Solutions

1

Introduction

In this chapter, we will discuss about liquid solutions and their formation. This will be followed by studying the properties of solutions, like vapour pressure and colligative properties. We will begin with types of solutions and expressions for concentration of solutions in different units.

Thereafter, we will state and explain Henry's law and Raoult's law, distinguish between ideal and non-ideal solution and deviation of real solutions from Raoult's law. We will also discuss abnormal colligative properties alongwith association and dissociation of solute.

Types of Solutions

All the three states of matter (solid, liquid and gas) may behave either as solvent or solute. When a solution is composed of only two chemical substances, it is termed as binary solution. Depending upon the state of solute or solvent, binary solutions can be classified as:

Types of Solutions	Solute	Solvent	Common Examples
Gaseous Solutions	Gas Liquid Solid	Gas Gas Gas	Mixture of oxygen and nitrogen gases Chloroform mixed with nitrogen gas Camphor in nitrogen gas
Liquid Solutions	Gas Liquid Solid	Liquid Liquid Liquid	Oxygen dissolved in water Ethanol dissolved in water Glucose dissolved in water
Solid Solutions	Gas Liquid Solid	Solid Solid Solid	Solution of hydrogen in palladium Amalgam of mercury with sodium Copper dissolved in gold

Some Important Definitions

- **Mixture -** When two or more chemically non-reacting substances are mixed, they form mixture.
- **Heterogeneous Mixture -** It consists of distinct phases, and the observed properties are just the sum of the properties of individual phases.
- **Homogeneous Mixture -** It consists of a single phase which has properties that may differ from one of the individual components.
- **Solution -** The homogeneous mixture of two or more components such that at least one component is a liquid is called solution.
- **Solvent -** It is the constituent of solution which has same physical state as that of solution and generally present in greater amount than all the other components.
- **Solute -** The component of a solution other than solvent is called solute, may or may not have same physical state as that of solution. Generally it is in smaller amount.

  ***Example* -** In a sugar syrup (liquid solution) containing 60% sugar (solid) and 40% water (liquid), water is termed as solvent, due to same physical state as that of solution.

Expressing the Strength of Solution

For a given solution the amount of solute dissolved per unit volume of solution is called concentration of solute. Strength of solution is the amount of solute in grams dissolved in one litre of solution. It is generally expressed in g/litre.

Other methods of expressing the strength of solution are:

1. **Mass percentage –**

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

$$\text{Mass \% of solvent} = \frac{\text{Mass of solvent}}{\text{Total mass of solution}} \times 100$$

2. **Volume percentage –**

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

$$\text{Volume \% of solvent} = \frac{\text{Volume of solvent}}{\text{Total volume of solution}} \times 100$$

3. **Molality (m) -** It is no. of moles of solute dissolved in 1 kg of the solvent.

$$\text{m} = \frac{(\text{Number of moles of solute})}{(\text{Mass of solvent \{in kg\}})}$$

4. **Molarity (M) -** It is no. of moles of solute dissolved in 1 litre of solution.

$$\text{M} = \frac{(\text{Number of moles of solute})}{(\text{Mass of soution \{in litre\}})}$$

5. **Normality (N) -** It is no. of gram-equivalents of solute dissolved in 1 litre of solution

$$\text{N} = \frac{(\text{Number of gram equivalents of solute})}{(\text{Volume of solution \{in litre\}})}$$

6. **Formality -** Ionic solutes do not exist in the form of molecules. These molecular mass is expressed as Gram-formula mass. Molarity for ionic compounds is actually called as **formality.**

7. **Mole fraction –**

$$\text{Mole fraction of solute} = \frac{(\text{Number of moles of solute})}{(\text{Total moles of solution})}$$

$$\text{Mole fraction of solvent} = \frac{(\text{Number of moles of solvent})}{(\text{Total moles of solution})}$$

For a binary solution,

mole fraction of solute + mole fraction of solvent = 1.

8. **Parts per million (ppm) –**

It is defined in two ways

ppm = mass fraction × 10^6

ppm = mole fraction × 10^6

Solubility

Solubility of a substance is its maximum amount that can be dissolved in a specified amount of solvent at a specified temperature. It depends upon the nature of solute and solvent as well as temperature and pressure. Let us consider the effect of these factors in solution of a **solid** or a **gas** in a **liquid**.

1. Solubility of Solid in Liquid

A solute dissolves in a solvent if the intermolecular interactions are similar in them, i.e., like dissolves like.

Polar solute dissolves in polar solvent and non-polar solute in non-polar solvent. For e.g., sodium chloride and sugar dissolves readily in water and napthalene and anthracene dissolves readily in benzene.

Solute + Solvent ⟶ Solution

i. **Dissolution:** When a solid solute is added to the solvent, some solute dissolves and its concentration increases in solution. This process is called **dissolution**.

ii. **Crystallization**: Some solute particles collide with solute particles in solution and get separated out. This process is called **crystallization**.

iii. **Saturated solution**: Such a solution in which no more solute can be dissolved at the same temperature and pressure is called a **saturated solution.**

iv. **Unsaturated solution:** An unsaturated solution is one in which more solute can be dissolved at the same temperature.

v. **Effect of temperature**: In general, if in a nearly saturated solution, the dissolution process is endothermic, the solubility should increase with rise in temperature, if it is exothermic, the solubility should decrease with rise in temperature.

vi. **Effect of pressure**: Solids and liquids are highly incompressible, so pressure does not have any significant effect on solubility of solids and liquids.

vii. **Supersaturated solution**: When more solute can be dissolved at higher temperature in a saturated solution, then the solution becomes supersaturated.

2. Solubility of Gas in Liquid

All gases are soluble in water as well as in other liquids to a greater or lesser extent. The solubility of a gas in liquid depends upon the following factors Nature of the gas, Nature of solvent, Temperature and Pressure.

Generally, the gases which can be easily liquified are more soluble in common solvents. For e.g., CO2 is more soluble than hydrogen or oxygen in water. The gases which are capable of forming ions in aqueous solutions are much more soluble in water than other solvents. For e.g., HCl and NH3 are highly soluble in water but not in organic solvents (like benzene) in which they do not ionize.

i. **Effect of temperature:** Solubility of most of the gases in liquids decreases with rise in temperature. In dissolution of a gas in liquid, heat is evolved and thus this is an exothermic process. The dissolution process involves dynamic equilibrium and thus follows **Le Chatelier's** principle. As dissolution is exothermic the solubility of gas should decrease with rise in temperature.

ii. **Effect of pressure: Henry's law**: At constant temperature, the solubility of a gas in a liquid is directly proportional to the pressure of the gas.

$$p = KH\ x$$

KH = Henry's law constant.

Applications of Henry's law

1. In manufacture of soft drinks and soda water, CO_2 is passed at high pressure to increase its solubility.
2. To minimise the painful effects accompanying the decompression of deep sea divers. O_2 diluted with less soluble. He gas is used as breathing gas.
3. At high altitudes, the partial pressure of O_2 is less then that at the ground level. This leads to low concentrations of O_2 in the blood of climbers which causes '**anoxia**'.

Vapour Pressure of Solution

It is the pressure exerted by vapour on the surface layer of liquid at equilibrium between vapour and liquid.

Factors affecting Vapour Pressure

i. **Nature of liquid -** Liquid with higher intermolecular attraction forces form less amount of vapour and hence lower vapour pressure and vice-versa.

ii. **Temperature -** Vapour pressure increases with temperature of liquid. This is because, as temperature increases, kinetic energy of the molecules increases, hence, more molecules leave the surface of the liquid and come into vapour phase.

Raoult's Law

According to Raoult's law, for a solution of volatile liquids, the relative lowering of vapour pressure of solution is directly proportional to its mole fraction of dissolved solvent in solute.

$$\frac{P^\circ - P}{P^\circ} = X_A$$

Ideal and Non-Ideal Solution

The binary liquid-liquid solution may be classified into two types:

(1) Ideal solutions

(2) Non-ideal solutions

1) Ideal Solutions

An **ideal solution** may be defined as the solution which obeys Raoult's law over the entire range of concentration.

a) Such solutions are formed by mixing two components which are identical in molecular size, in structure and have almost identical intermolecular forces.

b) The intermolecular interactions between the components (A – B attractions) are of same magnitude as the intermolecular interactions in pure components (A- A and B-B attractions).

According to Raoult's law, the partial vapour pressure of two components of the solution may be given as :

$$p_A = p_A^\circ x_A$$

$$p_B = p_B^\circ x_B$$

Total pressure p is given by

$p = p_A + p_B$

$p = p_A^\circ x_A + p_B^\circ x_B$

The ideal solutions have also the following characteristics:

1) **Heat change on mixing is zero:** Since there is no change in magnitude of the attractive forces in the two components present, the heat change on mixing i.e. $\Delta_{mixing}H$ in such solutions must be zero.

2) **Volume change on mixing is zero:** In ideal solutions, the volume of the solution is the sum of the volumes of the components before mixing i.e. there is no change in volume on mixing or $\Delta_{mixing} V$ is zero.

The solutions generally tends to become ideal when they are dilute.

The characteristics of an ideal solution may be summed up as follows:

(i) It must obey Raoult's law.

(ii) $\Delta_{mixing} H$ should be zero.

(iii) $\Delta_{mixing} V$ should be zero.

Example of Ideal Solutions

(i) Benzene and toluene

(ii) n-hexane and n-heptane

(iii) Bromoethane and iodoethane

(iv) Chlorobenzene and bromobenene

Solutions which obey Raoult's law are called **ideal liquid solution.**

Composition in Vapour Phase

The composition of vapour phase in equilibrium with the solution is determined by the partial pressure of the components. If y1and y2 are the mole fraction of the two components 1 and 2 respectively in the vapour phase, then according to Dalton's law of partial pressures:

Partial pressure of a component =Mole fraction of the component x Total pressure

$$p_1 = y_1 p$$

$$p_2 = y_2 p$$

In general, $P_i = y_i p_{total}$

Mole fraction of component 1 in vapour phase $y_1 = p_1/p$

Mole fraction of component 2 in vapour phase, $y_2 = p_2/p$

Mole fraction of a component in vapour phase =

Partial vapour pressure of component / Total Vapour Pressure

2) Non-Ideal Solutions

The solutions which do not obey Raoult's law over the entire range of concentration are called **non-ideal solutions**. Therefore, for such solutions

$$p_A \neq p_A^\circ x_A$$

$$p_B \neq p_B^\circ x_B$$

The vapour pressure of such solutions is either higher or lower than that predicted by Raoult's law.

In non-ideal solutions, there is a noticeable change in volume and heat energy when the two components are mixed.

Most of the solutions are non-ideal because they deviate from ideal behaviour to more or less extent.

Thus, for non-ideal solutions,

a) none of the components obey Raoult's law over the entire composition range, i.e.

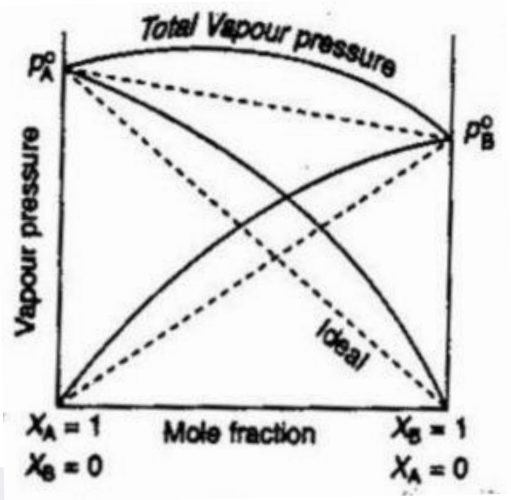
$$p_A \neq p_A^\circ x_A \text{ and } p_B \neq p_B^\circ x_B$$

b) (i) $\Delta_{mixing} H$ is not equal to zero

(ii) $\Delta_{mixing} V$ is not equal to zero

Ideal solution	Non-Ideal solution
The interactions between the components are similar to those in the pure components.	The interaction between the components are different from those of the pure components.
There is no enthalpy change on mixing. $\Delta_{mixing}H = 0$	There is no enthalpy change on mixing. $\Delta_{mixing}H \neq 0$
There is no volume change on mixing. $\Delta_{mixing} V = 0$	There is no volume change on mixing. $\Delta_{mixing} V \neq 0$
Each component obeys Raoult's law at all temperatures and concentrations, $p_A = p_A^\circ x_A$ and $p_B = p_B^\circ x_B$	Their components do not obey Raoult's law. They show positive and negative deviations from Raoult's law. $p_A \neq p_A^\circ x_A$ and $p_B \neq p_B^\circ x_B$

Types of Non-ideal Solutions



Non-ideal solutions show positive and negative deviations from the ideal behaviour depending upon their nature.

(1) Non-Ideal solutions showing positive deviations from Raoult's law

Consider a binary solution of two components A and B.

If the A-B interactions in the solutions are weaker than the A-A and B-B interactions in the two liquids forming the solution, then the escaping tendency of A and B types of molecules from the solution becomes more than from pure liquids. As a result, each component of solution has a partial vapour pressure greater than expected on the basis of Raoult's law. The total vapour pressure will be greater than corresponding vapour pressure expected in case of ideal solution of the same composition. This type of behaviour of solution is described as positive deviations from Raoult's law.

pA >pA° xA and

pB >pB° xB

The total vapour pressure,

p= pA+ pB is always greater than (pA° xA + pB° xB)

Examples of solutions showing positive deviations are :

(i) Ethyl alcohol and cyclohexane

(ii) Acetone and carbon disulphide

(iii) Benzene and acetone

(iv) Carbon tetrachloride and choloroform

(v) Acetone and ethyl alcohol

(vi) Ethyl alcohol and water.

Explanation for positive deviations

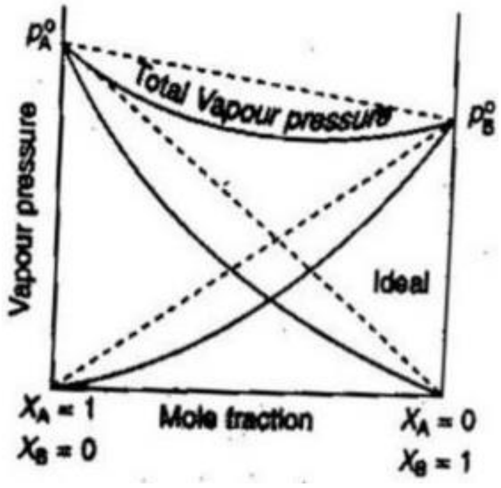
In ethyl alcohol, the molecules are held together due to hydrogen bonding. When cyclohexane is added to ethyl alcohol, the molecules of cyclohexane tend to occupy the spaces between ethyl alcohol molecules. Consequently, some hydrogen bonds in alcohol molecules break and the attractive forces in alcohol molecules are weakened. The escaping tendency of alcohol and cyclohexane molecules from the solution increases. Consequently, the vapour pressure of the solution is greater than the vapour pressure as expected according to Raoult's law.

(i) Δmixing H is positive because energy is required to break A-A or B-B attractive forces. Therefore, dissolution process is endothermic.

(ii) Because of the decrease in the magnitude of intermolecular forces in solutions, the molecules will be loosely held and, therefore, there will be increase in volume on mixing. Thus, Δmixing V will be positive.

(iii) Since the dissolution process in endothermic, heating will increase the solubility of such a solution.

(2) Non-Ideal solutions showing negative deviations from Raoult's law.



In such solutions, the A-B interactions are stronger than the A-A and B-B interactions present in the two liquids forming the solution. Due to stronger A-B interactions, the escaping tendency of A and B types of molecules from the solution becomes less than from pure liquids. Consequently, each component of the solution has a partial vapour pressure less than expected on the basis of Raoult's law. As a result , the total vapour pressure becomes less than the corresponding vapour pressure expected in case of ideal solution.

$pA < pA° xA$ and

$pB < pB° xB$

$p= pA+ pB$ is always less than $(pA° xA + pB° xB)$

Examples of Negative Deviation

(i) Acetone and chloroform

(ii) Chloroform and diethyl ether

(iii) Chloroform and nitric acid

(iv) Acetone and aniline

(v) Water and nitric acid

(vi) Diethyl ether and chloroform.

Explanation for Negative Deviations

When acetone and chloroform are mixed there are new attractive forces due to intermolecular hydrogen bonding. Thus the attractive forces become stronger and the escaping tendency of each liquid from the solution decreases. Therefore, the vapour pressure of the solution is less than that expected for an ideal solution.

(i) ΔmixingH is negative because energy is released due to increase in attractive forces. Therefore, dissolution process is exothermic and heating the solution will decrease solubility.

(ii) Because of the increase in the magnitude of forces of attraction in solutions, the molecules will be loosely held more tightly. Therefore, there will be decrease in volume on mixing. Thus, ΔmixingV will be negative.

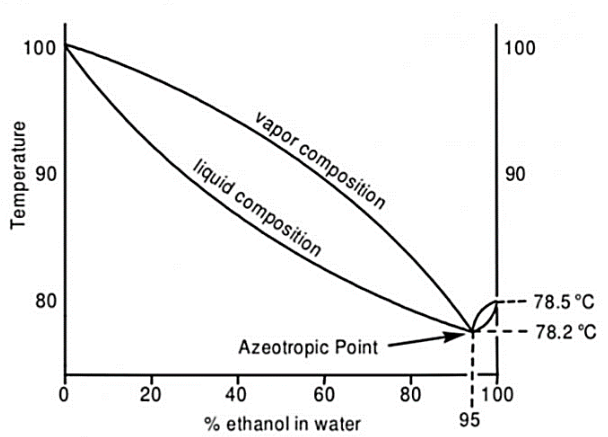
Difference between Ideal and Non-Ideal solution

Solution having positive deviation	Solution having negative deviation
A-B forces are less than A-A and B-B forces.	A-B forces are more than A-A and B-B forces.
$pA > pA° xA$ and $pB > pB° xB$	$pA < pA° xA$ and $pB < pB° xB$
ΔmixingH is positive	ΔmixingH is negative
Dissolution is endothermic	Dissolution is exothermic
Heating increases solubility	Heating decreases solubility
ΔmixingV will be positive.	ΔmixingV will be negative.

a) Some solution exhibit very large positive deviation from Raoult's law that there is a maximum in the vapour pressure curve which is above the vapour pressure of either pure components.

For one of the intermediate composition, the total vapour pressure of such a solution will be the highest and the boiling point will be the lowest. At this point, the composition of liquid and vapour phase is same and the liquid mixture boils at constant temperature and remains unchanged in composition. Therefore, this liquid mixture distills over as if it is a pure liquid. Solution acquires the property of boiling at constant temperature and remains unchanged in composition.

The solutions (liquid mixtures) which boil at constant temperature and can distil unchanged in composition are called azeotropes or azeotropic mixtures. Thus, the azeotropes distil over as if it were pure liquids. These types of solutions are called minimum boiling azeotropes.



For example: Ethanol and water form minimum boiling azeotrope. It has maximum in the vapour pressure curve and hence a minimum in the boiling point diagram. In this boiling point diagram, we indicate the composition of the vapour phase by the upper curve and composition of the liquid phase by the lower curve.

The boiling point diagram shows an azeotropic composition at $x(H_2O)=0.056$ and $x(C_2H_5OH) = 0.944$ at a temperature.of 351 K (or 78°C) which is lower than that of pure ethanol 351.5 K (or 78.5°C) and water 378 K (or 100°C).

Fractional distillation of solutions lying on either side of this azeotropic composition is capable of separating them into at best, one pure component and a azeotropic mixture having the minimum boiling point.

b) In the case of solutions showing negative deviations, total vapour pressure becomes less than the corresponding ideal solution of same composition. The boiling points of such solutions are increased.

For one of the intermediate composition, the total vapour pressure will be the least and the boiling point will be the highest. At this composition, the solution also boils at constant temperature without a change in composition. This is also called azeotrope.

The solutions which show negative deviations from Raoult's law are called **maximum boiling azeotropes** because they have a composition having maximum boiling point

For example: hydrochloric acid and water form maximum boiling point azeotrope at the composition $x(H_2O)=0.889$ and $x(HCl)=0.111$ (or 20.2% HCl) which boils at 381.6 K (or 108.6°C) which has higher than that of pure water.

Nitric acid (HNO_3) and water also form maximum boiling azeotrope. The azeotrope has the approximate composition 68% nitric acid and 32% water by mass with a boiling point of 393.5 K.

Thus, the azeotropes are liquid mixtures of definite composition, which boil at constant boiling point. These cannot be separated into pure components by fractional distillation.

Colligative Properties

The properties of dilute solution which depends only on number of particles of solute (molecules or ions) present in the solution and not on their nature, are called colligative properties. The important **colligative properties** are;

1. Relative lowering of vapour pressure
2. Elevation of boiling point
3. Depression in freezing point
4. Osmotic pressure

i. Relative Lowering of Vapour Pressure

When a non-volatile solute is added to a solvent, its vapour pressure gets **lowered.** If this pressure is divided by pressure of pure solvent, this is called **relative lowering of vapour pressure.**

According to **Raoult's law,**

$$\frac{P^\circ - P}{P^\circ} = X_A$$

where, P° = V.P. of pure solvent

P° – P = lwering in vapour pressure

$$\frac{P^\circ - P}{P^\circ} = \frac{n_A}{n_A + n_B} .... \left[X_A = \frac{n_A}{n_A + n_B} \right]$$

For dilute solution $n_A + n_A \approx n_A$

$$\frac{P^\circ - P}{P^\circ} = \frac{n_A}{n_B}$$

$$\frac{P^\circ - P}{P^0} = \frac{W_A}{M_A} \times \frac{M_B}{W_B}$$

where,
W_A = weight of solute
W_B = weight of solvent
M_A = molecular weight of solute
M_B = molecular weight of solvent

ii. Relative Elevation of boiling point

A liquid boils at the temperature at which its vapour pressure is equal to the atmospheric pressure. The boiling point of a solution of non-volatile solute is always higher than that of the boiling point of pure solvent in which the solution is prepared. Similar to lowering of vapour pressure, the elevation of boiling point also depends on the number of solute particles rather than their nature.

Let T° be the boiling point of pure solvent and T be the boiling point of solution. The increase in boiling point $\Delta Tb = T - T^\circ$ is known as **elevation in boiling point**.

For dilute solutions, the ΔT_b is directly proportional to the molal concentration of the solute in a solution. Thus

$$\Delta T_b \propto m$$

$$\Delta T_b = K_b m$$

K_b is molal **elevation constant** (Ebullioscopic constant). The unit of K_b is K kg mol^{-1}.

Substituting the value of molality in above equation, we get

$$\Delta T_b = \frac{K_b \times 1000 \times w_2}{M_2 \times w_1}$$

$$M_2 = \frac{K_b \times 1000 \times w_2}{\Delta T_b \times w_1}$$

Where, w_1 = mass of solvent, w_2 = mass of solute and M_2 = molar mass of solute

iii. Depression in freezing point

Freezing point is the temperature at which vapour pressure of liquid phase becomes same as that of solid phase. The decrease in freezing point of a solvent on the addition of a non-volatile solute is known as **depression in freezing point**.

Let T° be the freezing point of pure solvent and T be the freezing point of solution. The decrease in freezing point $\Delta T_f = T^\circ - T$ is known as depression in freezing point.

For dilute solutions, the ΔT_f is directly proportional to the molal concentration of the solute in a solution. Thus

$$\Delta T_f \propto m$$

$$\Delta T_f = Kf \cdot m$$

Here K_f is molal depression constant or cryoscopic constant

Substituting the value of molality in above equation, we get

$$\Delta T_f = \frac{K \times w_2 \times 1000}{M_2 \times w_1}$$

$$M_2 = \frac{K \times w_2 \times 1000}{\Delta T_f \times w_1}$$

Where, w_1 = mass of solvent, w_2 = mass of solute and M_2 = molar mass of solute

iv. Osmotic pressure

Osmosis is the spontaneous flow of the solvent molecules from a less concentrated solution (dilute) to a more concentrated solution through a **semi-permeable membrane**. The driving force of osmosis is called **osmotic pressure**. Osmotic pressure may be defined as "the minimum excess pressure that has to be applied on the solution to prevent the osmosis".

