Topic 1: Types of Solutions, Expressing Concentration of Solutions and Solubility

Summary

- **Solution:** A homogeneous mixture of two (or more) substances.
- **Binary solution:** A solution consisting of two components. The component which is present in larger quantity is called **solvent** and the component which is small in quantity is called **solute.**

Solute	Solvent	Example
Gas	Gas	Air
Gas	Liquid	Aerated water
Gas	Solid	Hydrogen in palladium
Liquid	Liquid	Alcohol in water, benzene in toluene
Liquid	Solid	Mercury in zinc amalgam
Liquid	Gas	CO_2 dissolved in water
Solid	Liquid	Sugar in water, common salt in water
Solid	Gas	Smoke
Solid	Solid	Various alloys

Types of solutions:

- **Unsaturated solution:** A solution in which more solute can be dissolved without raising temperature.
  - **Saturated solution:** A solution in which no solute can be dissolved any more at a given temperature.
  - **Supersaturated solution:** A solution which contains more solute than that would be required to do saturation at a given temperature.
  - **Aqueous solution:** In this type of solution, water is present as solvent. For example, salt solution.
  - **Non-aqueous solution:** In this type of solution, there is another solvent apart from water. For example, iodine dissolved in alcohol.
- **Solubility:** The maximum amount of a solute that can be dissolved in a given amount of solvent at a given temperature.

  The solubility of a solute in a solvent depends upon the following:
  - Nature of the solute
  - Nature of the solvent
  - Temperature of the solution: If the dissolution process is endothermic, solubility of solid in liquid increases with increase in temperature, and in endothermic process, solubility decreases.
  - Pressure (in case of gases): Solubility of gases increase with increase in pressure but it has no effect on solids in liquids.

Methods of Expressing Concentration of Solutions:

- **Mass Percentage (W / w)**

$$\text{W/ w\%} = \frac{\text{Mass of solute}}{\text{Total mass of solution}} \times 100$$

- **Percentage by volume (V / v%)**

  $$V/\ v\% = \frac{\text{Volume of solute}}{\text{Total volume of solution}} \times 100$$

- **Mass by volume percentage (*w*/*v*)**

  $$w\ /\ v\% = \frac{\text{Mass of solute}}{\text{Volume of solution}} \times 100$$

- **Mole fraction (x)**: It is defined as the ratio of the number of moles of a component to the total number of moles of all the components. For a binary solution, if the number of moles of A and B are n_A and n_B respectively, the mole fraction of A will be

  $$\chi_A = \frac{n_A}{n_A + n_B}, \chi_B = \frac{n_B}{n_A + n_B}$$

- **Parts per million (ppm):** It is defined as the parts of a component per million parts of the solution.

  $$\text{ppm} = \frac{\text{number of parts of the component}}{\text{total number of parts of all the components}} \times 10^6$$

  It can be expressed in different ways like mass to mass, volume to volume and mass to volume.

  $$\text{ppm}(\text{mass to mass}) = \frac{\text{Mass of a component}}{\text{Total mass of solution}} \times 10^6 \quad \text{ppm}(\text{volume to volume}) = \frac{\text{Volume of a component}}{\text{Total volume of solution}} \times 10^6$$

  $$\text{ppm}(\text{mass to volume}) = \frac{\text{Mass of a component}}{\text{Volume of solution}} \times 10^6$$

- **Molarity (M):** It is the number of moles of solute present in 1L (dm^3) of the solution.

  $$M = \frac{\text{Number of moles of solute}}{\text{Volume of solution}} = \frac{W_B \times 1000}{M_B \times V(ml)}$$

- **Molality (m):** It is the number of moles of solute per kilogram of the solvent.

  $$m = \frac{\text{Number of moles of solute}}{\text{Mass of solvent}} = \frac{W_B \times 1000}{W \times W_A}$$

- **Normality (N):** The number of gram equivalents of solute present in 1 L of solution.

  $$\text{Normality} = \frac{\text{Number of gram equivalent of solute}}{\text{Volume of solution in L}}$$

  Number of gram equivalents of solute = $\frac{\text{Mass of solute in gram}}{\text{Equivalent weight}}$

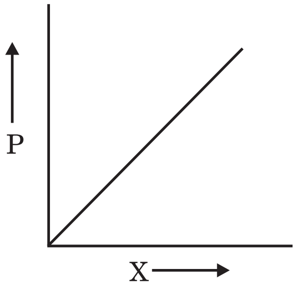
- **Relationship between Molarity and Molality:**

  $$m = \frac{1000M}{M \times M_B - 1000d}$$

- **Henry's law**: The partial pressure of a gas in vapour phase (p) is proportional to the mole fraction of the gas (χ) in a solution. It is a special case of Raoult's law.

  $\rho = K_H\chi$, K_H is the Henry's constant

  Higher the value of K_H, lower the solubility of gas in the liquid.



Slope of the line gives the value of K_H

- **Limitations of Henry's law:** This law is applicable only when

  The law does not apply for gases which undergo association or dissociation in the solution.

  This law is not applied for gases at high pressure and low temperature.

  The law does not apply for gases which undergo any chemical change.
- **Applications of Henry's law:**

  At high altitudes, low blood oxygen makes people weak and cause a problem called anoxia.

  Bottles of soft drinks are sealed under high pressure to increase the solubility of CO_2

  Scuba divers use air diluted with helium, nitrogen and oxygen to avoid toxic effects of nitrogen in blood.

PREVIOUS YEARS'
EXAMINATION QUESTIONS
TOPIC 1

▶ 1 Mark Questions

1. Give one example each of lyophobic sol and lyophilic sol. **[DELHI 2014]**

▶ 2 Mark Questions

[DELHI 2013]

2. State Henry's law. What is the effect of temperature on the solubility of a gas in a liquid. **[DELHI 2014]**

3. Define an ideal solution and write, one of its characteristics. **[DELHI 2014]**

4. State Henry's law correlating the pressure of a gas and its solubility in a solvent and mention two applications for the law. **[DELHI 2016]**

5. (i) Gas (A) is more soluble in water than Gas (B) at the same temperature. Which of the two gases will have the higher value of K_H (Henry's constant) and why?

(ii) In non-ideal solution, what type of deviation shows the formation of maximum boiling azeotropes? **[ALL INDIA 2016]**

▶ 5 Mark Questions

6. (a) Differentiate between molality and molarity of a solution. How does a change in temperature influence their values?

(b) Calculate the freezing point of an aqueous solution containing 10.50 g of $MgBr_2$ in 200 g of water. (Molar mass of $MgBr_2$ = 184 g) (K_f for water $= 1.86K\ kgmol^{-1}$)

OR

(a) Define the terms osmosis and osmotic pressure. Is the osmotic pressure of a solution a colligative property? Explain

(b) Calculate the boiling point of a solution prepared by adding 15.00 g of NaCl to 250.0 g of water. (K_b for water $= 0.512K\ kgmol^{-1}$, Molar mass of $NaCl = 58.44g$)

[DELHI 2011]

7. (a) State the following:

1. Henry's law about partial pressure of a gas in a mixture.
2. Raoult's law in its general form in reference to solutions.

(b) A solution prepared by dissolving 8.95 mg of a gene fragment in 35.0 mL of water has an osmotic pressure of 0.335 torr at 25°C. Assuming the gene fragment is non-electrolyte, find its molar mass.

Topic 2: Vapour Pressure of Liquid Solutions, Ideal and Non-ideal Solutions

Summary

- **Vapour Pressure:** Vapour pressure of a liquid solution is the amount of pressure that the vapours exert on the liquid solvent when they are in equilibrium and at a fixed temperature. It changes with the temperature of the surroundings and the nature of the liquid.
- **Raoult's Law:** The law states that the partial pressure is directly proportional to the mole fraction of the solute component. So, according to Raoult's Law, the partial pressure of A will be

  $P_A \propto x_A$

  $P_A = P_A{}^0 x_A$

  Where $P_A{}^0$ is the vapour pressure of pure liquid component A.

  Similarly partial pressure of B will be

  $P_B \propto x_B$

  $P_B = P_B{}^0 x_B$

  Where $P_B{}^0$ is the vapour pressure of pure liquid component B. The total pressure (P_{total}) of the solution placed in a container is the sum of partial pressures of its respective components. That is

  $P_{total} = P_A + P_B$

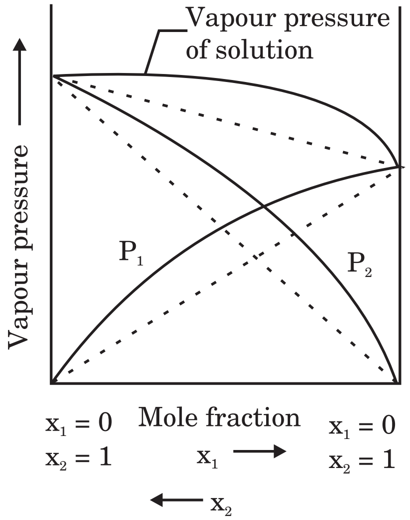
  $P_{total} = P_A{}^0 x_a + P_B{}^0 x_B$
- **Raoult's Law as a Special Case of Henry's Law:**

  According to Raoult's law, vapour pressure of volatile component is given by, $p_i = x_i p_i^o$

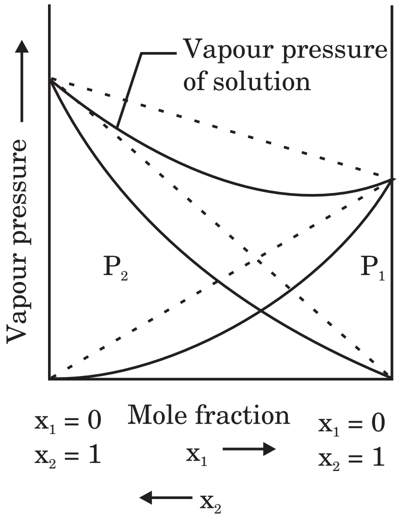
  According to Henry's law, the gaseous component is volatile that it exist as a gas and solubility depends on Henry's law:

  $p_A = K_H x_A$
- **Positive and negative deviation from Raoult's law:**

  Positive deviation leads to increase in vapour pressure. In positive deviation, A-B interactions are weaker than interaction between B-B or A-B. Examples: Acetic acid and toluene, Methanol and chloroform, etc.



Negative deviation leads to decrease in vapour pressure. In negative deviation, A-A and B-B intermolecular forces are weaker than interaction between A-B. Examples: Chloroform and benzene, chloroform and methyl acetate, etc.



- **Ideal Solution:** These are the solutions which obey Raoult's law over the entire range of concentration.

  Two properties of Raoult's law:

  $\Delta_{mix}H = 0$ and $\Delta_{mix}V = 0$

  Examples of ideal solutions are: Ethyl bromide and ethyl chloride, benzene and toluene.
- **Non-ideal Solutions:** These solutions do not obey Raoult's law over the range of concentration.

  If the vapour pressure of such a solution is higher, then the solution exhibits positive deviation and if it is lower, then the solution exhibits negative deviation.
- **Azeotropes:** Binary mixtures which have same composition in liquid and vapour phase and boil at constant temperature are called azeotropes.
- **Minimum boiling azeotrope:** Solutions which show large positive deviation from Raoult's law. For example: Ethanol-water mixture.
- **Maximum boiling azeotrope:** Solutions which show large negative deviation from Raoult's law. For example: Nitric acid and water.

PREVIOUS YEARS'
EXAMINATION QUESTIONS
TOPIC 2

1 Mark Questions

1. Some liquids on mixing form 'azeotropes'. What are 'azeotropes'? **[DELHI 2014]**

2 Mark Questions

2. State the following:
   - *(i)* Raoult's law in its general form in reference to solutions.
   - *(ii)* Henry's law about partial pressure of a gas in a mixture. **[ALL INDIA 201]**
3. State Raoult's law for the solution containing volatile components. What is the similarity between Raoult's law and Henry's law? **[DELHI 2014]**
4. What is meant by positive deviations from Raoult's law? Give an example. What is the sign of $\Delta_{mix}H$ for positive deviation?

   OR

   Define azeotropes. What type of azeotrope is formed by positive deviation from Raoult's law? Give an example. **[DELHI 2015]**

Topic 3: Colligative Properties, Determination of Molecular Mass and Abnormal Molar Mass

Summary

Colligative properties depend on the number of solute particles but do not depend on its chemical identity. When a non volatile solute is added to volatile solvent, vapour pressure decreases. The properties of such solutions are:

- **Relative lowering of vapour pressure of solvent:** A relation between vapour pressure of solution, mole fraction and vapour pressure of the solvent is as follows:

  $p_i = x_i p_i^o$

  Reduction in vapour pressure of solvent is given by:
  $\Delta p_i = \left(1 - x_i\right) p_i^o = x_j p_i^o$

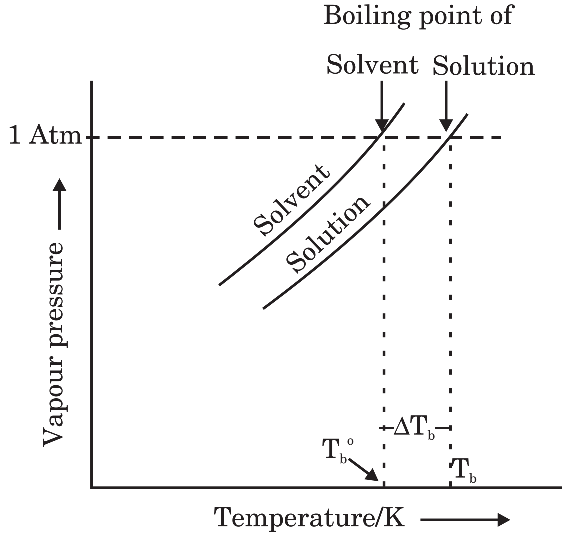
  $$\frac{\Delta p_i}{p_i^o} = \frac{p_i^o - p_i}{p_i^o} = x_j$$

  This expression is called relative lowering of vapour pressure which equals mole fraction of the solute.

- **Elevation of boiling point:** Boiling point of a solution is always higher than the boiling point of the pure solvent. The elevation of boiling point depends on the number of solute molecules.

  The difference between the boiling point of solution and boiling point of pure solvent gives the elevation of boiling point.
  $\Delta T_b = T_b - T_b^o$

  For dilute solutions, $\Delta T_b = K_b m$, where K_b is called Boiling Point Elevation Constant, and m is molality.

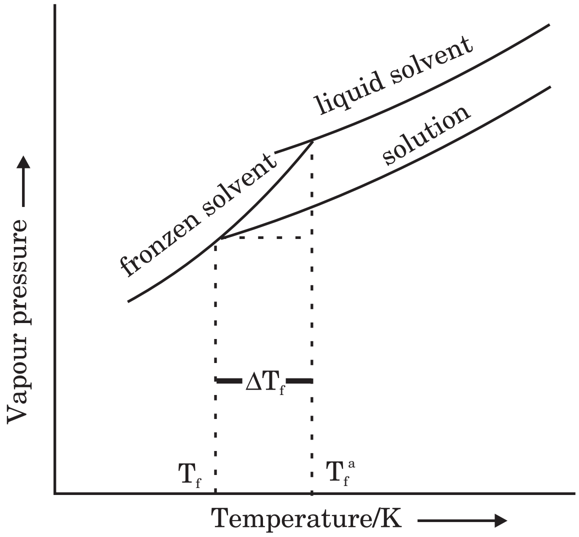


ΔT_b denotes elevation of boiling point of solvent

- **Depression of freezing point:** Lowering of vapour pressure causes depression of freezing point. The difference between the freezing point of pure solvent and freezing point of solvent when non volatile solute is dissolved in it gives the depression in freezing point.

  $\Delta T_f = T_f^o - T_f$

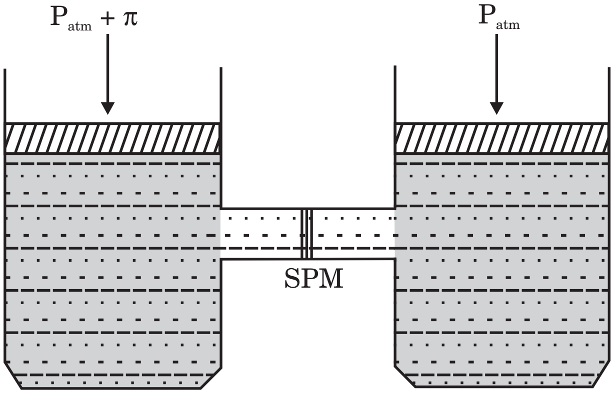
  For dilute solutions, $\Delta T_f = K_f m$, where K_f is the freezing point depression constant



- **Osmosis:** The flow of solvent molecules from pure solvent to solution is called osmosis. Some extra pressure applied which just stops the flow of solvent is called osmotic pressure.

  Osmotic pressure of solution

  $\pi = \frac{n}{VRT}$, where $\pi = CRT$ as the osmotic pressure

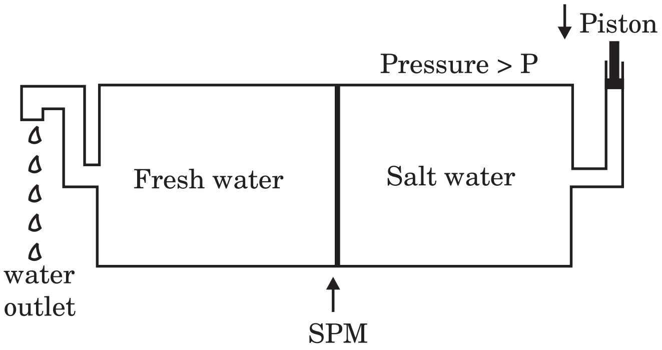


Solution Solvent

Excess pressure is equal to the osmotic pressure

- **Isotonic solutions:** Any two solutions having same osmotic pressure are called isotonic solutions. No osmosis occurs between such solutions which are separated by semi permeable membrane.
- **Hypertonic and hypotonic solutions:** When cells shrink due to water flowing out of the cell due to more salt concentration, then the solution is called hypertonic solution. When water flows into the cell due to less salt concentration, then the solution is called hypotonic solution.

- **Reverse Osmosis:** Pressure larger than the osmotic pressure when applied on the solution side causes reverse osmosis. It is used for water purification.



- **Abnormal Molar Mass:** A molar mass higher or lower than the normal molar mass is called abnormal molar mass.
- **Van't Hoff factor:** The Van't Hoff factor is the ratio between the actual concentration of particles produced when the substance is dissolved, and the concentration of a substance as calculated from its mass.

$$i = \frac{\text{observed (experimental) value of a colligative property}}{\text{Normal (calculated) value of the same colligative property}}$$

PREVIOUS YEARS'

EXAMINATION QUESTIONS

TOPIC 3

1 Mark Questions

1. What are isotonic solutions? **[DELHI 2014]**
2. Out of $BaCl_2$ and KCl, which one is more effective in causing coagulation of a negatively charged colloidal sol? Give reason. **[DELHI 2015]**

2 Mark Questions

3. A 1.00 molal aqueous solution of trichloroacetic acid (CCl_3COOH) is heated to its boiling point. The solution has the boiling point of 100.18 °C. Determine the Van't Hoff factor for trichloroacetic acid. (K_b for water = $0.512\ K\ kg\ mol^{-1}$)

   OR

   Define the following terms:

   1. Mole fraction
   2. Isotonic solutions
   3. Van't Hoff factor
   4. Ideal solution **[ALL INDIA 2012]**

4. Write the dispersed phase and dispersion medium of the following colloidal system?

   (i) Smoke (ii) Milk.

   OR

   What are lyophilic and lyophobic colloids? Which of these, sols can be easily coagulated on addition of small amounts of electrolytes?

   [DELHI 2013]

5. Calculate the mass of compound (molar mass = 256 g mol^{-1}) to be dissolved in 75 g of benzene to lower its freezing point by 0.48 K ($K_f = 5.12\ K\ kg\ mol^{-1}$)

   [DELHI 2014]

6. Calculate the freezing point of a solution containing 60 g of glucose (Molar mass = 180 g mol^{-1}) in 250g of water. (K_f of water = 1.86 K kg/mol^{-1})

   [ALL INDIA 2018]

3 Mark Questions

7. Calculate the amount of KCl which must be added to 1kg of water so that the freezing point is depressed by 2K.

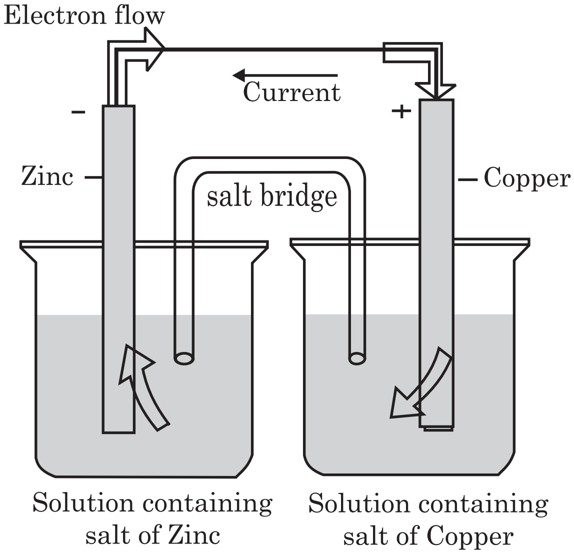
   [ALL INDIA 2011]

   (K_f for water = 1.86 K kg/mol^{-1})

Topic 1: Electrochemical Cells, Galvanic cells and Nernst Equation

Summary

- Electrolytic conduction: The conduction of an electrical current by the movement of ions.
- Electrolyte: A substance that dissociates into ions in solution and hence conducts electricity.
- Degree of ionization: The ratio of the number of ions of a solute to the total number of molecules of that solute in a solution.
- Specific resistivity: It is the resistance offered by a material or solution occupying one cm^3 volume.
- Specific conductance or conductivity (κ): It is the conductance of a material between two electrodes of cross sectional area 1 cm^2, separated by 1 cm distance.
- Electrochemical cell: It is a device that generates a potential difference between electrodes using redox reactions.
- Galvanic cell or voltaic cell: The Galvanic Cell is a device which transforms chemical energy into electric energy.
- Daniel cell: A galvanic cell in which one electrode is Zn plate in $ZnSO_4$ (or Zn^{++} ion) solution and the other is Cu plate in $CuSO_4$ (or Cu^{++} ion) solution. Following diagram shows a Daniel cell:



- Salt Bridge: A salt bridge is a combination of two noncovalent interactions i.e. electrostatic interactions and hydrogen bonding. Since, noncovalent interactions are weak interactions, formation of salt bridges provide an additional level of stabilizing interactions that can add important contribution to the overall stability of a molecule.
- Standard electrode potential (E°): It is defined by measuring the potential relative to a standard hydrogen electrode using 1 mol solution at 25 °C and 1 bar pressure.
- Emf of a cell can also be defined as the work done or required for transforming a unit positive charge from negative to positive terminal within the cell.

$$E_{cell} = E_{cathode} - E_{anode}$$

- The standard reduction potentials of a number of electrodes are measured using standard hydrogen electrode as the reference electrode. These various electrodes can be arranged in increasing order of their reduction potentials which is called electrochemical series.

Application of electrochemical series:

- ➢ Calculation of the standard EMF of the cell
- ➢ Predicting the feasibility of a redox reaction
- ➢ Comparison of the reactivities of metals.

Debye-Huckel-Onsagar equation:

It is for a strong electrolyte

$\Lambda = \Lambda^0 - AC^{\frac{1}{2}}$

$\Lambda =$ Equivalent conductivity at given concentration.

$\Lambda^0 =$ Equivalent conductivity at infinite dilution.

$C =$ Concentration

and A is a constant

- Redox reaction: When both reduction and oxidation reactions go side-by-side, it is known as a redox reaction.
- Redox couple: It is defined as having together the oxidized and reduced form of a substance taking part in and oxidation or reduction half reaction.

Nernst Equation:

It is used when the concentration of species in the electrode reaction is not equal to 1M.

$aA + bB \xrightarrow{ne^-} mM + nN$

The Nernst equation at 298 K can be written as

$$E_{cell} = E^0{}_{cell} - \frac{0.059}{n} \log \frac{[M]^m [N]^n}{[A]^a [B]^b}$$

- Gibb's Energy:

$\Delta G^0 = nFE^0{}_{cell}$

For spontaneous cell reaction, ΔG must be negative.

$\Delta G^0 = -2.303 RT \log K$

PREVIOUS YEARS'

EXAMINATION QUESTIONS

TOPIC 1

2 Mark Questions

1. The chemistry of corrosion of iron is essentially an electro-chemical phenomenon. Explain the reactions occurring during the corrosion of iron in the atmosphere. **[DELHI 2011]**
2. Complete the following chemical equations:
   (i) $Cr_2O_7{}^{2-} + H^+ + I^- \longrightarrow$
   (ii) $MnO_4{}^- + NO_2{}^- + H^+ \longrightarrow$
   [DELHI 2012]
3. The standard electrode potential (E°) for Daniel cell is +1.1V. Calculate the ΔG° for the reaction
   $Zn(s) + Cu^{2+}(aq) \longrightarrow Zn^{2+}(aq) + Cu(s)$
   $\left(1F = 96500 C\, mol^{-1}\right)$ **[ALL INDIA 2013]**

3 Mark Questions

4. Complete the following chemical equations:
   (i) $MnO_4{}^- + C_2O_4{}^{2-} + H^+ \rightarrow$
   (ii) $KMnO_4 \xrightarrow{heated}$
   (iii) $Cr_2O_7{}^{2-} + H_2S + H^+ \rightarrow$
   [DELHI 2011]

Topic 2: Conductance of Electrolytic Solutions or Ionic Solution and its Measurement

Summary

Conductance

- The electrical resistance of an object is given by $R = \rho \frac{l}{A}$ where l is the length and the area of cross section is A. ρ is called as resistivity.
- Conductance (G): It is the tendency of a material to allow current through it. It is the reciprocal of resistance. It depends on the following factors
  - ➢ Temperature
  - ➢ Nature an structure of the metal
  - ➢ Number of valence electrons per atom
- The conductance of electricity by ions present in thesolutions is called electrolytic or ionic conductance. The conductivity of electrolytic (ionic) solutions depends on following factors
  - ➢ Temperature
  - ➢ Concentration of electrolyte
  - ➢ The nature of electrolyte added
  - ➢ The nature of solvent and its viscosity
  - ➢ Size of ions produced and their solvation

Measurement of conductivity of Ionic Solutions

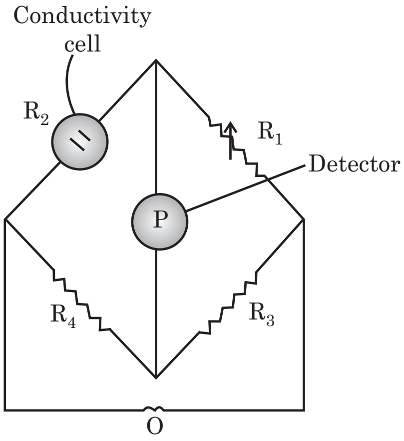
Measuring resistance of ionic solution using Wheatstone bridge faces two problems

- A solution cannot be connected to the bridge like a metallic wire. This problem is solved by using a specially designed vessel which is called conductivity cell.
- The composition of the solution is changed by passing direct current. This problem is solved by using alternating current source of power.

Cell constant (G*): The ratio of the distance between the electrodes to the cross sectional area of the electrodes is known as cell constant.

$$G = \frac{l}{A} = R\kappa$$

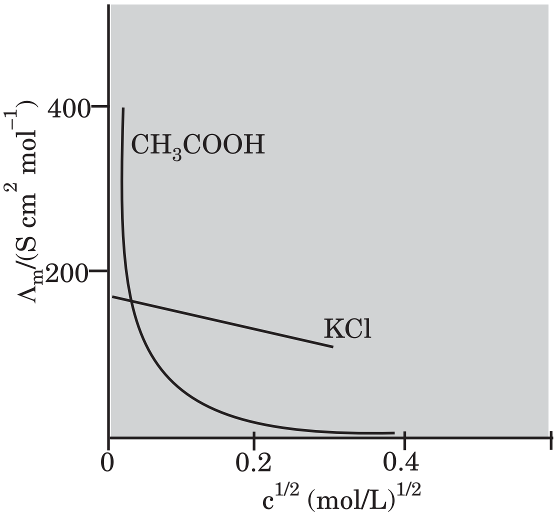
After determining the cell constant, it is used for measurement of resistance or conductivity of the solution using the circuit shown below:



Unknown Resistance $R_2 = \frac{R_1 R_4}{R_3}$

Variation of conductivity and molar conductivity with concentration

- **Strong Electrolytes**
  - On dilution, the number of ions per unit volume that carry the current in a solution decreases. Hence, conductivity and molar conductivity decreases with decrease in concentration for strong and weak electrolytes.
  - Molar conductivity increases with decrease in concentration as the total volume of solution containing one mole ofelectrolyte also increases.
  - Λ increases with dilution and is shown as $\Lambda_m = E_m{}^o - Ac^{\frac{1}{2}}$ where $E_m{}^o$ is limiting molar conductivity.



- **Kohlrausch's law of independent migration of ions.**

  Limiting molar conductivity of an electrolyte at infinite dilution is expressed as the sum of contributions from the individual ions.
  $\Lambda_m{}^{\infty} = v_+\lambda_+{}^{\infty} + v_-\lambda^{\infty}$ where v_+, v_- are the number of cations and anions per formula of electrolyte.