Osmotic pressure of a solution ∝ molar concentration of solute in that solution

$$\pi \propto c$$

$$\pi = cRT$$

where, R = Gas constant = 0.0821 lit atm K^{-1} $mole^{-1}$

T = Temperature

c = Molar concentration

$$\pi = \frac{n}{V}RT \ldots\ldots \left[c = \frac{n}{V}\right]$$

$$\pi = \frac{W_B}{M_B}\frac{RT}{V}$$

W_B = wt. of solute

M_B = Molar mass of solute

van't Hoff Factor

To calculate the extent of association or dissociation, van't Hoff in 1886 introduced a factor 'i' called van't Hoff factor. **van't Hoff factor** 'i' is defined as ratio of the experimental value of colligative property to the calculated value of colligative property.

$$i.e., \mathrm{i}\frac{\text{Experiment ecolligatival properties}}{\text{Calculated ecolligativ properties}}$$

Abnormal Molar Masses

Abnormal Molecular Masses

The accurate values of molar masses can be obtained only if the following two conditions are met.

(i) The solutions should be dilute

The solutions used for measuring colligative properties must not be too concentrated. In the concentrated solutions, the particles begin to interact with each other as well as with the solvent. As a result, the vapour pressure and therefore, other colligative properties depend upon the nature of the solute and not just on the number of solute particles.

(ii) The solute must not dissociate or associate in solution

The equations derived for measuring the colligative properties are for non-electrolyte solutes which do not undergo any dissociation or association in the solution.

Discrepancies in determination of molar mass arise when the solute dissociate or associate on dissolving in a solvent. This is because due to the association or the dissociation of the solute molecules in the solution, the number of molecules undergo a change.

The discrepancy in molar mass is called abnormal molar mass. The abnormal molar masses is due to association or dissociation of solute particles.

Association of Solute Particles

In certain solvents, generally non-polar, the solute molecules undergo association i.e. two, three or even more molecules exist in combination with each other to form bigger molecules. For example: suppose n simple molecules combine to form an associated molecule as:

$$nA \Leftrightarrow A_n$$

Therefore, the total number of molecules in solution become less than the number of molecules of the substance added and, therefore, colligative properties will be lower. Since the colligative properties are inversely proportional to the molar mass of the solute, the molar masses in such cases will be greater than the theoretical values.

For example: In benzene solvent, both ethanoic acid (acetic acid) and benzoic acid exist as dimers as:

$$2CH_3COOH \Leftrightarrow (CH_3COOH)_2$$

$$2C_6H_5COOH \Leftrightarrow (C_6H_5COOH)_2$$

The molar masses of ethanoic acid and benzoic acid have been found to be nearly 120 and 244 which are about double than their normal values of 60 and 122. The association of solute molecules in a solution is generally due to the hydrogen bonding between these molecules.

For example: benzoic acid and ethanoic acid exist as dimers due to the formation of hydrogen bonds. Due to association of ethanoic acid or benzoic acid, the ΔTf or ΔTb value will be about half of the normal value. Therefore, the molar mass calculated on the basis of ΔT will be about twice the expected value.

Dissociation of Solute Molecules

Molecules of certain substances (acids, bases and salts) dissociate or ionise in a solvent to give two or more particles.

For example: AB dissociates to give double number of particles as:

$$AB \Leftrightarrow A+ + B-$$

The total number of particles increases in solution and, therefore, the colligative properties of such solutions will be large. Since colligative properties are inversely proportional to molar mass, the observed molar mass will be less than the theoretical value.

For example, KCl dissociates to give K+ and Cl– ions.

$$KCl \Leftrightarrow K+ + Cl-$$

If we dissolve 1 mol of KCl (74.5 g) in water, we expect 1 mol of K+ and 1 mol of Cl– ions to be produced in the solution. Therefore, there would be 2 mol of particles in the solution instead of 1 mol. Consequently, the colligative properties would also be about double than expected.

For example: if we ignore interionic attraction, 1 mol of KCl in 1 kg of water would be expected to increase the boiling point by 2 X 0.52 K (Kb= 0.52 Km-1) = 1.04 K.

Van't Hoff Factor

In 1886, Van't Hoff introduced a factor called Van't Hoff factor, **i** , to express the extent of association or dissociation of solutes in solution. It is the ratio of the normal and observed molar masses (or abnormal molar mass) of the solute, i.e.

$$i = \frac{\text{Normal molar mass}}{\text{Observed molar mass}}$$

In case of association, observed molar mass being more than the normal, the factor **i** has a value less than 1.

But in case of dissociation, the Van't Hoff factor is more than 1 because the observed molar mass has a lesser value.

In case of solutes which do not undergo any association or dissociation in a solvent, the Van't Hoff factor i will be equal to 1 because the observed and normal molar masses will be same.

Since the molar masses are inversely proportional to the colligative property. Van't Hoff factor may also be expressed as:

$$i = \frac{\text{Observed colligative property}}{\text{Normal collegative property}}$$

Relative lowering in vapour pressure = i xsolute = Δp / p°

Elevation in boiling point , Δ Tb =i Kb m

Depression in freezing point = Δ Tf = i Kf m

Osmotic pressure π = i cRT

Van't Hoff Factor and Extent of Dissociation or Association in an Electrolytic Solution

Van't Hoff factor can be used to calculate the extent of dissociation or association in terms of degree of dissociation or association of a substance in solution.

(i) Degree of dissociation: It is defined as the fraction of total substance that undergoes dissociation into ions, i.e.

Degree of dissociation = No. of moles of the substance dissociated / Total number of moles of the substance taken

Suppose a molecule of an electrolyte gives n ions after dissociation. Then if we start with 1 mole of the solute, and α is the degree of dissociation, then at equilibrium:

Number of moles of solute left undissociated =1-α

Number of moles of ions formed = nα

Total number of moles of particles 1-α+ nα

Van't Hoff factor, i =

Observed number of moles of solute / Normal number of moles of solute

Total number of moles at equilibrium = 1 – α + $n\alpha$

$$\therefore \quad i = \frac{1-\alpha+n\alpha}{1}$$

$$\Rightarrow \quad \alpha = \frac{i-1}{n-1}$$

Knowing the value of i from observed molar mass and normal molar mass, degree of dissociation, α can be calculated.

For the electrolytes of the type AB, such as KCl, NaCl, etc,.the number of particles in solution i.e. n = 2

For the electrolytes of the type AB, like $CaCl_2$, $Ba(NO_3)2$ etc, the value of n=2, so that

α = (i-1) /2

(ii) Degree of association: It is defined as the fraction of total number of molecules which combine to form associated molecules, i.e.

$$\textbf{Degree of association} = \frac{\textbf{No. of moles of the substance associated}}{\textbf{Total number of moles of substance taken}}$$

For example: suppose n simple molecules of the solute associate to form the associated molecule A.

$$nA = A_n$$

If we start with 1 mole of A and α is the degree of association, the concentration of the species after association is

[An] = α/n

[A] =1-α

Total number of moles after association = 1-α+ α/n

Thus, the colligative properties will correspond to (1-α+ α/n) mole particles rather than one mole of particles.

Van't Hoff factor, i , is : Observed number of moles of solute / Normal number of moles of solute

= 1-α + α/n / 1

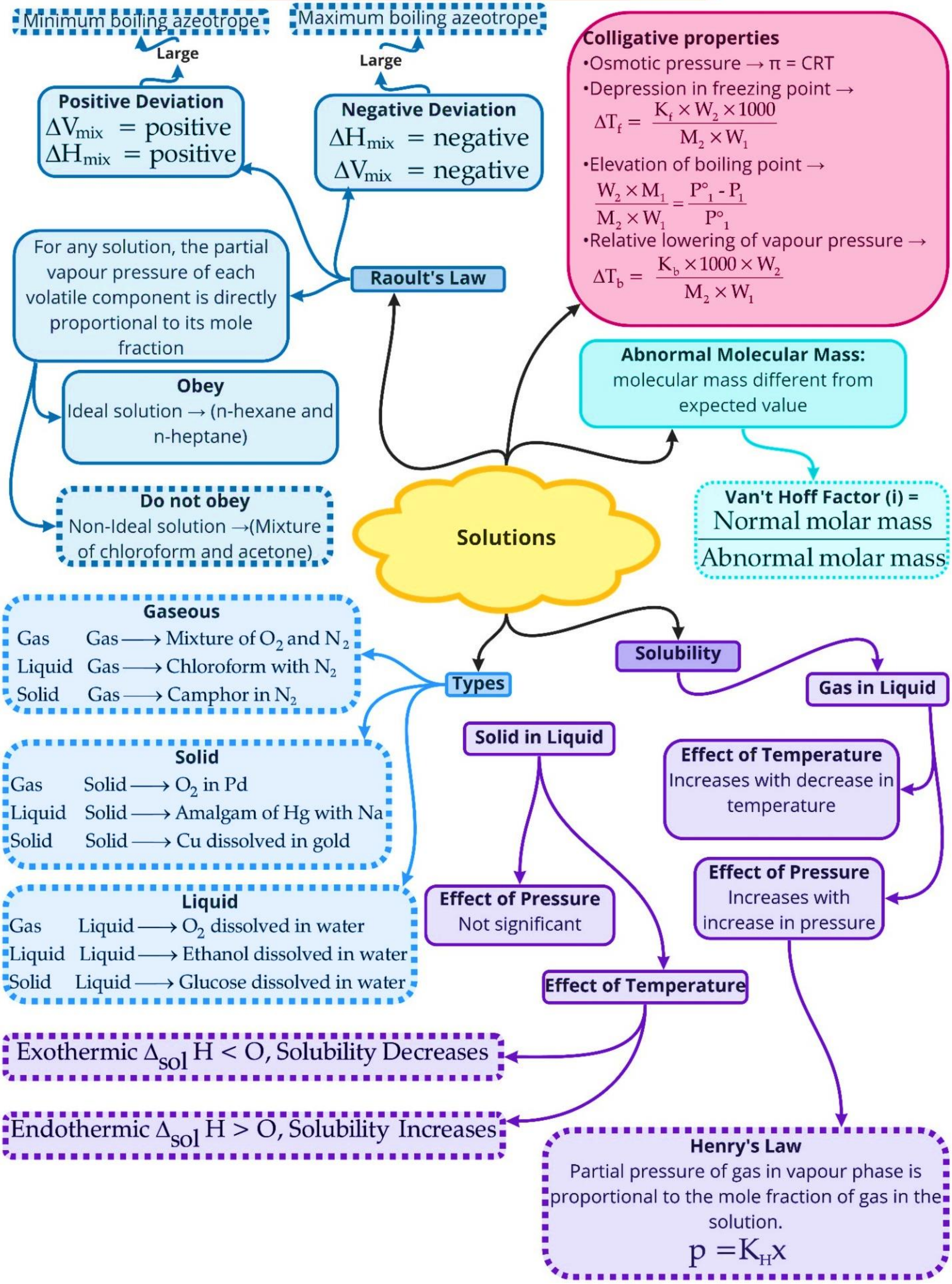
= 1+ α (1/n -1)

α =(i-1) /(1/n -1)

$$I = \frac{\textbf{Normal molar mass}}{\textbf{Observed molar mass}}$$

Knowing n the number of simple molecules which combine to give associated molecule, observed molar mass, degree of association(α) can be calculated.

Class : 12th Chemistry
Chapter-2 : Solutions (Part_1)



Solutions

Minimum boiling azeotrope ← Large ← **Positive Deviation**
$\Delta V_{mix} = \text{positive}$
$\Delta H_{mix} = \text{positive}$

Maximum boiling azeotrope ← Large ← **Negative Deviation**
$\Delta H_{mix} = \text{negative}$
$\Delta V_{mix} = \text{negative}$

Raoult's Law

For any solution, the partial vapour pressure of each volatile component is directly proportional to its mole fraction

Obey
Ideal solution → (n-hexane and n-heptane)

Do not obey
Non-Ideal solution →(Mixture of chloroform and acetone)

Colligative properties

- Osmotic pressure → π = CRT
- Depression in freezing point →

$$\Delta T_f = \frac{K_f \times W_2 \times 1000}{M_2 \times W_1}$$

- Elevation of boiling point →

$$\frac{W_2 \times M_1}{M_2 \times W_1} = \frac{P^\circ_1 - P_1}{P^\circ_1}$$

- Relative lowering of vapour pressure →

$$\Delta T_b = \frac{K_b \times 1000 \times W_2}{M_2 \times W_1}$$

Abnormal Molecular Mass:
molecular mass different from expected value

Van't Hoff Factor (i) =

$$\frac{\text{Normal molar mass}}{\text{Abnormal molar mass}}$$

Types

Gaseous
Gas Gas ⟶ Mixture of O_2 and N_2
Liquid Gas ⟶ Chloroform with N_2
Solid Gas ⟶ Camphor in N_2

Solid
Gas Solid ⟶ O_2 in Pd
Liquid Solid ⟶ Amalgam of Hg with Na
Solid Solid ⟶ Cu dissolved in gold

Liquid
Gas Liquid ⟶ O_2 dissolved in water
Liquid Liquid ⟶ Ethanol dissolved in water
Solid Liquid ⟶ Glucose dissolved in water

Solubility

Solid in Liquid

Effect of Pressure
Not significant

Effect of Temperature

Exothermic $\Delta_{sol} H < O$, Solubility Decreases

Endothermic $\Delta_{sol} H > O$, Solubility Increases

Gas in Liquid

Effect of Temperature
Increases with decrease in temperature

Effect of Pressure
Increases with increase in pressure

Henry's Law
Partial pressure of gas in vapour phase is proportional to the mole fraction of gas in the solution.

$$p = K_H x$$

Class : 12th Chemistry
Chapter-2 : Solutions (Part_2)

Solutions

Parts per million : For trace quantities

$$\frac{\text{No. of parts of components} \times 10^6}{\text{Total no. parts of components of solution}}$$

Normality: Number of gram equivalents of the solute dissolved in one litre of solution

$$\frac{\text{No. of gram equivalentof solute} \times 100}{\text{Volume of solution}}$$

$$\downarrow$$

Gram Equivalents of solute

$$= \frac{\text{Mass of solute}}{\text{Equivalent weight}}$$

$$\downarrow$$

$$\text{Equivalent weight} = \frac{\text{Molecular mass}}{\text{Valency}}$$

Mass by volume percentage (w/v)

$$\frac{\text{Mass of solute}}{\text{Volume of solution}} \times 100$$

Mass percentage w/w

$$\frac{\text{Mass of component in solution}}{\text{Total mass of solution}} \times 100$$

Volume percentage v/v

$$\frac{\text{Volume of component}}{\text{Total volume of solution}} \times 100$$

Mole fraction

$$\frac{\text{No. of moles of component}}{\text{Total No. of moles of all components}}$$

Molality: Number of moles of solute per kilogram of the solvent

$$\frac{\text{No. of moles of solute} \times 100}{\text{Mass of solvent}}$$

Molarity: Number of moles of solute in 1L solution

$$\frac{\text{No. of moles of solute} \times 100}{\text{Volume of solution}}$$

Important Questions

Multiple Choice Questions

1. Which of the following units is useful in relating concentration of solution with its vapour pressure?
   (a) mole fraction
   (b) parts per million
   (c) mass percentage
   (d) molality
2. On dissolving sugar in water at room temperature, solution feels cool to touch. Under which of the following cases dissolution of sugar will be most rapid?
   (a) Sugar crystals in cold water.
   (b) Sugar crystals in hot water.
   (c) Powdered sugar in cold water.
   (d) Powdered sugar in hot water.
3. At equilibrium the rate of dissolution of a solid solute in a volatile liquid solvent is
   (a) less than the rate of crystallisation
   (b) greater than the rate of crystallisation
   (c) equal to the rate of crystallisation
   (d) zero
4. A beaker contains a solution of substance 'A'. Precipitation of substance 'A' takes place when small amount of 'A' is added to the solution. The solution is ………………
   (a) saturated
   (b) supersaturated
   (c) unsaturated
   (d) concentrated
5. Maximum amount of a solid solute that can be dissolved in a specified amount of a given liquid solvent does not depend upon .
   (a) temperature
   (b) nature of solute
   (c) pressure
   (d) nature of solvent
6. Low concentration of oxygen in the blood and tissues of people living at high altitude is due to
   (a) low temperature
   (b) low atmospheric pressure
   (c) high atmospheric pressure
   (d) both low temperature and high atmospheric pressure
7. Considering the formation, breaking and strength of hydrogen bond, predict which of the following mixtures will show a positive deviation from Raoult's law?
   (a) Methanol and acetone.
   (b) Chloroform and acetone.
   (c) Nitric acid and water.
   (d) Phenol and aniline.
8. Colligative properties depend on
   (a) the nature of the solute particles dissolved in solution.
   (b) the number of solute particles in solution.
   (c) the physical properties of the solute particles dissolved in solution.
   (d) the nature of solvent particles.
9. Which of the following aqueous solutions should have the highest boiling point?
   (a) 1.0 M NaOH
   (b) 1.0 M Na_2SO_4
   (c) 1.0 M NH_4NO_3
   (d) 1.0 M KNO_3
10. The unit of ebullioscopic constant is
    (a) K kg mol^{-1} or K $(molality)^{-1}$
    (b) mol kg K^{-1} or K^{-1} (molality)
    (c) kg mol^{-1} K^{-1} or K^{-1} $(molality)^{-1}$
    (d) K mol kg^{-1} or K (molality)
11. In comparison to a 0.01 M solution of glucose, the depression in freezing point of a 0.01 M $MgCl_2$ solution is ………..
    (a) the same
    (b) about twice
    (c) about three times
    (d) about six times
12. An unripe mango placed in a concentrated salt solution to prepare pickle shrivels because ………..
    (a) it gains water due to osmosis.
    (b) it loses water due to reverse osmosis.
    (c) it gains water due to reverse osmosis.
    (d) it loses water due to osmosis.

13. At a given temperature, osmotic pressure of a concentrated solution of a substance
    (a) is higher than that of a dilute solution.
    (b) is lower than that of a dilute solution.
    (c) is same as that of a dilute solution.
    (d) cannot be compared with osmotic pressure of dilute solution.
14. Which of the following statements is false?
    (a) Two different solutions of sucrose of same molality prepared in different solvents will have the same depression in freezing point.
    (b) The osmotic pressure of a solution is given by the equation $\pi = cRT$ (where c is the molarity of the solution).
    (c) Decreasing order of osmotic pressure for 0.01 M aqueous solutions of barium chloride, potassium chloride, acetic acid and sucrose is $BaCl_2 > KCl > CH_3COOH >$ sucrose.
    (d) According to Raoult's law, the vapour pressure exerted by a volatile component of a solution is directly proportional to its mole fraction in the solution.
15. The values of Van't Hoff factors for KCl, NaCl and K_2SO_4, respectively, are
    (a) 2, 2 and 2
    (b) 2, 2 and 3
    (c) 1,1 and 2
    (d) 1, 1 and 1

Very Short Question:

1. Define the term – solubility?
2. What is the effect of pressure on solubility of a gas?
3. State Henry's Law.
4. State Raoult's Law.
5. What are the factors on which vapour pressure depends?
6. The vapour pressure of solvent gets lowered, when a non- volatile solute is added to it. Why?
7. Name two ways by which vapour pressure of a liquid can be lowered.
8. Define solution?
9. Define the following terms:
    (a) Molality
    (b) Molarity
10. How does change in temperature changes the molarity and molality values?

Short Questions:

1 Find the molality and molarity of a 15% solution of H_2SO_4 when its density is
    a) 1.10 glcm^3 & molar mass = 98 amu.
2. Calculate the mole fraction of ethanol and water in a sample of rectified spirit which contains 46% ethanol by mass?
3. Calculate the % composition in terms of mass of a solution obtained by mixing 300g of a 25% & 400 g of a 40% solution by mass?
4. One litre of sea water weight 1030g and 6×10^{-3} g contains about of dissolved O_2. Calculate the concentration of dissolved oxygen in ppm?
5. The density of 85% phosphoric acid is 1.70 g/cm^3. What is the volume of a solution that contains 17g of phosphoric acid?
6. Define the term azeotrope?
7. Obtain a relationship between relative lowering of vapour pressure and mole fraction of solute?
8. Draw the graphs of both deviations from ideal behaviours?
9. A weak electrolyte AB in 5% dissociated in aqueous solution? What is the freezing point of a 0.10 molar aqueous solution of AB? $K_f = 1.86$ deg/molal?
10. Henry's law constant for the molality of methane in 4.27 × 105 mmHg benzene at 298 K is . Calculate the solubility of methane in benzene at 298 K under 760 mm Hg.

Long Questions:

1. The vapour pressure of CS_2 500°C at is 854 mm Hg. A solution of 2.0g sulphur in 100g of has a vapour pressure CS_2 of 848.9 mm Hg. Calculate the formula of sulphur molecule

2. Calculate the mass percentage of benzene (C_6H_6) and carbon tetrachloride (CCl_4) if 22 g of benzene is dissolved in 122 g of carbon tetrachloride.

3. Calculate the mole fraction of benzene in solution containing 30% by mass in carbon tetrachloride.

4. Calculate the molarity of each of the following $CO(NO_3)_2\ 6H_2O$ solutions: (a) 30 g of. in 4.3 L of solution (b) 30 mL of 0.5 M H_2SO_4 diluted to 500mL.

5. Calculate (a)molality (b)molarity and (c)mole fraction of KI if the density of 20% (mass/mass) aqueous KI 1.202 g ml^{-1} is.

Assertion and Reason Questions:

1. In these questions, a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following choices.
   - a) Assertion and reason both are correct statements and reason is correct explanation for assertion.
   - b) Assertion and reason both are correct statements but reason is not correct explanation for assertion.
   - c) Assertion is correct statement but reason is wrong statement.
   - d) Assertion is wrong statement but reason is correct statement.

   Assertion: Camphor is used as a solvent in the determination of molecular masses of naphthalene, anthracene, etc.

   Reason: Camphor has high molal elevation constant.

2. In these questions, a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following choices.
   - a) Assertion and reason both are correct statements and reason is correct explanation for assertion.
   - b) Assertion and reason both are correct statements but reason is not correct explanation for assertion.
   - c) Assertion is correct statement but reason is wrong statement.
   - d) Assertion is wrong statement but reason is correct statement.

   Assertion: Reverse osmosis is used in the desalination of sea water.

   Reason: When pressure more than osmotic pressure is applied, pure water is squeezed out of the sea water through the membrane.

Case Study Questions:

1. Read the passage given below and answer the following questions:

The solubility of gases increases with increase of pressure. William Henry made a systematic investigation of the solubility of a gas in a liquid. According to Henry's law "the mass of a gas dissolved per unit volume of the solvent at constant temperature is directly proportional to the pressure of the gas in equilibrium with the solution". Dalton during the same period also concluded independently that the solubility of a gas in a ti quid solution depends upon the partial pressure of the gas. If we use the mole fraction of gas in the solution as a measure of its solubility, then Henry's law can be modified as "the partial pressure of the gas in the vapour phase is directly proportional to the mole fraction of the gas in the solution"

The following questions are multiple choice questions. Choose the most appropriate answer:

(i) Henry's law constant for the solubility of methane in benzene at 298K is 4.27 x 10^5mm Hg. The solubility of methane in benzene at 298K under 760mm Hg is:
   - a) 4.27×10^{-5}
   - b) 1.78×10^{-3}
   - c) 4.27×10^{-3}
   - d) 1.78×10^{-5}

(ii) The partial pressure of ethane over a saturated solution containing 6.56×10^{-2}g of ethane is I bar. If the solution contains 5.00×10^{-2}g of ethane then what will be the partial pressure (in bar) of the gas?
   - a) 0.762
   - b) 1.312
   - c) 3.81
   - d) 5.0

(iii) K_H (K bar) values for $Ar_{(g)}$, $CO_{2(g)}$, $HCHO_{(g)}$ and $CH_{4(g)}$ are 40.39, 1.67, 1.83×10^{-5} and 0.413 respectively. Arrange these gases in the order of their increasing solubility. Arrange these gases in the order of their increasing solubility.
   - a) HCHO < CH_4 < CO_2 < Ar
   - b) HCHO < CO_2 < CH_4 < Ar
   - c) Ar < CO_2 < CH_4 < HCHO
   - d) Ar < CH_4 < CO_2 < HCHO

(iv) When a gas is bubbled through water at 298K, a very dilute solution of the gas is obtained. Henry's law constant for the gas at 298K is 150 kbar. If the gas exerts a partial pressure of 2 bar, the number of millimoles of the gas dissolved in IL of water is:

a) 0.55

b) 0.87

c) 0.37

d) 0.66

(v) Which of the following statements is correct?

a) K_H increases with increase of temperature.

b) K_H decreases with increase of temperature.

c) K_H remains constant with increase of temperature.

d) K_H first increases then decreases, with increase of temperature.