Application of Kohlrausch's law

  - Calculation of limiting conductivities of weak electrolytes
  - Determination of degree of ionization (α) of weak electrolyte

- **Weak Electrolytes**
  - Weak electrolytes have lower degree of dissociation at higher concentrations and hence for such electrolytes, the change in Λ_m with dilution is due to increase in the degree of dissociation and consequently the number of ions in total volume of solution that contains 1 mol of electrolyte. For weak electrolyte is obtained using Kohlrausch's Law.
  - $E_m{}^o$
  - $K_a = \dfrac{c\Lambda_m{}^2}{\Lambda_m{}^o\left(\Lambda_m{}^o - \Lambda_m\right)}$

Topic 3: Electrolysis, Batteries, Fuel Cells and Corrosion

Summary

- Electrolysis is the passage of electricity through an electrolyte, in which cations move to the cathode to get reduced, and anions move towards the anode to get oxidized.
- Faraday's Laws of Electrolysis
  - ➢ Faraday's First Law of Electrolysis

  The mass of the substance (m) which occurs at any electrode is directly proportional to the quantity of electricity or charge (Q) passed.

  $m = ZIt$, where Z= Electrochemical equivalent

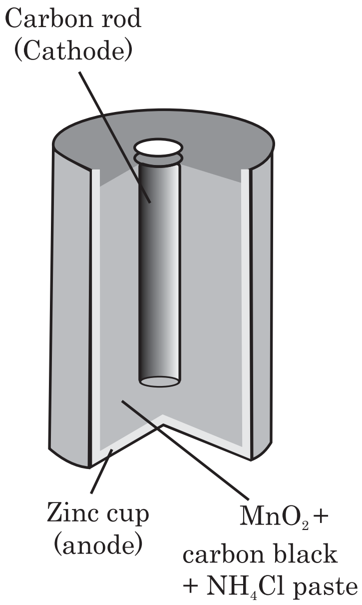
  - ➢ Faraday's second Law of Electrolysis

  When the same quantity of electricity is passed through different electrolytes, the masses of different ions liberated at the electrodes are directly proportional to their chemical equivalents (Equivalent weights)

  $$\frac{w}{E_1} = \frac{w}{E_2}$$

- The product of electrolysis depends on the types of electrode used and the physical state of the material.
- Batteries: It is a source of electrical energy where one or more cells are connected in series.
  - ➢ Primary Battery: They are non-chargeable batteries like Dry cell and Lechlanche Cell.

Dry cell



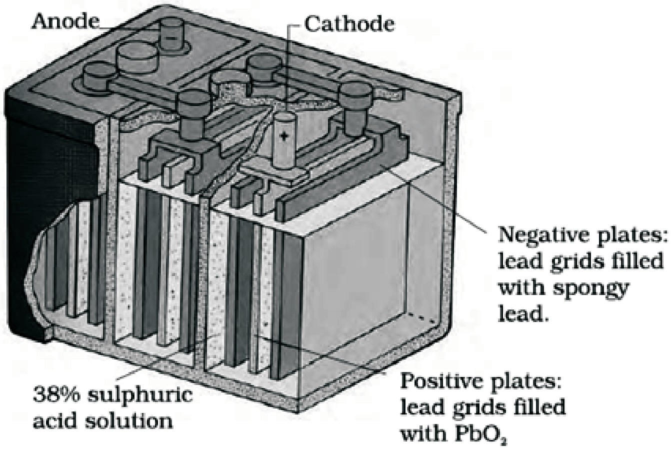
At anode: $Zn_{(s)} \rightarrow Zn^{2+}{}_{(aq)} + 2e^-$

At cathode: $MnO_{2(s)} + NH_{4(aq)}{}^+ + 2e^- \rightarrow MnO(OH) + NH_3$

The net reaction: $Zn + MnO_{2(s)} + NH_{4(aq)}{}^+ \rightarrow Zn^{2+} + MnO(OH) + NH_3$

- ➢ Secondary Battery: These are the chargeable cells like lead storage battery and nickel-cadmium cells.

Lead storage battery:



Anode: Spongy lead

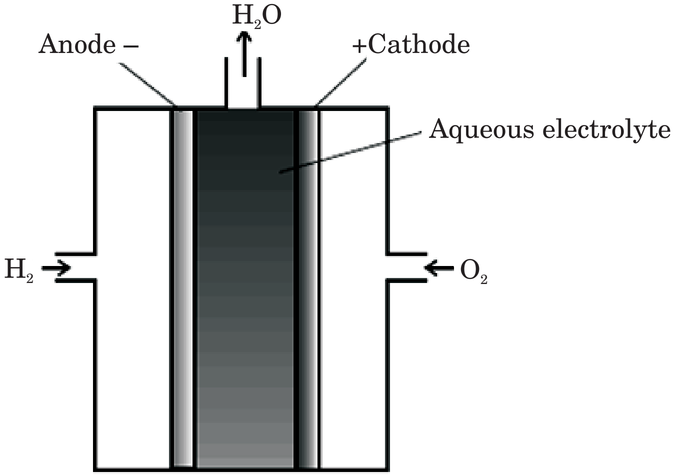
Cathode: Lead packed with lead dioxide

Electrolyte: Aqueous solution of S_2SO_4

At anode: $Pb_{(S)} + SO_4{}^{2-}{}_{(aq)} \rightarrow PbSO_{4(S)} + 2e^-$

At cathode: $PbSO_{4(S)} + 2e^- \rightarrow Pb_{(S)} + SO_4{}^{2-}{}_{(aq)}$

- Fuel cell: These are the cells which convert energy from fuels like methane, hydrogen into electrical energy. Following diagram shows a fuel cell.



Anode: $\left[H_{2(g)} + 2OH_{(aq)}{}^- \rightarrow 2H_2O_{(l)} + 2e^-\right] \times 2$

Cathode: $O_{2(g)} + 2H_2O_{(l)} + 4e^- \rightarrow 4OH^-{}_{(aq)}$

Net reaction: $O_{2(g)} + 2H_{2(g)} \rightarrow 2H_2O_{(l)}$

- Corrosion: The conversion of metals into undesirable compounds (usually oxides) on reaction with moisture and other gases.

Rusting of Iron:

$$Fe_{(S)} + 2H^+_{(aq)} + \frac{1}{2}O_{2(g)} \rightarrow Fe^{2+}_{(aq)} {}_{-}+ H_2O_{(l)}$$

$$2Fe^{2+}_{(S)} + \frac{1}{2}O_{2(g)} + 2H_2O_{(l)} \rightarrow Fe_2O_{3(S)} + 4H^+$$

$$Fe_2O_{3(S)} + xH_2O_{(l)} \rightarrow Fe_2O_3{\bullet}xH_2O$$

Corrosion can be prevented using following measures

- Alloying
- Barrier protection by covering the surface with paint.
- Sacrificial protection by galvanization

PREVIOUS YEARS'

EXAMINATION QUESTIONS

TOPIC 3

2 Mark Questions

1. What type of a battery is lead storage battery? Write the anode and the cathode reactions and the overall reactions occurring in a lead storage battery. **[ALL INDIA 2011]**

2. (*a*) Following reactions occur at cathode during the electrolysis of aqueous silver chloride solution:

$$Ag^+(aq) + e^- \longrightarrow Ag(s); E^\circ = +0.80V$$

$$H^+(aq) + e^- \longrightarrow \frac{1}{2}H_2(g); E^\circ = 0.00V$$

On the basis of their standard reduction electrode potential (E°) values, which reaction is feasible at the cathode and why?

(*b*) Define limiting molar conductivity. Why conductivity of an electrolyte solution decreases with decrease in concentration? **[DELHI 2015]**

3. Calculate the time to deposit 1.5 g of silver at cathode when a current of 1.5 was passed through the solution of $AgNO_3$. (Molar mass of $Ag = 108\ g\ mol^{-1}$, $1F = 96500\ C\ mol^{-1}$) **[ALL INDIA 2015]**

4. What type of cell is a lead storage battery? Write the anode and the cathode reactions and the overall cell reaction occurring in the use of a lead storage battery?

OR

Construct the redox equation from the two half cell reactions and predict if this reaction favours formation of reactants or product shown in the equation. **[DELHI 2017]**

5. Write the name of the cell which is generally used in transistors. Write the reactions taking place at the anode and cathode of this cell. **[ALL INDIA 2017]**

5 Mark Questions

6. (a) What type of a battery is lead storage battery? Write the anode and cathode reactions and the overall cell reaction occurring in the operation of a lead storage battery.

(b) Calculate the potential for half-cell containing

$0.10\ M\ K_2Cr_2O_7(aq),\ 0.20\ M\ Cr^{3+}(aq)$

and $1.0 \times 10^{-4}\ M\ H^+(aq)$

The half-cell reaction is

$$Cr_2O_7{}^{2-}(aq) + 14\ H^+(aq) + 6\ e^- \longrightarrow 2\ Cr^{3+}(aq) + 7\ H_2O\ (l)$$

and the standard electrode potential is given as $E_o = 1.33\ V$

OR

(a) How many moles of mercury will be produced by electrolyzing 1.0 $M\ Hg\ (NO_3)_2$ solution with a current of 2.00A for 3 hours? $\left[Hg(NO_3)_2 = \ 200.6\ g\ mol^{-1}\right]$

Topic 1: Rate of a Chemical Reaction and Factors Influencing Rate of a Reaction

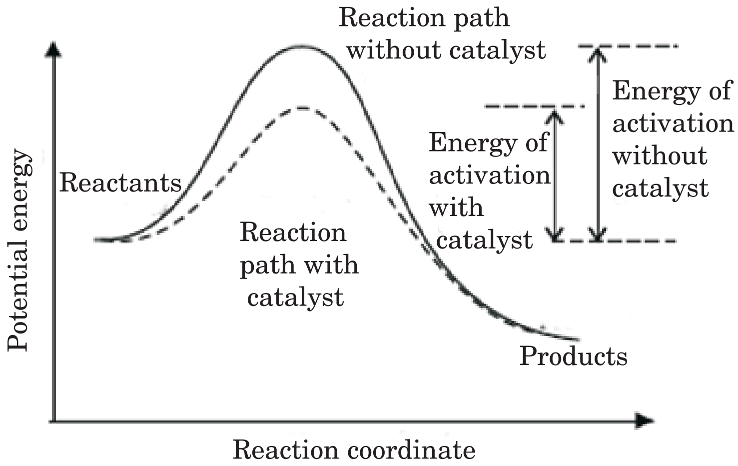
Summary

- **Chemical Kinetics**: The study of chemical reactions, their rates, effect of various factors on rate of reaction is considered under chemical kinetics.
- **Rate of Reaction:** The change in concentration of reactant or product with respect to time is called the rate of reaction.

  For the reaction, R → P

  Rate of disappearance of R $= -\frac{\Delta[R]}{\Delta t}$; Rate of appearance of P $= \frac{\Delta[P]}{\Delta t}$

  Units of rate of reaction are concentration × time^{-1}. Unit of concentration varies according to the state of the reactant. For gases, concentration is expressed as partial pressures, for liquids, concentration is in mol L^{-1}.
- Rate of chemical reaction can be instantaneous or average. Rate of reaction at a particular moment of time is instantaneous rate while the rate of reaction over a time interval is average rate.
- **Factors affecting the rate of a chemical reaction:** There are various factors which affect the rate of reaction.
  - **Pressure of the reaction:** Pressure varies directly with the rate of reaction. As the pressure is increased, volume decreases and concentration increases. Therefore with increase in concentration, rate of reaction increases.
  - **Temperature of the reaction:** Temperature varies directly with the rate of reaction. As the temperature of the reaction increases, rate increases and vice versa.
  - **Concentration of the reaction:** As the concentration of the reactants increases, rate of reaction increases and if the concentration of the reactants is less then rate of reaction decreases.
  - **Surface area of the reactants:** For reactions which takes place on the surface of the reactant, the rate of reaction increases with increase in surface.
  - **Presence of catalyst:** Rate of reaction increases on adding catalyst. It is because the catalyst decreases the activation energy of the reaction.



  - **Nature of reactants:** Simpler molecules separate easily and take part in chemical reaction while molecules which are complex take time to separate the bonds and the rate of reaction thus decreases.

- **Rate Law:** It is an expression where rate of chemical reaction is written in terms of concentration of the reactants with each term raised to some power which may or may not be same as the stoichiometric coefficients of the reacting species.

  For example: For the reaction, $2NO\ (g) + O_2\ (g) \rightarrow 2NO_2\ (g)$

  Rate = $k\ [NO]^2\ [O_2]$

  Here k is the rate constant.
- **Molecularity:** It is defined as the number of reacting species (molecules, atoms or ions) in an elementary reaction. It cannot be a non integer or zero.
- **Elementary or complex reactions:** If a reaction takes place in a single step, it is an elementary reaction while a reaction involving series of elementary reactions is called complex reaction.
- **Rate determining step:** The step which takes place slowly is called the rate determining step.

PREVIOUS YEARS'

EXAMINATION QUESTIONS

TOPIC 1

1 Mark Question

1. Define 'order of a reaction'. **[ALL INDIA 2011]**

2 Mark Questions

2. What do you understand by the rate law and rate constant of a reaction? Identify the order of a reaction if the units of its rate constant are:

   (i) $L^{-1}\ mol\ s^{-1}$

   (ii) $L\ mol^{-1}\ s^{-1}$ **[ALL INDIA 2011]**

3. What do you understand by the 'order of a reaction'? Identify the reaction order from each of the following units of reaction rate constant:

   (i) $L^{-1}\ mol\ s^{-1}$

   (ii) $L\ mol^{-1}\ s^{-1}$ **[ALL INDIA 2012]**

4. For a reaction:

$$H_2 + Cl_2 \longrightarrow 2HCl$$

Rate = k

   (i) Write the order and molecularity of this reaction.

   (ii) Write the unit of 'k'.

[ALL INDIA 2016]

5. For the reaction

$$2N_2O_5(g) \longrightarrow 4NO_2(g) + O_2(g),$$

the rate of formation of $NO_2\ (g)$ is $2.8 \times 10^{-3}\ Ms^{-1}$. Calculate the rate of disappearance of $N_2O_5\ (g)$. **[ALL INDIA 2018]**

6. Distinguish between 'rate expression' and 'rate constant' of a reaction. **[DELHI 2011]**

7. Write two differences between 'order of reaction' and 'molecularity of reaction'. **[DELHI 2014]**

8. What is meant by the 'rate constant, k' of a reaction? If the concentration be expressed in mol L^{-1} units and time in seconds, what would be the units for k

   (i) for a zero order reaction and

   (ii) for a first order reaction? **[DELHI 2016]**

9. Define the following:

   (i) Elementary step in a reaction

   (ii) Rate of a reaction **[DELHI 2017]**

3 Mark Questions

10. For the first order thermal decomposition reaction, the following data were obtained

$$C_2H_5CI(g) \longrightarrow C_2H_4(g) + HCl(g)$$

Time/sec	Total pressure/atm
0	0.30
300	0.50

Calculate the rate constant. (Given: $log2 = 0.301$, $log3 = 0.4771$, $log4 = 0.6021$) **[ALL INDIA 2016]**

11. For the reaction:

$$2NO(g) + Cl_2(g) \longrightarrow 2\ NOCl(g)$$

Experiment no.	Initial $[NO]$ (M)	Initial $[Cl_2]$ (M)	Initial rate of disappearance of Cl_2 (M/min)
1	0.15	0.15	0.60
2	0.15	0.30	1.20
3	0.30	0.15	1.20
4	0.25	0.25	?

Topic 2: Integrated Rate Equation, Pseudo First Order Reaction

Summary

- Order of reaction: It is defined as the sum of powers of the concentration of reactants in the rate law expression. It can be zero and even fraction.

  Units of rate constant are different for reactions of different order.

Reaction	**Order**	**Units of rate constant**
Zero order reaction	0	mol L^{-1} s^{-1}
First order reaction	1	s^{-1}
Second order reaction	2	mol^{-1} Ls^{-1}

- **Integrated rate equations:** A relation between directly measured experimental data and rate constant is given by integrated rate equation. There are different rate equations for different order of reactions.
  - **Zero order reaction:** Rate of reaction is independent of the concentration of the reactants.

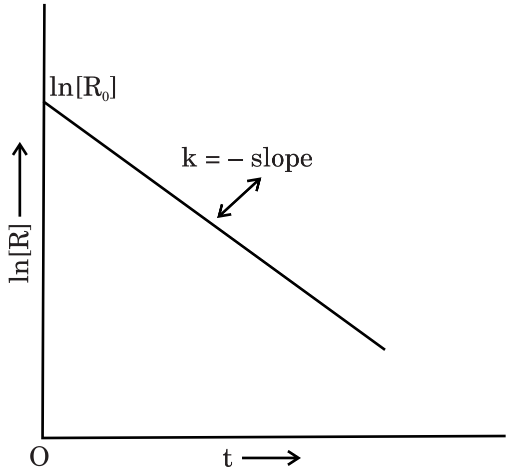
    For the reaction, $2NH_3(g) \xrightarrow[Pt\ catalyst]{1130K} N_2(g) + 3H_2(g)$

    Rate = $k\ [NH_3]^0 = k$
  - **First order reaction:** Rate of reaction is directly proportional to the first power of the concentration of the reactants.

    For the reaction, $C_2H_4(g) + H_2(g) \rightarrow C_2H_6(g)$

    Rate = $k\ [C_2H_4]$

    $$k = \frac{2.303}{t}\log\frac{[A_o]}{[A]}$$



Graph showing the relation between $ln\ [R]$ and t for first order reaction

  - **Second order reaction:** In this rate law the sum of powers of concentration terms in rate law is equal to 2.

    For example: $A + B \rightarrow C + D$

    $$\frac{dx}{dt} = k[A]'[B]'$$

- Pseudo first order reaction: The reaction is not of first order but certain conditions makes the reaction of first order.

  For example: Reaction of ethyl acetate with water.

  $$CH_3COOHC_2H_5 + H_2O \xrightleftharpoons{H^+} CH_3COOH + C_2H_5OH$$

  It should be of second order but water is in very less quantity so it is pseudo first order reaction.

- **Half life of a reaction:** The time in which concentration of the reactant reduces to half of the initial concentration is called half-life of a reaction. It is represented as $t_{½}$.

  For a zero order reaction, the rate constant at $t_{½}$,

  $$k = \frac{[R]_o}{2t_{1/2}}$$

  For a first order reaction, the rate constant at $t_{½}$

  $$t_{1/2} = \frac{0.693}{k}$$

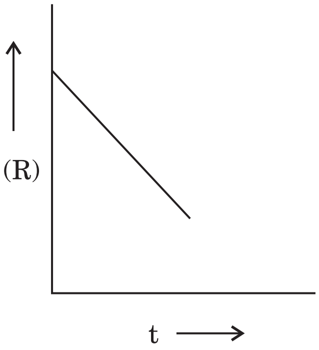
PREVIOUS YEARS'

EXAMINATION QUESTIONS

TOPIC 2

2 Mark Questions

1. The thermal decomposition of HCO_2H is a first order reaction with a rate constant of $2.4 \times 10^{-3} s^{-1}$ at a certain temperature. Calculate how long will it take for three-fourths of initial quantity of HCO_2H to decompose.
   ($log0.25 = -0.6021$) **[ALL INDIA 2011]**
2. For a reaction $A + B \rightarrow P$, the rate law is given by $r = k[A]^{1/2}[B]^2$
   (a) What is the order of this reaction?
   (b) A first order reaction is found to have a rate constant $k = 5.5 \times 10^{-14} s^{-1}$. Find the half-life of the reaction. **[ALL INDIA 2013]**
3. For a chemical reaction $R \rightarrow P$, the variation in the concentration (R) vs. time (t) plot is given as



   (i) Predict the order of the reaction.
   (ii) What is the slope of the curve?
   [ALL INDIA 2014]
4. Define the following terms:
   (i) Pseudo first-order reaction
   (ii) Half-life period of reaction ($t_{1/2}$).
   [DELHI 2014]
5. Explain the following terms:
   (i) Rate constant (k)
   (ii) Half life period of reaction ($t_{1/2}$)
   [DELHI 2014]
6. A reaction is of first order in reactant A and of second order in reactant B. How is the rate of this reaction affected when
   (i) the concentration of B alone is increased to three times
   (ii) the concentrations of A as well as B are doubled? **[DELHI 2018]**

3 Mark Questions

7. A first order reaction takes 20 minutes for 25% decomposition. Calculate the time taken when 75% of the reaction will be completed?
   (Given: $log2 = 0.3010$, $log3 = 0.4771$, $log4 = 0.6021$)
   [ALL INDIA 2017]
8. A first order decomposition reaction takes 40 minutes for 30% decomposition. Calculate its $t_{1/2}$ value. **[DELHI 2016]**

Topic 3: Temperature Dependence of the Rate of a Reaction, Collision Theory of Chemical Reactions

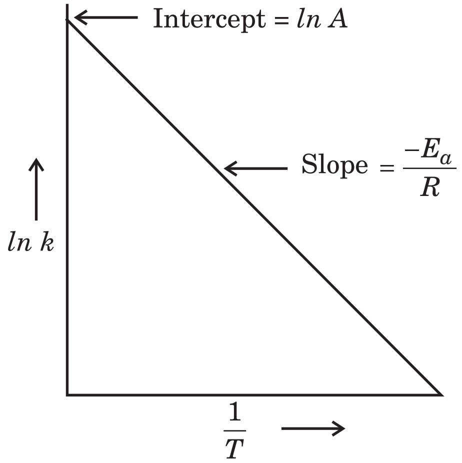
Summary

Electrostatic potential:

- The rate of a reaction depends on temperature. As the temperature increases, rate of reaction increases.
- **Activation Energy:** It is the energy of reactant molecules so that collision of molecules leads to formation of products. It cannot be negative.
- **Threshold energy:** It is the minimum energy required by the reactants to form products.
- **Arrhenius equation:** The relation between rate of reaction and temperature is given in the Arrhenius equation.

  $$k = Ae^{\frac{-E_a}{RT}}$$

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



- **Collision Theory:** According to this theory, It is assumed that reactant molecules are hard spheres and reaction occurs when reactant molecules collide with each other.

  Number of collisions per second per unit volume gives collision frequency.

  Rate $= Z_{AB}e^{\frac{-E_a}{RT}}$

  Where Z_{AB} is the collision frequency

  When molecules collide with sufficient kinetic energy to facilitate breaking of bonds to form products, it is called effective collisions.

  Rate of reaction $= f \times z$

  Where f is the frequency of effective collisions.
- Collision theory ignores the structural aspect and considers molecules as hard spheres which is a drawback of collision theory.

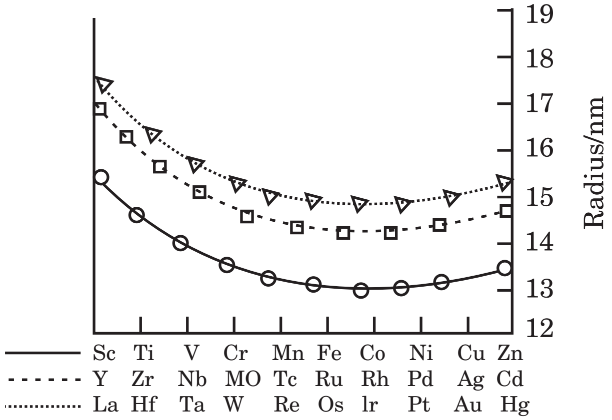
Summary

d-block elements

- The elements of group 3-12 which have incompletely filled *d*-orbitals in the ground state are called d- block elements.
- They are also called transitional elements as their properties are in between those of s and p block elements.
- The electronic configuration is given as $(n-1)\,d^{1-10}\,ns^{1-2}$.

General properties

- **Physical Properties**
  - ➢ They are all metals, malleable and ductile(except Hg)
  - ➢ They display high tensile strength, high thermal and electrical conductivity
- **Variation in atomic and ionic sizes**
  - ➢ With increasing atomic number, ions of the same charge in given series experience decrease in radius as when a new electron enters a *d* orbital, the nuclear charge increases by unity.
  - ➢ 4*f* orbitals must be filled before 5*d* orbitals which leads to a regular decrease in atomic radii known as Lanthanoid contraction which is responsible for increasing atomic sizes with increasing atomic number.



- **Ionisation Enthalpy**

  The ionization enthalpy in a group decreases from 3*d* to 4*d* series and increases from 4*d* to 5*d* series because of Lanthanoid contraction.
- **Oxidation states**
  - ➢ Transition elements show a great variety of oxidation states in their compounds due to incomplete filling of *d*-orbitals.
  - ➢ Elements in the middle of the group have the maximum number of oxidation states, example: Manganese exhibits oxidation states from +2 to +7.
- **Trends in** $\frac{M^{2+}}{M}$ **electrode potential**

  No regular trend is shown in $E°$ values as ionization and sublimation enthalpy have no regular trend.

- **Magnetic Properties**
  - ➢ The two types of elements are diamagnetic and paramagnetic.
  - ➢ Diamagnetic substances have paired electrons only like Zn whereas paramagnetic substances have atleast one unpaired electron
- **Colored compound formation**

  The transition elements form colored ions as they have unpaired *d*-electrons.

  When light is absorbed in the visible region, it causes excitation of unpaired *d*-electrons which causes formation of colored compounds.
- **Alloy Formation**
  - ➢ *d*- block elements form alloy due to:

    Availability of d-orbitals for bond formation

    High ionic charges

    Similar sizes of the metal ions
  - ➢ Some of the alloys are Steel and Brass.
- **Chemical Reactivity**
  - ➢ Transition metals differ in chemical reactivity.
  - ➢ Many of them are sufficiently electropositive to dissolve in mineral acids while few of them stay unaffected by simple acids.
- **Catalytic Properties**
  - ➢ Many of the transition metals and their compounds acts as catalyst, especially oxides.
  - ➢ Some of the commonly used catalysts are Iron, Nickel, Cobalt, Platinum and their compounds.
- **Interstitial Compound Formation**
  - ➢ These are the compounds formed when small atoms (*H*, *C*, and *N*) get trapped inside the crystal lattices of metals. Example: TiC, Fe_3H, Mn_4N.
  - ➢ They are chemically inert, have a good metallic conductivity and are extremely hard.

Compounds of Transition Elements

- **Potassium dichromate ($K_2Cr_2O_7$)**
  - ➢ It is a crystalline solid orange in color.
  - ➢ It is prepared from the chromate ore using the following reactions:

    $4FeCr_2O_4 + 8Na_2CO_3 + 7O_2 \rightarrow 8Na_2CrO_4 + 2Fe_2O_3 + 8CO_2$

  The sodium chromate solution is acidified with sulphuric acid

  $2Na_2CrO_4 + 2H^+ \rightarrow Na_2Cr_2O_7 + 2Na^+ + H_2O$

  The solution is treated with potassium chloride.

  $Na_2Cr_2O_7 + 2KCl \rightarrow K_2Cr_2O_7 + 2NaCl$
  - ➢ It is used in preparation of azo compounds and in leather industry.
- **Potassium Permanganate ($KMnO_4$)**
  - ➢ It is a crystalline solid dark purple in color.
  - ➢ It is prepared commercially as

$$MnO_2 + 2e^- \xrightarrow[\text{Oxidised with air}]{\text{Fused with KOH}} MnO_4^{2-}$$

$$MnO_4^{2-} \xrightarrow[\text{in alkaline solution}]{\text{Electrolytic oxidation}} MnO_4^- + 1e^-$$

  - ➢ It is used in titration, bleaching of silk and in organic synthesis.
- The *f* block elements comprises of two series of elements called Lanthanoids and Actinoids.

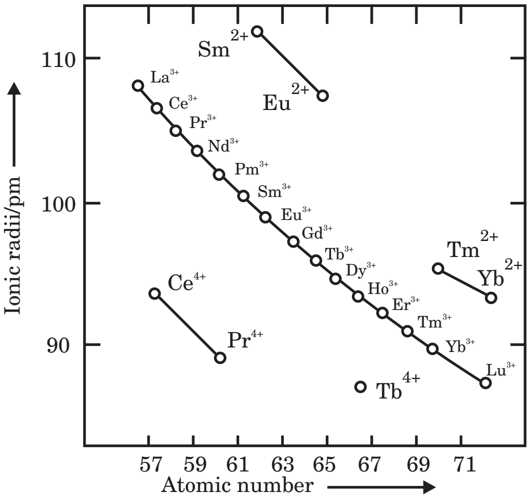
- The general electronic configuration for *f* block elements is $(n-2)f^{1-14}(n-1)d^{0-1}ns^2$.

$$\begin{cases} n=6 & \text{for Lanthanoid} \\ n=7 & \text{for Actinoid} \end{cases}$$

Lanthanoids

- **General Properties**
  - They are soft metals silvery white in color.
  - They are good conductors of electricity.
- **Atomic and ionic sizes**

  There is an overall decrease in atomic and ionic radii from Lanthanium to Lutelium (with increasing atomic number) due to Lanthanoid Contraction.



- **Oxidation States**

  Some of the elements exhibit +2 and +4 oxidation states but mainly they show +3 oxidation state.

Actinoids

- **General Properties**
  - Actinoids are radioactive elements.
  - They have high melting point and are highly electropositive.
- **Atomic and ionic radii**
  - With increasing atomic number, the electrons are added to the 5f shell resulting in increase in nuclear charge causing the shell to shrink which is known as actinoid contraction.
  - Due to actinoid contraction, atomic and ionic radii decrease with increasing atomic number
- **Oxidation States**
  - They generally exhibit +3 oxidation state but the distribution in oxidation states is uneven.
  - They exhibit higher oxidation states of +4, +5, +6, +7.

Comparison of Lanthanoids with Actinoids

Lanthanoids	Actinoids
They are less reactive than actinoids.	They are highly reactive metals.
4*f* orbital is progressively filled.	5*f* orbital is progressively filled.
They show limited oxidation state +2, +3, +4	A variety of oxidation states is shown. +3, +4, +5, +6, +7
They are non-radioactive except promethium.	They are radioactive elements.

Applications of *d* and *f* block elements

- Plutonium is used in atomic reactors and in atomic bombs.
- Oxides of lanthanoids are used as abrasives in cleaning of glass
- Iron is extensively used as a building material.
- *d* and *f* block elements are used as catalysts in various reactions.
- MnO_2 is used in dry battery cells.

PREVIOUS YEARS'

EXAMINATION QUESTIONS

1 Mark Question

1. What is meant by 'lanthanoid contraction'?

[ALL INDIA 2011]

2 Marks Questions

2. How would you account for the following:

(i) Cr^{2+} is reducing in nature while with the same d-orbital configuration $(d^4)Mn^{3+}$ is an oxidising agent.

(ii) In a transition series of metals, the metal which exhibits the greatest number of oxidation states occurs in the middle of the series. [**ALL INDIA** 2011]

3. Complete the following chemical equations:

(i) $MnO_4^{-}(aq)+S_2O_3^{2-}(aq)+H_2O\ (l)\longrightarrow$

(ii) $Cr_2O_7^{2-}(aq)+Fe^{2+}(aq)+H^{+}(aq)\longrightarrow$

OR

State reasons for the following:

(i) Cu (I) ion is not stable in an aqueous solution.

(ii) Unlike $Cr^{3+}, Mn^{3+}, Fe^{3+}$ and the subsequent other M^{3+} ions of the 3d series of elements, the 4d and the 5d series metals generally do not forms stable cationic species.

[ALL INDIA 2011]

4. Assign reasons for each of the following:

1. Transition metals generally form coloured compounds.
2. Manganese exhibits the highest oxidation state of +7 among the 3d series of transition elements. **[DELHI 2011]**

5. Assign reasons for the following:

1. Copper (I) ion is not known in aqueous solution.
2. Actinoids exhibit greater range of oxidation states than lanthanoids. **[DELHI 2011]**

6. Complete the following chemical equations:

(i) $Cr_2O_7^{2-}+H^{+}+I^{-}\longrightarrow$

(ii) $MnO_4^{-}+NO_2^{-}+H^{+}\longrightarrow$

[ALL INDIA 2013]

7. (a) Which metal in the first transition series (3d series) exhibits + 1 oxidation state most frequently and why?

(b) Which of the following cations are coloured in aqueous solutions and why?

Sc^{+3}, V^{+3}, Ti^{+4}, Mn^{+2}

(Atomic Nos. Sc = 21, V = 23,
Ti = 22, Mn = 25) **[DELHI 2013]**

8. What are the transition elements? Write two characteristics of the transition elements.
[DELHI 2015]

9. Why do transition elements show variable oxidation states? How is the variability in oxidation states of d-block different from that of the p-block elements? **[ALL INDIA 2015]**

10. Complete the following chemical reaction equations:

(i) $MnO_4^{-}(aq)\ +\ C_2O_4^{2-}(aq)\ +\ H^{+}(aq)\longrightarrow$

(ii) $Cr_2O_7^{2-}(aq)\ +\ Fe^{2+}(aq)\ +H^{+}(aq)\longrightarrow$

[DELHI 2015]

11. Complete and balance the following chemical equations:

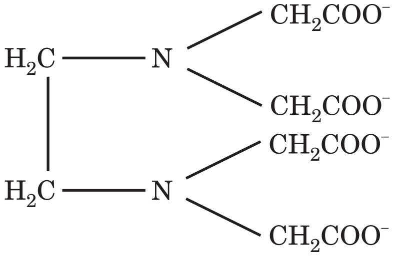
(a) $Fe^{2+}+MnO_4^{-}+H^{+}\longrightarrow$

(b) $MnO_4^{-}+H_2O+I^{-}\longrightarrow$

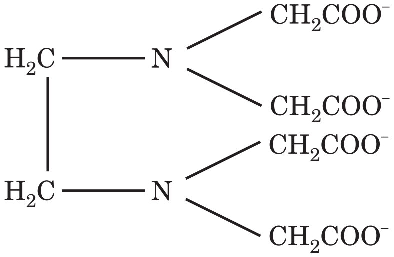
[ALL INDIA 2018]

Summary

- Coordination compounds are formed when metal atoms bound with anions or neutral molecules to form a compound. For example: $\left[Co\left(NH_3\right)_6\right]^{3+}$, $\left[Ni(CO)_4\right]$, $\left[CoCl_2\left(NH_3\right)_4\right]^{+}$, etc.
- **Double Salt:** It differs from coordination compound in such a way that they dissociate into constituent ions when dissolved in water while coordination compounds will not break into its respective ions. Some examples of double salt are Mohr's salt ($FeSO_4$. $(NH_4)_2SO_4.6H_2O$), Potash alum KAl $(SO_4)_2.12H_2O$, etc.
- **Coordination entity:** A central metal ion or atom bonded to a fixed number of ions or molecules forms a coordination entity. For example: $[Co\ (NH_3)_6]^{3+}$ is a coordination entity where a cobalt ion is surrounded by six ammonia molecules.
  - ➢ Here cobalt ion is the **central ion.**
  - ➢ The ammonia molecules arranged in a pattern around the central ion are called **ligands**.
  - ➢ When ligand is bound to metal atom/ ion by single donor atom then it is **unidentate ligand** as in this example ammonia is unidentate.
  - ➢ When a ligand is bound to two donor atoms, it is **didentate ligand**. For example: $C_2O_4^{2-}$ or $H_2NCH_2CH_2NH_2$
  - ➢ When several donor atoms are present in a single ligand, it is **a polydentate ligand**. For example: Ethylenediaminetetraacetate ion which contains several donor atoms.

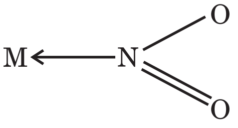


  - ➢ **Denticity** is the number of ligating groups in a ligand.
  - ➢ When two or more donor atoms are used by ligands to bind a metal ion, it is called a **chelate ligand**. For example:



  - ➢ Ligands which can ligate through two different atoms are called **ambidentate ligands**. Some examples are: SCN^- which can coordinate through sulphur or nitrogen atom. NO_2^- can coordinate through nitrogen or oxygen.

$M \longleftarrow SCN$ thiocyanato $\quad M \longleftarrow NCS$ isothiocyanato



$M \longleftarrow O - N = O$

- Ligands can also be classified on the basis of charge. It is of three types:

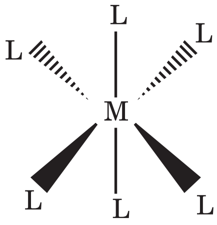
  Cationic ligands: The ligands which carry positive charge are cationic ligands. For example:

  $N_2H_5^+$, NO_2^+ .

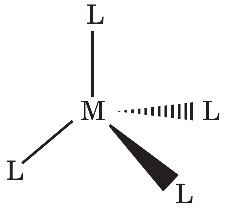
  Anionic ligands: The ligands which carry negative charge are anionic ligands. For example: OH^-, CN^-, etc.

  Neutral ligands: Ligands which do not carry any charge are neutral ligands. For example: NH_3, N_2, NO, etc.

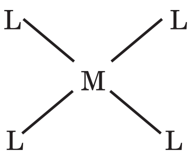
- **Coordination sphere:** It is a collective term for central atom/ ion and ligands written together in square brackets. For example: $[Co\ (NH_3)_6]^{3+}$, $K_4\ [Fe\ (CN)_6]$ (here $[Fe\ (CN)_6]^{4-}$ is a coordination sphere while K^+ is a counter ion).
- **Coordination number:** Metal atom/ ion is bonded to some ligand donor atoms. The number of donor atoms linked to the metal gives the coordination number. For example, in the compound $[Co\ (NH_3)_6]^{3+}$, coordination number of Co is 6 and in the compound $[Co\ (en)_3]^{3+}$, coordination number is 6 because *en* (ethane-1, 2-diamine) is a didentate ligand.
- **Coordination Polyhedron:** The ligand atoms are arranged around the central atom in a definite pattern which forms a coordination polyhedron. Some of the common examples are: square planar, octahedral, tetrahedral, etc.



Octahedral



Tetrahedral



Square planar

- **Oxidation number of central atom:** The charge on the central atom when all the ligands are removed along with the elctron pairs shared with it gives the oxidation number of central atom. For example: oxidation number of copper in $[Cu\ (CN)_4]^{3+}$ is 1 and it is written in Roman numeral as $Cu\ (I)$.
- **Homoleptic and heteroleptic complexes:** When a complex is bound to more than one donor groups, it is a heteroleptic complex. For example: $[Co\ (NH_3)_6]Cl_3$

  When the metal in a complex is bound to just one type of donor atom, it is a homoleptic complex. For example: $[Cu\ (CN)_4]^{3+}$
- **Nomenclature of Coordination Compounds:** It is based on the recommendations of the International Union of Pure and Applied Chemistry (IUPAC). There are some rules for naming coordination compounds which are as follows:
  - Cation is named first while naming any coordination entity.
  - Ligands are written before the central atom/ion in alphabetical order.
  - Anioinc ligands are written with –o at the end. There are some terms for some specific molecules written in (). aqua is used for H_2O, ammine for NH_3 , nitrosyl for NO and carbonyl for CO.
  - Number of individual ligands in the coordination entity are represented by some prefixes like mono, di, tri, etc.
  - Oxidation number of the central atom/ion is written in Roman numerals inside parentheses.
  - Cations are named same as the element in complex ion while anions end with –ate.

    For example: Co is written as cobalt if it acts as cation and cobaltate if it is present as anion.
- **Isomerism:** The phenomenon of compounds which have same molecular formula but different structural formulae which are isomers is known as isomerism. For example: C_2H_6O can be written as C_2H_6OH and CH_3OCH_3.

- **Types of isomerism:** Isomerism can either be structural or stereo.
  - **Structural Isomerism:** It can be divided into four types:

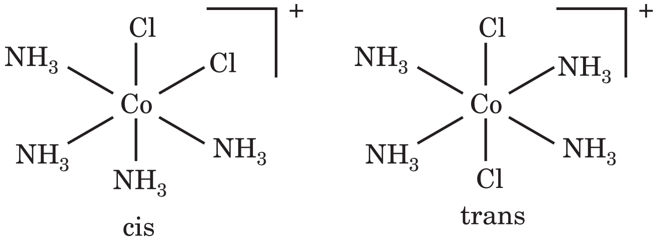
    Ionisation isomerism: When isomers have same molecular formula but different ions in solution, it is called ionisation isomerism. For example: $[Co\ (NH_3)_5SO_4]Br$ and $[Co\ (NH_3)_5Br]SO_4$.

    Linkage isomerism: It arises in compounds which contain ambidentate ligand. For example: $[Co\ (NH_3)_5\ (NO_2)]Cl_2$ where nitrile ligand is bound through oxygen to give red color and nitrile ligand is bound through nitrogen to give yellow color.

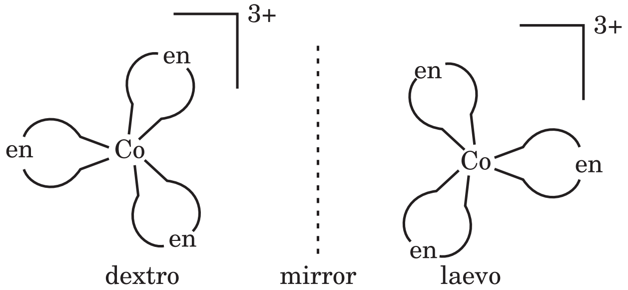
    Coordination isomerism: Ligands interchange between cationic and anionic entities of different metal ions in a complex. Such isomerism is a type of coordination isomerism. For example: $[Co\ (NH_3)_6][Cr\ (C_2O_4)_3]$ and $[Cr\ (NH_3)_6][Co\ (C_2O_4)_3]$

    Hydration isomerism: In this type of isomerism, isomers have same molecular formula but different number of molecules of water. For example: $[Cr\ (H_2O)_5Cl]\ Cl.\ H_2O$ and $[Cr\ (H_2O)_4Cl_2]Cl.\ 2H_2O$
  - **Stereo Isomerism:** It can be of two types:

    Geometrical isomerism (cis-trans isomerism): For a tetra co-ordinated square planar complex, trans-isomer has same groups on opposite sides while cis-isomer has same group on same sides. For example: cis and trans isomer of $[Co\ (NH_3)_4Cl_2]^+$



Optical isomerism: Optical isomers also called enantiomers are mirror images which cannot be superimposed on one another. The molecules or ions involved in this isomerism are called chiral. Depending on the direction of rotation of plane polarised light in a polarimeter, there are two forms dextro (d) and laevo (l).



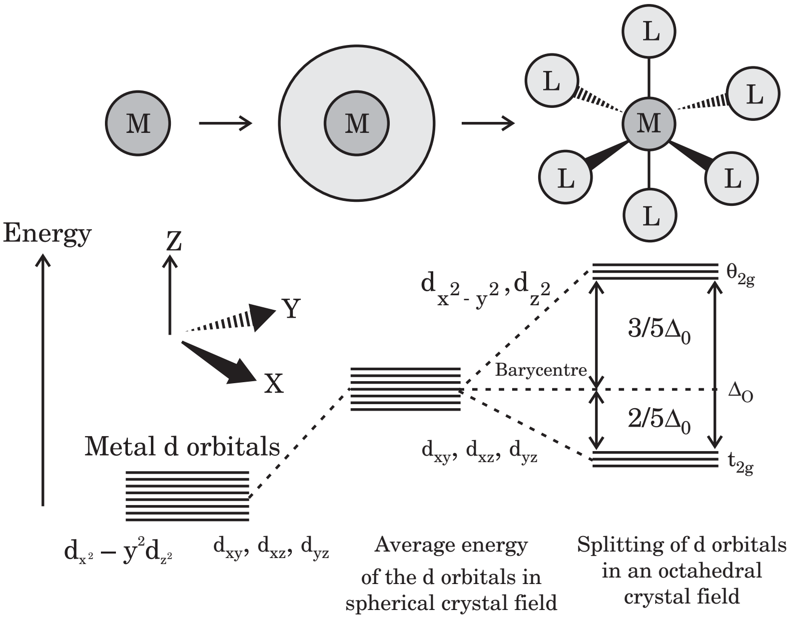
Optical isomers of $[Co(en)_3]^{3+}$

- Bonding in coordination compounds can be explained by different theories like Valence Bond Theory (VBT), Werner's Theory, Crystal Field Theory (CFT), Ligand Field Theory (LFT), and Molecular Orbit Theory (MOT).
- **Werner's Theory of Coordination Compounds:**

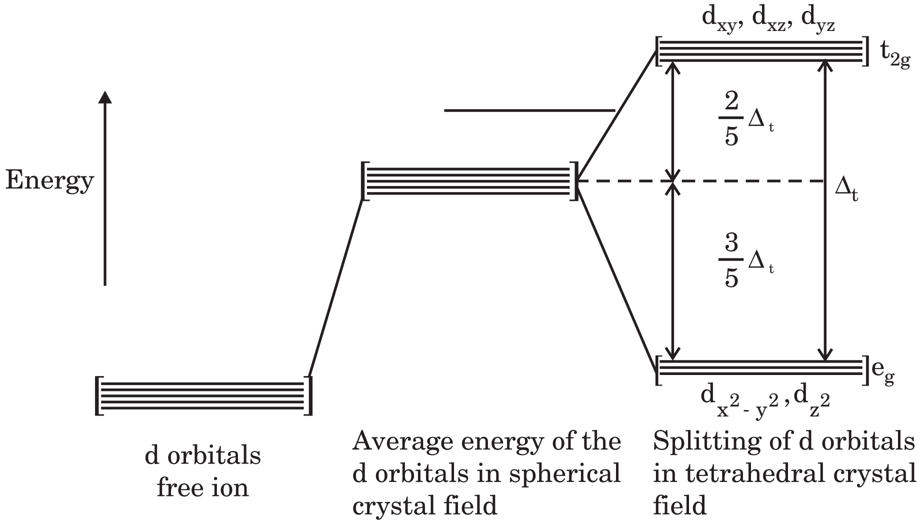
  This theory explained the nature of bonding in complex compounds. Primary and Secondary valency are the different kinds of valencies shown by metals.
  - Primary valency is equal to the oxidation state of the metal which is satisfied by anions.
  - Secondary valencies are similar to coordination number which is satisfied by opposite charged ions, neutral molecules or cations.

- **Limitations of Werner's theory:**
  - ➢ It does not explain the reason of only some elements forming complexes.
  - ➢ It does not explain the magnetic nature of complexes.
  - ➢ It does not explain the directional nature of coordination complexes.
- **Valence Bond Theory:**
  - ➢ A suitable number of vacant orbitals must be present for the formation of coordinate bond in the central metal atom/ion.
  - ➢ *s, p* or *d*-orbitals are appropriately used for hybridization by central metal ion depending on the number of ligands.
  - ➢ The ligands which donate electron pair overlap with the hybridized orbitals.
  - ➢ Outer or inner orbital complexes are formed on the basis of outer or inner *d*-orbitals used.
- **Limitations of Valence Bond Theory:**
  - ➢ Detailed magnetic properties of complex compounds are not explained.
  - ➢ Optical absorption spectra of coordination compounds are not explained by this theory.
  - ➢ It does not differentiate between strong and weak ligands.
  - ➢ Thermodynamic or kinetic stabilities of coordination compounds is not explained by this theory.
  - ➢ Geometry of 4 coordinate complex (square planar or tetrahedral) is not predicted.
- **Crystal Field Theory:**
  - ➢ Ligands are point charges according to this theory.
  - ➢ *d*-orbitals of metal ion split on approaching ligands.
  - ➢ In tetrahedral complexes, t_{2g} orbitals have high energy.
  - ➢ Splitting of *d*-orbitals is large when ligands produce strong fields and splitting is small when ligands produce weak fields.
  - ➢ Ligands are arranged according to increasing field strength as follows:

    $I^- < Br^- < SCN^- < Cl^- < S^{2-} < F^- < OH^- < C_2O_4^{2-} < H_2O < NCS^- < EDTA^{4-} < NH_3 < en < CN^- < CO$

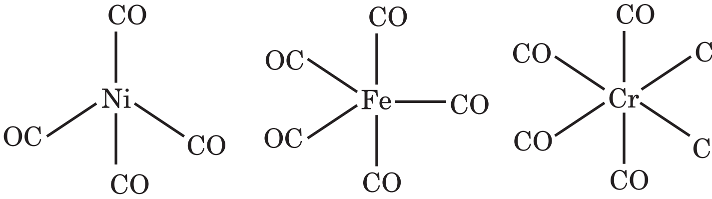


Splitting octahedral crystal field



- ➢ There is high energy of e_g orbitals in octahedral and lower energy in tetrahedral complexes.

- **Limitations of crystal field theory:**
  - ➢ It does not consider the covalent bonding between ligand and central atom.
  - ➢ According to this theory anionic ligands exert greatest splitting effect but actually the splitting is small.
- **Bonding in metal carbonyls:** Homoleptic carbonyls are formed by transition metals. Some examples are pentacarbonyliron (0) is trigonalbipyramidal, tetracarbonylnickel (0) is tetrahedral and hexacarbonyl chromium (0) is octahedral.



$Ni(CO)_4$ Tetrahedral

$Fe(CO)_5$ Trigonal bipyramidal

$Cr(CO)_6$ Octahedral

- Metal-carbon bond possess both *s* and *p* character. There is a synergic effect between the metal and ligand bond which strengthens the bond.
- **Stability of Coordination compounds:** The degree of association between two species gives the stability of complex in solution. Stability is expressed by magnitude of equilibrium constant. Larger the stability constant/ association constant, higher the proportion of the product in solution.

  Consider a reaction: $A + 4B \rightleftharpoons AB_4$

  Here *A* is surrounded by solvent molecules, *B* and the reaction goes in the following order using stability constants:

$$A + B \rightleftharpoons AB \qquad K_1 = \frac{[AB]}{[A][B]}$$

$$AB + B \rightleftharpoons AB_2 \qquad K_2 = \frac{[AB_2]}{[AB][B]}$$

$$AB_2 + B \rightleftharpoons AB_3 \qquad K_3 = \frac{[AB_3]}{[AB_2][B]}$$

$$AB_3 + B \rightleftharpoons AB_4 \qquad K_4 = \frac{[AB_4]}{[AB_3][B]}$$

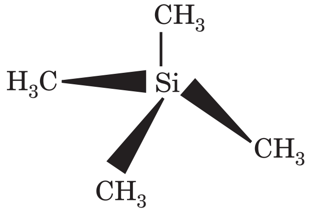
Here K_1, K_2,...... are stepwise stability constants.

$$\beta_4 = \frac{[AB_4]}{[A][B]^4}$$, β_4 is overall stability constant

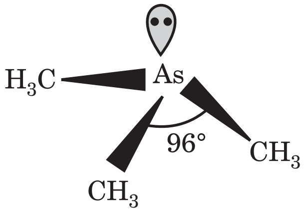
$\beta_4 = K_1 \times K_2 \times K_3 \times K_4$

Dissociation constant or instability constant is the reciprocal of association/ stability constant.

- **Classification of organometallic compounds:** These are divided into two groups as main group organometallics and *d*- and *f*- block organometallics.
  - ➢ **Main Group organometallics:** These are *s*- and *p*- block organometallics. Here are some examples with diagram: Tetramethyl silane, trimethyl arsene, etc.



$Si(CH_3)_4$



$As(CH_3)_3$

  - ➢ *d*- and *f*- block organometallics: The elements of *d*- and *f*- block form these kind of organometallics. Some examples are: Pentamethyl cyclopentadienyl ligand (C_5Me_5) forms *f*- block compounds, $[PtCl_3\ (C_2H_4)^-]$, $(C5H_5)_2Fe$, etc.
- **Applications of complex compounds:**
  - ➢ These compounds are used in qualitative and quantitative analysis.
  - ➢ Stability constants of calcium and magnesium complexes are different which can be used for selective estimation of calcium and magnesium ions.
  - ➢ Purification of metals is carried out by formation and decomposition of coordination compounds.
  - ➢ Extraction processes are carried out using complex formation.
  - ➢ These compounds are used as catalysts. For example, Wilkinson catalyst (rhodium complex) is used for hydrogenation of alkenes.
  - ➢ Medicinal chemistry make use of chelate therapy.

PREVIOUS YEARS'
EXAMINATION QUESTIONS

1 Mark Questions

1. Which of the following is more stable complex and why?

$\left[Co\left(NH_3\right)_6\right]^{3+}$ and $\left[Co\left(en\right)_3\right]^{3+}$ **[DELHI 2014]**

2. Give an example of linkage isomerism.

3. Write the coordination number and oxidation state of Platinum in the complex $\left[Pt\left(en\right)_2 Cl_2\right]$.

[ALL INDIA 2018]

2 Marks Questions

4. Explain the following giving an appropriate reason in each case.

1. O_2 and F_2 both stabilize higher oxidation states of metals but O_2 exceeds F_2 in doing so.
2. Structures of xenon fluorides cannot be explained by Valence Bond approach.

[DELHI 2012]

5. Write the IUPAC name of the complex $[Cr(NH_3)_4Cl_2]^+$. What type of isomerism does it exhibit? [DELHI 2014]

6. (i) Write down the IUPAC name of the following complex: $\left[Cr\left(NH_3\right)_2 Cl_2\left(en\right)\right]Cl$

(en = ethylenediamine)

(ii) Write the formula for the following complex: Pentaamminenitrito-o-Cobalt(III).

[DELHI 2015]

Topic 1: Introduction, Nomenclature and Preparation of Haloalkanes and Haloarenes

Summary

Haloalkanes are hydrogen atoms in aliphatic hydrocarbons replaced by halogens, whereas Haloarenes are hydrogen atoms replaced in benzene ring by halogens. In haloalkanes, halogen gets connected with the carbon through $(CO_2 + H_2O)$ hybridisation, while in Haloarenes, it is connected with CO_2 hybridisation.

Classification

- **On the Basis of Number of Halogen Atoms**

  It depends on the number of halogen atoms attached to the structure. It may be mono, di, tri or tetra etc. For example,

C_2H_5X

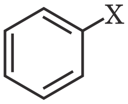
Monohaloalkane

$$\begin{array}{c}CH_2X\\ |\\ CH_2X\end{array}$$

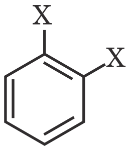
Dihaloalkane

$$\begin{array}{c}CH_2X\\ \|\\ CHX\\ \|\\ CH_2X\end{array}$$

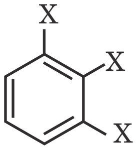
Triyhaloalkane



Monohaloarene



Dihaloarene



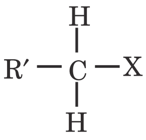
Trihaloarene

- **Compounds Containing** $\text{ppm}\left(\text{mass to mass}\right) = \dfrac{\text{Mass of a component}}{\text{Total mass of solution}} \times 10^6$ **C-X Bond (X= F, Cl , Br, I)**

  - Alkyl halides or haloalkanes (R-X): The series is represented as

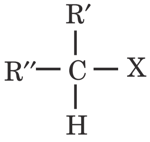
    $\text{ppm}\left(\text{volume to volume}\right) = \dfrac{\text{Volume of a component}}{\text{Total volume of solution}} \times 10^6.$

    It has further 3 categories, i.e., primary, secondary or tertiary depending on the nature of carbon to which halogen is attached.



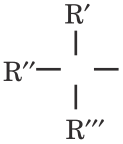
$$\begin{array}{c}H\\ |\\ R'-C-X\\ |\\ H\end{array}$$

Primary (1°)



$$\begin{array}{c}R'\\ |\\ R''-C-X\\ |\\ H\end{array}$$

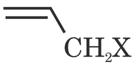
Secondary (2°)

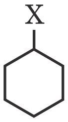


$$\begin{array}{c}R'\\ |\\ R''- \quad -\\ |\\ R'''\end{array}$$

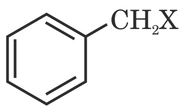
Tertiary (3°)

  - Allylic halides: The halogen atom is attached to the carbon atom just adjacent to carbon-carbon double bond.

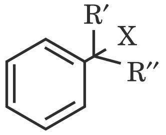




- Benzylic halides: The halogen atom is attached to the carbon atom right next to an aromatic ring.



(1°)

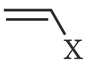


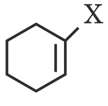
R′ = CH$_3$, R″ = H(2°)

R′ = R″ = CH3(3°)

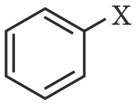
- **Compounds Containing** $\text{ppm}\left(\text{mass to volume}\right) = \frac{\text{Mass of a component}}{\text{Volume of solution}} \times 10^6$ **C-X Bond**

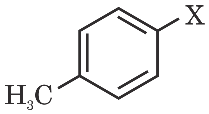
  - Vinylic halides: The halogen atom is attached to the carbon atom just adjacent to carbon-carbon double bond (C=C).





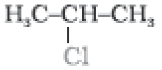
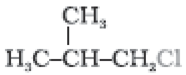
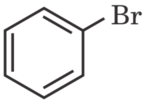
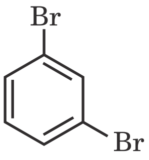
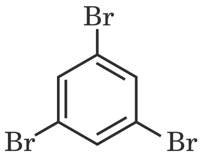
  - Aryl halides: The halogen atom is attached to the carbon atom right next to an aromatic ring.





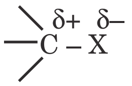
Nomenclature

Alkyl halides are named as halo-substituted hydrocarbons in the IUPAC system of nomenclature. Haloarenes are the common as well as IUPAC names of aryl halides.

Structure	IUPAC Names	Common Names
$CH_3CH_2CH_2Br$	1-Brompropane	n-Propyl bromide
 $H_3C{-}\underset{\displaystyle Cl}{\underset{\vert}{C}H}{-}CH_3$	2-Chloropropane	Isopropyl chloride
 $H_3C{-}\overset{\displaystyle CH_3}{\overset{\vert}{C}H}{-}CH_2Cl$	1-Chloro-2-methylpropane	Isobutyl chloride
	Bromobenzene	Bromobenzene
	1,3-Dibromobenzene	m-Dibromobenzene
	1,3,5-Tribromobenzene	sym-Tribromobenzene
$H_3C{-}CHCl_2$	1,1-Dicholoroethane	Ethylidene Chloride

Nature of C-X Bond

They form a polarised bond as the carbon atom bears a partial positive charge whereas the halogen atom bears a partial negative charge.



Methods of preparation

- **From Alcohols**

  Alkyl halides are most commonly prepared from alcohols as the hydroxyl group of an alcohol can be easily replaced by any halogen atom.

$$\text{R–OH} + \text{HX} \xrightarrow{ZnCl_2} \text{R–X} + H_2O$$

$$\text{R–OH} + \text{NaBr} + H_2SO_4 \longrightarrow \text{R–Br} + NaHSO_4 + H_2O$$

$$3\text{R–OH} + PX_3 \longrightarrow 3\text{R–X} + H_3PO_3 \quad (X = Cl, Br)$$

$$\text{R–OH} + PCl_5 \longrightarrow \text{R–Cl} + POCl_3 + HCl$$

$$\text{R–OH} \xrightarrow[X_2=Br_2, I_2]{\text{red } P/X_2} \text{R–X}$$

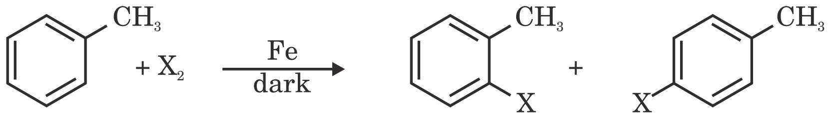
$$\text{R–OH} + SOCl_2 \longrightarrow \text{R–Cl} + SO_2 + HCl$$

From Hydrocarbons

- ➢ **By free radical halogenation:** Under certain conditions we can obtain mixture of isomeric mono and polyhaloalakanes**.**

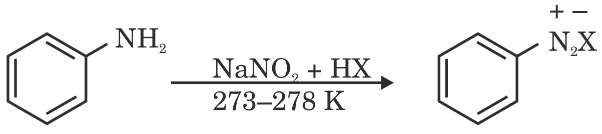
$$CH_3CH_2CH_2CH_3 \xrightarrow[\text{or heat}]{Cl_2/\text{UV light}} CH_3CH_2CH_2CH_2Cl + CH_3CH_2CHClCH_3$$

- ➢ **By electrophilic substitution:** This requires the presence of Lewis acid catalyst like iron or iron(III) chloride. Chloride and bromide compounds can be prepared from this method but not fluoro compounds due to the high reactivity of fluorine.