2. Read the passage given below and answer the following questions

Few colligative properties are:

1. Relative lowering of vapour pressure: depends only on molar concentration of solute (mole fraction) and independent of its nature.
2. Depression in freezing point: it is proportional to the molal concentration of solution.
3. Elevation of boiling point: it is proportional to the molal concentration of solute.
4. Osmotic pressure: it is proportional to the molar concentration of solute

A solution of glucose is prepared with 0.052 g at glucose in 80.2 g of water. (KJ = 1.86K kg mol^{-1} and K_b = 5.2K kg mol^{-1})

The following questions are multiple choice questions. Choose the most appropriate answer:

(i) Molality of the given solution is.

a) 0.0052m

b) 0.0036m

c) 0.0006m

d) 1.29m

(ii) Boiling point for the solution will be.

a) 373.05K

b) 373.15K

c) 373.02K

d) 373.02K

(iii) The depression in freezing point of solution will be.

a) 0.0187K

b) 0.035K

c) 0.082K

d) 0.067K

(iv) Mole fraction of glucose in the given solution is.

a) 6.28×10^{-5}

b) 6.28×10^{-4}

c) 0.00625

d) 0.00028

(v) If same amount of sucrose ($C_{12}H_{22}O_{11}$) is taken instead of glucose, then.

a) Elevation in boiling point will be higher.

b) Depression in freezing point will be higher.

c) Depression in freezing point will be lower.

d) Both (a) and (b).

Answers key

MCQ answers:

1. **Answer:** (a) mole fraction
2. **Answer:** (d) Powdered sugar in hot water.
3. **Answer:** (c) equal to the rate of crystallisation
4. **Answer:** (b) supersaturated
5. **Answer:** (c) pressure
6. **Answer:** (b) low atmospheric pressure
7. **Answer:** (a) Methanol and acetone.
8. **Answer:** (b) the number of solute particles in solution.
9. **Answer:** (b) 1.0 M Na_2SO_4
10. **Answer:** (a) $K\ kg\ mol^{-1}$ or $K\ (molality)^{-1}$
11. **Answer:** (c) about three times
12. **Answer:** (d) it loses water due to osmosis.
13. **Answer:** (a) is higher than that of a dilute solution.
14. **Answer:** (a) Two different solutions of sucrose of same molality prepared in different solvents will have the same depression in freezing point.
15. **Answer:** (b) 2, 2 and 3

Very Short Answers:

1. The maximum amount of a substance that can be dissolved in a specified amount of solvent is called its solubility.
2. The solubility of a gas increases with increases of pressure.
3. **Answer:** Henry's Law states that at a constant temperature the solubility of a gas in a liquid is directly proportional to the pressure of the gas.
4. **Answer:** Raoult's Law states that for a solution of volatile liquids, the partial vapour pressure of each component in the solution is directly proportional to its mole fraction.
5. **Answer:** The factors on which vapour pressure depends are –

   1) Temperature of the liquid.

   2) Nature of the liquid.
6. **Answer:** When a non-volatile solute is added to a solvent, the surface area for escape of solvent molecules decreases and vapour pressure gets lowered.
7. **Answer:** The two ways by which vapour pressure can be lowered are –

   1) By decreasing the temperature.

   2) By adding a non- volatile solute.
8. Solutions are homogeneous mixtures of two or more than two components.
9. (a) Molality is defined as the number of moles of the solute per kilogram of solvent.

$$\text{Molality(m)} = \frac{\text{Moles of solutes}}{\text{Mass of solvent in Kg}}$$

   (b) Molarity (M) = Number of moles of solute dissolved in one litre of solution.

$$\text{Molalrity(M)} = \frac{\text{No. of Moles of solute}}{\text{Volume of solution in litre}}$$

10. As the temperature increases, volume increases and molarity decreases whereas molality does not change with any change in temperature.

Short Answers:

1. **Answer**

Volume = mass/density

= 100 g/1.10 glcm3 = 90.9 cm3

$$\text{Molalrity} = \frac{\text{No. of Moles of } H_2SO_4}{\text{Volume of solution}} \times 1000$$

$$= \frac{(15/98)}{90.9} \times 1000 = 1.68\,m$$

$$\text{Molality} = \frac{\text{Moles of solute}}{\text{Mass of solvent in kg}}$$

$$= \frac{(15/98)}{85g} \times 1000 = 1.8\ \text{M}$$

2. **Answer:**

Mass of ethanol = 46g

Mass of water = 100 – 46 = 54g

$$X_A = \frac{X_A}{X_A + X_B}$$

Mole fraction of ethanol,

$$= \frac{\frac{46}{46}}{\frac{46}{46} + \frac{54}{18}} = \frac{1}{1+3} = \frac{1}{4} = 0.25$$

Mole fraction of water = 1-0.25 = 0.75

3. Answer:

Mass of solute in 400g of 40%

$$=\frac{40}{100}\times 400=160g$$

Total mass of solute = 160+75 = 235g

Total mass of solution = 400+300 = 700g

Mass % of solute $\frac{\text{mass of solute}}{\text{total mass of solution}}\times 100$

$$=\frac{235}{700}\times 100=33.57\%$$

Mass % of solvent = 100 – 33.57 = 66.43%

4. Answer:

Mass of O_2 = 6 × 10^{-3} g

ppm of O_2 in 1030 g sea water

$$=\frac{\text{mass of } O_2}{\text{mass of sea water}}\times 10^6$$

$$=\frac{6\times 10^{-3}}{1030}\times 10^6=5.8\text{ ppm}$$

5. Answer :

85g phosphoric acid is present in 100g of solution.

17g of phosphoric acid is present in

$$\frac{100}{85}\times 17=20\text{ g of solution}$$

Volume of 17g of 85% acid $=\frac{\text{mass}}{\text{density}}$

$$=\frac{20g}{1.70\ glcm^3}=11.8\ cm^3$$

6. Answer

A solution at certain concentration when continues to boil at constant temperature without change in its composition in solution & in vapour phase is called an azeotrope.

7. Answer:

According to Raoult's Law –

$$P_1=x_1p_1^0$$

$$\Delta P=P_1^0-P=P_1^0-P_1^0X_1$$

$$=\Delta P=P_1^0=P_1^0(1-X_1)$$

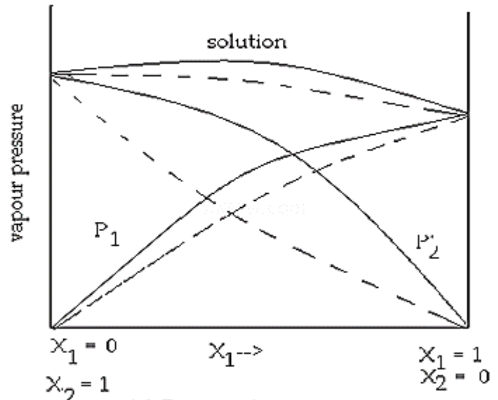
$$\Delta P_1=P_1^0X_2(X_1+X_2=1)$$

$$\frac{\Delta P_1}{P_1^0}=X_2$$

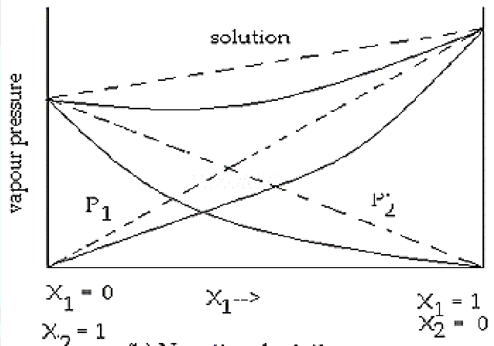
$$=\frac{P_1^0-P_1}{P_1^0}=X_2$$

Relative lowering of vapour pressure.

8. Answer:



(a) Positive deviation.



(b) Negative deviation

9. Answer :

Degree of dissociation ´ of AB = $\frac{5}{100}=0.05$

AB → A^+ + B^-

M 0 0

No. of moles dissolved

No. of moles after dissociations

m (1- α) m α m α

0.1(1–0.05) 0.1 × 0.05 0.1 × 0.0

Total moles = 0.1(1 – 0.05) + (0.1 × 0.05) + (.1 × 0.05)

= 0.095 + 0.005 + 0.005 = 0.105 m

$\Delta T_f = K_f$ m

= 1.86 0. × 105 = 0.1953 deg.

T_f = 0°C – 0.1953 = 0.1953°C

10. Answer :

p = 760 mm Hg

k_H = 4.27 × 105 mm Hg

According to Henry's law,

$p = k_H x$

$$x = \frac{p}{k_H}$$

$$= \frac{760\,mm\,Hg}{4.27 \times 10^5\,mm\,Hg}$$

$= 177.99 \times 10^{-5}$

$= 178 \times 10^{-5}$ (approximately)

Hence, the mole fraction of methane in benzene is 178×10^{-5}.

Long Answers:

1. **Answer:**

$$P_A^0 = 854\,mm\ \ P_A^0 = 848\,m,\ W_B = 2.0\,g$$

$$W_A = 100\,g\ M_B = ?$$

$$M_A = 12 + 2(32) = 76\,g/mol/CS^2$$

$$\frac{P_A^0 - P_A}{P_A^0} = X_B = \frac{W_B}{M_B} / \frac{W_A}{M_A}$$

$$= M_B = W_B \times \frac{W_A}{M_A} \times \frac{P_A^0}{P_A - P_A}$$

$$= 2 \times \frac{100}{76} \times \frac{854}{854 - 848.9}$$

= 254.5 g/mol.

Let the formula = *Sx*

$$X \times 32 = 254.5\,g/mol$$

$$X = \frac{254.5}{32}$$

=7.95

=8.

= Formula = S_8

2. **Answer:**

Mass percentage of

$$C_6H_6 = \frac{\text{Mass of } C_6H_6}{\text{Total mass of the solution}} \times 100\%$$

$$= \frac{\text{Mass of } C_6H_6}{\text{Mass of } C_6H_6 + \text{Mass of } CCl_4} \times 100\%$$

$$= \frac{22}{22 + 122} \times 100\%$$

=15.28%

Mass percentage of CCl_4

$$= \frac{\text{Mass of } CCl_4}{\text{Total mass of the solution}} \times 100\%$$

$$= \frac{\text{Mass of } CCl_4}{\text{Mass of } C_6H_6 + \text{Mass of } CCl_4} \times 100\%$$

= 84.72%

Alternatively,

Mass percentage of CCl_4 = (100 – 15.28) %

= 84.72%

3. **Answer:**

Let the total mass of the solution be 100 g and the mass of benzene be 30g.

∴ Mass of carbon tetrachloride = (100 – 30) g = 70 g

Molar mass of benzene (C_6H_6) = (6 × 12 + 6 ×) g mol^{-1}

= 78 g mol^{-1}

$$\therefore \text{Number of moles of } C_6H_6 = \frac{30}{78}\,\text{mol}$$

= 0.3846 mol

Molar mass of carbon tetrachloride

(CCl_4) = 1 × 2 + 4 × 355 = 154 g mol^{-1}

∴ Number of moles of = 0.4545 mol

Thus, the mole fraction of C_6H_6 is given as:

$$CCl_4 = \frac{70}{154}\,\text{mol}$$

$$\frac{\text{Number of moles of } C_6H_6}{\text{Number of moles of } C_6H_6 + \text{Number of moles } CCl_4}$$

$$= \frac{0.3846}{0.3846 + 0.4545}$$

= 0.458

4. **Answer:**

Molarity is given by:

$$\text{Molarity} = \frac{\text{Moles of solute}}{\text{Volume solution in litre}}$$

(a) Molar mass of $CO(NO_3)_2 .6H_2O$ 59 + 2 (14 + 3 × 16) + 6 × 18

= 291 g mol^{-1}

Therefore, Moles of

$$CO(NO_3)_2 \cdot 6H_2O = \frac{30}{291}\,\text{mol} = 0.103\text{ mol}$$

$$\text{Therefore, } = \frac{0.103\text{ mol}}{4.3\text{ L}} \text{ molarity}$$

= 0.023 M

(b) Number of moles present in 1000 mL of 0.5 H_2SO_4 = 0.5 mol M

∴Number of moles present in 30 mL of 0.5 M

$$H_2SO_4 = \frac{0.5\times30}{1000}\text{mol}$$

= 0.015 mol

Therefore, molarity $\frac{0.015}{0.5\,\text{L}}\text{mol} = 0.03\,\text{M}$

5. Answer:

(a) Molar mass of KI = 39 + 127 = 166 g mol^{-1}
20% (mass/mass) aqueous solution of KI means 20 g of KI is present in 100 g of solution.
That is, 20 g of KI is present in (100 – 20) g of water = 80 g of water

Therefore, molality of the solution

$$= \frac{\text{Moles of KI}}{\text{Mass of water in kg}}$$

$$\frac{\frac{20}{166}}{0.05}\text{m}$$

= 1.506 m

= 1.51 m (approximately)

(b) It is given that the density of the solution = 1.202 g ml^{-1}

Therefore, Volume of 100 g solution

$$= \frac{\text{Mass}}{\text{Density}}$$

$$= \frac{100\,\text{g}}{1.202\,\text{g ml}^{-1}} = 83.19\text{ mL}$$

= 83.19×10^{-3} L

Therefore, molarity of the solution

$$= \frac{\frac{20}{166}\text{mol}}{83.19\times10^{-3}\,\text{L}}$$

(c) Moles of KI = $\frac{20}{166} = 0.12\,\text{mol}$

Moles of water = $\frac{80}{18} = 4.44\,\text{mol}$

Therefore, mole fraction of KI

$$= \frac{\text{Moles of KI}}{\text{Moles of KI} + \text{Moles of water}}$$

$$= \frac{0.12}{0.12+4.44} = 0.0263$$

Assertion and Reason Answers:

1. (c) Assertion is correct statement but reason is wrong statement.

Explanation:

Camphor has high molal depression constant.

2. (a) Assertion and reason both are correct statements and reason is correct explanation for assertion.

Explanation:

If a pressure larger than the osmotic pressure is applied to the solution side, the pure solvent flows out of the solution to the solvent through semi-permeable membrane and this phenomenon is called reverse osmosis.

Case Study Answers:

1. Answer :

(i) (b) 1.78×10^{-3}

Explanation:

$K_H = 4.17 \times 10^5$ mm HG

p = 760 mm Hg

According to Henry's law, $P = K_H \times X_{CH_4}$

$$X_{CH_4} = \frac{P}{K_H} = \frac{760}{4.27\times10^5} = 1.78\times10^{-3}$$

(ii) (a) 0.762

Explanation:

According to Henry's law, m = $K_H \times p$

6.56 × 10–2 = $K_H \times 1$

For another case, 5 × 10–2 = 6.56 × 10–2 × p

$$p = \frac{5\times10^{-2}}{6.56\times10^{-2}} = 0.762\,\text{bar}$$

(iii) (c) Ar < CO_2 < CH_4 < HCHO

Explanation:

Higher the value of K_H at a given pressure, the lower is the solubility of the gas.

(iv) (c) 0.37

Explanation:

The mole fraction of the gas in solution,

$$X = \frac{n}{n+55.5}\text{ or, }\frac{n}{55.5} = \frac{1}{150\times10^3}$$

[n + 55.5 ≈ 55.5, as *n* is very small]

$$n = \frac{55.5}{150}\times10^{-3} = 0.37\text{ millimoles}$$

(v) (a) K_H increases with increase of temperature.

2. Answer :

(i) (b) 0.0036 m

Explanation:

$$m = \frac{0.052}{180} \times \frac{1000}{80.2} = 0.0036$$

(ii) (c) 373.02 K

Explanation:

$\Delta T_b = k_b \times m = 5.2 \times 0.0036 = 0.0187$ K

Tb = 373 + 0.0187 = 373.0187 K $\approx$ 373.02 K

(iii) (d) 0.067 K

Explanation:

$\Delta T_f = k_f \times m = 1.86 \times 0.0036 = 0.067$ K

(iv) (a) 6.28×10^{-5}

Explanation:

$$\text{Moles of water} = \frac{80.2}{18} = 4.455$$

Mole of fraction of glucose

$$= \frac{0.00028}{4.45 + 0.00028} = 6.28 \times 10^{-5}$$

(v) Depression in freezing point or elevation in boiling point is proportional to molarity, which is proportional to number of moles. For some amount, higher the molar mass of solute, lower will be number of moles. Hence, lower will be the colligative property.

❖❖

Electrochemistry

2

Classification of Electrolytes

Electrochemistry

The branch of science which deals with the production of electricity from energy released during spontaneous chemical reactions and the use of electrical energy to bring about non- spontaneous chemical transformations is called electrochemistry.

Redox Reaction

Oxidation is a process which involves loss of electrons and reduction is a process which involves gain of electrons.

The reactions which involve both oxidation and reduction are called redox reactions. In these reactions, electrons are transferred from one reactant to another.

The substance which can lose one or more electrons (*i.e.,* get oxidised) is called reducing agent or reductant while the substance which can gain one or more electrons (*i.e,* get reduced) is called oxidising agent or oxidant.

Thus, in a redox reaction, one substance acts as a reducing agent and itself gets oxidised while another substance acts as an oxidising agent and itself gets reduced.

For example: A redox reaction is the reaction between zinc and copper (II) salt occurring in a battery. In this reaction, zinc loses electrons and gets oxidised whereas Cu^{2+} ions gain electrons and get reduced.

$Zn(s) + Cu_{2+} \longrightarrow Zn_{2+} (aq) + Cu (s)$

Zinc acts as a reducing agent or reductant while Cu^{2+} ions act as oxidising agent or oxidant.

Some other examples of redox reactions are

$$Zn + 2HCl \longrightarrow ZnCl_2 + H_2$$

$$5Fe_{2+} + 8\,H+ MnO^{4^-} \longrightarrow 5\,Fe_{3+} + Mn_{2+} + 4\,H_2O$$

Metallic and Electrolytic conductance

The substances which allow the passage of electric current are called conductors. The best conductors are metals such as copper, silver, tin, etc.

The substances which do not allow the passage of electric current through them are called non-conductors or insulators.

Some common examples of insulators are rubber, glass, ceramics, wood, wax, etc.

Types of Conductors

The conductors are broadly classified into two types:

(1) Metallic conductors or Electronic conductors

These are metallic substances which allow the electricity to pass through them without undergoing any chemical change. Metals and their alloys have very large conductivity and are called conductors.

For example: copper, silver etc.

The flow of electric current through metallic conductors is due to the flow of electrons in the metal atoms. Electrical conductance through metals is called metallic conductance or electronic conductance.

The electronic conductance depends on

(1) the nature and structure of the metal

(2) the number of valence electrons per atom

(3) the density of metal and

(4) temperature (it decreases with increase of temperature)

(2) Electrolytes or Electrolytic conductors

These are substances which allow the electricity to pass through them in their molten states or in the form of their aqueous solutions and undergo chemical decomposition.

For example: acids, bases and salts are electrolytes.

The flow of electric current through an electrolytic solution is called electrolytic conduction.

In this type of conduction, charge is carried by ions. Therefore, it is also called ionic conductance. The conduction will not occur unless the ions of the electrolyte are free to move.

Therefore, these substances do not conduct electricity in the solid state but conduct electricity in the molten state or in their aqueous solutions due to the movement of ions.

Non-electrolytes: The substances, which do not conduct electricity either in their molten state or through their aqueous solutions are called non-electrolytes.

For example: sugar, glucose, ethyl alcohol, urea, etc.

Metallic conduction Electrolytic conduction

- It is carried by the movement of electrons It is carried by the movement of ions.
- It does not involve the transfer of any matter. It involves the transfer of matter as ions.
- It involves no change in the chemical properties of the conductor. It involves the decomposition of the electrolyte as a result of the chemical reaction.
- It decreases with increase in temperature. It increases with increase in temperature.

Classification of Electrolytes

On this basis, electrolytes are broadly divided into two types : strong electrolytes and weak electrolytes.

(1) **Strong electrolytes:** The electrolytes which are almost completely dissociated into ions in solution are called strong electrolytes.

For example: NaCl, KCl, HCl, NaOH, $NH4NO_3$ etc.

(2) **Weak electrolytes:** The electrolytes which do not ionise completely in solution are called weak electrolytes.

For example: CH_3COOH, H_2CO_3, H_3BO_3, HCN, $HgCl_2$, $ZnCl_2$, NH_4OH, etc.

In weak electrolytes, an equilibrium is established between the unionised electrolyte and the ions formed in solution.

The extent of ionisation of a weak electrolyte is expressed in terms of degree of ionisation or degree of dissociation. It is defined as the fraction of total number of molecules of the electrolyte which ionise in the solution. It is generally denoted by alpha (α), for strong electrolytes, α is almost equal to 1 and for weak electrolytes, it is always less than 1.

Factors Affecting Electrical Conductivity

The electrical conductivity of the solutions of electrolytes depends upon the following factors:

(i) Interionic attractions: These depend upon the interactions between the ions of the solute molecules, i.e. solute-solute interactions. If the solute-solute interactions are large, the extent of dissociation will be less. These interactions are also responsible for the classification of electrolytes as strong electrolytes and weak electrolytes.

(ii) Solvation of ions: These depend upon the interactions between the ions of the solute and the molecules of the solvent and are called solute-solvent interactions. If the solute-solvent interactions are strong, the ions of the solute will be highly solvated and their electrical conductivity will be low.

(iii) Viscosity of the solvent: The viscosity of the solvent depends upon the solvent-solvent interactions. Larger the solvent-solvent interactions, large will be the viscosity of the solvent.

The average kinetic energy of the ions of the electrolyte increases with increase in temperature. Consequently, the conductance of electrolytic solutions increases with rise in temperature. The conductance of electronic conductors decreases with increase in temperature.

Conductivity of electrolytic (or ionic) solution depends upon the following factors:

(i) **Nature of electrolyte:** The conductance of an electrolyte depends upon the number of ions present in the solution. Therefore, the greater the number of ions in the solution, the greater is the conductance. The number of ions produced by an electrolyte depends upon its nature.

The strong electrolytes dissociate almost completely into ions in solutions and therefore, their solutions have high conductance.

Weak electrolytes, dissociate to only small extents and give lesser number of ions. Therefore, the solutions of weak electrolytes have low conductance.

(ii) **Nature of the solvent:** Electrolytes ionize more in polar solvents. Therefore greater the polarity of the solvent, larger is the ionization and hence greater is the conductance.

(iii) **Size of the ions produced and their solvation:** If the ions are strongly solvated, their effective size will increase and hence their conductance will decrease.

(iv) **Concentration of the electrolytic solution:** The molar conductance of electrolytic solution varies with the concentration of the electrolyte. The molar conductance of an electrolyte increases with decrease in concentration or increase in dilution.

(v) **Temperature:** The conductivity of an electrolyte depends upon the temperature. With increase in temperature, the conductivity of an electrolyte increases.

Electrolytic Conduction

When a voltage is applied to the electrodes dipped into an electrolytic solution, ions of the electrolyte move and, therefore, electric current flows through the electrolytic solution.

The power of the electrolytes to conduct electric current is termed conductance or conductivity. Electrolytic solutions also obey Ohm's law.

Ohm's Law

This law states that the current flowing through a conductor is directly proportional to the potential difference across it, i.e.

$$I \propto V$$

where I is the current strength (in amperes) and V is the potential difference applied across the conductor (in volts)

$I = V/R$ or

$V = IR$

where R is the constant of proportionality and is known as resistance of the conductor. It is expressed in ohms and is represented as Ω. The strength of current flowing through a conductor is directly proportional to the potential difference applied across the conductor and inversely proportional to the resistance of the conductor.

Resistance

It measures the obstruction to the flow of current. The resistance of any conductor is directly proportional to the length (l) and inversely proportional to the area of cross-section (a) so that

$$R \propto l/a \text{ or}$$

$$R=\rho\ (l / a)$$

where p (Greek, rho) is the constant of proportionality and is called specific resistance or resistivity. The resistance depends upon the nature of the material.

The unit of resistance is ohm (Ω). In terms of SI, base unit is equal to (kgm2/(s3A2)

Resistivity or specific resistance

$$R= \rho\ (1/ \alpha)$$

Now, l=1 cm, a =1 cm2, then R= ρ

Thus, resistivity is defined as the resistance of a conductor of 1 cm length and having area of cross-section equal to 1 cm2.

Resistivity or specific resistance is the resistance between opposite faces of one centimetre cube of the conductor. It is also expressed as resistance when it is 1 m long and its area of cross section is 1 m2 i.e., resistance of one metre cube of the conductor

1 Ω m = 100 Ω cm or

1 Ω cm = 0.01 Ω m

The units of resistivity are

ρ = R (a / l) = (ohm cm2) /cm = ohm cm

Its SI units are ohm metre (Ω m). But quite often ohm centimeter (Ω cm) is also used

Conductance

It is a measure of the ease with which current flows through a conductor. It is expressed as G. It is inverse of the resistance, i.e

$$G = 1 / R$$

The units of conductance are reciprocal ohm (ohm-1) or mho. Ohm is also abbreviated as Ω so that ohm-1 may be written as Ω-1

According to S.I. system, the units of electrical conductance are siemens,

S (i.e. 1S = 1 Ω-1)

Conductivity

The inverse of resistivity is called conductivity (or specific conductance). It is represented by the symbol, κ (Greek kappa)

The conductance of a solution of 1 cm length and having 1 sq cm as the area of cross-section. Conductivity is the conductance of one centimetre cube of a solution of an electrolyte.

$$\kappa = 1/ \rho$$

The units of conductivity are

κ = 1/ ρ

κ = 1/ ohm . cm

κ = ohm-1 cm-1

κ = Ω-1 cm-1

Molar Conductivity or Molar Conductance

Molar conductivity is defined as the conducting power of all the ions produced by dissolving one mole of an electrolyte in solution.

It is denoted by Λm (lambda).

$$\Lambda m = \kappa / M$$

where M is the molar concentration. If M is in the units of molarity i.e. moles per litre (mol L-1), then Λ may be expressed as :

$$\Lambda m = (\kappa \times 1000)/M$$

Units of Molar Conductance

The units of molar conductance can be derived from the formula,

$$\Lambda m = (\kappa x 1000)/M$$

The units of κ are S cm -1 and units of Λ are

$\Lambda m = S\ cm^{-1} x (cm^3 / mol\ L^{-1})$

$\Lambda m = S\ cm^2\ mol^{-1}$

Equivalent Conductivity

It is defined as the conducting power of all the ions produced by dissolving one gram equivalent of an electrolyte in solution.

It is expressed as Λe and is related to specific conductance as

$\Lambda e = (\kappa \times 1000) / C$

where C is the concentration in gram equivalent per litre (or normality). The units of equivalent conductivity are ohm cm2 (g equiv-1) as obtained from the formula:

$$\Lambda = (\kappa x 1000) / C$$

$\Lambda = [(S\ cm^{-1}) \times cm^3\ L^{-1}] / g\ equiv\ L^{-1}$

In terms of SI units, the units of equivalent conductivity are S m2 equiv-1 and Λ is expressed as:

$$\Lambda = \kappa / C$$

where κ, is in S m-1 and C is in g equiv m-3.

1) **Measurement of Conductance**

The conductance of a solution is reciprocal of the resistance, therefore, the experimental determination of the conductance of a solution involves the measurement of its resistance.

It consists of four arms containing the resistance R1, R2, R3 and R4. R2 is the variable resistance and R4 is the unknown resistance. When the current flows through the circuit, the variable resistance is so adjusted to get no current position. This is indicated by no deflection in the galvanometer and is called null point.

At null point

$$R2/R4 = R1/R3$$

Knowing the value of R1, R2, R3 ,unknown resistance R4 can be calculated.

$$R4 = (R2 \times R3) / R1$$

Conductivity of Solutions

What is Conductivity?

- Electrical resistance is represented by the symbol 'R', and it is measured in ohm (Ω).
- The electrical resistance of any object is directly proportional to its length (l) and inversely proportional to its area of cross-section (A), i.e.

$$R \propto \frac{I}{A} \text{ or } R = \rho\frac{I}{A}$$

where the constant of proportionality ρ is called resistivity (specific resistance).

- The inverse of resistance, R, is called conductance, G, and we have the relation

$$G = \frac{1}{R} = \frac{A}{\rho I} = \kappa\frac{A}{I}$$

where the constant κ is called conductivity (specific conductance).

- The SI unit of conductance is Siemens, represented by the symbol ‘S’, and it is equal to ohm^{-1} (also known as mho) or Ω^{-1}. The SI unit of conductivity (κ) is $S\ m^{-1}$.

Conductivity of Electrolytic (Ionic) Solutions

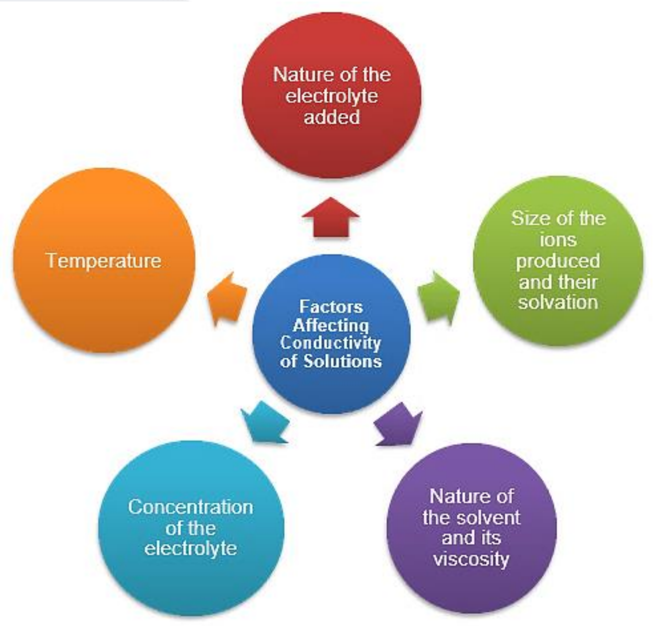
- Very pure water has small amounts of hydrogen and hydroxyl ions (~10^{-7}M) which lend it very low conductivity ($3.5 \times 10^{-5}\ S\ m^{-1}$).
- When electrolytes are dissolved in water, they dissociate to give their own ions in the solution; hence, its conductivity also increases.

Electrolytic or ionic conductance:

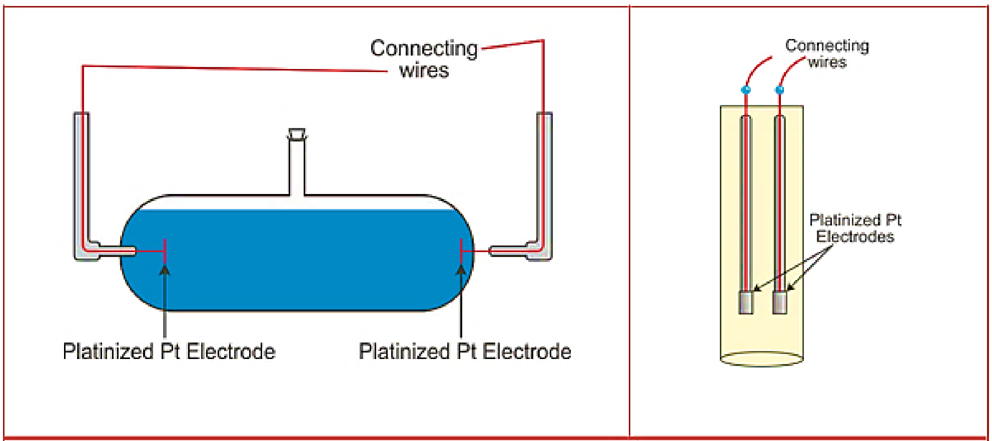
Conductance of electricity by ions present in solutions

Measurement of Conductivity of Ionic Solutions

- We first need to find the resistance of an ionic solution to measure conductivity.
- We face two problems when measuring the resistance of an ionic solution:
  1. Passing direct current (DC) changes the composition of the solution
  2. A solution cannot be connected to the bridge like a metallic wire or other solid conductor
- The first difficulty is resolved by using an alternating current (AC) source of power. The second problem is solved by using a specially designed vessel called **conductivity cell**.



Conductivity Cell:



Two different types of conductivity cells

- It consists of two platinum electrodes coated with platinum black (finely divided metallic Pt is deposited on the electrodes electrochemically).

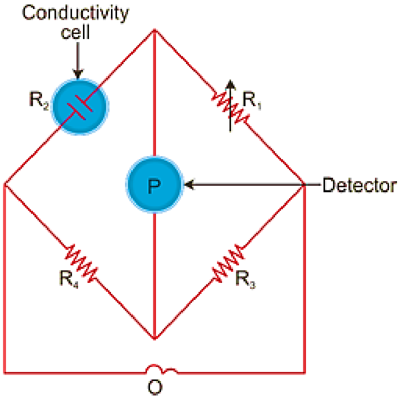
- These have area of cross-section equal to ‘A’ and are separated by distance ‘l’. The resistance of such a column of solution is then given by the equation:

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

- The quantity ‘l/A’ is called cell constant and is denoted by the symbol G*. It depends on the distance between the electrodes and their area of cross-section and has the dimension [L^{-1}].
- Hence, the cell constant G* is given by the equation:

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

- When the cell constant is determined, we can use it for measuring the resistance or conductivity of any solution.
- The set up for the measurement of the resistance is nothing but the well-known Wheatstone bridge.



Arrangement for measurement of resistance of a solution of an electrolyte

- It consists of two resistances R_3 and R_4, a variable resistance R_1 and the conductivity cell having the unknown resistance R_2.
- The Wheatstone bridge is fed by an oscillator O (a source of AC power in the audio frequency range 550−5000 cycles per second).
- P is a suitable detector (a headphone or other electronic device).
- The bridge is balanced when no current passes through the detector.
- Under these conditions,

$$\text{Unknown Resistance, } R_2 = \frac{R_1R_4}{R_3}$$

- When the cell constant and the resistance of the solution in the cell are determined, the conductivity of the solution is given by the equation:

$$\kappa = \frac{\text{Cell Constant}}{R} = \frac{G^*}{R}$$

Molar Conductivity

- Conductivity of solutions of different electrolytes in the same solvent and at a given temperature differs due to
  1. Charge and size of ions in which they dissociate
  2. Concentration of ions or ease with which the ions move under a potential gradient

- Therefore, it becomes necessary to define a quantity called molar conductivity denoted by the symbol (λ_m). It is related to the conductivity of the solution by the equation:

$$\text{Molar Conductivity } = \lambda_m = \frac{\kappa}{c}$$

- Unit of λm is in S m^2 mol^{-1}.
- Hence, molar conductivity can be given by the formula

$$\lambda_m\left(Sm^2mol^{-1}\right) = \frac{\kappa\left(Sm^{-1}\right)}{1000Lm^{-3} \times \text{Molarity}\left(molL^{-1}\right)}$$

Variation of Conductivity and Molar Conductivity with Concentration

- Both conductivity and molar conductivity change with the concentration of the electrolyte.
- Conductivity always decreases with a decrease in concentration for both weak and strong electrolytes. It is because the number of ions per unit volume which carry the current in a solution decreases on dilution.
- Molar conductivity increases with a decrease in concentration. This is because the total volume (V) of solution containing one mole of electrolyte also increases.
- The decrease in κ on dilution of a solution is more than compensated by an increase in itsvolume.

Molar conductivity (λ_m): Conductance of the electrolytic solution kept between the electrodes of a conductivity cell at unit distance but having area of cross section large enough to accommodate sufficient volume of solution which contains one mole of the electrolyte.

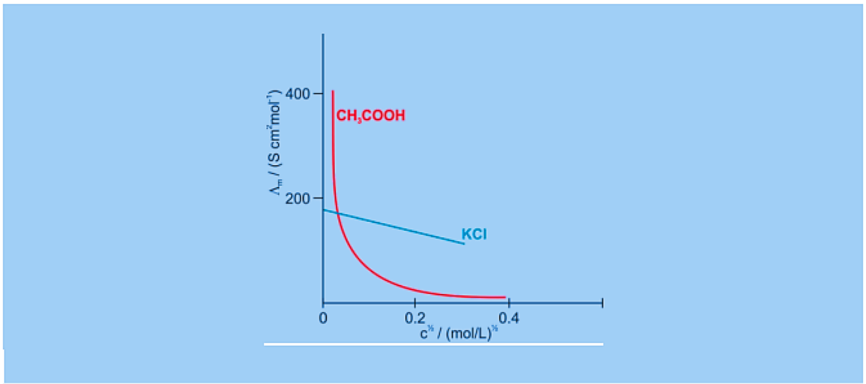
- When concentration approaches zero, the molar conductivity is known as limiting molar conductivity and is represented by the symbol λ_m^0.
- The variation in λ_m with concentration is different for strong and weak electrolytes.

Strong Electrolytes:

- λ increases slowly with dilution and can be represented by the equation:

$$\lambda_m = \lambda_m^0 - Ac^{1/2}$$

- It can be seen that if we plot λm against $c^{1/2}$, we obtain a straight line with intercept equal to λ^o_m and slope equal to '−A'.



Molar conductivity λ_m versus $c^{1/2}$ for acetic acid (weak electrolyte) and potassium chloride (strong electrolyte) in aqueous solutions

The value of the constant 'A' for a given solvent and temperature depends on the type of electrolyte.

Weak Electrolytes:

- Weak electrolytes such as acetic acid have a lower degree of dissociation at higher concentrations. Hence, for such electrolytes, the change in λ_m with dilution is due to
  1. Increase in the degree of dissociation
  2. The number of ions in total volume of solution which contains 1 mol of electrolyte
- In such cases, λ_m^o increases steeply on dilution, especially near lower concentrations. Therefore, it cannot be obtained by extrapolating λ_m to zero concentration.
- At infinite dilution, electrolyte dissociates completely ($\alpha = 1$), but at such low concentration, the conductivity of the solution is so low that it cannot be measured accurately. Therefore, λ_m^o for weak electrolytes is obtained by using Kohlrausch's law of independent migration of ions.
- Thus, at any concentration c, if α is the degree of dissociation, then it can be approximated to the ratio of molar conductivity, λ_m, at the concentration c to limiting molar conductivity λ_m^o.

$$\therefore \alpha = \frac{\lambda_m}{\lambda_m^0}$$

But we know that for a weak electrolyte,

$$K_a = \frac{c\alpha^2}{(1-\alpha)}$$

- By putting the value of α in the above equation, we get the equation:

$$K_a = \frac{C\lambda_m^2}{\lambda_m^0\left(1-\frac{\lambda_m}{\lambda_m^0}\right)} = \frac{C\lambda_m^2}{\lambda_m^0\left(\lambda_m^0-\lambda_m\right)}$$

Numerical

1) The resistance of a conductivity cell containing 0.001M KCl solution at 298 K is 1500Ω. What is the cell constant if conductivity of 0.001M KCl solution at 298K is 0.146×10^{-3} Scm^{-1}?

Answer :

Given Data:

R =1500Ω

$\kappa = 0.146 \times 10^{-3}$ Scm^{-1}

$G^* = ?$

Solution :

The cell cons tant is givenby the equation,

Cell constant=G^*=Rκ

$= 1500 \times 0.146 \times 10^{-3}$

$= 0.219$ m^{-1}

Hence, cell constant of given conductivity cell is 0.219 m^{-1}

2) Conductivity of 0.00241 M acetic acid is 7.896×10^{-5} Scm^{-1}. Calculate its molar conductivity and if λ_m^o for acetic acid is 390.5 Scm^2 mol^{-1}, what is its dissociation constant?

Answer:

Given data:

$\kappa = 7.896 \times 10^{-5}\ \mathrm{Scm^{-1}}$

c = 0.00241 M

$\lambda_m^0 = 390.5\ \mathrm{Scm^2\ mol^{-1}}$

$\lambda_m = ?$

$K_a =$

Solution:

The molar conductivity can be calculated by formula,

$$\lambda_m = \frac{\kappa}{C} = \frac{7.896 \times 10^{-5}}{0.00241}$$

$$\therefore \quad \lambda_m = 327.63 \times 10^{-4}\ \mathrm{Sm^2\ mol^{-1}}$$

The dissociation constant of acetic acid can be given by,

$$K_a = \frac{C\lambda_m^2}{\lambda_m^0\left(\lambda_m^0 - \lambda_m\right)}$$

$$= \frac{0.00241 \times (327.63 \times 10^{-4})^2}{390.5\,(390.5 - 327.63 \times 10^{-4})}$$

$$K_a = 1.696 \times 10^{-11}\ \mathrm{molL^{-1}}$$

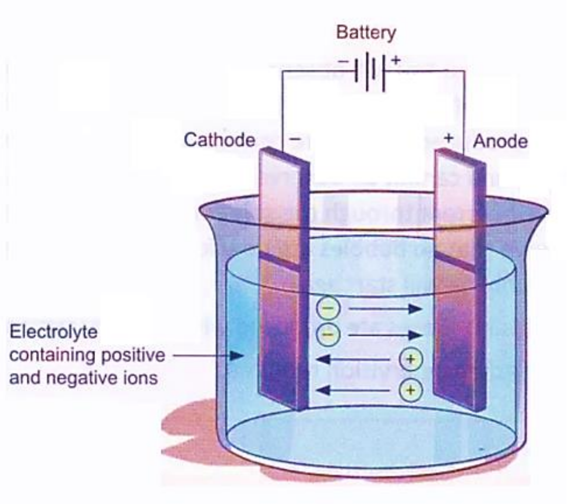
Hence, the molar conductivity of given solution is $327.63 \times 10^{-4}\ \mathrm{Sm^2\ mol^{-1}}$ and dissociation cons tant is 1.696 $\times 10^{-11}\ \mathrm{molL^{-1}}$.

Electrolytic Cells

Electrolysis is a process in which chemical changes take place by the passage of electric current. The cells used to carry out electrolysis are electrolytic cells

Process of electrolysis

1) The process of electrolysis is carried out by taking the solution of an electrolyte in a suitable vessel. The vessel is called electrolytic tank.
2) It is made up of either glass or of a material which is a bad conductor of electricity.
3) Two metallic rods or plates are suspended in the electrolytic solution. These are connected to the terminal of a battery with the help of metallic wires.
4) These metallic rods or plates allow the passage of current and are called electrodes. The electrode connected to the positive terminal of the battery is called anode while the electrode connected to the negative terminal of the battery is called cathode.



When an electrolyte is dissolved in water, it splits up into negative and positive ions. The positively charged ions are called cations and negatively charged ions are called anions.

On passing electric current through the solution, the ions are attracted by the oppositely charged electrodes. As a result, cations move towards cathode while anions move towards anode. This movement of ions in solution is known as electrolytic or ionic conduction and constitutes flow of current through the solution.

The anions on reaching the anode give up their electrons. On the other hand, cations take up the electrons from the cathode Therefore, cations and anions get discharged at the respective electrodes and are converted to neutral particles. This is known as primary change. The primary products may be collected as such or they undergo further changes to form molecules or compounds. These are called secondary products and the change is known as secondary change.

According to ionic theory, the electrolytes are present as ions in solution and the function of electricity is only to direct these ions to their respective electrodes. The electrolytes can be electrolysed only in the dissolved or molten state.

Faraday's Laws of Electrolysis

1) Faraday's first law of electrolysis

The amount of any substance deposited or liberated at any electrode is directly proportion to the quantity of electricity passed through the electrolytic solution. The amount of any sub stance obtained gives the amount of chemical reaction which occurs at any electrode during electrolysis.

Thus, if w gram of the substance is deposited on passing Q coulombs of electricity, then

$w \propto Q$

$w = ZQ$

where Z in a constant of proportionality and is called electrochemical equivalent. If a current of I amperes is passed for t seconds, then

$Q = I \times t$

$W = Z \times Q = Z \times I \times t$

$Q = 1$ coulomb

$I = 1$ ampere and $t = 1$ second, then

$w = Z \times 1 \times 1$

$w = Z$

Electrochemical equivalent of a substance may be defined as the mass of the substance deposited when a current of one ampere is passed for one second, i.e. a quantity of electricity equal to one coulomb is passed.

2) Faraday's second law of electrolysis

It states that when same quantity of electricity is passed through different electrolytic solutions connected in series, the weights of the substances produced at the electrodes are directly proportional to their chemical equivalent weights.

For example: When same current is passed through two electrolytic solutions, containing copper sulphate ($CuSO_4$) and silver nitrate ($AgNO_3$) connected in series, the weights of copper and silver deposited are :

According to Faraday's law, the amount of chemical change occurred i.e. the moles of substances deposited or liberated is proportional to the number of moles of electrons exchanged during the oxidation-reduction reactions that occur.

By knowing the amount of electricity passed, we can easily calculate the number of moles of products formed from the appropriate electrode reaction. From the moles of the products formed, we can calculate the masses their volumes if they are gases.

During the passage of electric current through molten NaCl, sodium gets deposited at cathode and chlorine is liberated at anode.

$NaCl \longrightarrow Na + \frac{1}{2}Cl_2$

During electrolysis, sodium ions move towards cathode, accept electrons and get deposited as:

$Na^+ (aq) + e^- \longrightarrow Na(s)$

The passage of one electron produces one sodium atom. The passage of 1 mol of electrons produce 1 mol of sodium (or 23 g).

Similarly, at anode, chloride ions give up electrons and produce Cl atoms as:

$Cl^{-} - e^{-} \longrightarrow \frac{1}{2} Cl2(g)$

$2\ Cl^{-} - 2e^{-} \longrightarrow Cl2(g)$

2 mol of electrons produce 1 mol of Cl2 or 1 mol of electrons produce 1/2 mol of Cl (35.5 g)

Charge on an electron = 1.602 x 10-19 C

Now 1 mole of electrons= 6.022 x 1023 electrons

Charge on 1 mole of electrons = 6.022 x 1023 × 1.602 x 10-19 C

The charge on one mole of electrons is called 1 Faraday, F.

Thus 1F = 96485 C or approximately 96500 C.

Thus, charge on n mol of electrons will be equal to

Q= nF

Now, the production of 1 mol of sodium or 23.0 g by reduction of sodium ions require 1 mol of electrons.

Therefore, amount of charge required,

Q= nF = 1 × 96500 C = 96500 C

Similarly, 1 mol of Cl2 is obtained by 2 mol of electrons or 2 × 96500 C of charge during electrolysis of NaCl. Similarly, in the reaction

$Ag+ + e^{-} \longrightarrow Ag(s)$

One mole of electrons is required for the reduction of 1 mol of silver ions. Therefore, the quantity of electricity required for reduction of 1 mol of Ag+ ions is 96500 C or 1 Faraday.

Now 1 mole of copper will be produced by 2 mol of electrons or 2 × 96500 C of charge:

$Cu2+ + 2e^{-} \longrightarrow Cu$

The amount of substance deposited or evolved can be calculated. For example: aluminium gets deposited as:

$Al3+ +3\ e^{-} \longrightarrow Al$

Thus, 1 mol of Al will be deposited by 3 mol of electrons or 3 Faraday of electricity.

When the same quantity of electricity is passed through different electrolyte solutions, connected in series, the weights of different substances produced at the electrodes can be calculated from the mole ratios of their electrode reactions.

Battery

A Battery is a device consisting of one or more electrical cells that convert chemical energy into electrical energy. Every battery is basically a galvanic cell where redox reactions take place between two electrodes which act as the source of the chemical energy.

Battery types

Batteries can be broadly divided into two major types.

- Primary Cell / Primary battery
- Secondary Cell / Secondary battery

Based on the application of the battery, they can be classified again. They are:

Household Batteries

These are the types of batteries which are more likely to be known to the common man. They find uses in a wide range of household appliances (such as torches, clocks, and cameras). These batteries can be further classified into two subcategories:

- Rechargeable batteries Nickel

  Examples: Cadmium batteries, Lithium-Ion
- Non-rechargeable batteries

  Examples: Silver oxide, Alkaline & carbon zinc

Industrial Batteries

These batteries are built to serve heavy-duty requirements. Some of their applications include railroad, backup power and more for big companies. Some examples are:

Nickel Iron

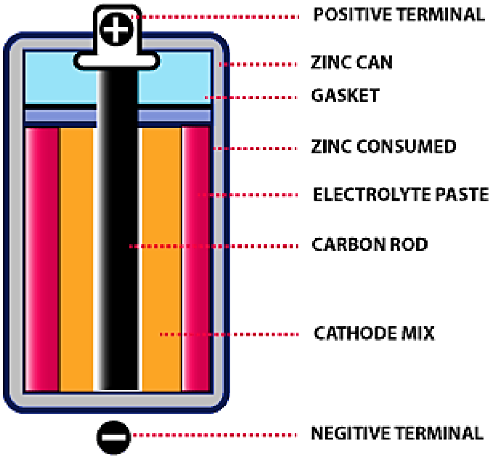
Wet Nickel Cadmium (NiCd)

Vehicle Batteries

These are more user-friendly and a less complicated version of the industrial batteries. They are specifically designed to power cars, motorcycles, boats & other vehicles. An important example of a vehicle battery is the Lead-acid battery.