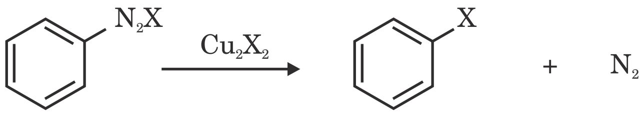


o-Halotoluene p-Halotouene

- ➢ **Sandmeyer's reaction:** This requires suspension of primary aromatic amine in cold aqueous mineral acid in the presence of sodium nitrate. A diazonium salt is formed which on reaction with cuprous chloride or bromide will replace diazonium group by Cl or Br.



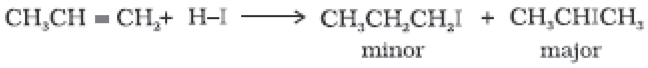
Benzene diazonium halide



Aryl halide
X = Cl, Br

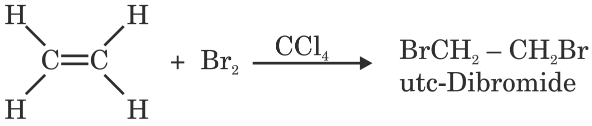
- **From alkenes**

  (i) Addition of hydrogen halides: This requires a reaction of alkyl halide with hydrogen chloride, bromide or iodide.



$$CH_3CH = CH_2 + H\text{–}I \longrightarrow \underset{\text{minor}}{CH_3CH_2CH_2I} + \underset{\text{major}}{CH_3CHICH_3}$$

  (ii) Addition of halogens: The following reaction takes place in presence of $M = \frac{\text{Number of moles of solute}}{\text{Volume of solution}} = \frac{W_B \times 1000}{M_B \times V(ml)}$.



- **Halogen Exchange**

  The reaction in which the alkyl iodides are prepared by the reaction of alkyl chlorides/ bromides with NaI in dry acetone is known as **Finkelstein Reaction.**

$$R\text{–}X + NaI \longrightarrow R\text{–}I + NaX$$

$X=Cl, Br$

  The reaction in which alkyl fluorides are prepared by the reaction of alkyl chlorides/ bromides with metallic fluoride is known as **Swarts Reaction**.

$$H_3C\text{–}Br + AgF \longrightarrow H_3C\text{–}F + AgBr$$

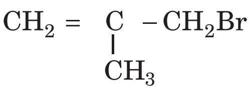
PREVIOUS YEARS'

EXAMINATION QUESTIONS

TOPIC 1

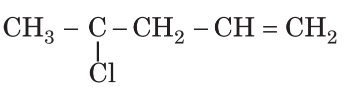
1 Mark Questions

1. Write the IUPAC name of the following compound: $CH_2 = CHCH_2Br$**[ALL INDIA 2011]**
2. How would you convert ethanol to ethene? **[ALL INDIA 2011]**
3. Give the IUPAC name of the following compound. **[ALL INDIA 2013]**



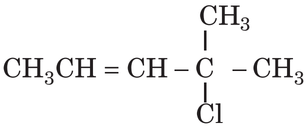
$$CH_2 = \underset{\underset{CH_3}{|}}{C} - CH_2Br$$

4. Write the IUPAC name of: **[DELHI 2013]**



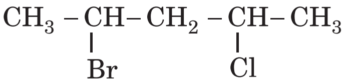
$$CH_3 - \underset{\underset{Cl}{|}}{C} - CH_2 - CH = CH_2$$

5. Write the IUPAC name of **[DELHI 2013]**

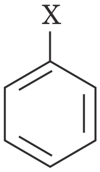
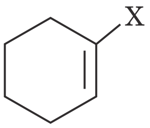


$$CH_3CH = CH - \overset{\overset{CH_3}{|}}{\underset{\underset{Cl}{|}}{C}} - CH_3$$

6. Write the IUPAC name of the following compound **[DELHI 2013]**



$$CH_3 - \underset{\underset{Br}{|}}{CH} - CH_2 - \underset{\underset{Cl}{|}}{CH} - CH_3$$

7. Write the IUPAC name of $(CH_3)_2CHCH(Cl)CH_3$. **[DELHI 2013]**
8. Write the structure of an isomer of compound C_4H_9Br which is most reactive towards reaction S_N1. **[ALL INDIA 2016]**
9. Out of the  and  which is an example of allylic halide? **[DELHI 2017]**

Topic 2: Properties of Haloalkanes and Haloarenes Including Polyhalogen Compounds

Summary

Physical Properties

- **Melting and boiling points**

  Because of the polarity of halogen compounds, the intermolecular forces of attraction are stronger due to which the boiling and melting points of chlorides, bromides and iodides are considerably higher than those of the hydrocarbons. The decreasing order of boiling points of some alkyl hydrides is: RI>RBr>RCl>RF. The boiling points of some isomers are high due to the symmetry.

- **Density**

  The density of alkyl hydrides increases with the number of carbon atoms and halogen atoms and their atomic masses.

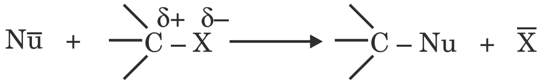
- **Solubility**

  The solubility of haloalkanes in water is quiet low because of strong hydrogen and carbon bond which is not easy to overcome or break. However, haloalkanes are soluble in solvent molecules because of the new intermolecular interactions between haloalkanes and solvent molecules which do not require much energy.

Chemical Reactions

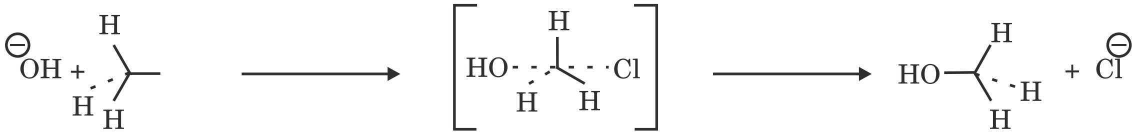
- **Reactions of Haloalkanes**
  - **Nucleophilic substitution reactions**

    A nucleophile reacts with a partial positive charge on a carbon atom of the haloalkanes, which then gets substituted by the nucleophile and separates out as halide ion.



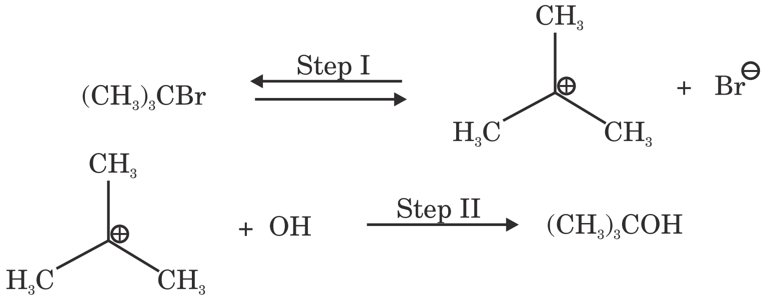
  - **Substitution nucleophilic bimolecular** ($m = \frac{\text{Number of moles of solute}}{\text{Mass of solvent}} = \frac{W_B \times 1000}{W \times W_A}$)

    In this case of nucleophilic substitution, a new carbon-OH bond is formed while simultaneously breaking the carbon-halide bond. Since both the steps take place simultaneously, this process is called **Inversion of configuration**.



  - **Substitution nucleophilic unimolecular** ($\text{Normality} = \frac{\text{Number of gram equivalent of solute}}{\text{Volume of solution in L}}$)

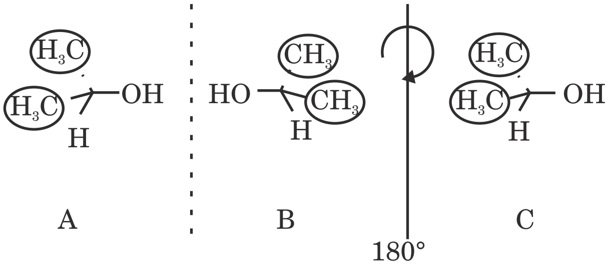
    These reactions require a presence of polar protic solvents like water or alcohol and follow the first order kinetics in which the reaction rate depends on only one reactant. This happens in two steps. In first step, bromide ion is separated out and then in the next step carbocation formed is attacked upon by the nucleophile.



- **Stereochemical aspects of nucleophilic substitution reactions**

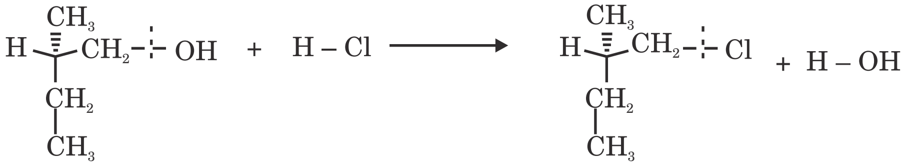
(i) Plane polarised light and optical activity: Those compounds which rotate the plane polarised light when passed through their solutions are called optically active compounds. If the light is rotated to the right by the compound, then it is called dextrorotatory and is represented by placing a positive sign before the degree of rotation. If the light is rotated to the left by the compound, then it is called laevorotatory and is represented by placing a positive sign before the degree of rotation. These isomers are called optical isomers and the phenomenon is called optical isomerism.

(ii) Molecular asymmetry, chirality and enantiomers: A carbon atom is called asymmetric carbon or stereocentre if the spatial arrangement of four groups around the central carbon is tetrahedral. The molecule so formed is referred to as asymmetric molecule. The super imposable objects when placed in front of the mirror are said to be achiral and the property is called as chirality. Those objects which are non-super imposable are known as chiral. For ex, propanol.



Enantiomers are stereoisomers which are related to each other as non-super imposable mirror images. When the rotation due to one isomer is cancelled by the rotation of other isomer in a mixture containing two equal enantiomers is known as racemic mixture and this process is known as racemisation.

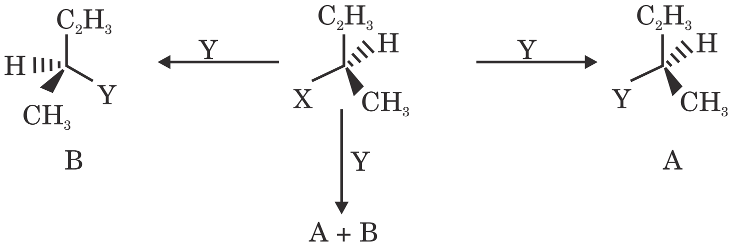
(iii) Retention: The preservation of integrity of the spatial arrangement of bonds during transformation or a chemical reaction is known as retention.



(–) –2-Methylbutan-1-ol

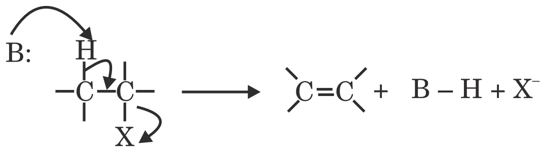
(+)-1-chloro-2-methylbutane

(iv) Inversion, retention and racemisation: If in a chemical reaction, compound A is produced, the process is called retention of configuration. If compound B is produced, then it is called inversion of configuration. If a mixture is produced, then the process is called racemisation.



- **Elimination reactions**

  This reaction requires the presence of alcoholic potassium hydroxide when a haloalkane with **β**-hydrogen is heated with it and the process is known as **β**-elimination.



B = Base ; X = Leaving group

- **Reaction with metals**

  The compounds obtained when chlorides or bromides react with certain metals are known as organo-metallic compounds. Grignard reagents of the form, RMgX, are obtained in such reactions.

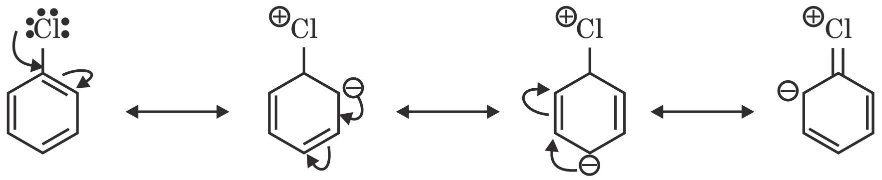
$$CH_3CH_2Br + Mg \xrightarrow{\text{dry ether}} \underset{\text{Grignard reagent}}{CH_3CH_2MgBr}$$

Wurtz reaction: The reactions in which alkyl halides reacts with sodium in dry ether to produce hydrocarbons with double the number of carbon atoms present in the halide.

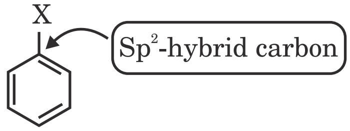
$$2RX + Na \longrightarrow RR + NaX$$

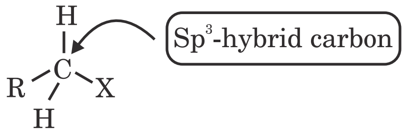
- **Reaction of Haloarenes**
  - **Nucleophilic substitution**

(i) **Resonance effect:** The electron pairs on halogen atom are in conjugation with π- electrons of the ring. The following resonating structures can be formed.



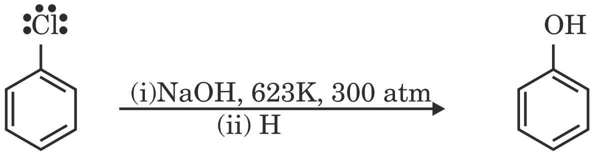
(ii) **Difference in hybridisation of carbon atom in C-X bond:** In haloalkanes, halogen gets connected with the carbon through sp^3 hybridisation, while in Haloarenes, it is connected with sp^2 hybridisation.

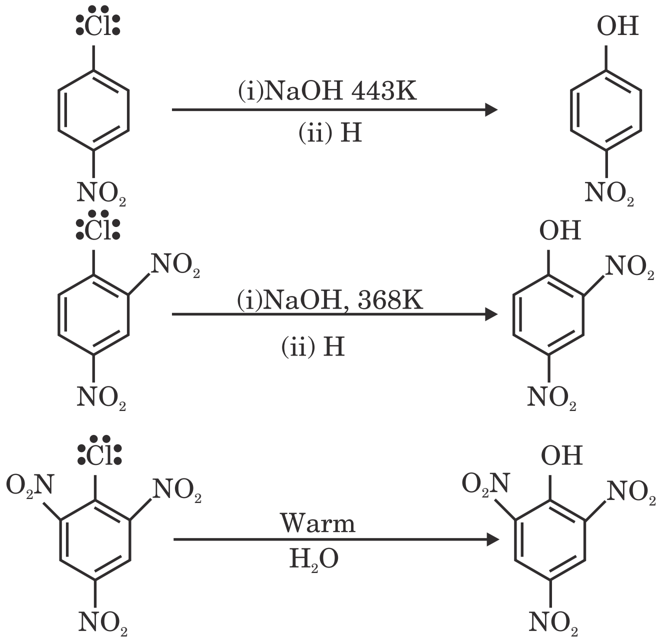




(iii) **Instability of phenyl cation:** In Haloarenes, the phenyl cation formed is not stabilized by resonance due to self-ionisation.

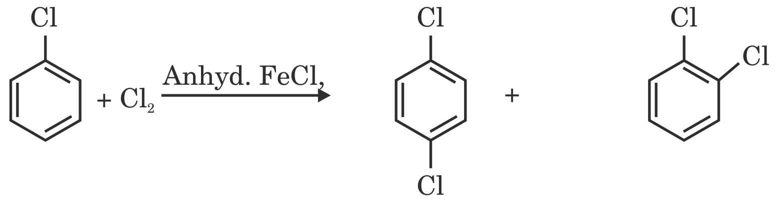
(iv) **Replacement by hydroxyl group:** Phenol is formed by heating chlorobenzene in aqueous sodium hydroxide solution.





- **Electrophilic substitution reactions**

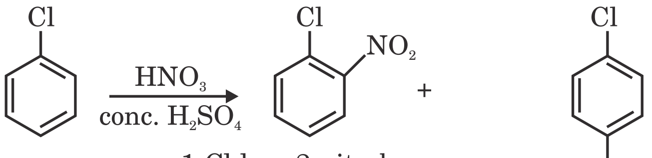
(i) Halogenation:



1, 4-Dichlorobenzene
(Major)

1, 2-Dichlorobenzene
(Minor)

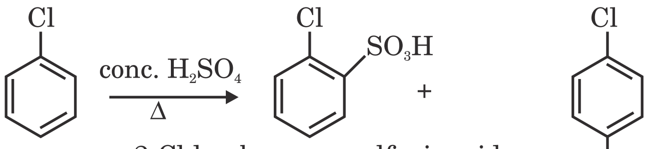
(ii) Nitration:



1-Chloro-2-nitrobenzene
(Minor)

1-Chloro-4-nitrobenzene
(Major)

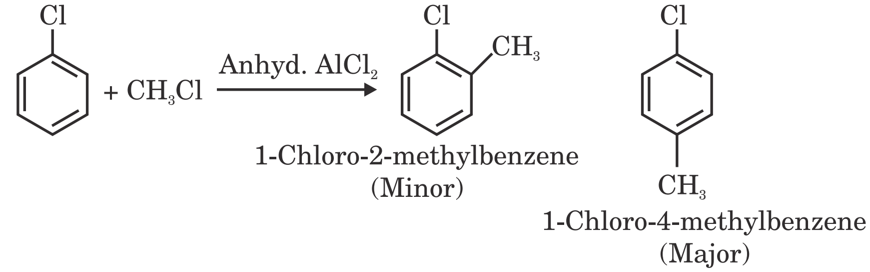
(iii) Sulphonation:



2-Chlorobenzene sulfonic acid
(Minor)

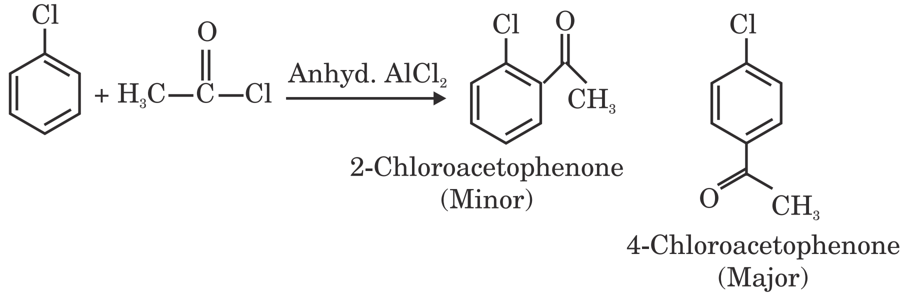
4-Chlorobenzene sulfonic acid
(Major)

(iv) Friedel-Crafts reaction:



1-Chloro-2-methylbenzene (Minor)

1-Chloro-4-methylbenzene (Major)



2-Chloroacetophenone (Minor)

4-Chloroacetophenone (Major)

- **Reaction with metals**

  (i) Wurtz-Fittig reaction

  Alkylarene is obtained on reaction of a mixture of alkyl halide and aryl halide with sodium in dry ether.

  (ii) Fittig reaction

  Analogous compounds are also formed in which two aryl groups are joined together.

- **Polyhalogen Compounds**
  - **Dichloromethane (Methylene chloride):** It is prepared industrially by the direct chlorination of methane.

$$CH_4 + 2Cl_2 \xrightarrow{h\upsilon} CH_2Cl_2 + 2HCl$$

Fractional distillation is used to separate the mixture so obtained. It is used as a solvent, as a paint remover, as a propellant in aerosols and also as a metal cleaning and finishing solvent.

  - **Trichloromethane (Chloroform):** It is manufactured by chlorination of methane followed by separation by fraction.

$$CH_4 + 3Cl_2 \xrightarrow[\text{Sunlight}]{h\upsilon} CHCl_3 + 3HCl$$

It is extensively used as solvent for waxes, resins, rubber, fats etc. Earlier, chloroform was used as anesthetic but at present this practice has been dropped as it is slowly oxidized by air in the presence of light to form highly poisonous phosgene gas. Therefore, it is stored in closed dark coloured bottles completely filled so that air is kept out.

- **Triiodomethane (Iodoform):** It is prepared by heating ethanol or acetone with sodium hydroxide or Na_2CO_3 and I_2 in water. It is insoluble in water and thus forms yellow precipitate of CHI_3.

$$CH\ CH_2OH + 6NaOH + 4I_2 \xrightarrow{\Delta} CHI_3 + 5NaI + HCOONa + 5H_2O$$

$$CH_3COCH_3 + 4NaOH + 3I_2 \xrightarrow{\Delta} CHI_3 + 3NaI + CH_3COONa + 3H_2O$$

It is used as an antiseptic for dressing wounds.

- **Tetrachloromethane (Carbon tetrachloride):** It is prepared by chlorination of methane and by action of chlorine on CS_2 in the presence of $AlCl_3$ as catalyst.

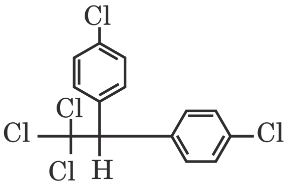
$$CS_2 + 3Cl_2 \xrightarrow[\Delta]{AlCl_3} CCl_4 + SCl_2$$

$$\left(\text{Sulphur dichloride}\right)$$

$$CH_4 + 4Cl_2 \xrightarrow{h\upsilon} CCl_4 + 4HCl$$

It is used in fire extinguisher. Also, it is used as solvent for fats, resins etc.

- **Freons:** The chlorofluorocarbon compounds of methane and ethane are collectively known as freons. They are extremely stable, unreactive, non-toxic, non-corrosive and easily liquefiable gases.
- **p, p'-Dichlorodiphenyltrichloroethane(DDT):** It is non-biodegradable and extremely stable. It is used as an insecticide. It is manufactured by the condensation of chlorobenzene with chloral in the presence of sulphuric acid. It was earlier used to control malaria and typhoid but due to its highly toxic nature, it was banned in India and USA.



DDT

PREVIOUS YEARS'

EXAMINATION QUESTIONS

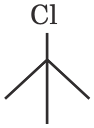
TOPIC 2

1 Mark Questions

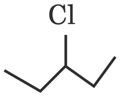
1. What happens when CH_3-Br is treated with KCN?

[DELHI 2013]

2. Which compound in the following pair undergoes faster S_N^1 reaction?



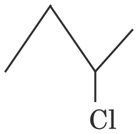
and

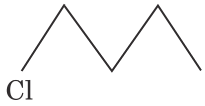


[DELHI 2013]

3. Identify the chiral molecule in the following pair:

[ALL INDIA 2014]

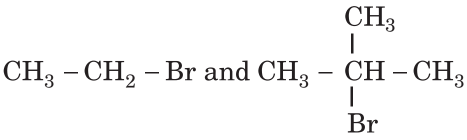




4. Which would undergo S_N2 reaction faster in the following pair: **[ALL INDIA 2015]**

$$C_6H_5CH_2CH_2CH_2Br \text{ and } C_6H_5-\underset{\displaystyle Br}{\underset{|}{CH}}-CH_3$$

5. Which would undergo S_N2 reaction faster in the following pair and why? **[DELHI 2015]**



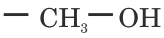
$$CH_3-CH_2-Br \text{ and } CH_3-\overset{\displaystyle CH_3}{\overset{|}{\underset{\displaystyle Br}{\underset{|}{CH}}}}-CH_3$$

Topic 1: Alcohols and Phenols

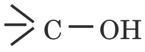
Summary

- **Alcohols:** Alcohols have the general formula as $C_nH_{2n+1}OH$ and they are obtained when one hydrogen atom in alkane is replaced by –OH group.
- **Classification of alcohols:**
  - Alcohols which have one hydroxyl group are called monohydric alcohols.
  - Alcohols which have 2 hydroxyl groups are called dihydric alcohols.
  - Alcohols which have 3 hydroxyl groups are called trihydric alcohols.
  - Alcohols which have many hydroxyl groups are called polyhyric alcohols.
  - Monohydric alcohols are further classified according to the hybridization of the carbon atom to which hydroxyl group is attached as shown below:

(i) **Compounds containing $C_{sp^3}-OH$ bond:** In this type of alcohols the –OH group is attached to an sp^3 hybridised carbon atom of an alkyl group.


Primary (1°)

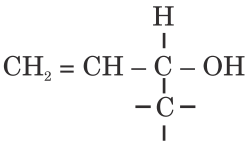

Secondary (2°)

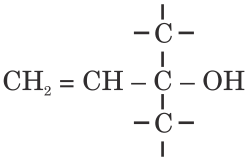

Tertiary (3°)

(ii) **Allylic alcohols:** In this type of alcohols the –OH group is attached to an sp^3 hybridised carbon next to the C-C double bond, which is an allylic carbon.

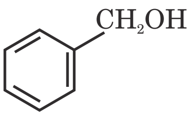
$CH_2=CH-CH_2-OH$

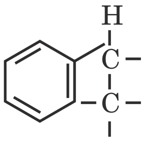
Primary

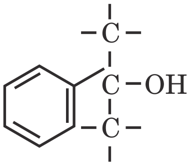

$$CH_2=CH-\overset{\displaystyle H}{\underset{\displaystyle -C-}{C}}-OH$$
Secondary


$$CH_2=CH-\overset{\displaystyle -C-}{\underset{\displaystyle -C-}{C}}-OH$$
Tertiary

(iii) **Benzylic alcohols:** In this type of alcohols the –OH group is attached to a sp^3-hybridised carbon atom attached to the benzene ring.


Primary

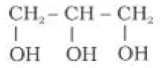
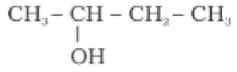

Secondary


Tertiary

(iv) **Vinylic alcohol:** In this type of alcohols –OH group is bonded to the C-C double bond i.e. to a vinylic carbon or to an aryl carbon.

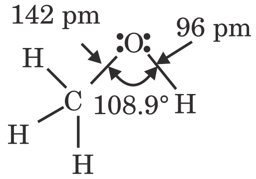
$CH_2=CH-OH$

- Common and IUPAC names of some alcohols are given below in the table:

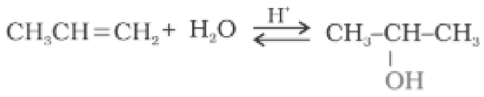
Compound	Common name	IUPAC name
CH_3-OH	Methyl alcohol	Methanol
$CH_3-CH_2-CH_2-OH$	n-Propyl alcohol	Propan-1-ol
 $\underset{OH}{CH_2}-\underset{OH}{CH}-\underset{OH}{CH_2}$	Glycerol	Propane-1, 2, 3-triol
 $CH_3-\underset{OH}{CH}-CH_2-CH_3$	Sec-Butyl alcohol	Butan-2-ol

- **Structure of alcohol:**

In alcohols, the oxygen of the –OH group is attached to sp^3 hybridized carbon by a sigma bond.

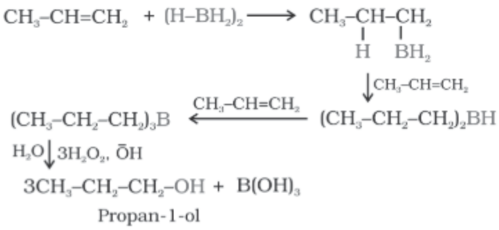


- **Preparation of Alcohols:**
  - **From alkenes:** alcohol is prepared when alkenes react with water in presence of acid as catalyst.



$$CH_3CH=CH_2+H_2O \overset{H^+}{\rightleftharpoons} CH_3-\underset{OH}{CH}-CH_3$$

  - **By hydroboration-oxidation:**



  - **From carbonyl compounds:**

(i) **By reduction of aldehydes and ketones:** Corresponding alcohols are produced by the reduction of aldehydes and ketones by addition of hydrogen in the presence of catalysts.

$$RCHO + H_2 \xrightarrow{Pd} RCH_2OH$$

$$RCOR' \xrightarrow{NaBH_4} R-\underset{OH}{CH}-R'$$

(ii) **By reduction of carboxylic acids and esters:** In the presence of strong agent, lithium aluminium hydride, carboxylic acids are reduced to primary alcohols.

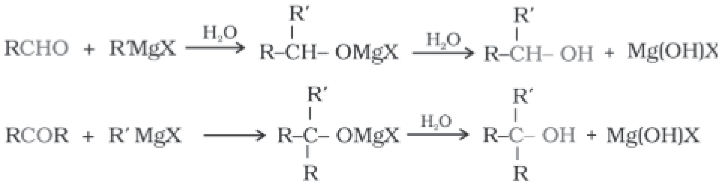
$$RCOOH \xrightarrow[\text{(ii) } H_2O]{\text{(i) } LiAlH_4} RCH_2OH$$

Commercially, acids are reduced to alcohols by first converting them to esters and then following catalytic hydrogenation.

$$RCOOH \xrightarrow[H^+]{R'OH} RCOOR' \xrightarrow[\text{Catalyst}]{H_2} RCH_2OH + R'OH$$

- **From Grignard reagents:** The reaction of Grignard reagent with formaldehyde produces a primary alcohol, with other aldehydes it reacts to give secondary alcohols and tertiary alcohols are produced on reaction of Grignard reagent with ketones.

$$HCHO + RMgX \rightarrow RCH_2OMgX \xrightarrow{H_2O} RCH_2OH + Mg(OH)X$$



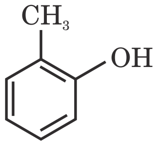
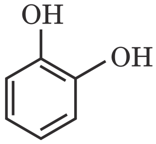
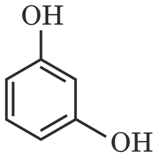
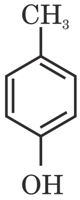
$$RCHO + R'MgX \xrightarrow{H_2O} R\text{–}\overset{R'}{\overset{|}{C}}H\text{– }OMgX \xrightarrow{H_2O} R\text{–}\overset{R'}{\overset{|}{C}}H\text{– }OH + Mg(OH)X$$

$$RCOR + R'MgX \longrightarrow R\text{–}\underset{R}{\underset{|}{\overset{R'}{\overset{|}{C}}}}\text{– }OMgX \xrightarrow{H_2O} R\text{–}\underset{R}{\underset{|}{\overset{R'}{\overset{|}{C}}}}\text{– }OH + Mg(OH)X$$

➢ **Phenols:**

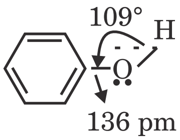
- It is the simplest hydroxyl derivative of benzene. In its substituted compounds the terms ortho (1, 2- disubstituted), meta (1, 3 –disubstituted) and para (1, 4- disubstituted) are often used in common names.