Primary Cell

PRIMARY BATTERY



Types Of Battery- Primary battery

These are batteries where the redox reactions proceed in only one direction. The reactants in these batteries are consumed after a certain period of time, rendering them dead. A primary battery cannot be used once the chemicals inside it are exhausted.

An example of a primary battery is the dry cell – the household battery that commonly used to power TV remotes, clocks, and other devices. In such cells, a zinc container acts as the anode and a carbon rod acts as the cathode. A powdered mixture of manganese dioxide and carbon is placed around the cathode. The space left in between the container and the rod are filled with a moist paste of ammonium chloride and zinc chloride.

The redox reaction that takes place in these cells is:

At Anode

$Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$

At Cathode

$2e^- + 2\,NH_4^+(aq) \rightarrow 2\,NH_3(g) + H_2(g)$

$2\,NH_3(g) + Zn^{2+}(aq) \rightarrow [Zn(NH_3)_2]^{2+}(aq)$

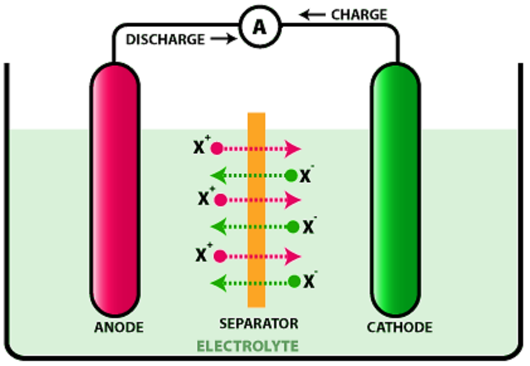
$H_2(g) + 2\,MnO_2(S) \rightarrow Mn_2O_3(S) + H_2O(l)$

Thus, the overall cell equation is:

$Zn(s) + 2\,NH_4^+(aq) + 2\,MnO_2(S) \rightarrow [Zn(NH_3)_2]^{2+}(aq) + Mn_2O_3(S) + H_2O(l)$

Another example of the primary cell is the mercury cell, where a zinc-mercury amalgam is used as an anode and carbon is used as a cathode. A paste of HgO is used as an electrolyte. These cells are used only in devices that require a relatively low supply of electric current (such as hearing aids and watches).

SECANDARY BATTERY



Secondary Cell

These are batteries that can be recharged after use by passing current through the electrodes in the opposite direction, i.e. from the negative terminal to the positive terminal.

Types of Battery – Secondary Cell

For example, a lead storage battery that is used in automobiles and inverters can be recharged a limited number of times. The lead storage battery consists of a lead anode and the cathode is a lead grid packed with lead dioxide. Sulphuric acid with a concentration of 38% is used as an electrolyte. The oxidation and reduction reactions involved in this process are listed below.

At Anode

$Pb \rightarrow Pb^{2+} + 2\ e^-$

$Pb + SO_4^{2-} \rightarrow PbSO_4(electrode) + 2\ e^-$

At Cathode

$2\ e^- + PbO_2 + 4\ H^+ \rightarrow Pb^{2+} + 2\ H_2O$

$2\ e^- + PbO_2 + 4\ H^+ + SO_4^{2-} \rightarrow PbSO_4(electrode) + 2\ H_2O$

In order to recharge these batteries, the charge is transferred in the opposite direction and the reaction is reversed, thus converting $PbSO_4$ back to Pb and PbO_2.

Another example of the secondary cell is the nickel-cadmium cell. These cells have high storage capacities and their lifespan is relatively long (compared to other secondary cells). However, they are difficult to manufacture and maintain.

Standard Hydrogen Electrode

The Standard Hydrogen Electrode is often abbreviated to SHE, and its standard electrode potential is declared to be 0 at a temperature of 298K. This is because it acts as a reference for comparison with any other electrode.

The half cell reaction of SHE can be written as follows:

$2H^+ (aq) + 2e^- \rightarrow H_2 (g)$

The reaction given above generally takes place on a platinum electrode. The pressure of the hydrogen gas present in this half cell equals 1 bar.

Uses of Platinum in the Standard Hydrogen Electrode

Platinum is used in the Standard Hydrogen Electrode due to the following reasons:

- Platinum is a relatively inert metal which does not corrode easily.
- Platinum has catalytic qualities which promote the proton reduction reaction.
- The surface of platinum can be covered with platinum black, a fine powder of platinum. This type of platinum electrode is called a platinized platinum electrode.
- Platinum also improves the reaction kinetics by adsorbing hydrogen at the interface.

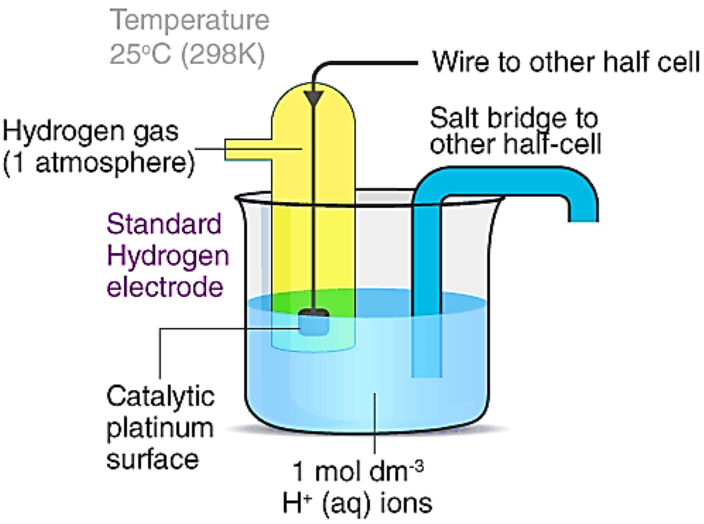
Standard Hydrogen Electrode Construction

The parts that make up a Standard Hydrogen Electrode are listed below.

- A platinum electrode is covered in finely powdered platinum black (platinized platinum electrode).
- A hydrogen blow.
- A solution of acid having an H+ molarity of 1 mole per cubic decimeter.
- SHE also contains a hydroseal which is used to prevent the interference of oxygen.
- The other half-cell of the entire Galvanic cell must be attached to the Standard Hydrogen Electrode through a reservoir in order to create an ionically conductive path. This can be done through a direct connection, through a narrow tube, or even through the use of a salt bridge.

Standard Hydrogen Electrode Diagram

A labelled diagram of a standard hydrogen electrode is provided below. In SHE, a salt bridge is used tso link SHE with the other half cell.



The platinized platinum surface has a very high adsorption activity. Therefore, this surface must be protected from atmospheric oxygen as well as from organic substances. Substances such as arsenic and sulphur compounds can deactivate or poison the catalyst.

Standard Electrode Potential

Standard electrode potential is a measurement of the potential for equilibrium. There is a potential difference between the electrode and the electrolyte called the potential of the electrode. When unity is the concentrations of all the species involved in a semi-cell, the electrode potential is known as the standard electrode potential.

Under standard conditions, the standard electrode potential occurs in an electrochemical cell say the temperature = 298K, pressure = 1atm, concentration = 1M. The symbol 'E^ocell' represents the standard electrode potential of a cell.

Significance of Standard Electrode Potential

- All electrochemical cells are based on redox reactions, which are made up of two half-reactions.
- The oxidation half-reaction occurs at the anode and it involves a loss of electrons.
- Reduction reaction takes place at the cathode, involving a gain of electrons. Thus, the electrons flow from the anode to the cathode.
- The electric potential that arises between the anode and the cathode is due to the difference in the individual potentials of each electrode (which are dipped in their respective electrolytes).
- The cell potential of an electrochemical cell can be measured with the help of a voltmeter. However, the individual potential of a half-cell cannot be accurately measured alone.
- It is also important to note that this potential can vary with a change in pressure, temperature, or concentration.
- In order to obtain the individual reduction potential of a half-cell, the need for standard electrode potential arises.
- It is measured with the help of a reference electrode known as the standard hydrogen electrode (abbreviated to SHE). The electrode potential of SHE is 0 Volts.
- The standard electrode potential of an electrode can be measured by pairing it with the SHE and measuring the cell potential of the resulting galvanic cell.
- The oxidation potential of an electrode is the negative of its reduction potential. Therefore, the standard electrode potential of an electrode is described by its standard reduction potential.
- Good oxidizing agents have high standard reduction potentials whereas good reducing agents have low standard reduction potentials.
- For example, the standard electrode potential of Ca^{2+} is -2.87 V. and that of F_2 is +2.87V. This implies that F_2 is a good oxidizing agent whereas Ca is a reducing agent.

Galvanic Cell (Voltaic Cell)

An electrochemical cell that converts the chemical energy of spontaneous redox reactions into electrical energy is known as a galvanic cell or a voltaic cell.

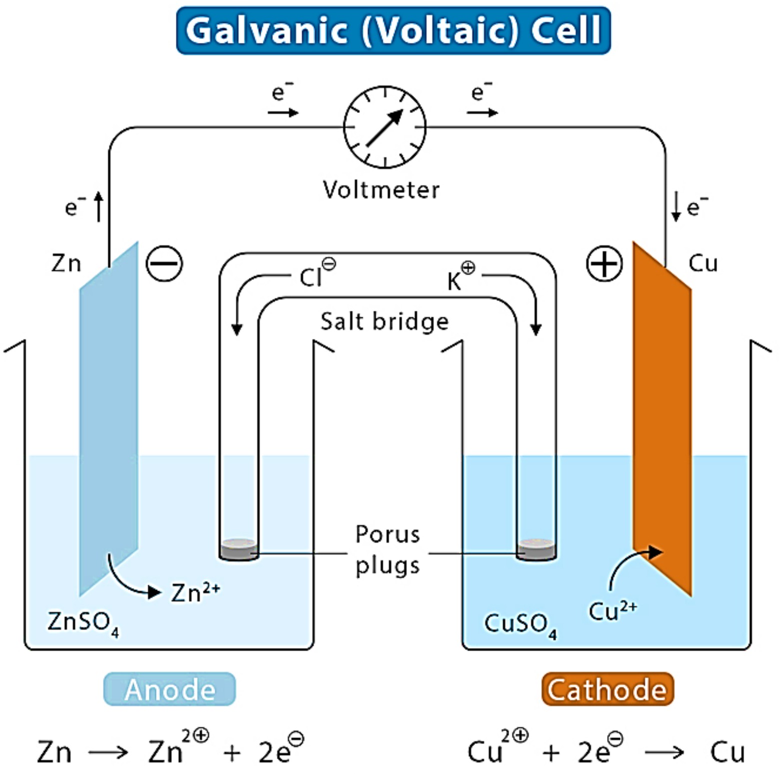
Galvanic cell Voltaic cell is an electrochemical cell that makes use of chemical reactions to generate electrical energy.

Let us understand how a voltaic or galvanic cell is created.

In oxidation-reduction reactions, electrons are moved from one species to another species. Energy is released if the reaction occurs spontaneously. Therefore, the released energy is used to do useful work. To tackle this energy, it is required to split the reaction into two separate half-reactions viz. oxidation and reduction. With the help of two different containers and wire, the reactions are put into them to drive the electrons from one end to the other end. This creates a voltaic cell.

Principle of Galvanic (Voltaic) Cell

Electric work done by a galvanic cell is mainly due to the Gibbs energy of spontaneous redox reaction in the voltaic cell. It generally consists of two half cells and a salt bridge. Each half cell further consists of a metallic electrode dipped into an electrolyte. These two half-cells are connected to a voltmeter and a switch externally with the help of metallic wires. In some cases, when both the electrodes are dipped in the same electrolyte, a salt bridge is not required.



Galvanic Cell (Voltaic Cell) Diagram

Parts of Galvanic Cell

Anode – Oxidation occurs at this electrode.

Cathode – Reduction occurs at this electrode.

Salt bridge – Contains electrolytes which are required to complete the circuit in a galvanic cell.

Half-cells – reduction and oxidation reactions are separated into compartments.

External circuit – Conducts the flow of electrons between electrodes

Load – A part of the circuit utilizes the electron to flow to perform its function.

Working of Galvanic Cell

- In a galvanic cell, when an electrode is exposed to the electrolyte at the electrode-electrolyte interface, the atoms of the metal electrode have a tendency to generate ions in the electrolyte solution leaving behind the electrons at the electrode. Thus, making the metal electrode negatively charged.
- While at the same time metal ions in the electrolyte solution too, have a tendency to deposit on a metal electrode. Thus, making the electrode positively charged.
- Under equilibrium condition, charge separation is observed and depending on the tendencies of two opposing reactions, the electrode can be positively or negatively charged. Hence, a potential difference is developed between the electrode and electrolyte. This potential difference is known as electrode potential.
- Out of two electrodes, the electrode at which oxidation takes place is called anode while the electrode at which reduction takes place is called cathode.
- The anode has a negative potential with respect to the solution while the cathode has a positive potential with respect to the solution.
- Thus, a potential difference develops between two electrodes of the galvanic cell. This potential difference is known as cell potential.
- When no current is drawn from the galvanic cell, cell potential is known as the electromotive force of the galvanic cell.
- When the switch is set on, due to the potential difference, electrons flow from the negative electrode to the positive electrode.

Electrolytic Cell

An electrolytic cell can be defined as an electrochemical device that uses electrical energy to facilitate a non-spontaneous redox reaction. Electrolytic cells are electrochemical cells that can be used for the electrolysis of certain compounds. For example, water can be subjected to electrolysis (with the help of an electrolytic cell) to form gaseous oxygen and gaseous hydrogen. This is done by using the flow of electrons (into the reaction environment) to overcome the activation energy barrier of the non-spontaneous redox reaction.

The three primary components of electrolytic cells are:

Cathode (which is negatively charged for electrolytic cells)

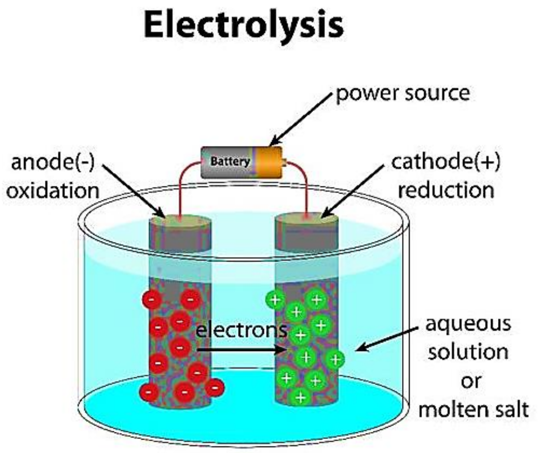
Anode (which is positively charged for electrolytic cells)

Electrolyte

The electrolyte provides the medium for the exchange of electrons between the cathode and the anode. Commonly used electrolytes in electrolytic cells include water (containing dissolved ions) and molten sodium chloride.

Diagram and Working of an Electrolytic Cell

Molten sodium chloride (NaCl) can be subjected to electrolysis with the help of an electrolytic cell, as illustrated below.



Here, two inert electrodes are dipped into molten sodium chloride (which contains dissociated Na+ cations and Cl– anions). When an electric current is passed into the circuit, the cathode becomes rich in electrons and develops a negative charge. The positively charged sodium cations are now attracted towards the negatively charged cathode. This results in the formation of metallic sodium at the cathode.

Simultaneously, the chlorine atoms are attracted to the positively charged cathode. This results in the formation of chlorine gas (Cl_2) at the anode (which is accompanied by the liberation of 2 electrons, finishing the circuit). The associated chemical equations and the overall cell reaction are provided below.

Reaction at Cathode: $[Na^+ + e^- \rightarrow Na] \times 2$

Reaction at Anode: $2Cl^- \rightarrow Cl_2 + 2e^-$

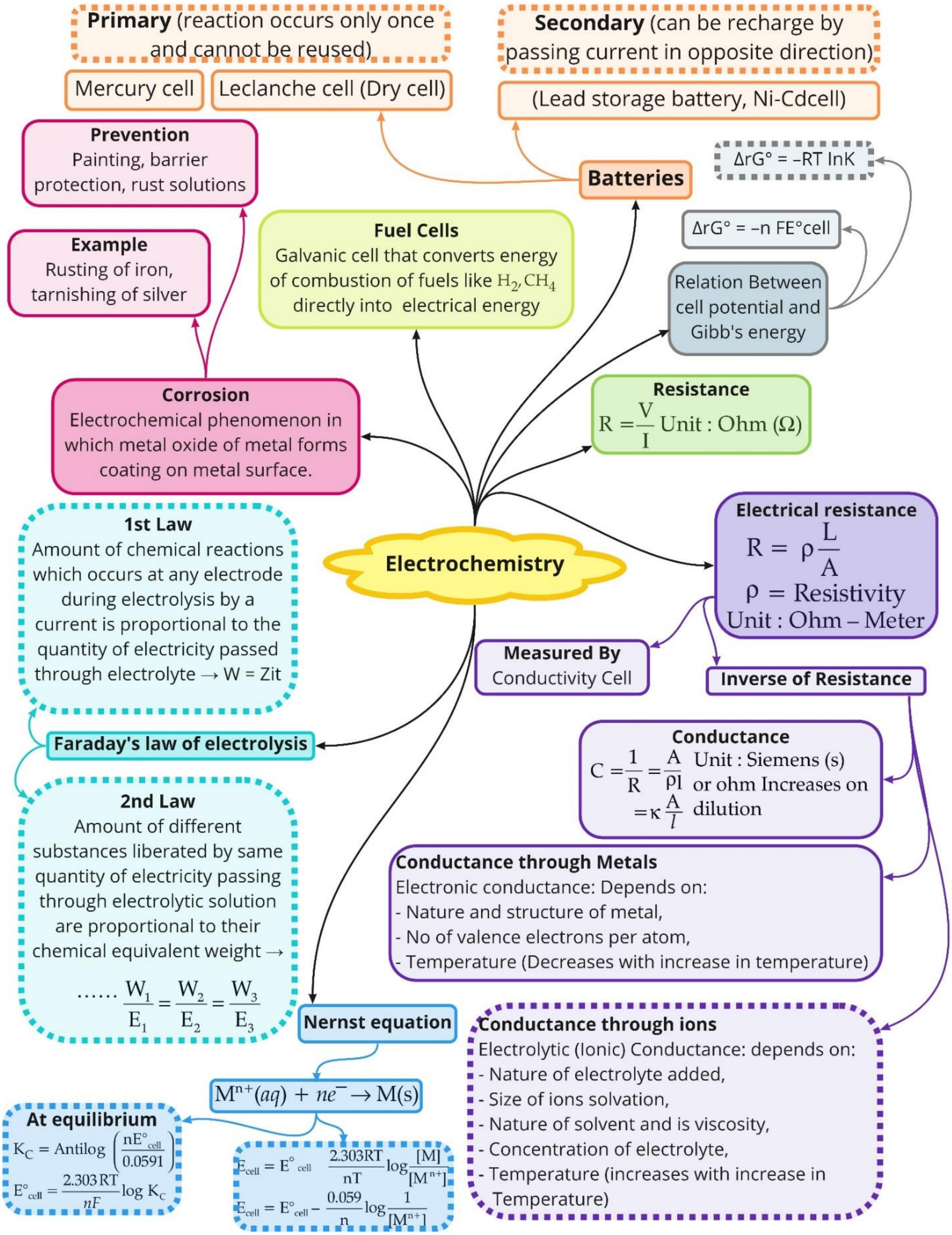
Cell Reaction: $2NaCl \rightarrow 2Na + Cl_2$

Thus, molten sodium chloride can be subjected to electrolysis in an electrolytic cell to generate metallic sodium and chlorine gas as the products.

Applications of Electrolytic Cells

- The primary application of electrolytic cells is for the production of oxygen gas and hydrogen gas from water. They are also used for the extraction of aluminium from bauxite.
- Another notable application of electrolytic cells is in electroplating, which is the process of forming a thin protective layer of a specific metal on the surface of another metal.
- The electrorefining of many non-ferrous metals is done with the help of electrolytic cells. Such electrochemical cells are also used in electrowinning processes.
- It can be noted that the industrial production of high-purity copper, high-purity zinc, and high-purity aluminium is almost always done through electrolytic cells.

Class : 12th Chemistry
Chapter-3 : Electrochemistry (Part_1)



Electrochemistry

Batteries

Primary (reaction occurs only once and cannot be reused)
- Mercury cell
- Leclanche cell (Dry cell)

Secondary (can be recharge by passing current in opposite direction)
- (Lead storage battery, Ni-Cdcell)

Fuel Cells
Galvanic cell that converts energy of combustion of fuels like H_2, CH_4 directly into electrical energy

Relation Between cell potential and Gibb's energy
- $\Delta rG° = -n\,FE°cell$
- $\Delta rG° = -RT\ lnK$

Resistance
$R = \frac{V}{I}$ Unit : Ohm (Ω)

Corrosion
Electrochemical phenomenon in which metal oxide of metal forms coating on metal surface.

Example
Rusting of iron, tarnishing of silver

Prevention
Painting, barrier protection, rust solutions

Electrical resistance
$R = \rho\frac{L}{A}$
ρ = Resistivity
Unit : Ohm – Meter

Measured By
Conductivity Cell

Inverse of Resistance

Conductance
$C = \frac{1}{R} = \frac{A}{\rho l} = \kappa\frac{A}{l}$ Unit : Siemens (s) or ohm Increases on dilution

Conductance through Metals
Electronic conductance: Depends on:
- Nature and structure of metal,
- No of valence electrons per atom,
- Temperature (Decreases with increase in temperature)

Conductance through ions
Electrolytic (Ionic) Conductance: depends on:
- Nature of electrolyte added,
- Size of ions solvation,
- Nature of solvent and is viscosity,
- Concentration of electrolyte,
- Temperature (increases with increase in Temperature)

Faraday's law of electrolysis

1st Law
Amount of chemical reactions which occurs at any electrode during electrolysis by a current is proportional to the quantity of electricity passed through electrolyte → W = Zit

2nd Law
Amount of different substances liberated by same quantity of electricity passing through electrolytic solution are proportional to their chemical equivalent weight →

$$\ldots\ldots \frac{W_1}{E_1} = \frac{W_2}{E_2} = \frac{W_3}{E_3}$$

Nernst equation

$$M^{n+}(aq) + ne^- \rightarrow M(s)$$

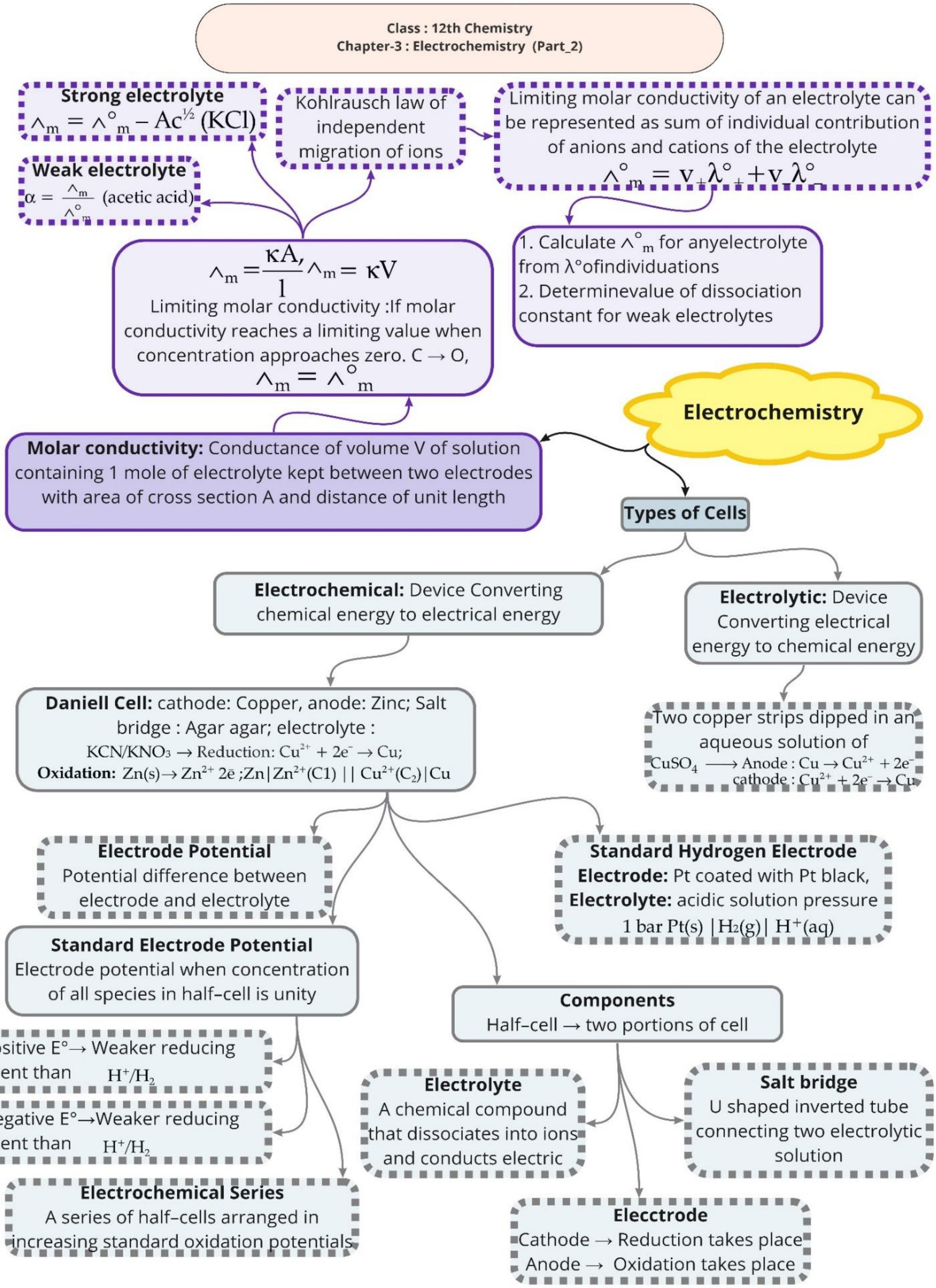
$$E_{cell} = E°_{cell}\ \frac{2.303RT}{nT}\log\frac{[M]}{[M^{n+}]}$$

$$E_{cell} = E°_{cell} - \frac{0.059}{n}\log\frac{1}{[M^{n+}]}$$

At equilibrium

$$K_C = \text{Antilog}\left(\frac{nE°_{cell}}{0.0591}\right)$$

$$E°_{cell} = \frac{2.303\,RT}{nF}\log K_C$$



Class : 12th Chemistry
Chapter-3 : Electrochemistry (Part_2)

Strong electrolyte
$\wedge_m = \wedge^\circ_m - Ac^{1/2}$ (KCl)

Weak electrolyte
$\alpha = \frac{\wedge_m}{\wedge^\circ_m}$ (acetic acid)

Kohlrausch law of independent migration of ions

Limiting molar conductivity of an electrolyte can be represented as sum of individual contribution of anions and cations of the electrolyte
$\wedge^\circ_m = v_+\lambda^\circ_+ + v_-\lambda^\circ_-$

1. Calculate $\wedge^\circ_m$ for anyelectrolyte from λ°ofindividuations
2. Determinevalue of dissociation constant for weak electrolytes

$\wedge_m = \frac{\kappa A,}{l} \wedge_m = \kappa V$
Limiting molar conductivity :If molar conductivity reaches a limiting value when concentration approaches zero. C → O,
$\wedge_m = \wedge^\circ_m$

Molar conductivity: Conductance of volume V of solution containing 1 mole of electrolyte kept between two electrodes with area of cross section A and distance of unit length

Electrochemistry

Types of Cells

Electrochemical: Device Converting chemical energy to electrical energy

Electrolytic: Device Converting electrical energy to chemical energy

Daniell Cell: cathode: Copper, anode: Zinc; Salt bridge : Agar agar; electrolyte :
KCN/KNO_3 → Reduction: $Cu^{2+} + 2e^- \rightarrow Cu$;
Oxidation: $Zn(s) \rightarrow Zn^{2+}\ 2\bar{e}$;$Zn|Zn^{2+}(C1)\ ||\ Cu^{2+}(C_2)|Cu$

Two copper strips dipped in an aqueous solution of
$CuSO_4 \longrightarrow$ Anode : $Cu \rightarrow Cu^{2+} + 2e^-$
cathode : $Cu^{2+} + 2e^- \rightarrow Cu$

Electrode Potential
Potential difference between electrode and electrolyte

Standard Hydrogen Electrode
Electrode: Pt coated with Pt black,
Electrolyte: acidic solution pressure
1 bar $Pt(s)\ |H_2(g)|\ H^+(aq)$

Standard Electrode Potential
Electrode potential when concentration of all species in half-cell is unity

Components
Half-cell → two portions of cell

Positive E°→ Weaker reducing agent than H^+/H_2

Negative E°→Weaker reducing agent than H^+/H_2

Electrochemical Series
A series of half-cells arranged in increasing standard oxidation potentials

Electrolyte
A chemical compound that dissociates into ions and conducts electric

Salt bridge
U shaped inverted tube connecting two electrolytic solution

Elecctrode
Cathode → Reduction takes place
Anode → Oxidation takes place

Important Questions

Multiple Choice Questions-

1. If the conductivity and conductance of a solution is same then its cell constant is equal to:
   (a) 1
   (b) 0
   (c) 10
   (d) 1000
2. The units of conductivity are.
   (a) ohm^{-1}
   (b) ohm^{-1} cm^{-1}
   (c) ohm^{-2} cm^2 $equiv^{-1}$
   (d) ohm^{-1} cm^2
3. The resistance of 0.1 N solution of acetic acid is 250 ohm, when measured in a cell of cell constant 1.15 cm^{-1}. The equivalent conductance (in ohm^{-1} cm^2 $equivalent^{-1}$) of 0.1 N acetic acid is
   (a) 18.4
   (b) 0.023
   (c) 46
   (d) 9.2
4. In infinite dilution of aqueous solution of BaCl2, molar conductivity of Ba^{2+} and Cl^- ions are = 127.32 S cm^2/mol and 76.34 S cm^2/mol respectively. What is A°m for BaCI2 at same dilution?
   (a) 280 S cm^2 mol^{-1}
   (b) 330.98 S cm^2 mol^{-1}
   (c) 90.98 S cm^2 mol^{-1}
   (d) 203.6 S cm^2 mol^{-1}
5. The specific conductance of 0.1 M NaCl solution is 1.06×10^{-2} ohm^{-1} cm^{-1}. Its molar conductance in ohm^{-1} cm^2 mol^{-1} is
   (a) 1.06×10^2
   (b) 1.06×10^3
   (c) 1.06×10^4
   (d) 53
6. The limiting molar conductivities A° for NaCl, KBr and KCl are 126, 152 and 150 S cm^2 mol^{-1} respectively. The A° for NaBr is
   (a) 278 S cm^2 mol^{-1}
   (b) 976 S cm^2 mol^{-1}
   (c) 128 S cm^2 mol^{-1}
   (d) 302 S cm^2 mol^{-1}
7. $\lambda(\text{CICH}_2\text{COONa})$ = 224 ohm^{-1} cm^2 gm eq^{-1}, λ(NaCl) = 38.2 ohm^{-1} cm^2 gm eq^{-1}. λ(HCl) = 203 ohm^{-1} cm^2 gm eq^{-1}, what is the value of $\lambda(\text{CICH}_2\text{COOH})$?
   (a) 288.5 ohm^{-1} cm^2 gm eq^{-1}
   (b) 289.5 ohm^{-1} cm^2 gm eq^{-1}
   (c) 388.8 ohm^{-1} cm^2 gm eq^{-1}
   (d) 59.5 ohm^{-1} cm^2 gm eq^{-1}
8. The limiting molar conductivities of HCl, CH_3COONa and NaCl are respectively 425, 90 and 125 mho cm^2 mol^{-1} at 25 °C. The molar conductivity of 0.1 M CH3COOH solution is 7.8 mho cm^2 mol^{-1} at the same temperature. The degree of dissociation of 0.1 M acetic acid solution at the same temperature is
   (a) 0.10
   (b) 0.02
   (c) 0.15
   (d) 0.03
9. The values of limiting ionic conductance of H and HCOO– ions are respectively 347 and 53 S cm^2 mol^{-1} at 298 K. If the molar conductance of 0.025 M methanoic acid at 298 K is 40 S cm^2 mol^{-1}, the dissociation constant of methanoic acid at 298 K is
   (a) 1×10^{-5}
   (b) 2×10^{-5}
   (c) 1.5×10^{-4}
   (d) 2.5×10^{-4}
10. The ionisation constant of a weak electrolyte is 2.5×10^{-5} and molar conductance of its 0.01 M solution is 19.6 S cm^2 mol^{-1}. The molar conductance at infinite dilution (S cm^2 mol^{-1}) is
   (a) 402
   (b) 392
   (c) 306
   (d) 39.2

Very Short

1. Can you store AgCl solution in Zinc pot?
2. Define the term – standard electrode potential?
3. What is electromotive force of a cell?
4. Can an electrochemical cell act as electrolytic cell? How?

5. Single electrode potential cannot be determined. Why?
6. What is SHE? What is its electrode potential?
7. What does the positive value of standard electrode potential indicate?
8. What is an electrochemical series? How does it predict the feasibility of a certain redox reaction?
9. Give some uses of electrochemical cells?
10. State the factors that affect the value of electrode potential?

Short Questions:

1. What is the cell potential for the cell at 25°C

Cr/Cr^{3+} 10.1 $m//Fe^{2+}$ (0.01 $m)/Fe$

$E^{0}{}_{cr+/cr} = -0.74V \cdot E^{0}Fe^{2+} / Fe = -0.44V$.

2. Calculate $\Delta G°$ for the reaction 25°C

$Zn(s)1Zn^{2}$ + $[0.0004m]11cd^{2}$ + $(0.2m)1cd(s)$

$E^{0\ 2+}_{Zn}{}_{/Zn} = -0.763V$

$E^{0\ 2+}_{cd}{}_{/cd} = -0.403v$

$F = 96500\ C\ Mol^{-1}$

$R = 8.314\ J/K$

3. Calculate Equilibrium constant K for the reaction

$298K\ Zn(s) + Cu^{2+}(aq) \rightleftarrows Zn^{2+} / (aq) + Cu\ E^{0\ 2+}_{Zn} 1Zn$

= -0.076v, $E^{0}Cu^{2} + /Cu + 0.34v$.

4. For what concentration of Ag + (aq) will the emf of the given cell be zero at 25°C if the concentration of $CU^{2+}(aq)$ is 0.1 M?

$Cu(s)/Cu^{2+}(0.1\ M)//Ag^{+}(aq)/Ag(s)$

$E^{0}\ Ag^{+}/Ag = +0.80V$

$E^{0\ 2+/Cu}_{Cu} = 0.34\ V$

5. Calculate the standard free energy change for the cell- reaction.

$Fe^{2+}(aq) + Ag^{+}(s)\,a' \rightarrow Fe^{3} + (aq) + Ag(s)$

How is it related to the equilibrium

constant of the reaction?

$E^{0\ 3+}_{Fe} / Fe^{2+} = +0.77V$

$E^{0\ +1/Ag}_{Ag} = +0.08V$

$F = 96500\ C/mol.$

6. How much charge is required for the following reductions:

(i) 1 mol of to Al.

(ii) 1 mol of to Cu.

(iii) 1 mol of to.

7. How much electricity in terms of Faraday is required to produce

(i) 20.0 g of Ca from molten .

(ii) 40.0 g of Al from molten

8. How much electricity is required in coulomb for the oxidation of

(i) 1 mol of to .

(ii) 1 mol of FeO to

9. A solution of $Ni(NO_3)_2$ is electrolysed between platinum electrodes using a current of 5 amperes for 20 minutes. What mass of Ni is deposited at the cathode?

10. Depict the galvanic cell in which the reaction takes place. Further show:

(i) Which of the electrode is negatively charged?

(ii) The carriers of the current in the cell.

(iii) Individual reaction at each electrode.

Long Questions:

1. Explain construction and working of standard Hydrogen electrode? (b) Write any two differences between amorphous solids and crystalline solids.

2. The molar conductivity of 0.025 mol L-1 methanoic acid is 46.1 S cm^{2} mol^{-1}. Calculate its degree of dissociation and dissociation constant. Given $\lambda°H^{+}$ = 349.6 S cm^{2} mol^{-1} and $\lambda°(HCOO-)$ = 54.6S cm^{2} mol^{-1}.

3. Explain how rusting of iron is envisaged as setting up of an electrochemical cell.

4. Calculate the standard cell potentials of galvanic cells in which the following reactions take place:

5. Write the Nernst equation and emf of the following cells at 298 K.

6. Define conductivity and molar conductivity for the solution of an electrolyte. Discuss their variation with concentration.

Assertion and Reason Questions:

1. In these questions, a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following choices.

a) Assertion and reason both are correct statements and reason is correct explanation for assertion.

b) Assertion and reason both are correct statements but reason is not correct explanation for assertion.

c) Assertion is correct statement but reason is wrong statement.

d) Assertion is wrong statement but reason is correct statement.

Assertion: At the end of electrolysis using platinum electrodes, an aqueous solution of copper sulphate tums colourless.

Reason: Copper in $CuSO_4$ is converted to $Cu(OH)_2$ during the electrolysis.

2. In these questions, a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following choices.

a) Assertion and reason both are correct statements and reason is correct explanation for assertion.

b) Assertion and reason both are correct statements but reason is not correct explanation for assertion.

c) Assertion is correct statement but reason is wrong statement.

d) Assertion is wrong statement but reason is correct statement.

Assertion: Zinc displaces copper from copper sulphate solution.

Reason: E^{o} of zinc is -0.vV and that of copper is +0.34V.

Case Study Questions:

1. The concentration of potassium ions inside a biological cell is at least twenty times higher than the outside. The resulting potential difference across the cell is important in several processes such as transmission of nerve impulses and maintaining the ion balance. A simple model for such a concentration cell involving a metal M is,

$M_{(s)}$ | M^+(aq.; 0.05 molar) || M^+(aq; 1 molar) | $M_{(s)}$

The following questions are multiple choice questions. Choose the most appropriate answer:

(i) For the above cell,

a) $E_{cell} < 0; \Delta G > 0$

b) $E_{cell} > 0; \Delta G < 0$

c) $E_{cell} < 0; \Delta G^{\circ} > 0$

d) $E_{cell} > 0; \Delta G^{\circ} < 0$

(ii) If the 0.05 molar solution of M^+ is replaced by a 0.0025 molar M^+ solution, then the magnitude of the cell potential would be:

a) 130mV

b) 185mV

c) 154mV

d) 600mV

(iii) The value of equilibrium constant for a feasible cell reaction is:

a) < 1

b) = 1

c) > 1

d) Zero

(iv) What is the emf of the cell when the cell reaction attains equilibrium?

a) 1

b) 0

c) > 1

d) < 1

(v) The potential of an electrode change with change in:

a) Concentration ofions in solution.

b) Position of electrodes.

c) Voltage of the cell.

d) All of these.

2. All chemical reactions involve interaction of atoms and molecules. A large number of atoms/molecules are present in a few gram of any chemical compound varying with their atomic/ molecular masses. To handle such large number conveniently, the mole concept was introduced. All electrochemical cell reactions are also based on mole concept. For example, a 4.0 molar aqueous solution of NaCl is prepared and 500mL of this solution is electrolysed. This leads to the evolution of chlorine gas at one of the electrode. The amount of products formed can be calculated by using mole concept.

The following questions are multiple choice questions. Choose the most appropriate answer:

(i) The total number of moles of chlorine gas evolved is:
  a) 0.5
  b) 1.0
  c) 1.5
  d) 1.9

(ii) If cathode is a Hg electrode, then the maximum weight of amalgam formed from this solution is:
  a) 300g
  b) 446g
  c) 396g
  d) 296g

(iii) The total charge (coulomb) required for complete electrolysis is:
  a) 186000
  b) 24125
  c) 48296
  d) 193000

(iv) In the electrolysis, the number of moles of electrons involved are:
  a) 2
  b) 1
  c) 3
  d) 4

(v) In electrolysis of aqueous NaCl solution when Pt electrode is taken, then which gas is liberated at cathode?
  a) H_2gas
  b) Cl_2gas
  c) O_2gas
  d) None of these.

Answers key

MCQ answers:

1. Answer: (a) 1
2. Answer: (b) ohm^{-1} cm^{-1}
3. Answer: (c) 46
4. Answer: (a) 280 S cm^2 mol^{-1}
5. Answer: (a) 1.06×10^2
6. Answer: (c) 128 S cm^2 mol^{-1}
7. Answer: (c) 388.8 ohm^{-1} cm^2 gm eq^{-1}
8. Answer: (b) 0.02
9. Answer: (d) 2.5×10^{-4}
10. Answer: (b) 392

Very Short Answers:

1. No. We can't store AgCl solution in Zinc pot because standard electrode potential of Zinc is less than silver..

2. When the concentration of all the species involved in a half-cell is unity, then the electrode potential is called standard electrode potential.

3. **Answer:** Electromotive force of a cell is also called the cell potential. It is the difference between the electrode potentials of the cathode and anode.

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

4. **Answer:** Yes, An electrochemical cell can be converted into electrolytic cell by applying an external opposite potential greater than its own electrical potential.

5. **Answer:** A single half cell does not exist independently as reduction and oxidation occur simultaneously therefore single electrode potential cannot be measured.

6. **Answer:** SHE stands for standard Hydrogen electrode. By convention, its electrode potential is taken as 0 (zero).

7. **Answer:** The positive value of standard electrode potential indicates that the element gets reduced more easily than ions and its reduced form is more stable than Hydrogen gas.

8. The arrangement of metals and ions in increasing order of their electrode potential values is known as electrochemical series.The reduction half reaction for which the reduction potential is lower than the other will act as anode and one with greater value will act as cathode. Reverse reaction will not occur.

9. Electrochemical cells are used for determining the
   - pH of solutions

- solubility product and equilibrium constant
- in potentiometric titrations

10. Factors affecting electrode potential values are –

- Concentration of electrolyte
- Temperature.

Short Answers:

1. Answer

The cell reaction is

$2Cr + 3Fe^{2+}\ 6e^{-} \rightarrow 2Cr^{3+} + 3Fe$

Nernst Equation –

$$E_{cell} = \left(E^{0\ 2}_{Fe} + /_{Fe} - E^{0\ 3+}_{Cr}{}_{/Cr}\right)$$

$$-\frac{0.059}{6}\log\frac{\left[Cr^{3+}\right]^2}{\left[Fe^{2+}\right]^3}$$

$$= (-0.44\text{v} - (-0.74\text{v}) - \frac{0.059}{6}\log\frac{(0.10)^2}{(0.01)^3}$$

$$= 0.3V - \frac{0.059}{6}\log 10^4$$

= 0.3V – 0.0394V

= +0.2606 V

2. Answer:

The half-cell reactions are

Anode: $Zn(s) \rightarrow Zn^{2} + (aq) + 2e^{-}$

Cathode: $Ca^{2} + (aq) + 2e^{-} \rightarrow Cd(s)$

Nernst Equation

$$E_{cell} = \left(E^{0}_{cathode} - E^{0}_{anode}\right) - \frac{0.059}{n}\log\frac{[Zn^{2+}]}{[Cd^{2+}]}$$

= (- 0.403 – (-0.763) –

= 0.36V – 0.0798V = 0.4398V

$\Delta G^{\circ} = -nFE^{\circ}_{cell}$

= - 8488 J mol^{-1}

3. Answer:

From the reaction, n =2

$E^{0}_{cell} = E^{0}cu^{2} + /cu - E^{0}Zn^{2} + /Zn$

= + 0.34v – (-0.76v) = 1.10V

$$E^{0}_{cell} = \frac{2.303RT}{nF}\log k_c$$

At 298k, $E^{0}_{cell} \times \frac{n}{0.059}\log k_c$

$$\text{Log k}_c = E^{0}_{cell} \times \frac{n}{0.059}$$

$$1.10 \times \frac{2}{0.059} = 37.29$$

$K_c = Antilog\ 37.29$

$= 1.95 \times 10^{37}$

4. Answer:

$[Ag^{+}] = 5.3 \times 10^{-9}\ M$

5. Answer :

$E^{0}{}_{cell} = 0.03V$

6. Answer

(i) Therefore, Required charge = 3 F

= 289461 C

(ii) $Cu^{2+} + 2e^{-} \rightarrow Cu$

Therefore, Required charge = 2 F

= 2 × 96487 C

= 192974 C

(iii) $MnO^{-}{}_{4} \rightarrow Mn^{2+}$

i.e., $Mn^{7+} + 5e^{-} \rightarrow Mn^{2+}$

Therefore, Required charge = 5 F

= 5 × 96487 C

= 482435 C

7. Answer:

(i) According to the question,

Electricity required to produce 40 g of calcium = 2 F

Therefore, electricity required to produce 20 g of calcium =

= 1 F

(ii) According to the question,

$$Al^{3} + 3e^{-1} \rightarrow \frac{Al}{27g}$$

Electricity required to produce 27 g of Al = 3 F

Therefore, electricity required to produce

$$40\text{ g of Al} = \frac{3 \times 40}{27}F$$

= 4.44 F

8. Answer:

(i) According to the question,

Now, we can write:

$$O^2 \rightarrow \frac{1}{2}O_2 + 2e^-$$

Electricity required for the oxidation of 1 mol of H_2O to O_2 = 2 F

= 2 × 96487 C

= 192974 C

(ii) According to the question

$$Fe^{2+} \rightarrow Fe^{3+} + e^{-1}$$

Electricity required for the oxidation of 1 mol of FeO to Fe_2O_3 = 1F

= 96487 C

9. Answer :

Given,

Current = 5A

Time = 20 × 60 = 1200 s

Therefore, Charge = Current × time

= 5 × 1200

= 6000 C

According to the reaction,

$$Ni^{2+}_{(aq)} + 2e^- \rightarrow \underset{58.7\,g}{Ni_{(s)}}$$

Nickel deposited by 2 × 96487 C = 58.71 g

Therefore, nickel deposited by 6000

$$C = \frac{58.71 \times 6000}{2 \times 96487} g$$

= 1.825 g

Hence, 1.825 g of nickel will be deposited at the cathode.

10. Answer :

The galvanic cell in which the given reaction takes place is depicted as:

$$Zn_{(s)} \,|\, Zn^{2+}_{(aq)} \,||\, Ag^{+}_{(aq)} \,|\, Ag_{(s)}$$

(i) Zn electrode (anode) is negatively charged.

(ii) Ions are carriers of current in the cell and in the external circuit, current will flow from silver to zinc.

(iii) The reaction taking place at the anode is given by,

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

The reaction taking place at the cathode is given by,

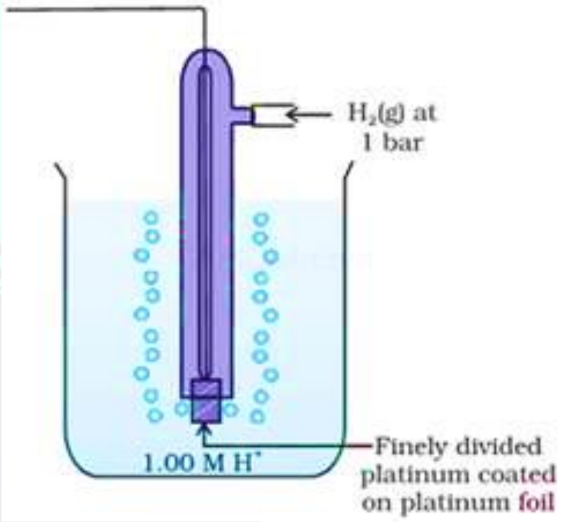
$$Ag^{+}_{(aq)} + e^- \rightarrow Ag_{(s)}$$

Long Answers:

1. Answer:

Construction: SHE consists of a platinum electrode coated with platinum black. The electrode is dipped in an acidic solution and pure Hydrogen gas is bubbled through it. The concentration of both the reduced and oxidized. Forms of Hydrogen is maintained at unity i.e) pressure of gas is 1 bar and concentration of Hydrogen ions in the solution is 1 molar.

Working – The reaction taking place in SHE is At 298 K , the emf of the cell constructed by taking SHE as anode and other half-cell as cathode, gives the reduction potential of the other half cell whereas for a cell constructed by taking SHE as anode gives the oxidation potential of other half cell as conventionally the electrode potential of SHE is zero.