➢ **Common name and IUPAC name of some phenols are given below in the table:**

Compound	**Common name**	**IUPAC name**
	o-Cresol	2-Methylphenol
	Catechol	Benzene-1, 2-diol
	Resorcinol	Benzene-1, 3-diol
	p-Cresol	4-Methyphenol

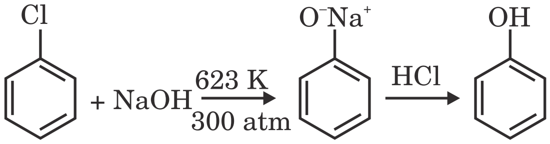
➢ **Structure of Phenols:**

In phenols, the –OH group is attached to the sp^2 hybridised carbon of an aromatic ring.

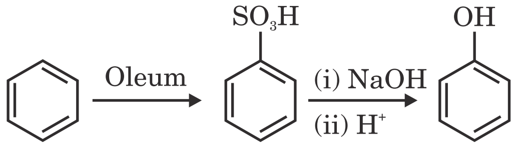


➢ **Preparation of Phenols:**

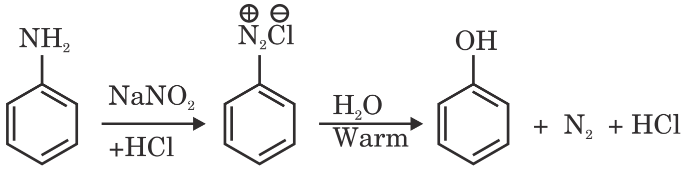
- **From haloarenes:**



- **From benzenesulphonic acid:**

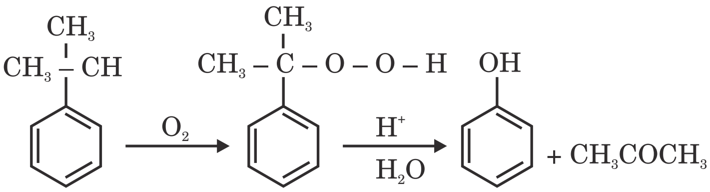


- **From diazonium salts:**



Aniline Benzene diazonium chloride

- **From cumene:**

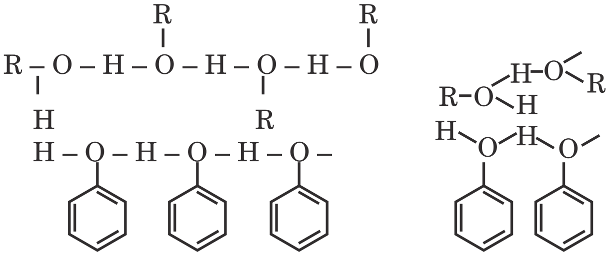


Cumene Cumene hydroperoxide

- **Physical properties of alcohols and phenols:**
  - **Boiling Points:** With increase in the number of carbon atoms van der Waal's forces increase which in turn increases the boiling point of alcohols and phenols. With increase of branching in carbon chain the Van der Waals forces decreases with decrease in surface area which in turn decreases the boiling point of alcohols.

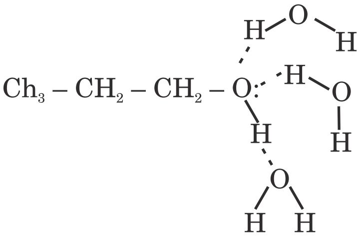
    The high boiling points of alcohols and phenols is mainly because of the presence of intermolecular hydrogen bonding in them which is lacking in ether and hydrocarbons.

    The –OH group in alcohols and phenols is involved in intermolecular hydrogen bonding as shown below:



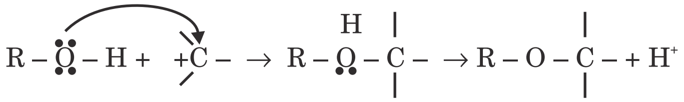
  - **Solubility:** Solubility of alcohols and phenols in water is because of their ability to form hydrogen bonds with water molecules.

    With increase in the size of the aryl/alkyl groups the solubility decreases.



Chemical Reactions

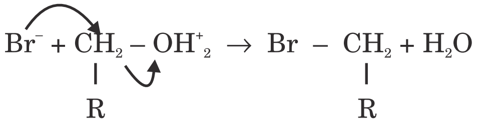
Alcohols react as nucleophiles and electrophiles. When alcohols react as nucleophile the bond between –OH is broken.



$$R-\ddot{O}-H + \overset{+}{C}- \rightarrow R-\underset{}{\overset{H}{\ddot{O}}}-\overset{|}{\underset{|}{C}}- \rightarrow R-O-\overset{|}{\underset{|}{C}}- + H^+$$

When they react as electrophile the bond between C-O is broken.

$$R-CH_2-OH+\overset{+}{H} \rightarrow R-CH_2-\overset{+}{O}H_2$$

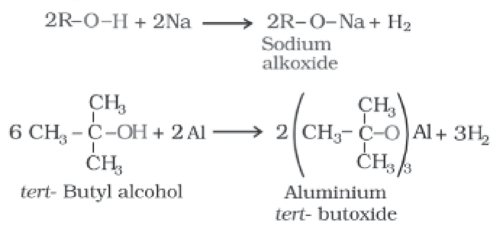


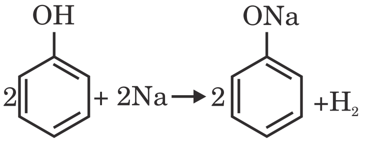
$$Br^- + \underset{R}{\underset{|}{CH_2}}-OH_2^+ \rightarrow Br-\underset{R}{\underset{|}{CH_2}} + H_2O$$

- **Reactions of alcohols and phenols involving cleavage of O-H bond:**

  1. **Acidity of alcohols and phenols:**

     (i) **Reaction with metals:** They react with active metals like sodium, potassium and aluminium to give corresponding alkoxides/phenoxides and hydrogen.

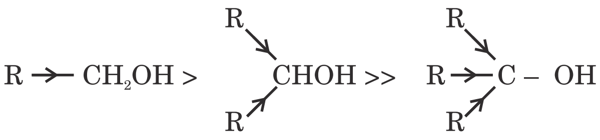




Phenol Sodium phenoxide

     (ii) **Acidity of alcohols:** The polar nature of O-H brings the acidic character in alcohols. The electron releasing group increase electron density on oxygen which decreases the polarity of O-H bond hence decreases the acid strength.

     The acid strength of alcohols decrease in the following order:



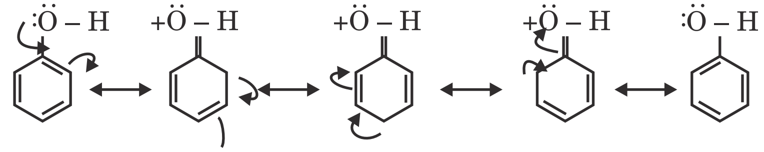
$$R \rightarrow CH_2OH > R_2 \rightarrow CHOH >> R_3 \rightarrow C-OH$$

Primary Secondary Tertiary

     Alcohols are weaker acids than water.

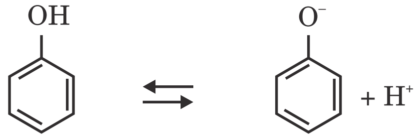
     Alcohols act as Bronsted bases due to the presence of unshared electron pairs on oxygen.

(iii) **Acidity of phenols:** Phenols are more acidic than alcohols and water. In phenol the hydroxyl group is attached directly to the sp^2 –hybridised carbon of the benzne ring which acts as an electron withdrawing group. Due to this, the charge distribution in phenol molecule, causes the oxygen of –OH group to be positive.

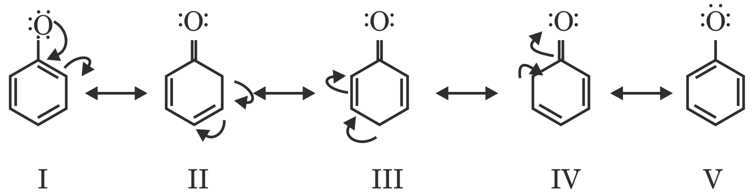


The ionization of an alcohol and a phenol takes place producing alkoxide and phenoxide ions as shown below:

$$R-\ddot{\underset{\cdot\cdot}{O}}-H \rightleftharpoons R-\ddot{\underset{\cdot\cdot}{O}}:^{-} \quad + H^{+}$$



In alkoxideion, the negative charge is localized on oxygen while in phenoxide ion, the charge is delocalized. The delocalization of negative charge makes phenoxide ion more stable and favours the ionization of phenol.



2. **Esterification:** Esters are formed when alcohols and phenols react with carboxylic acids, acid chlorides and acid anhydrides.

The reactions are given below:

$$Ar/RO-H \ + R'-COOH \overset{H^+}{\rightleftharpoons} Ar/ROCOR' + H_2O$$

$$Ar/R-OH + (R'CO)_2O \overset{H^+}{\rightleftharpoons} Ar/ROCOR' + R'COOH$$

$$R/ArOH + R'COCl \xrightarrow{Pyridine} R/ArOCOR' + HCl$$

- **Reactions involving cleavage of C-O bond in alcohols:**

Only alcohols undergo this type of reactions which involves cleavage of C-O bond. In phenols this type of reaction takes place only with zinc.

1. **Reaction with hydrogen halides:**

$$R-OH \ + \ HX \xrightarrow{ZnCl_2} R-X \ + \ H_2O$$

2. **Reaction with phosphorus trihalides:**

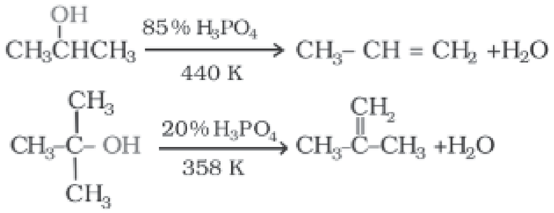
$$3R-OH + PX_3 \longrightarrow 3R-X + H_3PO_3 \qquad (X = Cl, Br)$$

3. **Dehydration:**

Dehydration of ethanol is given below:

$$C_2H_5OH \xrightarrow[443\ K]{H_2SO_4} CH_2 = CH_2 + H_2O$$

Dehydration of secondary and tertiary alcohols take place under milder condition and reaction is shown below:



$$CH_3\underset{}{\overset{OH}{C}}HCH_3 \xrightarrow[440\ K]{85\%\ H_3PO_4} CH_3-CH=CH_2 + H_2O$$

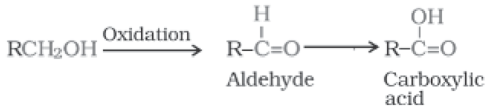
$$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-OH \xrightarrow[358\ K]{20\%\ H_3PO_4} CH_3-\overset{CH_2}{\overset{\|}{C}}-CH_3 + H_2O$$

The order of dehydration of alcohols is shown as:

Tertiary > Secondary > Primary

4. **Oxidation:**

Primary alcohol can be oxidized to aldehyde which on further oxidizing gives carboxylic acid which depends on the type of oxidizing agent used.



$$RCH_2OH \xrightarrow{Oxidation} \underset{\text{Aldehyde}}{R-\overset{H}{C}=O} \longrightarrow \underset{\text{Carboxylic acid}}{R-\overset{OH}{C}=O}$$

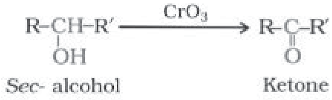
As an oxidizing agent CrO_3 can be used for isolating aldehyde.

$$RCH_2OH \xrightarrow{CrO_3} RCHO$$

Pyridinium chloromate (PCC) can be used an oxidizing reagent to get aldehyde from primary alcohols.

$$CH_3-CH=CH-CH_2OH \xrightarrow{PCC} CH_3-CH=CH-CHO$$

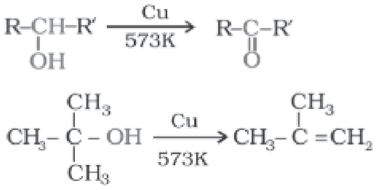
On oxidizing secondary alcohols gives ketone using CrO_3 as an oxidizing agent.



$$\underset{\textit{Sec-}\text{ alcohol}}{R-\underset{OH}{C}H-R'} \xrightarrow{CrO_3} \underset{\text{Ketone}}{R-\underset{O}{\underset{\|}{C}}-R'}$$

5. **Dehydrogenation:**

$$RCH_2OH \xrightarrow[573K]{Cu} RCHO$$



$$R-\underset{OH}{C}H-R' \xrightarrow[573K]{Cu} R-\underset{O}{\underset{\|}{C}}-R'$$

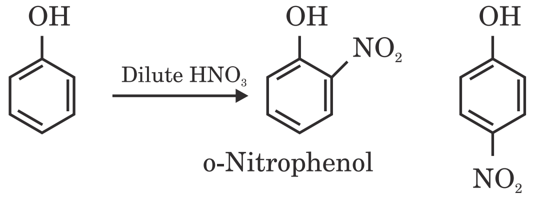
$$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-OH \xrightarrow[573K]{Cu} CH_3-\overset{CH_3}{C}=CH_2$$

- **Reactions of phenols:**

Following are the reactions of phenols:

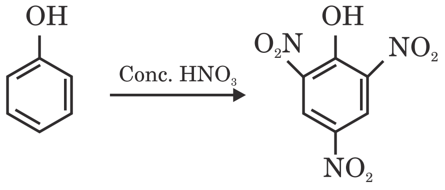
1. **Electrophilic aromatic substitution:**

(i) **Nitration:**



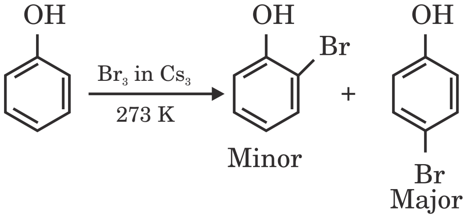
o-Nitrophenol

p-Nitrophenol

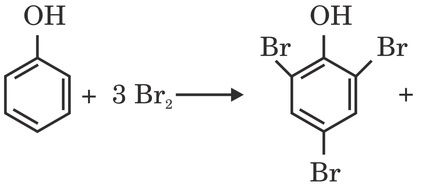


2.4.6-Trinitrophenol
(Picric acid)

(ii) **Halogenation:**

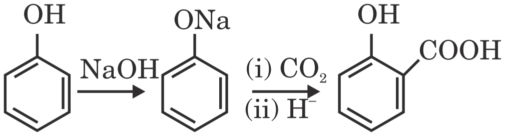


Treatment of phenol with bromine water is shown below:



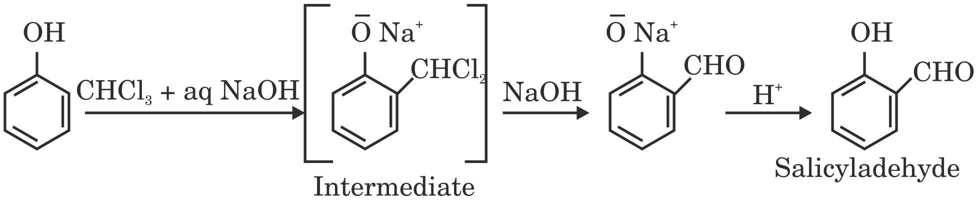
2,4,6-Tribomophenol

2. **Kolbe's reaction:**

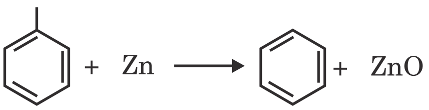


2-Hydroxybenzoic acid
(Salicylic acid)

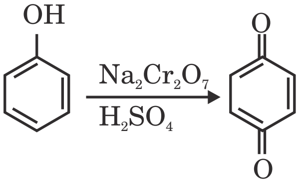
3. **Reimer- Tiemann reaction:**



4. **Reaction of phenol with zinc dust:**



5. **Oxidation:**



benzoquinone

- **Some commercially important alcohols are given below:**

1. **Methanol:**
   - **Physical properties:**

   Methanol is also known by the name 'wood spirit'.

   It is a colourless liquid which boils at 337 K.

   In paints, varnishes it is used as a solvent.

   - **Preparation of Methanol:**By catalytic hydrogenation of carbon monoxide.

$$CO + 2H_2 \xrightarrow[\substack{200\text{-}300\ \text{atm} \\ 573\text{-}673\ \text{K}}]{ZnO\text{-}Cr_2O_3} CH_3OH$$

2. **Ethanol:**
   - **Physical properties:**

   It is a colourless liquid which boils at 351 K.

   It is made unfit for drinking by mixing it with some copper sulphate which gives it some colour and pyride which gives it a foul smell. This complete process is called denaturation of alcohol.

   - **Preparation of Ethanol:**

   Ethanol is prepared by fermentation of glucose and fructose in presence of enzyme, Zymase, which is found in yeast.

   Glucose and fructose are produced from sugar in the presence of enzyme, invertase.

   The reactions are given below:

$$C_{12}H_{22}O_{11} + H_2O \xrightarrow{\text{Invertase}} \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Fructose}}{C_6H_{12}O_6}$$

$$C_6H_{12}O_6 \xrightarrow{\text{Zymase}} 2C_2H_5OH + 2CO_2$$

PREVIOUS YEARS'

EXAMINATION QUESTIONS

TOPIC 1

1 Mark Questions

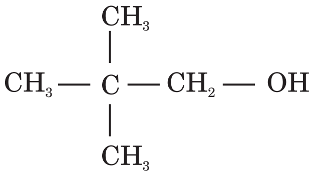
1. Draw the structure of hex-l-en-3-ol compound. **[DELHI 2012]**

2. Draw the structural formula of 2-methylpropan -2-ol molecule. **[ALL INDIA 2012]**

3. What happens when ethyl chloride is treated with aqueous KOH? **[DELHI 2013]**

4. Which of the following isomers is more volatile: o-nitrophenol or p-nitrophenol? **[DELHI 2014]**

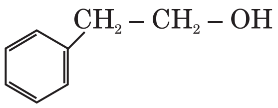
5. Write the IUPAC name of the given compound



$$CH_3 - \overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}} - CH_2 - OH$$

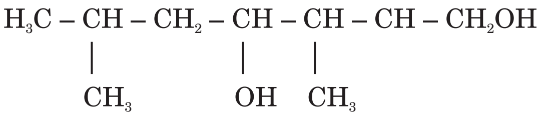
[ALL INDIA 2015]

6. Write IUPAC name of given compound:



[ALL INDIA 2016]

7. Write the IUPAC name of the following compound:



$$H_3C - \underset{\underset{\displaystyle CH_3}{|}}{CH} - CH_2 - \underset{\underset{\displaystyle OH}{|}}{CH} - \underset{\underset{\displaystyle CH_3}{|}}{CH} - CH - CH_2OH$$

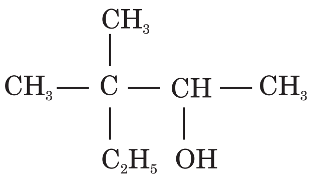
[DELHI 2016]

8. Give the IUPAC name of the following compound:

$$H_2C = CH - \underset{\underset{\displaystyle OH}{|}}{CH} - CH_2 - CH_2 - CH_3$$

[DELHI 2017]

9. Write the IUPAC name of the following:



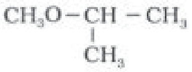
$$CH_3 - \overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle C_2H_5}{|}}{C}} - \underset{\underset{\displaystyle OH}{|}}{CH} - CH_3$$

[ALL INDIA 2018]

Topic 2: Ethers

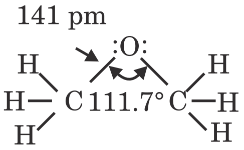
Summary

- They are represented by $R-0-R^{'}$ and have the general formula $C_nH_{2n+2}O$.
- **Ethers are classified into 2 categories:**
  - **Simple or symmetrical:** When the alkyl or aryl groups attached to the oxygen atom are the same. Example: $C_2H_5OC_2H_5$
  - **Mixed or unsymmetrical:** When the alkyl or aryl groups attached to the oxygen atom are different. Example: $C_2H_5OCH_3$
- **Common names and IUPAC names of some ethers are given below:**

Compound	**Common name**	**IUPAC name**
CH_3OCH_3	Dimethyl ether	Methoxymethane
$C_2H_5OCH_3$	Diethyl ether	Ethoxyethane
$C_6H_5OCH_3$	Methylphenyl ether	Methoxybenzene
 $CH_3O-\underset{\displaystyle CH_3}{CH}-CH_3$	Methyl isopropyl ether	2-Methoxypropane

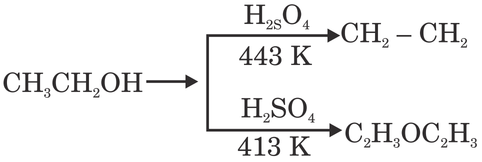
- **Structure of ether:**

The four electron pairs in ether, i.e. the two bond pairs and the two lone pairs of electrons are arranged approximately in tetrahedral arrangement as shown below:



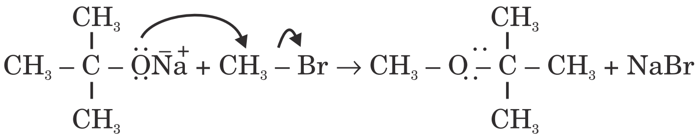
Methoxymethane

- **Preparation of Ethers:**
  - **By dehydration of alcohols:** In the presence of protic acid. The product which is formed in the reaction depends on the conditions of the reaction.



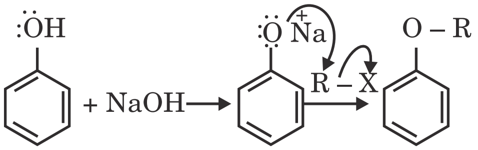
- **Williamson synthesis:** In this method alkyl halide reacts with sodium alkoxide.

$$R-X+R-\ddot{\underset{\cdot\cdot}{O}}\ Na \longrightarrow R-\ddot{\underset{\cdot\cdot}{O}}-R+Na\,X$$



$$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-\ddot{\underset{\cdot\cdot}{O}}\overset{-\ +}{Na}+CH_3-Br\rightarrow CH_3-\ddot{\underset{\cdot\cdot}{O}}-\underset{CH_3}{\overset{CH_3}{C}}-CH_3+NaBr$$

Phenols can also be converted to ethers using this method of preparation.

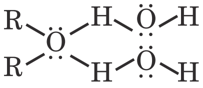


➢ Physical properties of ethers:

- The boiling point of ethers is lower than alcohols but is comparable to those of alkanes of the comparable molecular masses. The example is given below:

Formula	$CH_3(CH_2)_3CH_3$ n-Pentane	C_2H_5-O-C_2H_5 Ethoxyethane	$CH_3(CH_2)_3$-OH Butan-1-ol
b.p./K	309.1	307.6	390

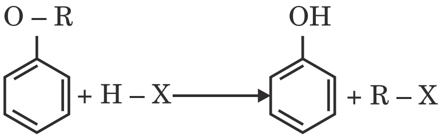
- The solubility of ethers in water is comparable to those of alcohols of the same molecular masses and this is because of the ability of the oxygen of the ether to form hydrogen bonds with water molecules.



➢ Chemical reactions of Ethers:

1. **Cleavage of C-O bond:** This cleavage takes place under severe conditions using excess of hydrogen halides.

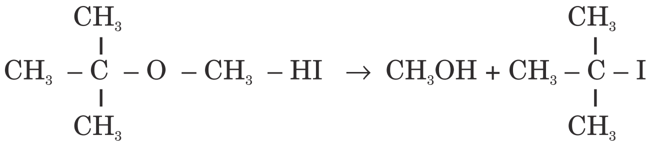
$$R\text{–}O\text{–}R + HX \longrightarrow RX + R\text{–}OH$$
$$R\text{–}OH + HX \longrightarrow R\text{–}X + H_2O$$



$$R\text{–}O\text{–}R' + HX \longrightarrow R\text{–}X + R'\text{–}OH$$

If one of the alkyl group is tertiary group then the halide formed will also be a tertiary halide.

Example:



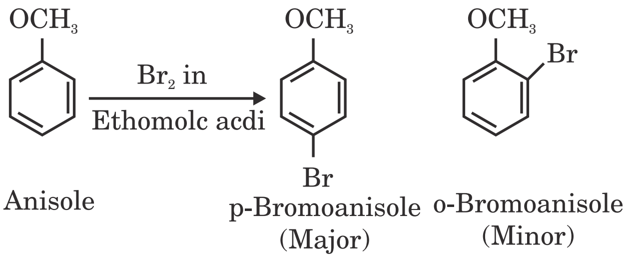
$$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-O-CH_3-HI \rightarrow CH_3OH + CH_3-\underset{CH_3}{\overset{CH_3}{C}}-I$$

The order of reactivity of hydrogen halides is given below:

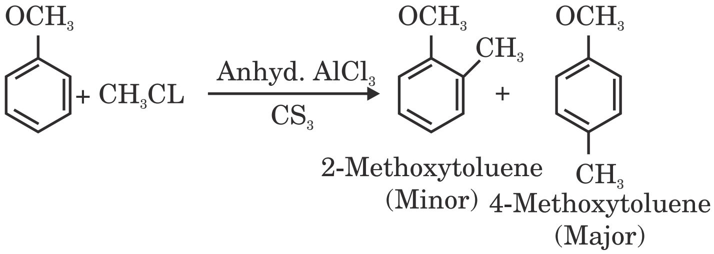
HI > HBr > HCl

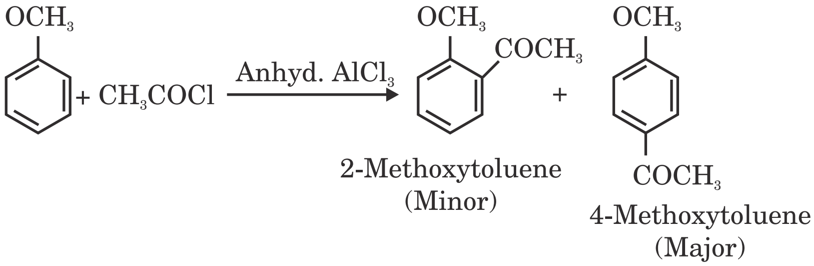
2. Electrophilic substitution:

(i) **Halogenation:**

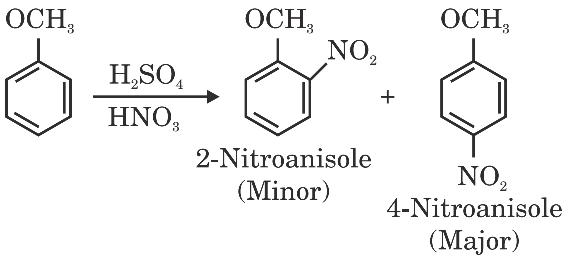


(ii) **Friedel – Crafts reaction:**





(iii) **Nitration:**

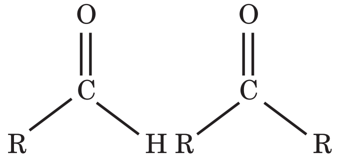


Topic 1: Aldehydes and ketones

Summary

They are the organic compounds containing carbon-oxygen double bond. (> C = O)

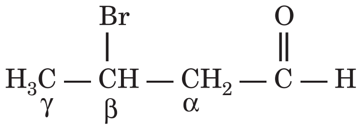
- The carbonyl group is bonded with a carbon and hydrogen in aldehydes and it is bonded to two carbon atoms in ketones.



Aldehyde Ketone

Nomenclature

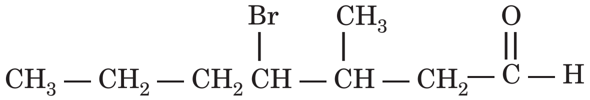
- **Common Names**
  - Instead of IUPAC names, common names are used for aldehydes and ketones.
  - The location of the substituent in the carbon chain is indicated by Greek letters α, β, γ etc, α-carbon being the one directly linked to the aldehyde group, carbon the next, and so on.



$$\underset{\gamma}{H_3C} - \underset{\beta}{\overset{Br}{\overset{|}{CH}}} - \underset{\alpha}{CH_2} - \overset{O}{\overset{\|}{C}} - H$$

β-Bromobutyraldehyde

- **IUPAC Names**
  - They are derived from IUPAC names of corresponding alkanes, by replacing ending e with –al in aldehydes and –one in ketones.
  - Longest carbon chain is numbered starting from the carbon of the aldehyde group while in case of ketones the numbering begins from the end nearer to the carbonyl group.



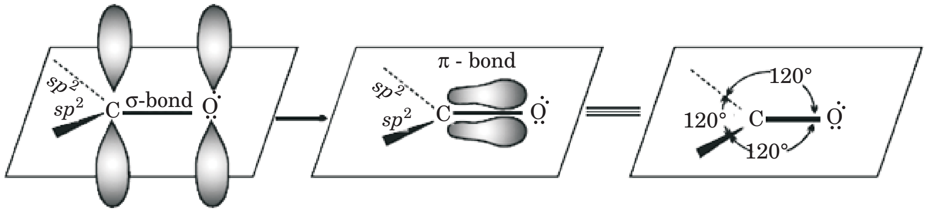
$$CH_3 - CH_2 - CH_2\ \overset{Br}{\overset{|}{CH}} - \overset{CH_3}{\overset{|}{CH}} - CH_2 - \overset{O}{\overset{\|}{C}} - H$$

4-Bromo-3-methylheptanal

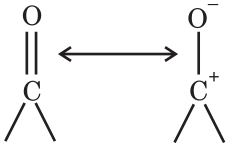
Structure of the Carbonyl Group

- The carbonyl carbon atom forms three sigma bonds and a π bond with oxygen and is sp^3 hybridized.

- The angles between the bonds is 120° as shown below

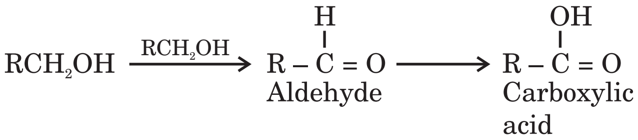


- As oxygen is more electronegative than oxygen, the carbon-oxygen double bond is polarized.



Preparation of Aldehydes and Ketones

- **Oxidation of alcohols**
- By oxidation of primary and secondary alcohols, aldehydes and ketones are prepared.

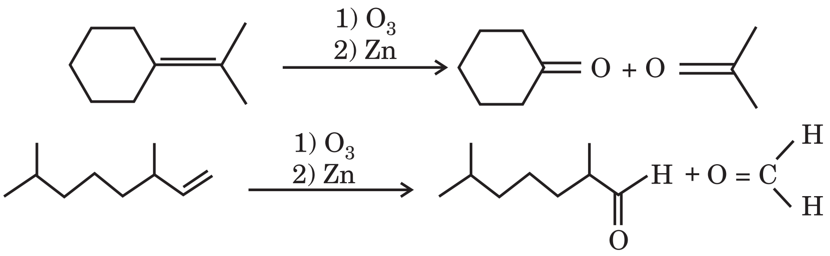


$$RCH_2OH \xrightarrow{RCH_2OH} \underset{\text{Aldehyde}}{R-\overset{H}{C}=O} \longrightarrow \underset{\text{Carboxylic acid}}{R-\overset{OH}{C}=O}$$

- Secondary alcohols are oxidized in presence of CrO^3 to ketones.
- **Dehydrogenation of alcohols**

$$\underset{1° \text{ Alcohol}}{R-CH_2-OH} \xrightarrow[573K]{Cu} \underset{\text{Aldehyde}}{RCHO + H_2}$$

- **Using hydrocarbons**
  - Using ozonolysis of alkenes



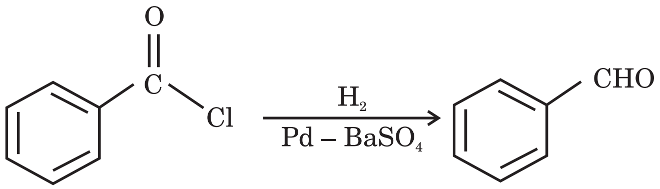
  - By hydration of alkynes

    Addition of water to ethyne in the presence of H_2SO_4 and $HgSO_4$ gives acetaldehyde

Preparation of Alhehydes

- **Rosenmund Reaction:**

Acid chloride is hydrogenated in presence of a catalyst (Palladium on Barium Sulphate)



Benzoyl chloride Benzaldehyde

- **Stephen Reaction:**

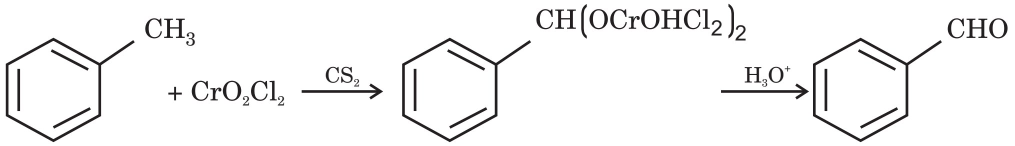
Nitrites are reduced to imine which on hydrolysis gives aldehyde.

$$RCN + SnCl_2 + HCl \longrightarrow RCH = NH \xrightarrow{H_3\overset{+}{O}} RCHO$$

- **From hydrocarbons**

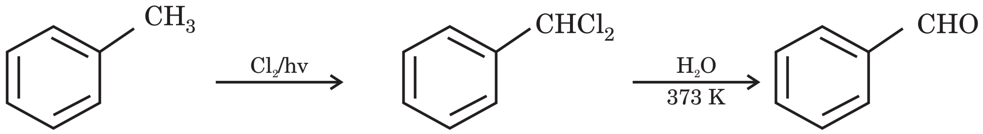
➢ By oxidation of methylbenzene

Etard Reaction:



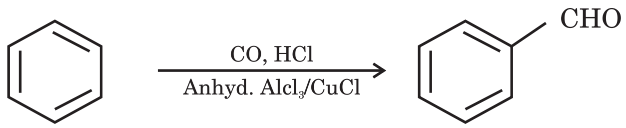
Toluene Chromium complex Benzaldehyde

By side chain chlorination followed by hydrolysis



Toluene Benzal chloride Benzaldehyde

Gatterman-Koch Reaction:

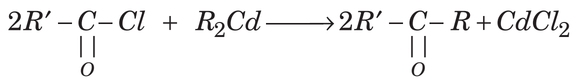


Benzal chloride Benzaldehyde

Preparation of Ketones

- **Using acyl chlorides**

$$2R - Mg - X \; + \; CdCl_2 \longrightarrow R_2Cd + 2Mg(X)Cl$$

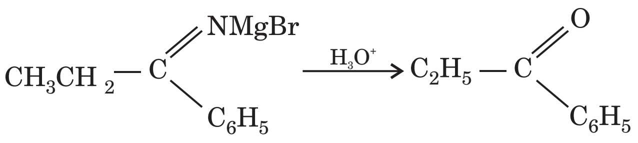


$$2R'-\underset{\underset{O}{||}}{C}-Cl + R_2Cd \longrightarrow 2R'-\underset{\underset{O}{||}}{C}-R + CdCl_2$$

- **Using nitriles**

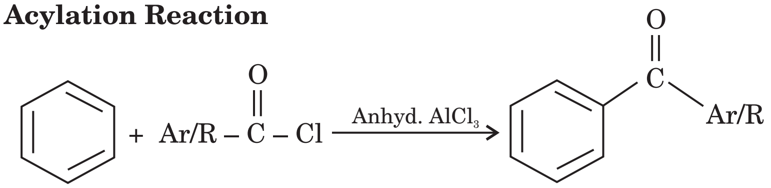
When nitriles are treated with Grignard reagent followed by hydrolysis, it gives ketones.

$CH_3 - CH_2 - C \equiv N + C_6H_5MgBr \xrightarrow{ether}$



Propiophenone
(1-Phenylpropanone)

- **Acylation Reaction**

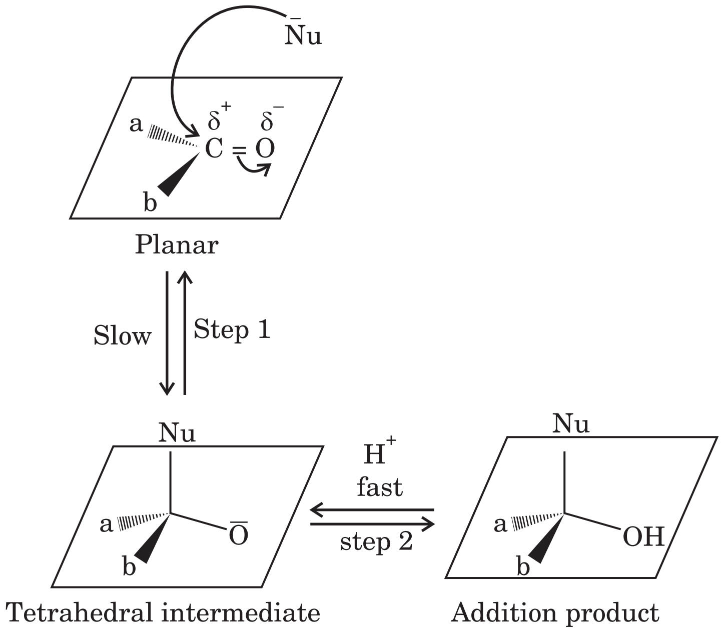


Physical Properties

- A large amount of aldehydes are liquids at room temperature.
- As aldehydes and ketones have hydrogen bonding capacity, they are soluble in water(upto 4 carbon atoms)
- Most of them have high boiling point when compared to hydrocarbons and higher than those of alcohols.

Chemical Properties

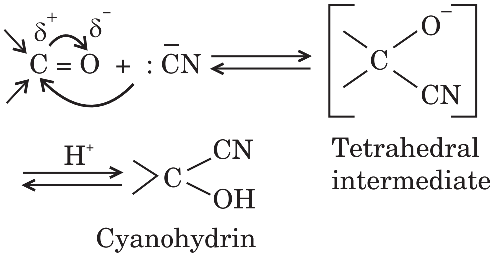
Nucleophilic Addition Reactions



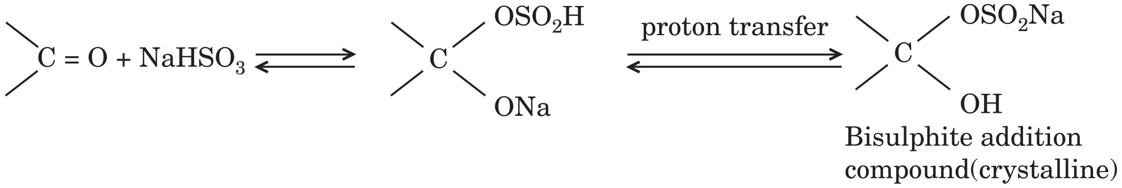
- **Addition of hydrogen cyanide:**

Cyanohydrins are obtained when aldehydes and ketones are treated with

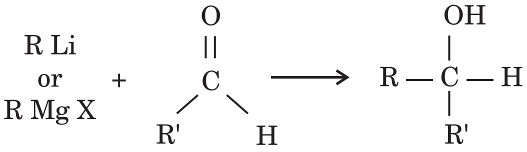
$$HCN + OH^- \rightleftharpoons :\overline{C}N + H_2O$$



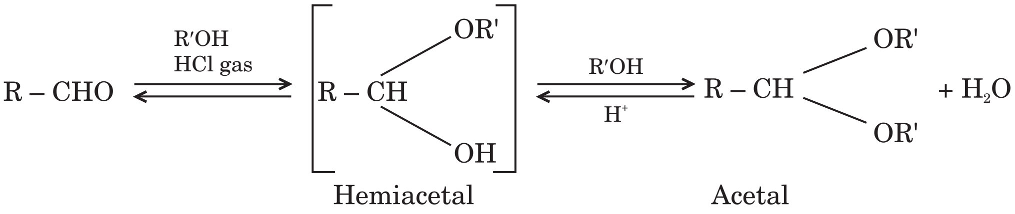
- **Addition of sodium hydrogensulphite**



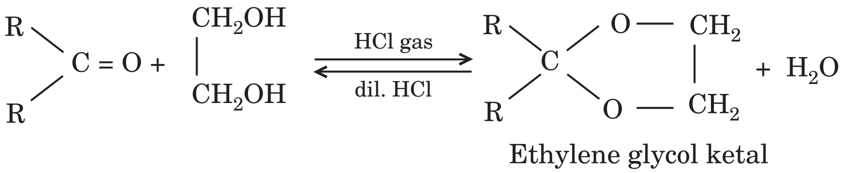
- **Addition of Grignard Reagent**



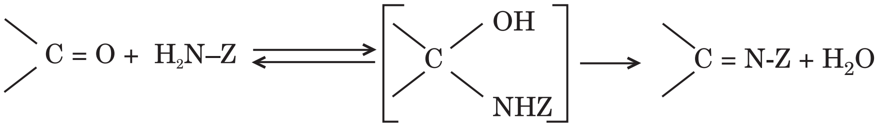
- **Addition of alcohols**



Ketones don’t react with monohydric alcohols but react with dihydric alcohols to give ketals.



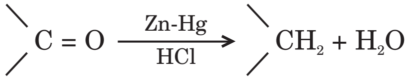
- **Addition of ammonia**



Reduction Reactions

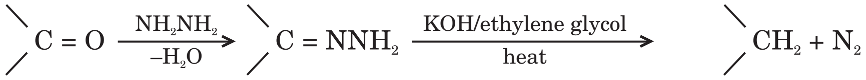
- **Clemmensen Reduction or Wolf Kishner Reduction:**

  The carbonyl group is reduced to CH_2 group as shown below



$$>C=O \xrightarrow[\text{HCl}]{\text{Zn-Hg}} >CH_2 + H_2O$$

(Clemmensen reduction)



$$>C=O \xrightarrow[-H_2O]{NH_2NH_2} >C=NNH_2 \xrightarrow[\text{heat}]{\text{KOH/ethylene glycol}} >CH_2 + N_2$$

(wolff-Kishner reduction)

- **Reduction to alcohols**

  In presence of $NaBH_4$, a primary alcohol is obtained while in presence of LiAIH_4, a secondary alcohol is obtained.

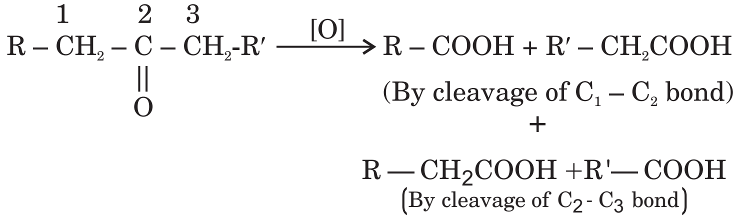
$$R-CHO+2[H]\xrightarrow{LiAlH_4}R-CH_2-OH$$

Oxidation

- On oxidation, aldehydes result in carboxylic acids on treatment with nitric acid, and mild oxidizing agents like Tollen's reagent and Fehling's reagent.

$$R-CHO\xrightarrow{[O]}R-COOH$$

- Ketones are oxidized by strong oxidizing agents at high temperatures which involves the cleavage of carbon-carbon bond.



$$R-\overset{1}{CH_2}-\underset{\underset{O}{\|}}{\overset{2}{C}}-\overset{3}{CH_2}\text{-}R' \xrightarrow{[O]} R-COOH+R'-CH_2COOH$$

(By cleavage of C_1-C_2 bond)

$+$

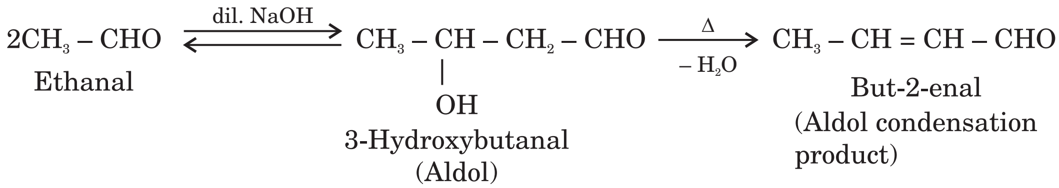
$$R-CH_2COOH+R'-COOH$$

(By cleavage of C_2 - C_3 bond)

Reactions due to α hydrogen

- Aldol Condensation

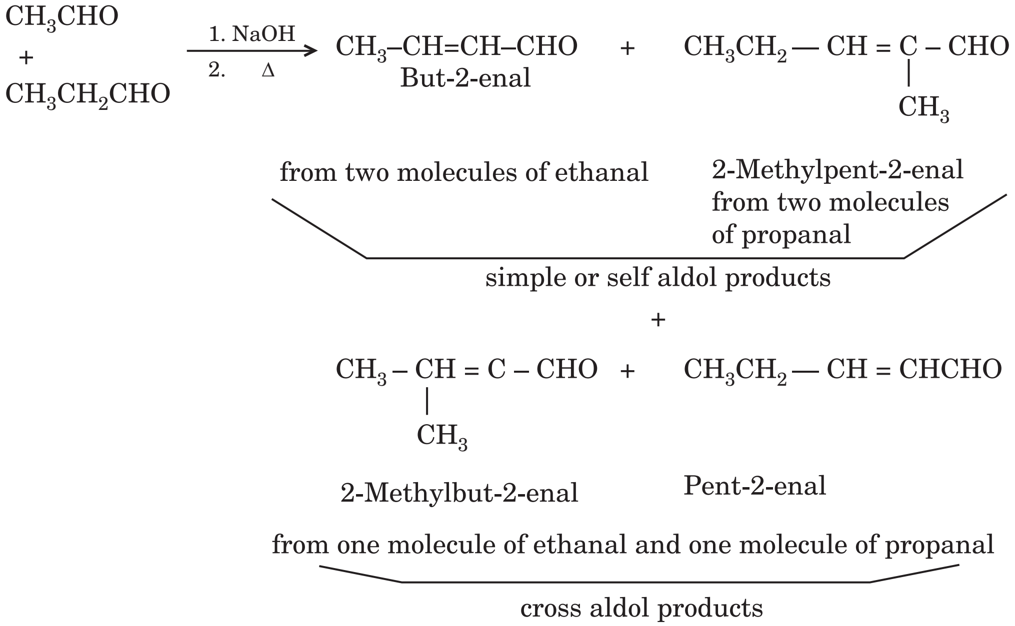
  β hydroxyl aldehydes or β hydroxyl ketones are obtained when Aldehydes and ketones having at least one α-hydrogen undergo a reaction in the presence of dilute alkali as catalyst.



$$\underset{\text{Ethanal}}{2CH_3-CHO} \xrightleftharpoons{\text{dil. NaOH}} \underset{\substack{\text{3-Hydroxybutanal}\\\text{(Aldol)}}}{CH_3-\underset{\underset{OH}{|}}{CH}-CH_2-CHO} \xrightarrow[-H_2O]{\Delta} \underset{\substack{\text{But-2-enal}\\\text{(Aldol condensation}\\\text{product)}}}{CH_3-CH=CH-CHO}$$

- **Cross Aldol Condensation**

  When two different aldehydes or/and ketones undergo aldol condensation, it is known as cross aldol condensation.



$$\begin{matrix}CH_3CHO\\ +\\ CH_3CH_2CHO\end{matrix} \xrightarrow[2.\ \Delta]{1.\ NaOH} \underset{\text{But-2-enal}}{CH_3{-}CH{=}CH{-}CHO} + CH_3CH_2{-}CH{=}\underset{\underset{CH_3}{|}}{C}{-}CHO$$

from two molecules of ethanal

2-Methylpent-2-enal from two molecules of propanal

simple or self aldol products

+

$$CH_3{-}\underset{\underset{CH_3}{|}}{CH}{=}C{-}CHO + CH_3CH_2{-}CH{=}CHCHO$$

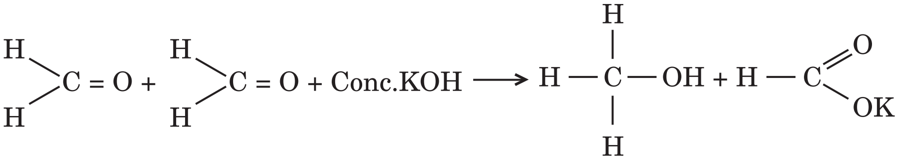
2-Methylbut-2-enal　　Pent-2-enal

from one molecule of ethanal and one molecule of propanal

cross aldol products

Other Reactions

- **Cannizzaro Reaction**:
  In this reaction, one molecule of the aldehyde is reduced to alcohol while another is oxidised to carboxylic acid salt.

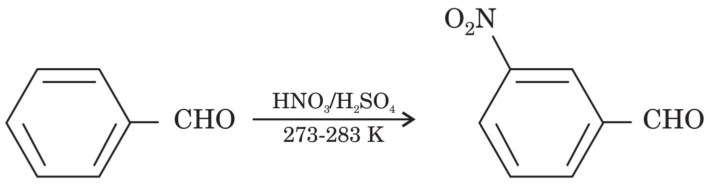


$$\begin{matrix}H\\ \ \end{matrix}\!\!>C=O + \begin{matrix}H\\ \ \end{matrix}\!\!>C=O + \text{Conc.KOH} \longrightarrow H{-}\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}}{-}OH + H{-}C\begin{matrix}{=}O\\ {-}OK\end{matrix}$$

Methanol　　Potassium formate

- **Electrophilic Substitution**

  Aromatic aldehydes and ketones undergo this reaction.



Benzaldehyde　　m-Nitrobenzaldehyde

Uses of Aldehydes and Ketones

- Formalin solution (Formaldehyde) is used in preserving biological specimens and to prepare polymer products.
- Many aldehydes and ketones have a pleasant smell and flavor.
- Acetaldehyde is used as a starting material to manufacture acetic acid, polymers and drugs.

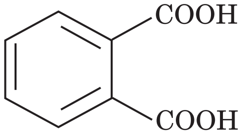
Topic 2: Carboxylic Acids

Summary

- These are the carbon compounds containing $-COOH$ functional group.
- Carboxylic acids may be aliphatic ($RCOOH$)or aromatic ($ArCOOH$) depending on the group, alkyl or aryl, attached to carboxylic carbon.

Nomenclature

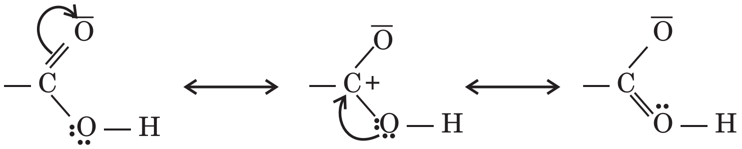
- Many of the carboxylic acids are known by their common names. Example: Ethanoic Acid is called as Acetic acid.
- In the IUPAC system, aliphatic carboxylic acids are named by replacing the ending –e in the name of the corresponding alkane with – oic acid.
- In numbering the carbon chain, the carboxylic carbon is numbered one. Example: The IUPAC name of is



is Benzene-1, 2-dicarboxylic acid.

Structure of Carboxyl Group

- The bonds are in one plane and the angle between the bonds is 120°.
- Due to difference in electrophilic nature, resonance is present as shown below:



Preparation of Carboxylic Acids

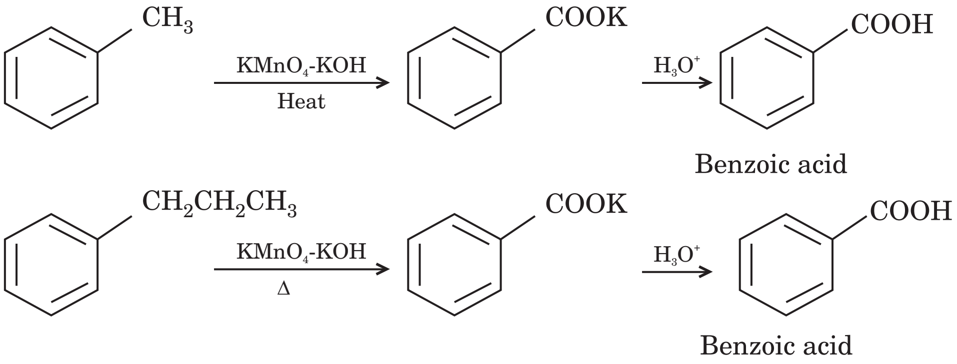
- **From primary alcohols and aldehydes**

  In the presence of oxidizing agents like potassium permanganate and potassium dichromate, primary alcohols are oxidized to carboxylic acids.

$$RCH_2OH \xrightarrow[\text{2. } H_3O^{\oplus}]{\text{1. alkaline } KMnO_4} RCOOH$$

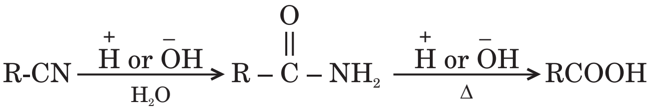
$$\underset{\text{1–Decanol}}{CH_3(CH_2)_8CH_2OH} \xrightarrow{CrO_3-H_2SO_4} \underset{\text{Decanoic acid}}{CH_2(CH_2)_8COOH}$$

- **From alkylbenzenes:**



- **Using nitriles and amides**

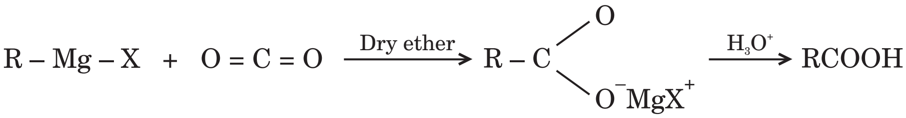
To stop the reaction at the amide stage, mild reaction conditions are used.



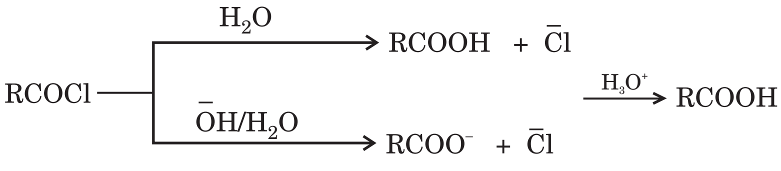
$$R\text{-}CN \xrightarrow[H_2O]{\overset{+}{H} \text{ or } \overset{-}{O}H} R-\overset{\overset{\large O}{||}}{C}-NH_2 \xrightarrow[\Delta]{\overset{+}{H} \text{ or } \overset{-}{O}H} RCOOH$$

- **Using Grignard Reagent**

Salts of carboxylic acids are formed when Grignard's reagent react with carbon dioxide(dry ice) which on acidification with mineral acid give carboxylic acids.



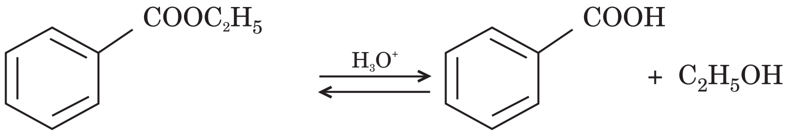
- **Using acyl halides and anhydrides**



$$\underset{\text{Benzoic anhydride}}{(C_6H_5CO)_2O} \xrightarrow{H_3O} \underset{\text{Benzoic acid}}{2C_6H_5COOH}$$

- **Using esters**

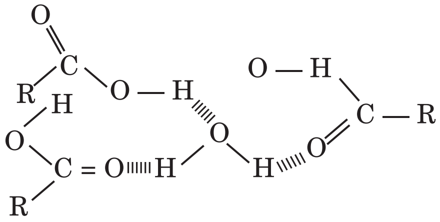
  Esters when subjected to acidic hydrolysis give carboxylic acids.



Ethyl benzoate Benzoic acid

Physical Properties

- Lower members are colorless liquid having pungent smell and the higher members are odourless waxy solid.
- The ability to form intermolecular hydrogen bonds causes carboxylic acids to have higher boiling point.



Hydrogen bonding of
RCOOH with H_2O

Chemical Reactions

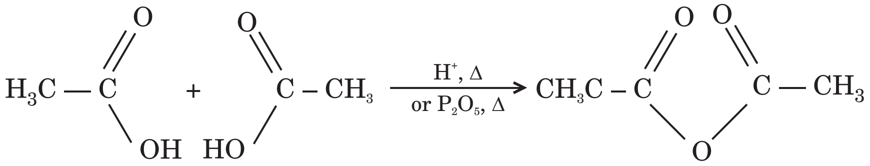
- **Reactions with metals and alkalies**

  On reacting with metals, the carboxylic acids evolve hydrogen.

$$2R-COOH+2Na \longrightarrow \underset{\text{Sodium carboxylate}}{2R-CO\bar{O}Na^{+}} + H_2$$

$$R-COOH+NaOH \longrightarrow R-CO\bar{O}Na^{+} + H_2O$$

- **Formation of anhydride**



Ethanoic acid Ethanoic anhydride

- **Esterification:**

  $RCOOH + PCl_5 \longrightarrow RCOCl + PCl_3 + HCl$

$$3RCOOH + PCl_3 \longrightarrow 3RCOCl + H_3PO_3$$

$$RCOOH + SOCl_2 \longrightarrow RCOCl + SO_2 + HCl$$

- **Reactions with** $PCl_5, PCl_3, SOCl_2$

The hydroxyl group gets replaced by chlorine atom.

$$RCOOH + R'OH \xrightleftharpoons{H^+,\ \Delta} RCOOR' + H_2O$$

- **Reaction with ammonia**

Reaction of carboxylic acids with ammonia gives ammonium salts which when heated further gives amides.

$$CH_3COOH + NH_3 \rightleftharpoons \underset{\text{Ammonium acetate}}{CH_3CO\bar{O}\overset{+}{N}H_4} \xrightarrow[-H_2O]{\Delta} \underset{\text{Acetamide}}{CH_3CONH_2}$$

Reactions involving –COOH group

- **Reduction**

Carboxylic acids, when reduced by diborane give primary alcohols.

$$R-COOH \xrightarrow[\text{(ii) } H_3O^+]{\text{(i) LiAIH}_4\text{ / ether or } B_2H_6} R-CH_2OH$$

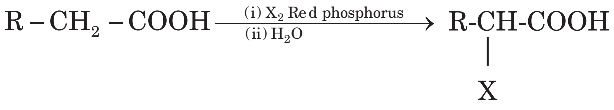
- Decarboxylation: The loss of carbon dioxide from carboxylic acids to form hydrocarbons when their sodium salts are heated with sodalime (NaOH and CaO in the ratio 3 :1) is called decarboxylation.

$$R-COONa \xrightarrow[\text{Heat}]{\text{NaOH \& CaO}} R-H + Na_2CO_3$$

Substitution Reactions

- **Halogenation (Hell Volhard-Zelinsky Reaction)**

Carboxylic acids which have an -hydrogen are halogenated at the α-position on treatment with chlorine or bromine in the presence of small amount of red phosphorus which results in α halocarboxylic acids.