2. Answer:

$$A_m = 16.1\,S\,cm^2\,mol^{-1}$$

$$\lambda°(H^+) = 349.6\,S\,cm^2\,mol^{-1}$$

$$\lambda°(HCOO^-) = 54.6\,S\,cm^2\,mol^{-1}$$

$$A^0_m(HCOOH) = \lambda°(H^+) + \lambda°(HCOO^-)$$

= 349.6 + 54.6 = 404.2 S cm^2 mol^{-1}

Now, degree of dissociation:

$$\alpha = \frac{A_m(HCOOH)}{A^0_m(HCOOH)}$$

$$= \frac{46.1}{404.2} = 0.114 \text{ (approximately)}$$

Thus, dissociation constant:

$$K = \frac{c\alpha^2}{(1-\alpha)}$$

$$= \frac{\left(0.025\,\text{molL}^{-1}\right)(0.114)^2}{(1-0.114)}$$

= 3.67 ´ 10^{-4} molL^{-1}

3. **Answer:**

In the process of corrosion, due to the presence of air and moisture, oxidation takes place at a particular spot of an object made of iron. That spot behaves as the anode. The reaction at the anode is given by,

Electrons released at the anodic spot move through the metallic object and go to another spot of the object.

There, in the presence of ions, the electrons reduce oxygen. This spot behaves as the cathode. These H+ ions come either from, which are formed due to the dissolution of carbon dioxide from air into water or from the dissolution of other acidic oxides from the atmosphere in water.

The reaction corresponding at the cathode is given

$$O_{2(g)} + 4H^+_{(aq)} \rightarrow 2Fe^{2+}_{(aq)} + 2H_2O_{(i)}$$

The overall reaction is:

$$2Fe_{(s)} + O_{2(g)} + 4H^+_{(aq)} \rightarrow 2Fe^{2+}_{(aq)} + 2H_2O$$

Also, ferrous ions are further oxidized by atmospheric oxygen to ferric ions. These ferric ions combine with moisture, present in the surroundings, to form hydrated ferric oxide $(Fe_2O_3 \times H_2O)$ i.e., rust.

Hence, the rusting of iron is envisaged as the setting up of an electrochemical cell.

4. **Answer (i)** $E^{\odot}_{Cr^{3+}/Cr} = 0.74V$

$$E^{\odot}_{Cd^{2+}/Cd} = 0.40V$$

The galvanic cell of the given reaction is depicted as:

$$Cr_{(s)}\,|\,Cr^{3+}_{(aq)}\,||\,Cd^{2+}_{(aq)}\,|\,Cd_{(s)}$$

Now, the standard cell potential is

$$E^{\odot}_{cell} = E^{\odot}_R - E^{\odot}_L$$

= 0.40 – (–0.74)

= +0.34 V

$$\Delta_r G^{\odot} = -nFE^{\odot}_{cell}$$

In the given equation,

n = 6

F = 96487 C mol – 1

$$E^{\odot}_{cell} = +0.34V$$

Then,

$$\Delta_r G^{\odot} = -6 \times 96487\,\text{C mol}^{-1} \times 0.34V$$

= –196833.48 CV mol^{-1}

= –196833.48 J mol^{-1}

= –196.83 kJ v

Again, $\Delta_r G^{\odot} = -RT\,\text{In}\,K$

$$\Delta_r G^{\odot} = -2.303\,RT\,\text{In}\,K$$

$$\log K = \frac{\Delta_r G}{2.303\,RT}$$

$$= \frac{196.83 \times 10^3}{2.303 \times 8.314 \times 298}$$

= 34.496

Therefore, K = antilog (34.496)

= 3.13 × 1034

(ii) $E^{\odot}_{Fe^{3+}/Fe^{2+}} = 0.77V$

$$E^{\odot}_{Ag^+/Ag} = 0.80V$$

The galvanic cell of the given reaction is depicted as:

$$Fe^{2+}_{(aq)}\,|\,Fe^{3+}(aq)\,||\,Ag^+_{(aq)}\,|\,Ag_{(s)}$$

Now, the standard cell potential is

$$E^{\odot}_{cell} = E^{\odot}_R - E^{\odot}_L$$

= 0.80 – 0.77

= 0.03 V

Here, n = 1.

Then, $\Delta_r G^{\odot} = -nFE^{\odot}_{cell}$

$$= 1 \times 69487\,\text{C mol}^{-1} \times 0.03V$$

= –2894.61 J mol^{-1}

= –2.89 kJ mol^{-1}

Again, $\Delta_r G^{\odot} = -2.303\,RT\,\text{In}\,K$

$$\log K = \frac{\Delta_r G}{2.303\,RT}$$

$$= \frac{-2894.61}{2.303 \times 8.314 \times 298}$$

= 0.5073

Therefore, K = antilog (0.5073)

= 3.2 (approximately)

5. **Answer (i)** For the given reaction, the Nernst equation can be given as:

$$E_{cell} = E^{\ominus}_{cell} = -\frac{0.0591}{n}\log\frac{[Mg^{2+}]}{[Cu^{2+}]}$$

$$=\{0.34-(-236)\}-\frac{0.0591}{2}\log\frac{.001}{.0001}$$

$$=2.7-\frac{0.0591}{2}\log 10$$

= 2.7 – 0.02955

= 2.67 V (approximately)

(ii) For the given reaction, the Nernst equation can be given as:

$$E_{cell} = E^{\ominus}_{cell} = -\frac{0.0591}{n}\log\frac{[Fe^{2+}]}{[H^{+}]^{2}}$$

$$=\{0-(-0.44)\}-\frac{0.0591}{2}\log\frac{0.001}{1^{2}}$$

= 0.44–0.02955(–3)

= 0.52865 V

= 0.53 V (approximately)

(iii) For the given reaction, the Nernst equation can be given as:

$$E_{cell} = E^{\ominus}_{cell} = -\frac{0.0591}{n}\log\frac{[Sn^{2+}]}{[H^{+}]^{2}}$$

$$=\{0-(-0.14)\}-\frac{0.0591}{2}\log\frac{0.050}{(0.020)^{2}}$$

= 0.14 – 0.0295 × log 125

= 0.14–0.062

= 0.078 V

= 0.08 V (approximately)

(iv) For the given reaction, the Nernst equation can be given as:

$$E_{cell} = E^{\ominus}_{cell} = -\frac{0.0591}{n}\log\frac{1}{[Br^{-}]^{2}\left[H^{+}\right]^{2}}$$

$$=(0-1.09)-\frac{0.0591}{2}\log\frac{1}{(0.010)^{2}(0.030)^{2}}$$

$$=-1.09-0.02955\times\log\frac{1}{0.00000009}$$

$$=-1.09-0.02955\times\log\frac{1}{9\times10^{-8}}$$

$$=-1.09-0.02955\times\log\left(1.11\times10^{7}\right)$$

= –1.09–0.02955(0.0453+7)

= –1.09–0.208

= –1.298 V

Assertion and Reason Answers:

1. (c) Assertion is correct statement but reason is wrong statement.

   Explanation:

   Cu^{2+} ions are deposited as Cu.

2. (a) Assertion and reason both are correct statements and reason is correct explanation for assertion.

Case Study Answers:

1. **Answer :**

(i) (b) $E_{cell} > 0; \Delta G < 0$

Explanation:

$$\underset{(1M)}{M} \rightarrow \underset{(0.05M)}{M^{+}} + e^{-}$$

For concentration cell, $E_{cell} = \frac{0.059}{1}\log\frac{0.05}{1}$

$$E_{cell} = \frac{0.059}{1}\log\left(5\times10^{-2}\right)$$

$$E_{cell} = \frac{0.059}{1}\left[(-2)+\log 5\right]-0.059(-2+0.698)$$

= –0.0595 (–1.302) = 000768

$\Delta G = -nFE_{cell}$

If E_{cell} is positive, ΔG is negative,

(ii) (c) 154mV

Explanation:

$$\frac{E_1}{E_2}=\frac{\log 0.05}{\log 0.0025}$$

$$\frac{E_1}{E_2}=\frac{\log 5\times10^{-2}}{\log 25\times10^{-4}}$$

E_1 = 0.0768

$$\frac{0.0168}{E_2}=\frac{-1.3}{-2.6}=\frac{1}{2}\ \text{or}\ E_2 = 154\text{mV}$$

(iii) (c) > 1

Explanation:

$$K = \text{antilog}\left(\frac{nE^{\circ}}{0.0591}\right)$$

For fesible cell, E° is positive, hence from the above equation, K > 1 for a feasible cell reaction.

(iv) (b) 0

(v) (a) Concentration of ions in solution.

2. Answer :

(i) (b) 1.0

Explanation:

$$^{n}\text{NaCl} = \frac{4 \times 500}{1000} = 2\,\text{mol}$$

$$\therefore\ ^{n}\text{Cl}_2 = 1\,\text{mol}$$

(ii) (b) 446g

Explanation:

^{n}Na deposited = 2 mol

$\therefore\ ^{n}\text{Na}-\text{Hg}$ formed = 2 mol

$\therefore$ Mass of amalgam formed = $2 \times 223 = 446$g

(iii) (d) 193000

Explanation:

$$\underset{(2F)}{2\text{Na}^+ + 2e^-} \rightarrow 2\text{Na}$$

Total charge requird = 2F = 2×96500 = 193000C

(iv) (a) 2

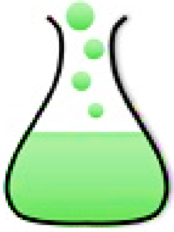
(v) (a) H_2 gas

❖ ❖

Chemical Kinetics

3

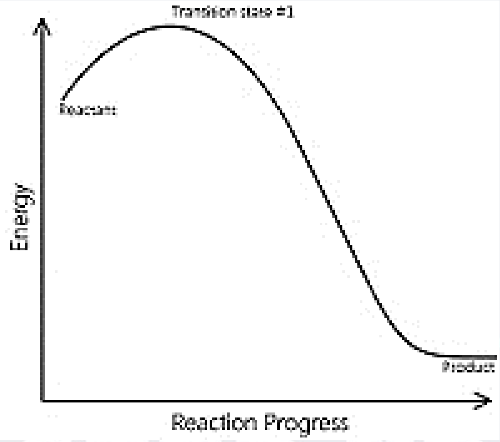
Introduction



The stream of chemistry that governs the rate of reactions along with their mechanisms is termed as Chemical kinetics derived from a Greek word meaning chemical movement.

Combination of two or more reactants to produce a new product is called reaction.

Elementary Reaction: The reaction that occurs in a single step to give the product is called an elementary reaction.



Complex reaction: The reactions that occur as a result of sequence of elementary reactions to give the product is called complex reactions.

Rate of reaction

The rate at which the concentration of reactant or product participating in a chemical reaction alters is called rate of reaction.

Rate of reaction = change in concentration/ time = (mol/litre)/time

Reactant (R) --> Product

Rate [R]

Rate = k[R]

k = rate constant or velocity constant.

Let one mole of the reactant A produce one mole of the product B.

Let at time t_1

[A]1 and [B]1 = Concentrations of A and B

Let at time t_2

[R]2 and [P]2 = Concentrations of A and B

Rate of disappearance of A = Decrease in concentration of R / Time taken = $-\Delta[A]/\Delta t$

Rate of appearance of B = Increase in concentration of P / Time taken = $+\Delta[B]/\Delta t$

When two or more reactants combine with each other the molecules of the respective reactants collide with each other to form the product. The collision between the molecules increases with the increase in concentration of the reactants and thereby increases the rate of reaction.

A + B --> C + D

Here molecules of reactant A and B collide to produce molecules of product C and D.

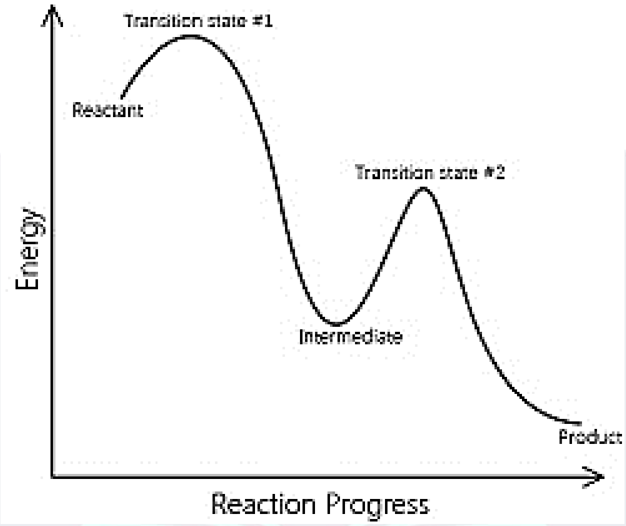
Therefore, we can conclude that rate of reaction is directly proportional to the concentration of the participating reactants.

Rate ∝ [A]x [B]y

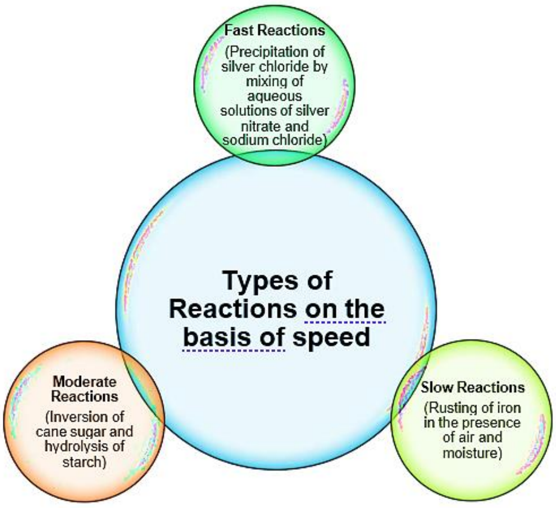
Or Rate = k[A]x [B]y

Hg(l) + Cl2 (g) --> HgCl2(s)

Rate of reaction= -Δ[Hg]/Δt = Δ[Cl2]/Δt = Δ[Hg Cl2]/Δt



Rate of Chemical Reaction



Rate of Chemical Reaction

The **rate of reaction** is the change in concentration of a reactant or production unit time.

- Alternatively, the rate of reaction can also be expressed as

The rate of decrease in concentration of any one of the reactants.

The rate of increase in concentration of any one of the products.

- Consider a hypothetical reaction, assuming that the volume of the system remains constant.

$$R \rightarrow P$$

One mole of the reactant R produces one mole of the product P.

- If $[R]_1$ and $[P]_1$ are the concentrations of R and P at time t_1 and $[R]_2$ and $[P]_2$ are theirconcentrations at time t_2, then

$$\Delta r = t_2 - t_1$$

$$\Delta[R] = [R]_2 - [R]_1$$

$$\Delta[P] = [P]_2 - [P]_1$$

The square brackets in the above expressions are used to express molar concentration.

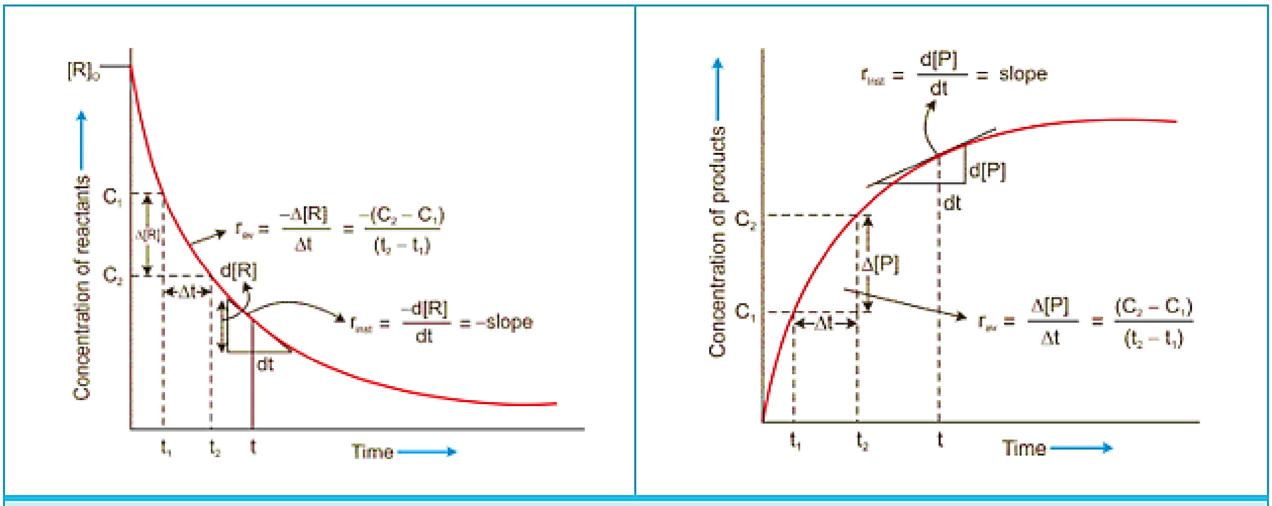
$$\text{Rate of disappearance of R} = \frac{\text{Decrease in concentration of R}}{\text{Time taken}} = -\frac{\Delta[R]}{\Delta t} \_\_\_\_\_(1)$$

- Δ[R] is a negative quantity because the concentration of reactants is decreasing.

$$\text{Rate of appearance of P} = \frac{\text{Increase in concentration of P}}{\text{Time taken}} = +\frac{\Delta[P]}{\Delta t} \_\_\_\_\_(2)$$

- Equations 1 and 2 represent the average rate of a reaction, r_{av}.

  This average rate depends on the change in concentration of reactants or products and the timetaken for that change to occur.



Instantaneous and average rate of a reaction

Units of Rate of a Reaction

- From Equations 1 and 2, it is clear that the units of rate are concentration time^{-1}.
- For example, if concentration is in mol L^{-1} and time is in seconds, then the units are mol L^{-1}s^{-1}.
- In gaseous reactions, the concentration of gases is expressed in terms of their partial pressures;hence, the units of the rate equation will be atm s^{-1}.

Instantaneous Rate of Reaction

- Consider the hydrolysis of butyl chloride (C_4H_9Cl).

$$C_4H_9Cl + H_2O \rightarrow C_4H_9OH + HCl$$

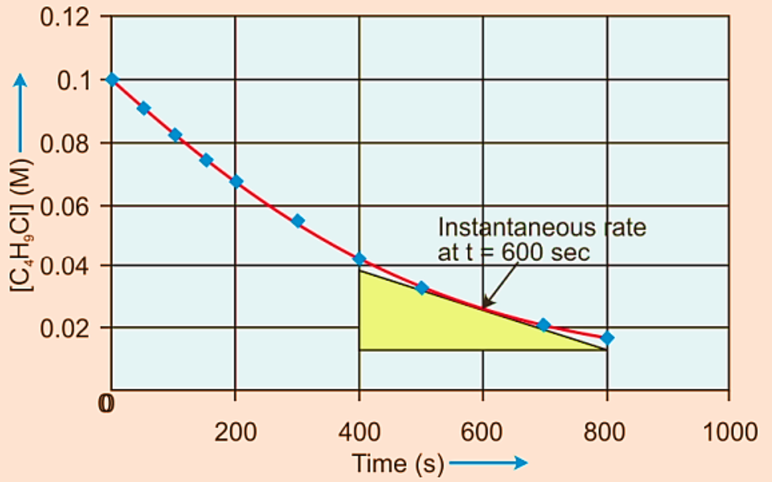
- We have provided the concentrations over different intervals of time below.

Time (s^{-1})	0	50	100	150	200	300	400	700	800
Concentration (mol L^{-1})	0.100	0.0905	0.0820	0.0741	0.0671	0.0549	0.0439	0.0210	0.017

- We can determine the difference in concentration over different intervals of time, and thus, wedetermine the average rate by dividing Δ[R] by Δt.
- It can be seen from experimental data that the average rate falls from 1.90×10^{-4} mol L^{-1}s^{-1} to 0.4×10^{-4} mol L^{-1}s^{-1}.
- However, the average rate cannot be used to predict the rate of reaction at a particular instant as itwould be constant for the time interval for which it is calculated.
- Hence, to express the rate at a particular moment of time, we determine the instantaneous rate.
- It is obtained when we consider the average rate at the smallest time interval, say dt, when Δt approaches zero.

Therefore, for an infinitesimally small dt, the instantaneous rate is given by:

$$r_{inst} = \frac{d[R]}{dt} = \frac{d[P]}{dt}$$



Instantaneous rate of hydrolysis of butyl chloride(C_4H_9Cl)

- By drawing the tangent at time t on either of the curves for the concentration of R versus time t or concentration of P versus time t and calculating the slope of the curve, we can determine the instantaneous rate of reaction.
- Hence, in this example, r_{inst} at 600 s is calculated by plotting the graph of the concentration of butylchloride as against time t.
- A tangent is drawn on the curve at a point t = 600 s.

$$\therefore r_{inst} \text{ at } 600s = \left[\frac{0.0165-0.037}{(800-400)}\right] molL^{-1} = 5.12\times10^{-5} molL^{-1}s^{-1}$$

At t = 250 s $\quad r_{inst} = 1.22 \times 10^{-4}\ molL^{-1}s^{-1}$

t = 350 s $\quad r_{inst} = 1.0 \times 10^{-4}\ molL^{-1}s^{-1}$

t = 450 s $\quad r_{inst} = 6.4 \times 10^{-5}\ molL^{-1}s^{-1}$

- Now consider a reaction,

$$Hg(l) + Cl_2(g) \rightarrow HgCl_2(s)$$

Here, the stoichiometric coefficients of the reactants and products are the same; hence, the rate of reaction is given as:

$$\text{Rate or reaction} = -\frac{\Delta[Hg]}{\Delta t} = -\frac{\Delta[Cl_2]}{\Delta t} = \frac{\Delta[HgCl_2]}{\Delta t}$$

Therefore, we can say that from the above equation that the rate of disappearance of any of the reactants is the same as the rate of appearance of the products.

- Consider another reaction,

$$2HI(g) \rightarrow H_2(g) + I_2(g)$$

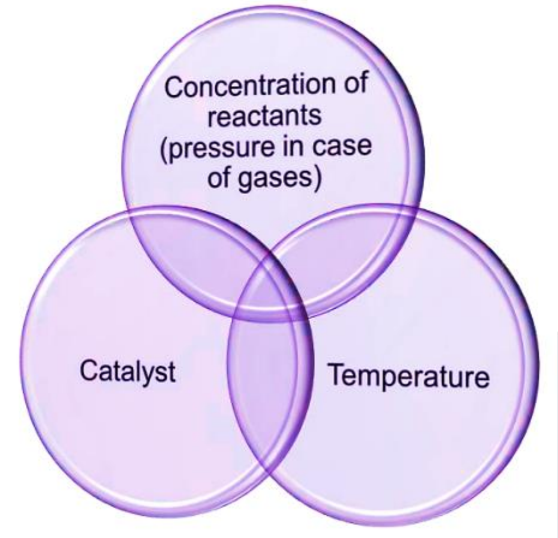
In this reaction, two moles of HI decompose to produce one mole each of H2 and I2, i.e. the stoichiometric coefficients of reactants or products are not equal to one; hence, we need to divide the rate of disappearance of any of the reactants or the rate of appearance of products by their respective stoichiometric coefficients.

Because the rate of consumption of HI is twice the rate of formation of H2 or I2, to make them equal, the term Δ[HI] is divided by 2.

The rate of this reaction is given by:

$$\text{Rate or reaction} = -\frac{1}{2}\frac{\Delta[HI]}{\Delta t} = \frac{\Delta[H_2]}{\Delta t} = \frac{\Delta[I_2]}{\Delta t}$$

- For a gaseous reaction at constant temperature, concentration is directly proportional to the partial pressure of a species, and hence, the rate can be expressed as the rate of change in partial pressure of the reactant or the product.



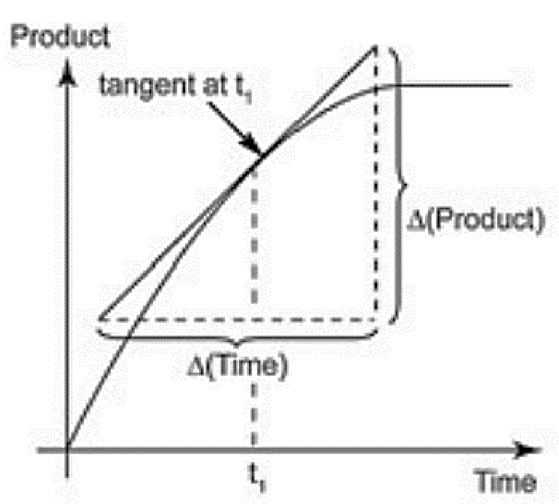
Instantaneous rate of reaction

The ratio of change in concentration in chemical reaction to the time period is termed as instantaneous rate of the reaction.