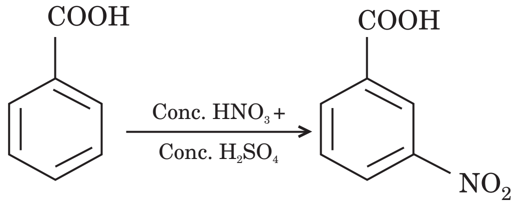


$$R-CH_2-COOH \xrightarrow[\text{(ii) } H_2O]{\text{(i) } X_2 \text{ Red phosphorus}} \underset{\displaystyle X}{\text{R-}\overset{}{\underset{|}{\text{CH}}}\text{-COOH}}$$

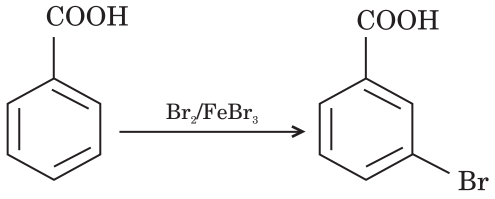
X = Cl, Br
α - Halocarboxvlic acid

- **Ring Substitution**

  In aromatic carboxylic acids, carboxyl group acts as a deactivating and meta-directing group.



m-Nitrobenzoic acid



m-Bromobenzoic acid

Applications of Carboxylic Acids

- Ethanoic acid is used as vinegar and as solvent.
- Methanoic acid is used in rubber, dyeing, leather,textile, and electroplating industries.
- Esters of benzoic acid are often used in perfume industry.
- For the manufacturing of soaps and detergents, higher fatty acids are used.

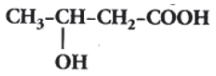
PREVIOUS YEARS'

EXAMINATION QUESTIONS

TOPIC 2

▶ 1 Mark Questions

1. Write the IUPAC name of the compound. **[DELHI 2014]**



$$\underset{\displaystyle OH}{\underset{|}{CH_3-CH}}-CH_2-COOH$$

2. Write the structure of 2-hydroxybenzoic acid. **[All INDIA 2014]**
3. Arrange the following compounds in an increasing order of their acid strengths:
   $(CH_3)_2\,CHCOOH,\ CH_3CH_2CH(Br)COOH,$
   $CH_3CH(Br)CH_2COOH$
   [DELHI 2016]

▶ 2 Marks Questions

4. How do you convert the following?
   Toluene to benzoic acid **[All INDIA 2018]**
   OR
   Account for the following:
   (a) Aromatic carboxylic acids do not undergo Friedel-Crafts reaction.
   (b) pK_a value of 4-nitrobenzoic acid is lower than that of benzoic acid. **[All INDIA 2018]**
5. Write chemical equation for the following conversions:
   (i) Nitrobenzene to benzoic acid.
   (ii) Benzyl chloride to 2-phenylethanamine.
   (iii)Aniline to benzyl alcohol. **[DELHI 2012]**

▶ 5 Marks Questions

6. (a) Illustrate the following name reactions giving suitable example in each case:
   (i) Clemmensen reduction
   (ii)Hell-Volhard-Zelinsky reaction
   (b) How are the following conversions carried out?

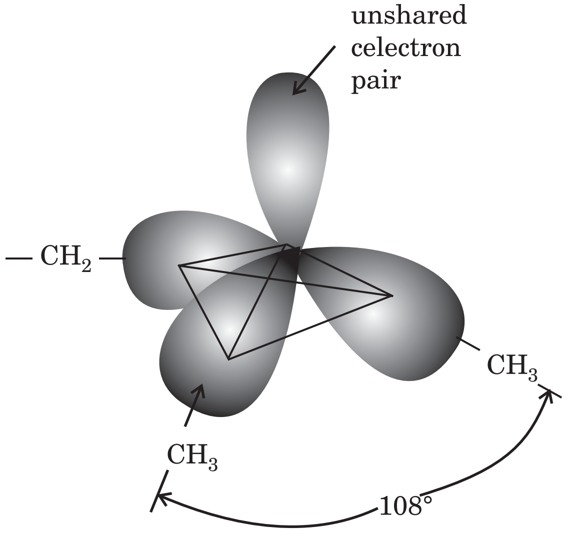
Topic 1: Introduction, Methods of Preparation and Physical Properties

Summary

- Amines: Amines can be considered as the amino derivatives of hydrocarbons or alkyl derivatives of ammonia. Amines are obtained by replacing one, two or three hydrogen atoms by alkyl and/or aryl groups. For example, $CH_3NH_2, C_2H_5NH_2, C_6H_5NH_2$ *etc.*
- Classification of amines:

$$\begin{array}{ccc} -NH_2 & -\overset{|}{N}H & -\overset{|}{N}- \\ \mathrm{Pr}imary & Secondary & Tertiary \\ \left(1^o\right) & \left(2^o\right) & \left(3^o\right) \end{array}$$

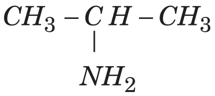
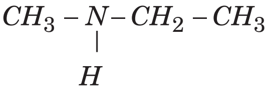
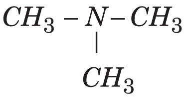
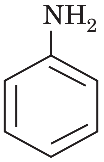
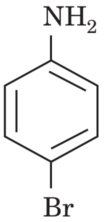
- Structure of amines:



Pyramidal shape of trimethylamine

Nitrogen orbitals in amines are sp^3 hybridised and the geometry of amines is pyramidal. The fourth orbital of nitrogen in all amines contains an unshared pair of electrons. Due to the presence of unshared pair of electrons, the angle $C-N-E$ is less than 109.5°.

- **Nomenclature of some alkylamines and arylamines:**

Amines	Common Names	IUPAC name
$CH_3-CH_2-NH_2$	Ethylamine	Ethanamine
$CH_3-CH_2-CH_2-NH_2$	n-Propylamine	Propan-1-amine
 $CH_3-\underset{\substack{\vert\\NH_2}}{C}H-CH_3$	Isopropylamine	Propane-2-amine
 $CH_3-\underset{\substack{\vert\\H}}{N}-CH_2-CH_3$	Ethylmethylamine	N-Methylethanamine
 $CH_3-\underset{\substack{\vert\\CH_3}}{N}-CH_3$	Trimethylamine	N,N-Dimethylmethaneamane
	Aniline	Aniline or benzenamine
	*p*-Bromoanaline	4-Bromobenzylamine Or 4-Bromoaniline

- Preparation of Amines:

➢ By reduction of nitro compounds:

$$\underset{}{R-NO_2+3H_2\xrightarrow{Ni}}\underset{1^o\ \text{amine}}{R-NH_2}+2H_2O$$

➢ By ammonolysis of alkyl halides:

$$R-X+NH_3\rightarrow\underset{(1^o)}{RNH_2}\xrightarrow{RX}\underset{(2^o)}{R_2NH}\xrightarrow{RX}\underset{(3^o)}{R_3N}\xrightarrow{RX}\underset{\substack{Quaternary\\ammonium\,salt}}{R_4\overset{+}{N}\overset{-}{X}}$$

The free amine can be obtained from the ammonium salt by treatment with a strong base:

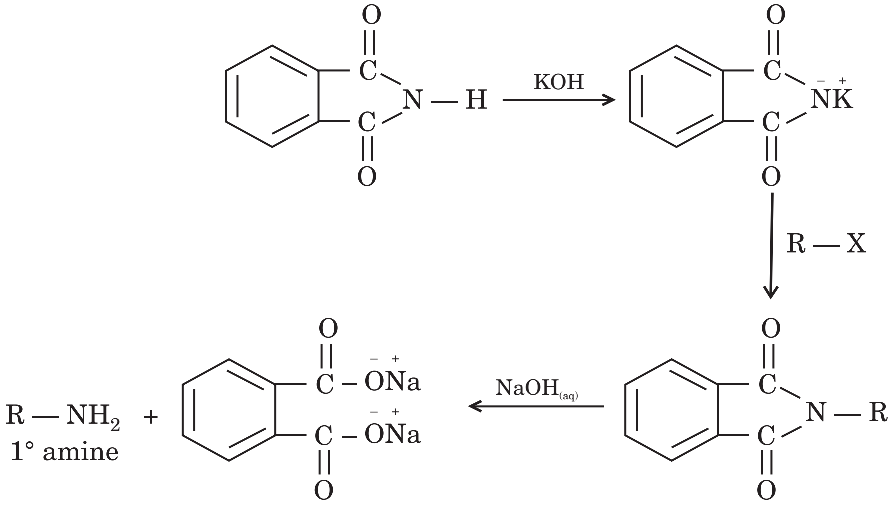
$$R-\overset{+}{N}H_3\overset{-}{X}+NaOH\rightarrow R-NH_2+H_2O+\overset{+}{Na}\overset{-}{X}$$

➢ By reduction of nitriles:

$$2H_2+R-C\equiv N\xrightarrow{Ni}R-CH_2-NH_2$$

$$R-C\equiv N+4[H]\xrightarrow[\text{or LiAlH}_4]{\text{Na(Hg)/C}_2\text{H}_5\text{OH}}\underset{1^{\circ}\text{ amine}}{R-CH_2-NH_2}$$

- ➢ Gabriel phthalmide synthesis:



- ➢ By reduction of amides:

$$R-\overset{O}{\overset{||}{C}}-NH_2\xrightarrow[(ii)\,H_2O]{(i)\,LiAlH_4}R-CH_2-NH_2$$

- ➢ By Hoffmann Bromamide degradation reaction:

$$R-\overset{O}{\overset{||}{C}}-NH_2+Br_2+4NaOH\longrightarrow R-NH_2+Na_2CO_3+2NaBr+2H_2O$$

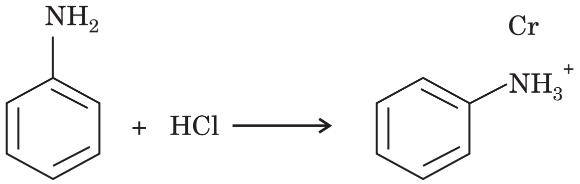
- Physical properties:
  - ➢ Lower members are combustible gases, members from C_3 to C_1 are volatile liquids and C_{12} onwards are gaseous. Lower aromatic amines are liquids.
  - ➢ Pure amines are colourless, although they develop colour on keeping in air for a long time.
  - ➢ With increase in molecular weight, the boiling point also increases. The order of boiling points of isomeric amines is, Primary > Secondary > Tertiary.
  - ➢ Lower members of amine are readily soluble in water. They decrease in water and increase in organic solvents with an increase in molecular weight.

Topic 2: Chemical Reaction of Amines and Diazonium Salts

Summary

- **Chemical properties:**
  - **Reactions due to alkyl group:**

$$R-\overset{\bullet\bullet}{N}H_2+HX\rightleftharpoons R-\overset{+}{N}H_3\,\overset{-}{X}\,(Salt)$$



Aniline Anilinium chloride

Amines, being basic in nature, react with acids to form salts. When these amine salts are treated with a base such as $NaOH$, they regenerate the parent amine.

$$\underset{\text{Amine Salts}}{R\overset{+}{N}H_3\,\overset{-}{X}}+\underset{\text{base}}{\overset{-}{O}H}\longrightarrow\underset{\text{parent amine}}{R\overset{\bullet\bullet}{N}H_2}+H_2O+\overset{-}{X}$$

Amine salts are soluble in water but insoluble in organic compounds like ether. This reaction helps in separating the amines from the non basic organic compounds insoluble in water.

The reaction of amines with mineral acids to form ammonium salts shows that these are basic in nature. The order of basic strength in case of methyl Substituted amines and ethyl substituted amines in aqueous solution is as follows:

$$(C_2H_5)_2NH>(C_2H_5)_3N>C_2H_5NH_2>NH_3$$

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

The $-NH_2$ group is attached directly to the benzene ring in aryl amines, which results in the unshared electron pair on nitrogen atom to be in conjugation with the benzene ring and thus making it less available for protonation.

In case of substituted aniline, it is observed that electron releasing groups increase basic strength whereas electron withdrawing groups decrease it.

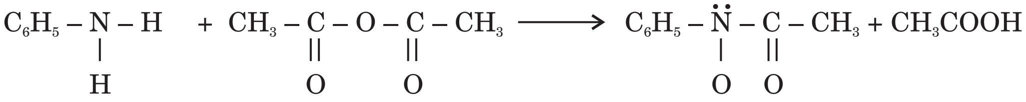
Alkylation:

$$CH_3-CH_2-NH_2\xrightarrow[-HBr]{+CH_3-CH_2-Br}(CH_3-CH_2)_2NH\xrightarrow[-HBr]{+CH_3-CH_2-Br}\underset{\textit{Triethylamine}}{(CH_3-CH_2)_3}$$

$$(CH_3-CH_2)_3N\xrightarrow[-HBr]{+CH_3-CH_2-Br}\underset{\substack{\textit{Tetraethyl}\\ \textit{ammonium bromide}}}{(CH_3-CH_2)_4\overset{+}{N}\overset{-}{Br}}$$

Acylation:

Aliphatic and aromatic primary and secondary amines react with acid chlorides, anhydrides and esters by nucleophillic substitution reaction. This reaction is known acylation.



$$C_6H_5-\underset{\displaystyle H}{\underset{|}{N}}-H + CH_3-\underset{\displaystyle O}{\underset{\|}{C}}-O-\underset{\displaystyle O}{\underset{\|}{C}}-CH_3 \longrightarrow C_6H_5-\underset{\displaystyle O}{\underset{|}{\ddot{N}}}-\underset{\displaystyle O}{\underset{\|}{C}}-CH_3 + CH_3COOH$$

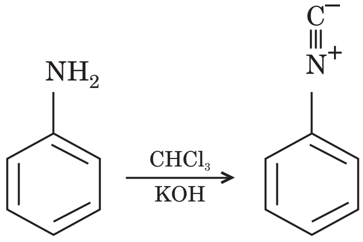
Benzenamine Ethanoic anhydride N-Phenylethanamide or Acetanilide

Benzoylation:

$$\underset{\textit{Methlamine}}{CH_3NH_2} + \underset{\substack{\textit{Benzoyl}\\ \textit{Chloride}}}{C_6H_5COCl} \longrightarrow \underset{\textit{N - Methylbenzamide}}{CH_3NHCOC_6H_5} + HCl$$

Carbylamine reaction: Secondary and tertiary amines do not give this reaction. This reaction is used as a test for primary amines.

$$R-NH_2+CHCl_3+3KOH\xrightarrow{Heat}R-NC+3KCl+3H_2O$$



Reaction with nitrous acid:

$$R-NH_2+HNO_2\xrightarrow{NaNO_2+HCl}\left[R-\overset{+}{N_2}\overset{-}{Cl}\right]\xrightarrow{H_2O}ROH+N_2+HCl$$

1^o amine

$$R_2NH + HNO_2 \longrightarrow R_2N-N=O + H_2O$$

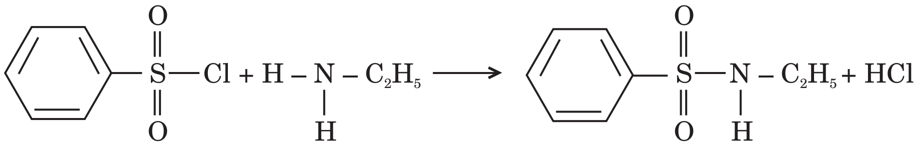
2^o amine N-Nitrosamine

$$\underset{3^o \text{ amine}}{R_3N} + HNO_2 \longrightarrow \underset{\text{Trialkyl ammonium nitrite}}{R_3NHNO_2}$$

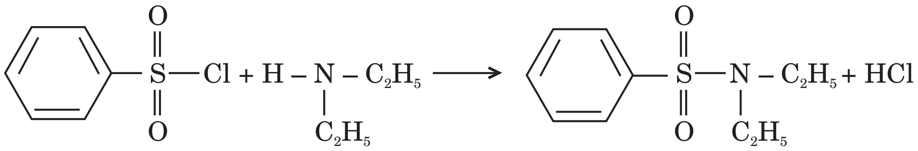
$$\underset{\text{Aromatic amine}}{C_6H_5-NH_2} \xrightarrow[273-278k]{NaNO_2+2HCl} \underset{\text{Benzenediazonium chloride}}{C_6H_5-\overset{+}{N}_2\overset{-}{Cl}} + NaCl + 2H_2O$$

Secondary and tertiary amines react with nitrous acid in a different manner.

Reaction with arylsulphonyl chloride:



N-Ethylbenzenesulphonamide
(soluble in alkali)

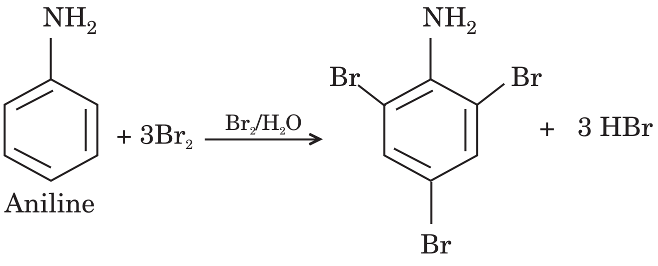


N, N-Diethylbenzenesulphonamide

Tertiary amines do not react with benzenesulphonyl chloride and therefore, benzenesulphonyl chloride is used to differentiate between primary, secondary and tertiary amines.

Bromination:

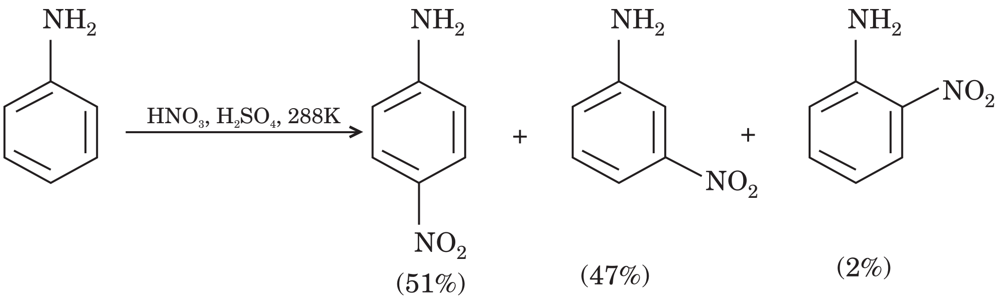
Aniline reacts with bromine water at room temperature to give a white precipitate of 2, 4, 6-tribromoanaline.



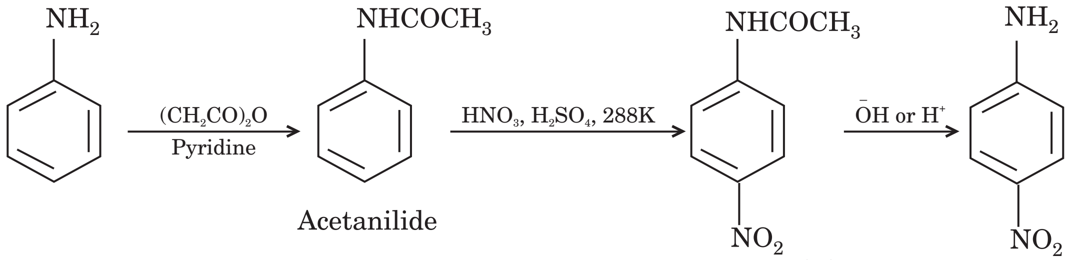
2, 4, 6- Tribromoaniline

Nitration:

Direct nitration of aniline yields nitro derivatives.



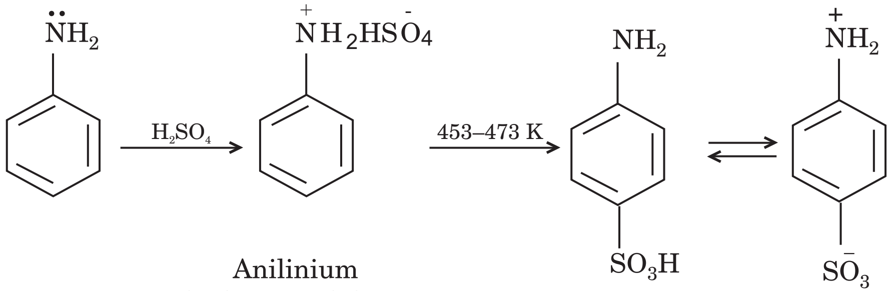
Preparation of monosubstituted aniline derivative by acetylation of group:


Acetanilide

p-Nitroacetanilide

p-Nitroaniline

Sulphonation:


Anilinium hydrogensulphate

Sulphanilic acid

Zwitter ion

Aniline does not undergo Friedel-Crafts reaction (alkylation and acetylation) due to salt formation with aluminium chloride.

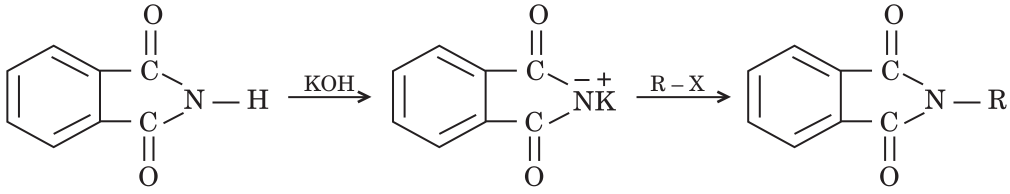
Ammonolysis:

Alkyl halide reacts with ammonia to form primary amine. The reaction of ammonia with alkyl halide is known as ammonolysis.

$$C_2H_5I \xrightarrow{NH_3/343K} C_2H_5NH_2 \xrightarrow[-HI]{C_2H_5I} (C_2H_5)_2$$

$$NH \xrightarrow[-HI]{C_2H_5I} (C_2H_5)_3N \xrightarrow[-HI]{C_2H_5I} \left[(C_2H_5)_4\overset{+}{N}\right]\overset{-}{I}$$

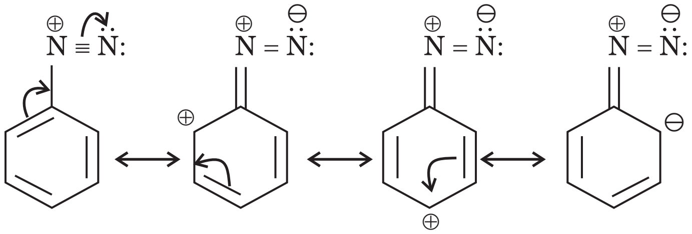
Gabriel Phthalimide Synthesis: In Gabriel phthalimide synthesis, phthalimide reacts with alcoholic KOH to get potassium phthalimide which reacts with alkyl halide to form N-alkyl phthalimide which on basic hydrolysis gives primary amine and phthalic acid.


Phthalimide

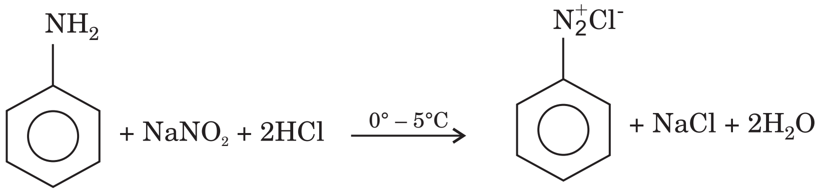
N-Alkyphthalimide

Friedel-Crafts reaction: Aniline does not undergo Friedel-Crafts reaction as it forms a salt with $AlCl_3$ which is a Lewis acid.

- **Diazonium salts:**
  - **General formula:** $R\overset{+}{N_2}\overset{-}{X}$, where R stands for an aryl group and $\overset{-}{X}$ ion may be for halides
  - **Stability of diazonium salts:** Primary aliphatic amines are highly unstable alkyldiazonium salts. Arenediazonium salts, made up of primary aromatic amines are more stable than alkyl diazonium slts due to the dispersal of the positive charge over the benzene ring.



  - **Preparation of diazonium salts:**



Benzene diazonium

  - **Chemical properties:**

Reactions involving displacement of nitrogen:

Replacement by halide or cyanide ion-

$$Ar\overset{+}{N_2}\overset{-}{X} \xrightarrow{CuCl/HCl} ArCl + N_2$$
$$Ar\overset{+}{N_2}\overset{-}{X} \xrightarrow{CuBr/HBr} ArBr + N_2$$
$$Ar\overset{+}{N_2}\overset{-}{X} \xrightarrow{CuCN/KCN} ArCN + N_2$$

Sandmeyer reaction

$$Ar\overset{+}{N_2}\overset{-}{X} \xrightarrow{Cu/HCl} ArCl + N_2 + CuX$$
$$Ar\overset{+}{N_2}\overset{-}{X} \xrightarrow{Cu/HBr} ArBr + N_2 + CuX$$

Gatterman's reaction

Replacement by iodide ion-

$$\underset{\text{Benzene diazonium chloride}}{Ar\overset{+}{N_2}\overset{-}{Cl}} + KI \longrightarrow \underset{\text{Iodobenzene}}{ArI} + KCl + N_2$$

Replacement by fluoride ion-

$$Ar\overset{+}{N_2}\overset{-}{Cl} + HBF_4 \longrightarrow Ar\overset{+}{N_2}\overset{-}{BF_4}$$

$$Ar\overset{+}{N_2}\overset{-}{BF_4} \xrightarrow{\Delta} Ar - F + BF_3 + N_2$$

Replacement by H-

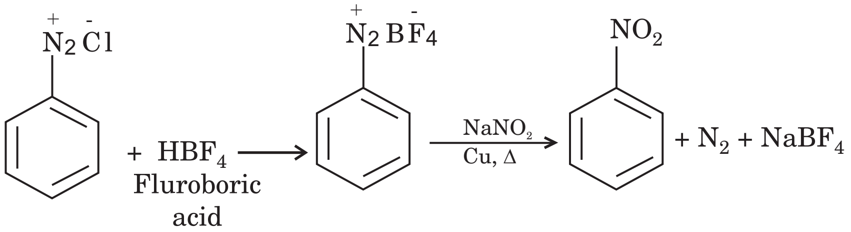
$$Ar\overset{+}{N_2}\overset{-}{Cl} + H_3PO_2 + H_2O \longrightarrow ArH + N_2 + H_3PO_3 + HCl$$

$$Ar\overset{+}{N_2}\overset{-}{Cl} + CH_3CH_2OH \longrightarrow ArH + N_2 + CH_3CHO + HCl$$

Replacement by hydroxyl group-

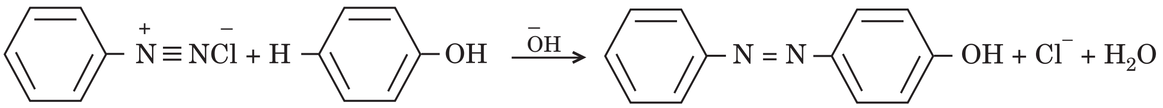
$$Ar\overset{+}{N_2}\overset{-}{Cl} + H_2O \xrightarrow{\Delta} \underset{Phenol}{ArOH} + N_2 + HCl$$

Replacement by $-NO_2$ group-

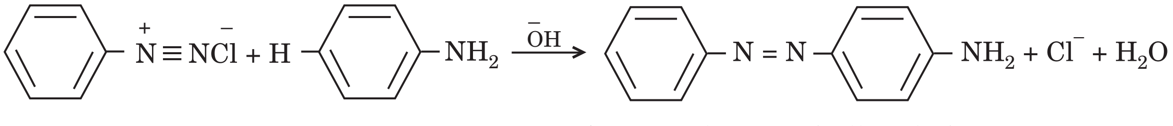


Reactions involving retention of diazo group:

Coupling reaction: The reaction of diazonium salts with phenols and aromatic amines to form azo compounds with the general formula, $Ar - N = N\,Ar$ is known as coupling reaction.



p-Hydroxyazobenzene (orange dye)



p-Aminoazobenzene (yellow dye)

- Importance of Diazonium salts: They are very good intermediates for the introduction of *–F, –Cl, Br, – I, – CN, OH, OH,* NO_2 groups into aromatic ring. Cyanobenzene can be prepared from diazonium salts.

- **Synthesis of organic compounds from diazonium salts:**

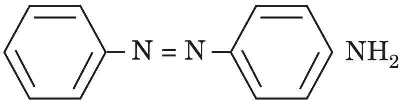
$$C_6H_5N_2Cl \xrightarrow{CH_3CH_2OH} C_6H_6$$

$$C_6H_5N_2Cl \xrightarrow{H_2O} C_6H_5OH$$

$$C_6H_5N_2Cl \xrightarrow{HBF_4} C_6H_5F$$

$$C_6H_5N_2Cl \xrightarrow{C_6H_6 / NaOH} C_6H_5C_6H_5$$

$$C_6H_5N_2Cl \xrightarrow{C_6H_5NH_2 / acid}$$



- Identification of primary, secondary and tertiary amines:

Test	Primary amine	Secondary amine	Tertiary amine
Reaction with nitrous acid.	Gives alcohol with effervescence of N_2 gas.	Gives only nitrosoamine which gives Liebermann's nitrosoamine test.	Forms nitrite in cold soluble in water and on heating gives nitrosoamine.
Recation with benzene sulphonyl chloride (Hiesenberg's reagent).	Gives N-alkyl benzene-sulphonamide which is soluble in alkali.	Gives N, N-dialkyl benzene sulphonamide which is insoluble in alkali.	No reaction.
Carbylamine test: Reaction with chloroform and alcoholic KOH.	Forms carbylamines or isocyanide (RNC) with characteristic unpleasant odour.	No reaction.	No reaction.
Hoffman's Mustard oil reaction: Recation with CS_2 and $HgCl_2$.	Forms N-substituted isotiocyanate with characteristic unpleasant smell of mustard oil.	No reaction.	No reaction.

Topic 1: Carbohydrates

Summary

- There are various complex biomolecules of which living systems are made up of. These biomolecules include carbohydrates, proteins, nucleic acids, lipids etc.
- Carbohydrates are primarily produced by plants and most of them have general formula, $C_x\,(H_2O)_y$. Example: the molecular formula of glucose is ($C_6H_{12}O_6$). Carbohydrates are classified into three groups on the basis of their behaviour on hydrolysis:
    - **Monosaccharides:** A carbohydrate that cannot be hydrolysed further to give simpler unit of polyhydroxy aldehyde or ketone. Example: glucose, fructose etc.
    - **Oligosaccharides:** A carbohydrate that yields two to ten units of monosaccharide units on hydrolysis. The most common oligosaccharides are disaccharides. The two monosaccharides units obtained on hydrolysis of a disaccharide may be same or different. Example: Sucrose of hydrolysis gives one molecule of glucose and one molecule of fructose whereas maltose of hydrolysis gives two molecules of glucose only.
    - **Polysaccharides :** These are the carbohydrates which yield a large number of monosaccharide units on hydrolysis. Example: Starch, cellulose etc. They are also called non-sugars.
- The carbohydrates which reduce Fehling's solution and Tollen's reagent are called **reducing sugars.** Example: Maltose.
- If the reducing group of monosaccharides i.e. aldehydic or ketonic groups are bonded they are called **non-reducing sugars.** Example: Sucrose.
- **Glucose:**

Preparation of glucose:

- From Sucrose: WhenSucrose is boiled with dilute HCl or H_2SO_4 in alcoholic solution, glucose and fructose are obtained in equal amounts.

$$C_2H_{22}0_{11} + H_20 \xrightarrow{H^+} C_6H_20_6 + C_6H_20_6$$

Sucrose Glucose Fructose

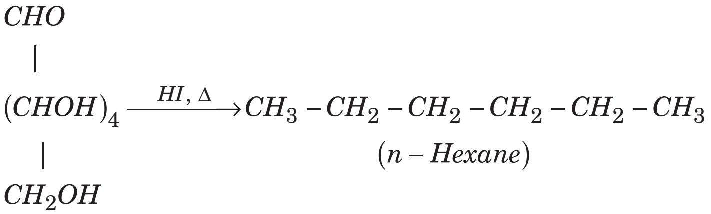
- **From starch:** Hydrolysis of starch by boiling it with dilute H_2SO_4 at 393 K under pressure.

$$\underset{\text{Satch or cellulose}}{(C_6H_{10}O_5)_n} + nH_2O \xrightarrow[393K;\ 2\text{–}3\ atm]{H^+} \underset{\text{Glucose}}{nC_6H_{12}O_6}$$

Structure of Glucose:

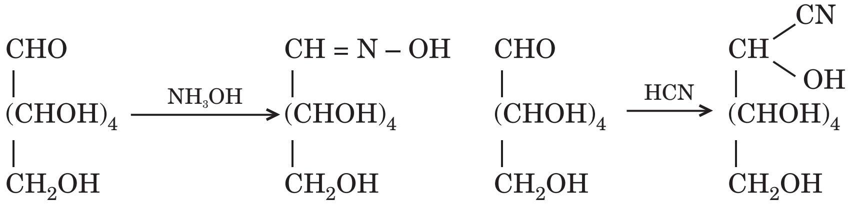
Glucose is also called dextrose. It is a monomer of many larger carbohydrates. The structure of glucose was assigned on the basis of the following facts:

- ➢ The molecular formula was found to be $C_6H_{12}O_6$.
- ➢ Prolonged heating of glucose with HI forms n-Hexane.



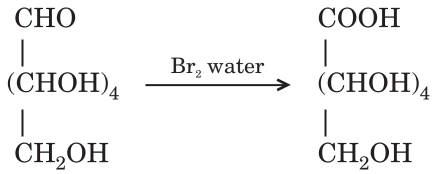
$$\begin{array}{l} CHO \\ | \\ (CHOH)_4 \\ | \\ CH_2OH \end{array} \xrightarrow{HI,\ \Delta} \underset{(n-Hexane)}{CH_3-CH_2-CH_2-CH_2-CH_2-CH_3}$$

- ➢ Glucose on reacting with hydroxylamine forms an oxime and adds molecule of hydrogen cyanide to give cyanohydrin. This confirms the presence of carbonyl group in glucose.



$$\begin{array}{l} CHO \\ | \\ (CHOH)_4 \\ | \\ CH_2OH \end{array} \xrightarrow{NH_3OH} \begin{array}{l} CH=N-OH \\ | \\ (CHOH)_4 \\ | \\ CH_2OH \end{array} \qquad \begin{array}{l} CHO \\ | \\ (CHOH)_4 \\ | \\ CH_2OH \end{array} \xrightarrow{HCN} \begin{array}{l} CH \diagup^{CN}_{\diagdown OH} \\ | \\ (CHOH)_4 \\ | \\ CH_2OH \end{array}$$

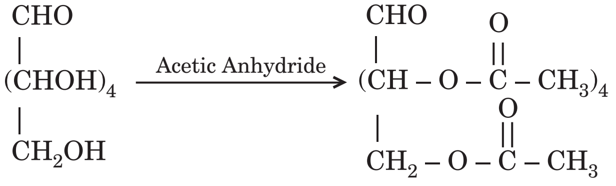
- ➢ On reacting with mild oxidizing agent like bromine water it oxidise to six carbon carboxylic acid. This indicates the presence of carbonyl group as an aldehydic group.



$$\begin{array}{l} CHO \\ | \\ (CHOH)_4 \\ | \\ CH_2OH \end{array} \xrightarrow{Br_2\ water} \begin{array}{l} COOH \\ | \\ (CHOH)_4 \\ | \\ CH_2OH \end{array}$$

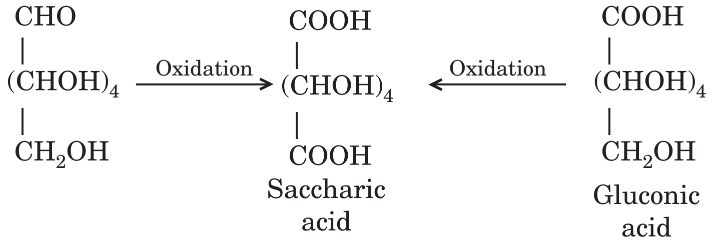
Gluconic acid

- ➢ To confirm the presence of five –OH groups glucose is acetylated with acetic anhydride to give glucose pentaacetate.



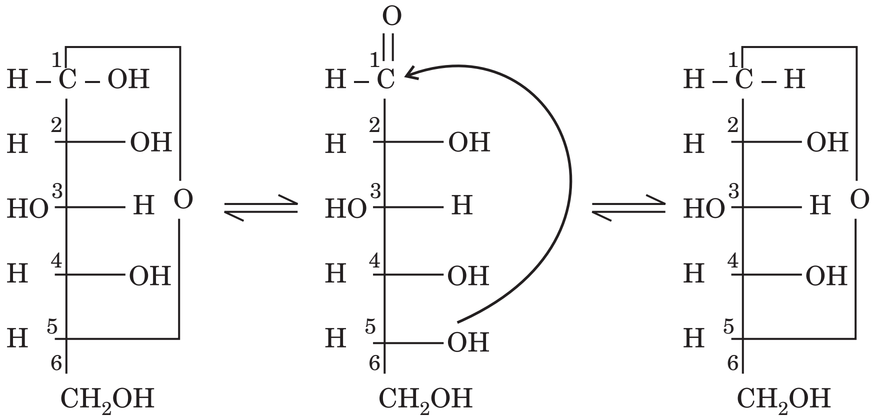
$$\begin{array}{l} CHO \\ | \\ (CHOH)_4 \\ | \\ CH_2OH \end{array} \xrightarrow{\text{Acetic Anhydride}} \begin{array}{l} CHO \\ | \\ (CH-O-\overset{\overset{\large O}{||}}{C}-CH_3)_4 \\ | \\ CH_2-O-\overset{\overset{\large O}{||}}{C}-CH_3 \end{array}$$

- To indicate the presence of a primary alcoholic (-OH) group in glucose, glucose as well as gluconic acid are both oxidized with nitric acid to yield dicarboxylic acid, saccharic acid.



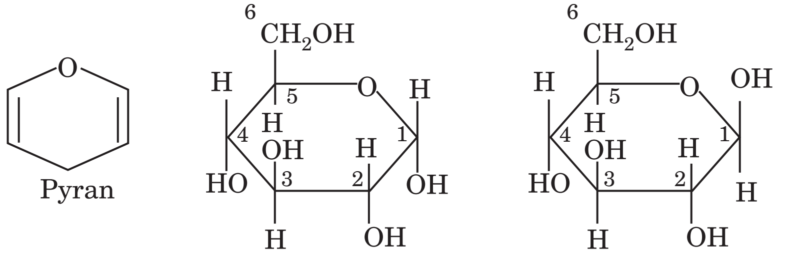
Cyclic Structure of Glucose:

- Glucose does not give 2, 4-DNP test, Schiff's test and does not form the hydrogensulphite addition product with $NaHSO_3$.
- The absence of free-CHO group is indicated as the pentaacetate of glucose does not react with hydroxylamine.
- Glucose exist in two different crystalline forms which are named as α and β. It was found that glucose forms a six-membered ring in which –OH at C5 in involved in ring formation.
- The cyclic structure is given below:



α – D – (+) – Glucose β – D – (+) – Glucose

- Haworth structure of glucose is given below:



α – D – (+) – Glucose β – D – (+) – Glucose

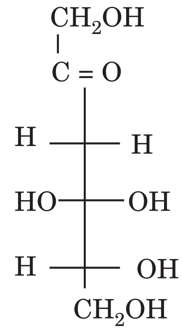
- **Fructose**

It is obtained along with glucose by the hydrolysis of sucrose.

- ➢ Structure of Fructose:

  Fructose has the molecular formula $C_6H_{12}O_6$. It is found to have a ketonic functional group at carbon 2 and six carbons which are in straight chain.

- ➢ The open chain structure of fructose is:



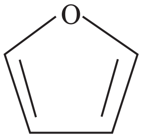
D – (–) – Fructose

- ➢ **Cyclic structure of fructose:**

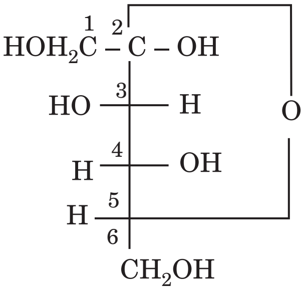
  Fructose exists in two cyclic forms and they are obtained by adding –OH at C5 to the ketonic group.

  The ring is a five membered ring.

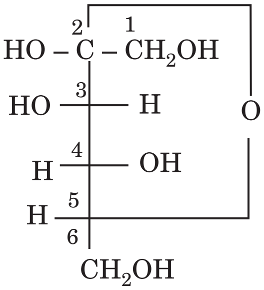
- ➢ **The structures are given below**



Furan

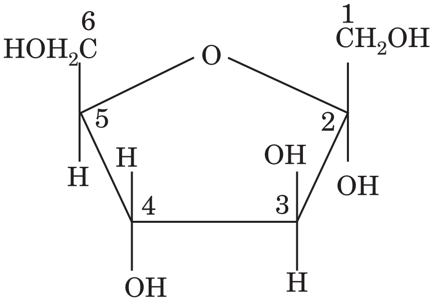


α – D – (–) – Fructofuranose

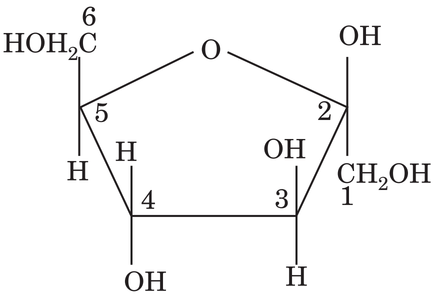


β – D – (–) – Fructofuranose

- ➢ **The Haworth structures of fructose are given below:**



α – D – (–) – Fructofuranose



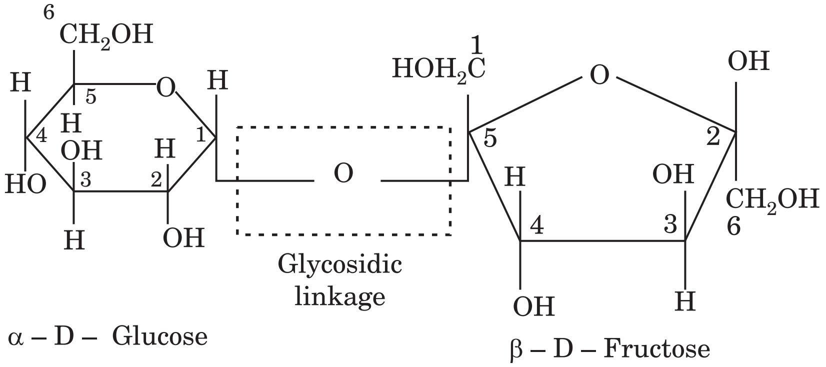
β – D – (–) – Fructofuranose

- Sucrose
  - ➢ Sucrose on hydrolysis gives equimolar mixture of D-(+)-glucose and D-(-) fructose.

$$C_2H_{22}0_{11} + H_20 \xrightarrow{H^+} C_6H_20_6 + C_6H_20_6$$

Sucrose D-(+)-Glucose D-(−)-Fructose

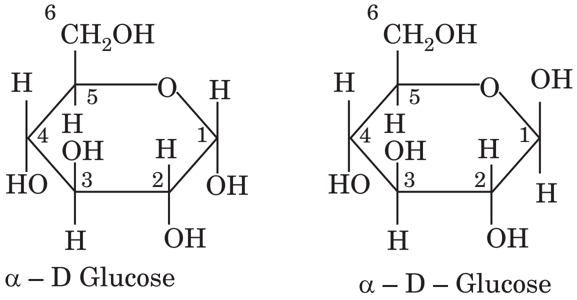
  - ➢ The structure of sucrose is given below:



Sucrose

  - ➢ The two monosaccharides in sucrose are held together by a glycosidic linkage. The product obtained on hydrolysis of sucrose is called invert sugar as the hydrolysis brings about a change in the sign of rotation from dextro (+) to laevo (-).

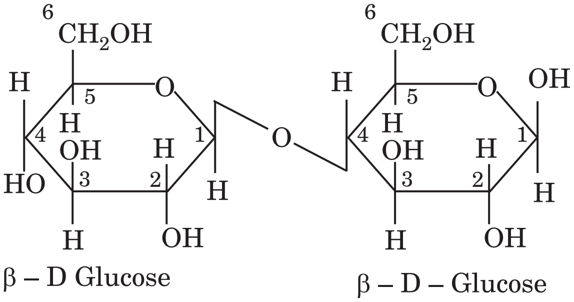
- Maltose:
  - ➢ Maltose has two α-*D*-glucose units. In maltose the C 1 of one glucose (I) is linked to C4 of another glucose unit (II).
  - ➢ **Structure of Maltose:**



Maltose

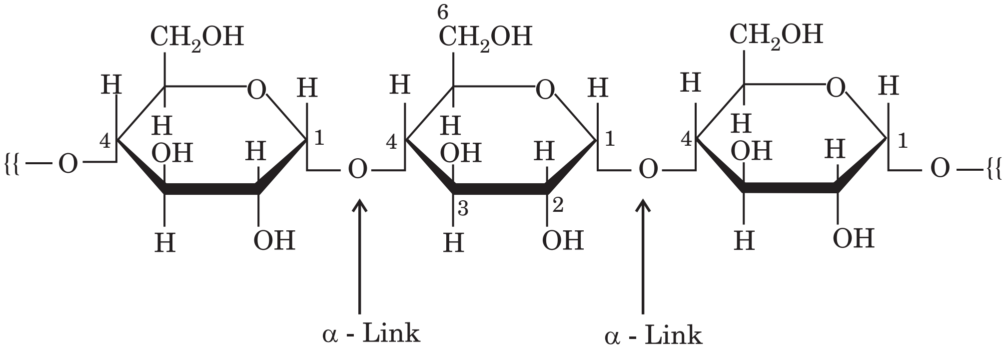
- Lactose:
  - ➢ It is commonly known as milk sugar as it is found in milk.

- **Structure of lactose:**



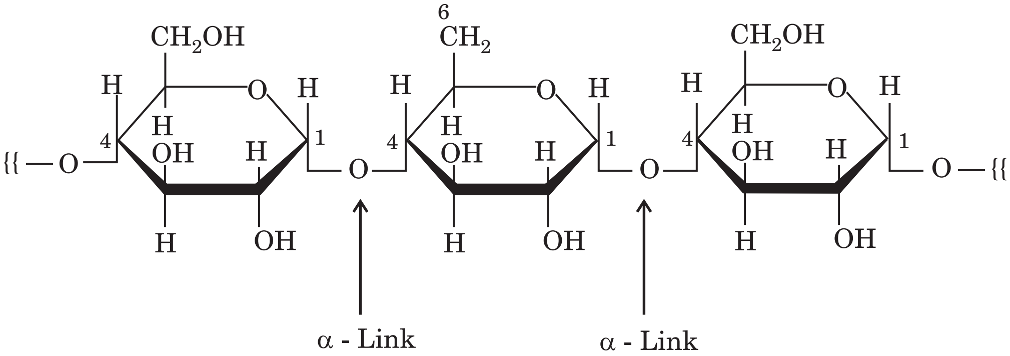
Lactose

- **Polysaccharides:** They contain a large number of monosaccharide units joined together by glycosidic linkage.
- Starch
  - It is the main storage polysaccharide of plants and important dietary source for human beings. It consists of two components namely Amylose and Amylopectin.
  - Amylose: It is water soluble component and constitutes 15-20% of starch. It is a long unbranched chain with 200-1000 α-*D*-(+)-glucose units held by C1-C4 glycosidic linkage.
  - **Structure of Amylose is given below:**

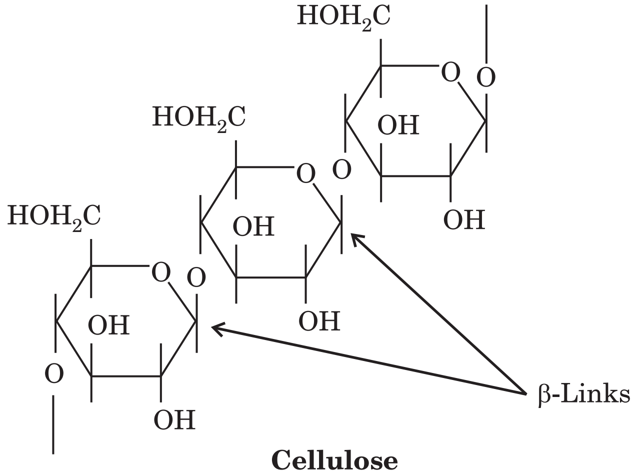


Amylose

  - Amylopectin: It is insoluble in water and constitutes 80-85% of starch. It is a branched chain polymer of   units in which chain is formed by C1-C4 glycosidic linkage whereas branching occurs by C1-C6 glycosidic linkage.
  - **Structure of Amylopectin is given below:**



- **Cellulose:**
  - It occurs exclusively in plants. It is an important constituent of cell wall of plant cells. Its fundamental unit is β-*D*-glucose which are joined by glycosidic linkage between C1 of one glucose unit and C4 of the next glucose unit.
  - **Structure of cellulose is:**



Cellulose

- **Glycogen:**
  - Carbohydrates are stored in animals as glycogen. Its structure is similar to amylopectin and is rather more branched therefore it is also known as animal starch. It is present in liver, muscles and brain.
- **Importance of carbohydrates:**
  - They are essential for both plants and animals as they are the source of energy.
  - They are used as storage molecules.
  - Cell wall of plants and bacteria is made of cellulose.
  - They also act as raw materials for many important industries like textiles, paper etc.

8. The following two reactions of glucose cannot be explained by the open chain structure of glucose.

(i) Despite having the aldehyde group glucose does not give 2, 4-DNP test. **[1]**

(ii) The pentacetate of glucose does not react with hydroxylamine indicating the absence of free –CHO group. **[1]**

9. (a) Value of being aware and informed. **[1]**

1. To be aware about adverse effect of carcinogen present in bread and bakery products. [½]
2. To replace the bakery product with some protein and vitamin rich food like fruits, salads etc. value of Taking Initiative. [½]

(b) Starch, Glycogen **[1]**

(c) Alpha helix, Beta pleated sheet **[1]**

(d) Riboflavin, Thiamine **[1]**

Topic 2: Protein, Vitamins and Nucleic Acids

Summary

- **Proteins:** They are the most abundant biomolecules of the living system. They form the fundamental basis of structure and functions of life.
- **Amino acids:** Amino acids contain amino $(-NH_2)$ and carboxyl $(-COOH)$ function groups.
- α-**Amino acids:** These are formed by the hydrolysis of proteins. In this the amino and the carboxyl function groups are attached to the same carbon.
- **Classification of amino acids:**

  Acidic, Basic and Neutral Amino Acids: Amino acids are classified as acidic, basic and neutral depending upon the relative number of amino and carboxyl groups in their molecules. If there are equal number of amino and carboxyl groups it makes it neutral; if there are more number of amino groups than carboxyl groups it makes it basic and if there are more number of carboxyl groups than amino groups it makes it acidic.
- **Non-Essential amino acids:** Those which can be generated in the body. Example: Gylycine.
- **Essential amino acids:** Those which cannot be generated in the body and must be obtained through diet. Example: Valine

- **Some amino acids are given below in the table:**

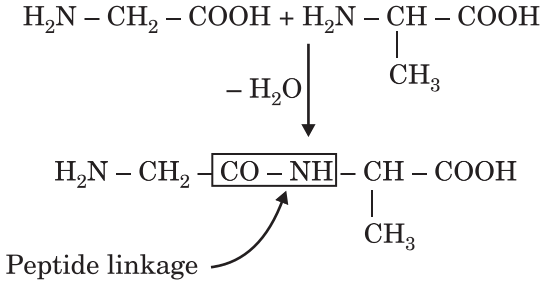
Name of amino acids	Characteristic feature of side chain, R	Three letter symbol	One letter code
1. Glycine	H	Gly	G
2. Alanine	$-CH_3$	Ala	A
3. Valine	$(H_3C)_2\,CH-$	Val	V
4. Leucine	$(H_3C)_2\,CH-CH_2-$	Leu	L
5. Glutamine	$H_2N-\overset{\overset{O}{\parallel}}{C}-CH_2-CH_2-$	Gln	Q
6. Phenylalanine	$C_6H_5-CH_2-$	Phe	F

- **Properties of amino acids:**
  - They are colourless, crystalline solids.
  - They are water soluble, have high melting point and behave like salts.

- **Structure of proteins:**

They are the polymers of α-amino acids and are connected to each other by peptide bond or peptide linkage.

Example: Formation of Glyclalanine



$$H_2N-CH_2-COOH+H_2N-\underset{\underset{CH_3}{|}}{CH}-COOH \xrightarrow{-H_2O} H_2N-CH_2-\boxed{CO-NH}-\underset{\underset{CH_3}{|}}{CH}-COOH$$

Glycylalanine (Gly-Ala)

- **Classification of proteins on the basis of molecular shape:**
  - **Fibrous proteins:** They are fibre like structure which is formed when the polypeptide chains run parallel and are held together by hydrogen disulphide bonds. They are insoluble in water. Example: Keratin
  - **Globular proteins:** This shape of protein is formed when the chains of polypeptides coil around to give a spherical shape. Such proteins are soluble in water. Example: Insulin.

- **Classification of proteins on the basis of structure and shape:**
  - **Primary structure of proteins:** Each polypeptide in a protein has amino acids linked with each other in a specific sequence and this sequence of amino acids is called primary structure of proteins.

- **Secondary structure of proteins:** It is the shape in which a long polypeptide chain can exist. They exist in two different types of structure:

  (i) *a – Helix*: In this polypeptide chain forms all possible hydrogen bonds by twisting into a right handed screw with the –NH group of each amino acid residue hydrogen bonded to the > C = O of an adjacent turn of the helix. Example: Keratin.

  (ii) β-structure : In this all peptide chains are stretched out to nearly maximum extension and then laid side by side which are held together by intermolecular hydrogen bonds. The structure resembles the pleated folds of drapery and therefore is known as β– pleated sheet .

- **Tertiary structure of proteins:** It shows the overall folding of the polypeptide chains. The forces which stabilize the 2 and 3 structures of proteins are hydrogen bonds, disulphide linkages, van der Walls and electrostatic forces of attraction.

- **Quaternary structure of proteins:** The spatial arrangement of the two or more polypeptide chains with respect to each other is known as quaternary structure.

- **Denaturation of Proteins:**

  When protein in its native form is given any physical change like change in temperature or chemical changes like change in pH, the hydrogen bonds are disturbed. Due to this, globules gets unfolded and helix gets uncoiled and protein loses its biological activity. The complete process is called denaturation of proteins. Example: coagulation of egg white on boiling.

- **Enzymes:** They are essential biocatalysts which are needed to catalyse biochemical reactions. Example: The enzyme that cataylses hydrolysis of maltose into glucose is maltase.

- **Vitamins:** These are the organic compounds that are required in the diet in small amounts to perform specific biological functions for normal maintenance of optimum growth and health of the organism.

  - **Classification of vitamins:**

    (i) **Fat soluble vitamins:** Vitamins which are soluble in fat and oils but insoluble in water. They are stored in liver and adipose tissues. Vitamin A, D, E and K are fat soluble.

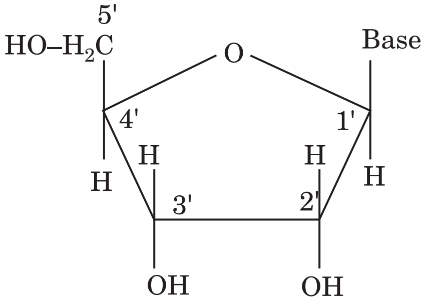
    (ii) **Water soluble vitamins:** Vitamins such as B group vitamins and vitamin C are soluble in water. These vitamins are readily excreted in urine and cannot be stored (except vitamin B12) in our body so they must be supplied regularly in diet.

- **Some important Vitamins, their sources and their deficiency diseases are shown below in the table:**

Name of Vitamins	Sources	Deficiency diseases
Vitamin A	Fish liver oil, butter and milk	Xerophthalmia, night blindness
Vitamin B_1 (Thiamine)	Yeast, milk, green vegetables and cereals	beriberi
Vitamin B_2 (Riboflavin)	Milk, egg white, liver, kidney	Cheilosis, digestive disorders
Vitamin B_6 (Pyridoxine)	Yeast, milk, egg york	Convulsions
Vitamin B_{12}	Meat, fish, egg and curd	Pernicious anaemia
Vitamin C	Citrus fruits, amla and green leafy vegetables	Scurvy
Vitamin D	Exposure to sunlight, fish and egg yolk	Rickets and osteomalacia
Vitamin E	Vegetable oils like wheat germ oil, sunflower oil etc.	Increased fragility of RBCs and muscular weakness
Vitamin K	Green leafy vegetables	Increased blood clotting time

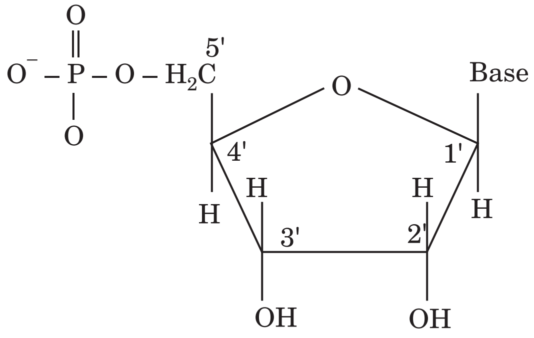
- **Nucleic Acids:**
  - ➢ These are the long chain polymers of nucleotides which help in synthesis of protein and transfer of genetic traits.
  - ➢ There are two types of nucleic acids:
    - (i) Deoxyribonucleic acid (DNA)
    - (ii) Ribonucleic acid (RNA)
- **Chemical composition of Nucleic Acids:**
  - ➢ Complete hydrolysis of DNA (or RNA) gives a pentose sugar, phosphoric acid and nitrogenous bases.
  - ➢ DNA contains four bases, which are adenine, guanine, cytosine and thymine.
  - ➢ In RNA also there are four bases. The first three bases (adenine, guanine and cytosine) are same as in DNA, but the fourth one is uracil.
- **Structure of Nucleic Acids:**
  - ➢ **Nucleoside:** The unit which is formed by the attachment of a base to position of sugar is known as nucleoside.

    Structure of nucleoside is given below:

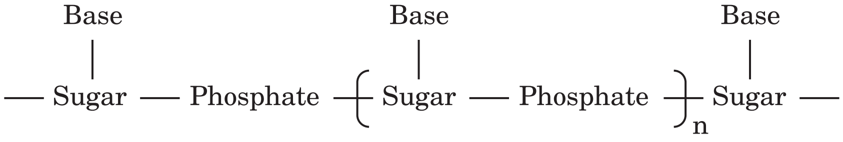


- **Nucleotide:** When nucleoside is linked to phosphoric acid at -position of sugar moiety.

  Structure of nucleotide is given below:



- The simplified version of nucleic acid chain is given below:



$$-\overset{\text{Base}}{\overset{|}{\text{Sugar}}}-\text{Phosphate}-\left[\overset{\text{Base}}{\overset{|}{\text{Sugar}}}-\text{Phosphate}-\right]_n\overset{\text{Base}}{\overset{|}{\text{Sugar}}}-$$

- **DNA:**
  - James Watson and Francis Crick gave a double strand helix structure for DNA.
  - There are two nucleic acid chains which are turned around each other and are held together by hydrogen bonds between pairs of bases.
  - The two strands in the DNA structure are complementary to each other due to the hydrogen bonding between specific pairs of bases.
- **RNA:**
  - In RNA helices are only single stranded which sometimes fold on themselves to form a double helix structure.
  - The three types of RNA molecules are given which perform different function.

    (i) Messenger RNA (m-RNA)

    (ii) Ribosomal RNA (r-RNA)

    (iii) Transfer RNA (t-RNA)
- **Biological functions of Nucleic Acids:**
  - DNA is responsible for maintaining the identity of different species of organisms.
  - Nucleic Acid helps in protein synthesis.
  - DNA is chemical basis for heredity.
  - DNA is regarded as reserve of genetic information.