-d[R]/dt = change in chemical concentration over short period of time/ the short time elapsed = (mol/litre) / time

It can be calculated from the slope of the tangent on a concentration- time graph.

For example, consider the following graph.



The rate of reaction at t = 40s in the above graph can be calculated by following method:

Rate of reaction = gradient of the tangent at 40s = (120-70)/(65-5) = 50/60= 0.83 cm3s^{-1}

Rate of reaction

The rate at which the concentration of reactant or product participating in a chemical reaction alters is called rate of reaction.

Rate of reaction = change in concentration/ time = (mol/litre)/time

Reactant (R) --> Product

Rate [R]

Rate = k[R]

k = rate constant or velocity constant.

Let one mole of the reactant A produce one mole of the product B.

Let at time t1

[A]1 and [B]1 = Concentrations of A and B

Let at time t2

[R]2 and [P]2 = Concentrations of A and B

Rate of disappearance of A = Decrease in concentration of R / Time taken = -Δ[A]/Δt

Rate of appearance of B = Increase in concentration of P / Time taken = +Δ[B]/Δt

When two or more reactants combine with each other the molecules of the respective reactants collide with each other to form the product. The collision between the molecules increases with the increase in concentration of the reactants and thereby increases the rate of reaction.

A + B --> C + D

Here molecules of reactant A and B collide to produce molecules of product C and D.

Therefore, we can conclude that rate of reaction is directly proportional to the concentration of the participating reactants.

$$\text{Rate} \propto [A]x\ [B]y$$

$$\text{Or Rate} = k[A]x\ [B]y$$

$$Hg(l) + Cl_2\ (g) \dashrightarrow HgCl_2(s)$$

$$\text{Rate of reaction} = -\Delta[Hg]/\Delta t = \Delta[Cl_2]/\Delta t = \Delta[Hg\ Cl_2]/\Delta t$$

Average rate of reaction

The average rate of the reaction is the ratio of change in concentration of reactants to the change in time. It is determined by the change in concentration of reactants or products and the time taken for the change as well. As the reaction precedes forward the collisions between the molecules of the participating reactants reduces thereby decreasing the average rate of the reaction.

Mathematically, Average rate of reaction = Change in concentration / Time = (mol/litre)/time

Problem 1. For the reaction R → P, the concentration of a reactant changes from 0.03 M to 0.02 M in 25 minutes. Calculate the average rate of reaction using units of time both in minutes and seconds.

Solution: R2= 0.02 M

R1= 0.03M

t2 - t1= 25 minutes

Δ[R]/Δt =Δ[R2-R1]/ t2- t1=- (0.02-0.03)/25 = 6.67 X 10-6 Ms-1

= 0.005ML-1 min-1

Problem 2. In a reaction, 2A → Products, the concentration of A decreases from 0.5 mol L-1 to 0.4 mol L-1 in 10 minutes. Calculate the rate during this interval?

Solution: -1/2 (Δ[A]/Δt) =-1/2(Δ[A2-A1]/Δt) =-1/2 (0.4-0.5/10)

=0.005ML-1 min^{-1}

= 5 X 10-3M min^{-1}

Rate expression

The representation of rate of reaction in terms of concentration of the reactants is called rate equation or rate expression.

For example, in the reaction

$$2NO(g) + O_2(g) \dashrightarrow 2NO_2$$

The rate expression is given as

$$\text{Rate} = k[NO]2[O2]$$

Let us consider another reaction

$$BrO_3^- + 5Br^- + 6H+ \dashrightarrow 3Br + 3\ H_2O$$

Rate expression for this reaction is given as

$$k[BrO_3^-][Br^-][H+]^2$$

Order of a Reaction

The order of a reaction is defined as:

the sum of the powers to which the concentration terms are raised in the rate law equation to express the observed rate of the reaction.

The power of the concentration of a particular reactant in the rate law is called the order of the reaction with respect to that reactant.

If the rate of a reaction,

$$aA + bB + cC \text{ ——> Products}$$

is given by the rate law as:

$$k[A]p\ [B]q\ [C]r$$

$$\text{Rate} = -dx\ /dt = k[A]p\ [B]q\ [C]r$$

then, the order of the reaction, n, is $n = p+q+r$

where p, q and r are the orders with respect to individual reactants and overall order of the reaction is sum of these exponents, i.e., $p + q + r$.

When n =1, the reaction is said to be first order reaction, if n = 2, the reaction is said to be second order reaction and so on.

Some Examples of Reactions of Different Orders

(a) Reactions of first order:

(1) Decomposition of nitrogen pentoxide (N2O5)

$2N_2O_5\ (g) \text{ ———> } 2\ NO_2\ (g) + ½\ O_2\ (g)$

Rate = $k\ [N_2O_5]$

(2) Decomposition of ammonium nitrite in aqueous solution

$NH_4NO_2 \text{ ————>} N_2+2H_2O$

Rate = $k[NH_4NO_2]$

(3) Decomposition of H_2O_2 in the presence of I^- ions

$H_2O_2 \text{ ————> } H_2O + ½\ O_2$

Rate = $k\ [H_2O_2]$

(b) Reactions of second order

(1) Decomposition of nitrogen peroxide

$2NO_2 \text{ ———> } 2NO + O_2$

Rate =$k\ [NO_2]2$

(2) Reaction between H_2 and I_2 to give HI

$H_2 + I_2 \text{ ———> } 2HI$

Rate =$k[H_2]\ [I_2]$

(c) Reactions of third order

(1) Reaction between nitric oxide and oxygen

$2NO + O_2 \text{ ———> } 2NO_2$

Rate = $k\ [NO]_2\ [O_2]$

(2) Reaction between nitric oxide and Cl_2

$2NO +Cl_2 \text{ ———>} 2NOCl$

Rate = $k\ [NO]_2\ [Cl2]$

(d) Reactions of fractional order

(1) Decomposition of acetaldehyde is a fractional order reaction

CH_3CHO ——-> $CH_4 + CO$

Rate = k $[CH_3CHO]^{3/2}$

Order = 3/2 or 1.5

(2) The reaction between hydrogen and bromine to form hydrogen bromide is a fractional order reaction.

H2(g) + Br2(g)——> 2HBr

Rate = k [H2] [Br2]½

Order = 1 + ½ = 1½

(e) Zero order reaction

A number of zero order reactions are known in which the rate of the reaction is independent of the concentration of the reactants.

For example: the decomposition of ammonia at the surface of metals like gold, platinum etc., is a zero order reaction.

$2NH_3$ ——-> $N_2 + 3H_2$

The rate of the reaction is independent of the concentration of ammonia, i.e.,

Rate = -dx/dt = k[NH3]0

Rate = k

order =0

Molecularity of a Reaction

For a chemical reaction to occur, the reacting molecules must collide with each other. The number of reacting species (molecules, atoms or ions) which collide simultaneously to bring about a chemical reaction is called molecularity of a reaction.

If a reaction involves the decomposition of only a single species, the molecularity is one or it is called unimolecular reaction.

For example:

1) The decomposition of hydrogen peroxide involves single species which undergoes the change to form the products. Hence, it is a unimolecular reaction.

$$H_2O_2 \text{ ——-> } H_2O + ½ O_2$$

2) Decomposition of ammonium nitrite

$$NH_4NO_2 \text{ ——-> } N_2 + 2H_2O$$

If the reaction involves the collision of two species, it is bimolecular and if three species take part in a collision leading to the formation of the products it is called trimolecular and so on.

The examples of bimolecular reactions are given below:

1) Dissociation of hydrogen iodide is a bimolecular reaction because two molecules collide to bring about the reaction.

$$2HI (g) \text{ ——-> } H_2 (g) + I_2 (g)$$

2) Combination of NO and O3 is a bimolecular reaction

$$NO(g) + O_3 (g) \text{ ——-> } NO_2 (g) + O_2 (g)$$

The examples of trimolecular reactions are

The reaction of nitric oxide and oxygen is a trimolecular reaction because it involves collision of three reacting molecules.

$$2NO(g) + O_2 (g) \text{ ——-> } 2 NO_2 (g)$$

Reactions involving three or more molecules are uncommon because such reactions requires the simultaneous collision of three or more than three molecules.

Simultaneous collision of three molecules means that the third molecule must collide the other two molecules at the same time when they are in the process of collision. The chances of the occurrence of such collisions are very small.

Some reactions involving more than three molecules are quite fast.

For example:

a) The reaction of bromide ions with bromate ions in the presence of an acid:

$$5Br^- (aq) + BrO_3^- (aq) + 6H+ (aq) \text{——>} 3 Br_2 (aq) + 3H_2O (l)$$

The experimentally measured rate law for this reaction is given as:

$$\text{Rate} = k[Br^-] [BrO_3^-] [H+]2$$

This rate is first order with respect to Br^- and BrO_3^- ion and second order with respect to H+ ions and the overall order of the reaction is 1+1+2=4.

b) The reaction of potassium chlorate with ferrous sulphate in the presence of sulphuric acid involves ten species.

$$KClO_3 + 6FeSO_4 + 3H_2SO_4 \text{——>} KCl + 3Fe_2(SO_4)3 + 3H_2O$$

The above reaction appears to be of tenth order but actually it is a second order reaction. If this reaction were to take place in a single step, the 10 particles (1 $KClO_3$, 6 $FeSO_4$, and 3 H_2SO_4) would have to collide simultaneously.

But chances of such events are extremely small, so much so that a reaction which takes place by such collision will not occur at all.

Type of reactions which take place through a sequence of two or more consecutive steps are called complex reactions.

The detailed description of various steps by which reactants change into the products is called mechanism of the reaction.

The steps which contribute to the overall reaction are called elementary processes.

Integrated Rate Expression

The concentration dependence of rate is called differential rate equation. Integrated rate equation gives a relation between directly measured experimental quantities i.e. concentrations at different times. The integrated rate equations are different for reactions of different orders.

The instantaneous rate of a reaction is given by differential rate law equations.

For example: For a general reaction

$$aA + bB \text{—–>} \text{Products}$$

the differential rate law equation is :

$$dx/dt = k[A]a\ [B]b$$

The differential form of rate law is transformed to integrated form of rate law by simple mathematics (calculus).

Zero Order Reaction

A reaction is said to be of zero order, if its rate is independent of the concentration of the reactants. Consider the general zero order reaction:

$$R \text{———>} \text{Product}$$

Let [R] be the concentration of the reactant R and k0 is the rate constant for the zero order reaction. For the zero order reaction, the rate of the reaction is independent of the concentration of R. Thus,

$$\text{Rate} = -\frac{d[R]}{dt} = k_0\ [R]^\circ = k_0$$

This form of rate law is known as differential rate equation, Rearranging the above equation,

$$-d[R] = k0\,dt$$

Integrating the above equation

$$-\int d[R] = k0 \int dt$$

$$-[R] = k0t + I$$

where I is the constant of integration. The value of I can be calculated from the initial concentration.

For example: the initial concentration of R be [R]0, at t=0

$$-[R]0 = k0 \times 0 + I$$

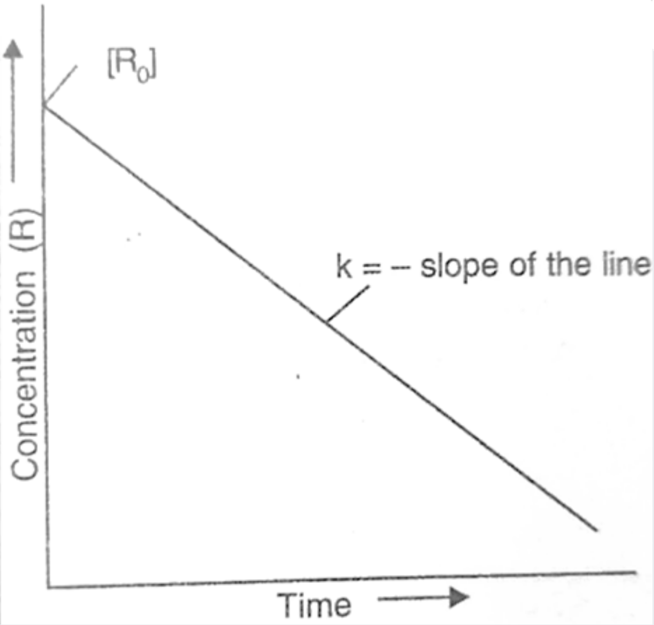
$$I = -[R]0$$

$$-[R] = K0t - [R]0$$

$$K0t = [R]0 - [R]$$

$$[R] = -K0t + [R]0$$

If we plot a graph between [R] against t, we get a straight line with slope as -k0 and intercept equal to [R]0.



Alternatively, rate constant, k0 can be calculated if we know the concentration of R at any time t and [R]0. Thus,

$$k0 = \{ [R]0 - [R] \} / t$$

where [R]0, is the initial concentration of R, [R] is the concentration at time t.

Alternatively, if the initial concentration of R is ‘a’ moles per litre and let x moles of reactants get changed to products in time t. Then, concentration of R left after time t be (a – x)

$$R \longrightarrow Products$$

$$[R]0 = a$$

$$[R] = a - x \text{ so that}$$

$$[R]0 - [R] = a - (a-x) = x$$

$$k0 = x/t$$

$$x = k0\,t$$

The amount of the substance reacted is proportional to the time.

Zero order reactions generally take place in heterogeneous systems. In such systems the reactant is adsorbed on the surface of a solid catalyst, where it is converted into product. The fraction of the surface of the catalyst covered by the reactant is proportional to the concentration of the reactants at low values.

After certain concentration limit of the reactant, the surface of the catalyst becomes fully covered. On further increasing the concentration of the reactant, the reaction rate does not change. The rate becomes independent of the concentration and, therefore, becomes zero order reaction.

Collision Theory

Pseudo Chemical Reactions

Some reactions are first order each with respect to two different reactants i.e.,

$$A+B \text{———>} \text{Products}$$

$$\text{Rate} = k[A]\,[B]$$

If one of the reactants is present in high concentration (solvent) then there is very little change in its concentration. The concentration of that reactant remains practically constant during the reaction.

For example, if [A] = 0.01 M and that of solvent water [B] = 55.5 M, the concentration of B changes only from 55.50 to 55.49 M even after the completion of the reaction.

The reaction, therefore, behaves as a first order reaction in A. Such reactions are called pseudo first order reactions.

Consider the hydrolysis of ethyl acetate:

$$CH_3COOC_2H_5 + H_2O \Leftrightarrow CH_3COOH + C_2H_5OH$$

The molecularity of the reaction is two because it involves two reacting species, namely ethyl acetate and water. However, the concentration of ethyl acetate changes during the reaction while water is present in such a large excess that its concentration remains practically unchanged. Therefore, the rate of the reaction depends only the order of the reaction is one.

$$\text{Rate} = k'\,[CH_3COOC_2H_5]\,[H_2O]$$

on the concentration of ethyl acetate and hence

$[H_2O]$ can be takes as constant so that

$$\text{Rate} = k\,[CH_3COOC_2H_5]$$

$$k = k'\,[H_2O]$$

Thus, the reaction appears to be second order but follows the first order kinetics. Such reactions which appear to be of higher order but actually follow lower order kinetics are called pseudo chemical reactions.

For example: The hydrolysis of cane sugar or inversion of cane sugar to give glucose

and fructose:

$$C_{1}2H_{22}O_{11} + H_2O \text{———>} C_6H_{12}O_6 + C_6H_{12}O_6$$

Molecularity is two while order is one.

Collision Theory

Collision theory was put forward by Max Trautz and William Lewis in 1916-18. It is based on kinetic theory of gases.

According to this theory,

1) The reactant molecules are assumed to be hard spheres and reaction is postulated to occur when molecules collide with each other.
2) The number of collisions that takes place per second per unit volume of the reaction mixture is known as collision frequency Z. The value of collision frequency is normally very high.
3) For instance, under ordinary conditions of temperature and pressure, in a gaseous system, the collision frequency of binary collisions is of the order of 1025 to 1028.
4) If all the collisions are effective in forming the products, the reactions must be completed in a very short time.
5) All the collisions among the reacting species at a temperature are not effective in bringing about the chemical reaction.

The collisions which actually produce the products and therefore, result in the chemical reactions are called effective collisions.

There are two important barriers to a reaction namely

(i) energy barrier (ii) orientation barrier

(i) **Energy barrier:** For the reacting species to make effective collisions, they should have sufficient energy to break the chemical bonds in the reacting molecules. The minimum amount of energy which the colliding molecules must possess is known as threshold energy. This means that only those collisions of reactants will give products which possess energies greater than threshold energy.

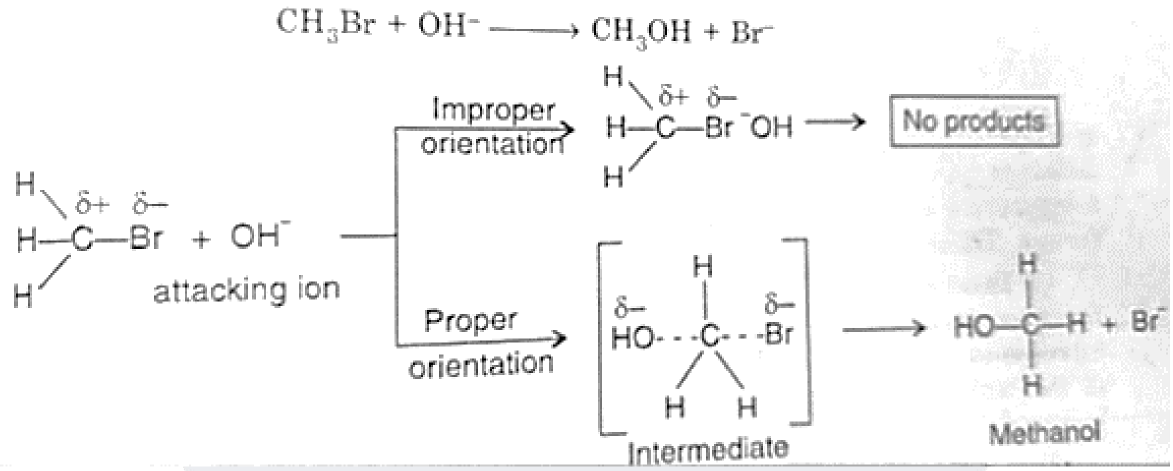
(ii) **Orientation barrier:** The colliding molecules should also have proper orientation so that the old bonds may break and new bonds are formed.

Consider the reaction

$$NO_2\,(g) + NO_2\,(g) \longrightarrow N_2O_4\,(g)$$

During this reaction, the products molecules are formed only when the colliding molecules have proper orientation at the time of collisions. These are called effective collisions.

When the molecules do not have proper orientation at the time of collision, they result in ineffective collisions and do not form the products.



Effect of Catalyst on Reaction Rate

The rate of a reaction can be increased by raising the temperature. However, temperature can be raised within certain limits because in certain cases, the reactants become unstable at higher temperatures and decompose.

Many reactions are made to proceed at an increased rate by the presence of some other substance.

For example: a mixture of H_2 and O_2 does not react at room temperature. However, in the presence of finely divided platinum, the reaction becomes quite vigorous.

Manganese dioxide, a black powder speeds up the thermal decomposition of potassium chlorate.

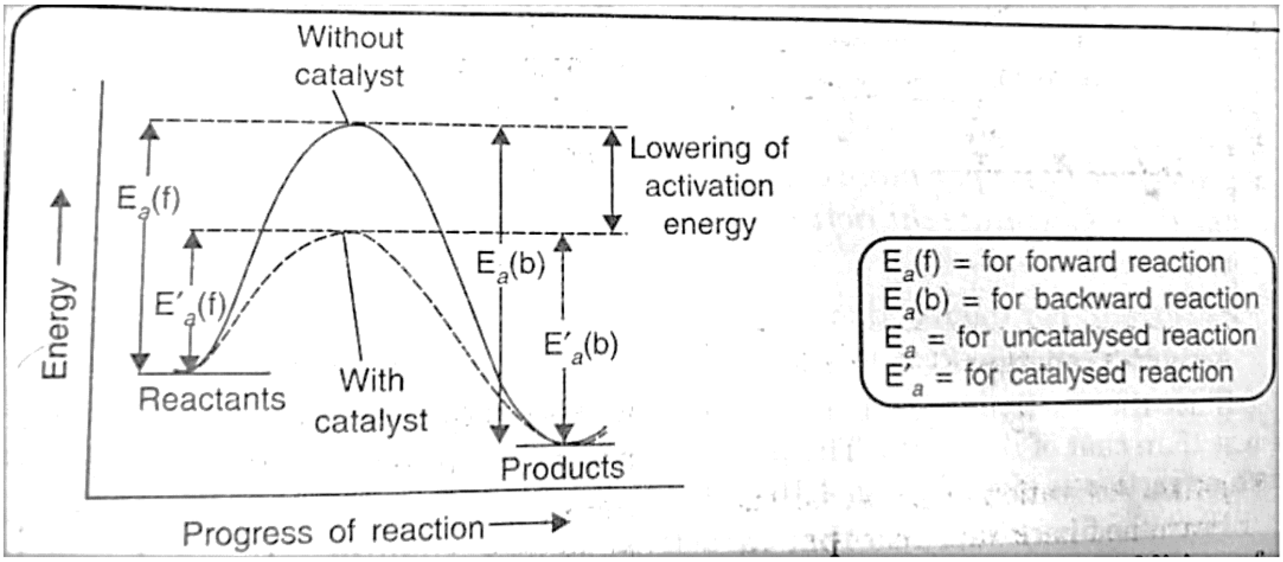
$$2\,KClO3\,(s) \longrightarrow 2KCl\,(s) + 3\,O_2$$

Catalysts

The substances which accelerate the rate of reactions without itself undergoing permanent change are called catalysts.

The substances which increase the rate of a reaction and can be recovered chemically unchanged in mass and composition after the reaction are called catalysts.

The phenomenon of increasing the rate of a reaction by the use of catalyst is called catalysis. A catalyst is not consumed in the reaction.



In a catalysed reaction the catalyst is used in one step and is regenerated in subsequent step and thus, it is used up again and again without undergoing any permanent change.

Catalyst provides an entirely new path for the reaction in which the reactants are converted to products quickly. The catalyst forms a new activated complex of lower potential energy. This means that the activation energy becomes lower for the catalysed reaction than that for uncatalysed reaction. The fraction of the total number of collisions possessing lower activation energy increased and hence, the rate of reaction also increase.

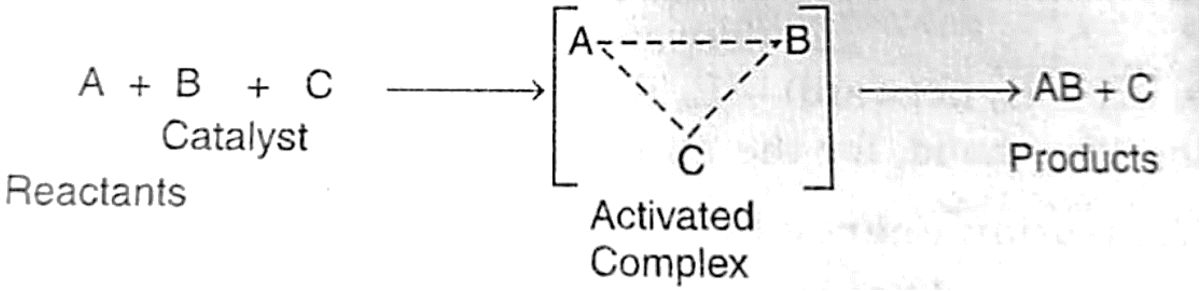
The solid line shows the path for uncatalysed reaction and dotted line shows the path adopted by catalysed reaction. Consider a hypothetical reaction

$$A + B \longrightarrow AB$$

The reaction proceeds through the formation of activated complex

$$A+B \longrightarrow [A...B] \longrightarrow AB$$

Addition of a catalyst C result into the formation of new activated complex of lower activation energy.



The Function of Catalyst

(1) A catalyst may undergo intermediate physical changes and it may even form temporary chemical bonds with the reactants but it is recovered unchanged in original form at the end of the reaction.

(2) A catalyst speeds up the reaction but it does not shift the position of equilibrium. The presence of a catalyst reduces the height of barrier by providing an alternative path for the reaction and lowers the activation energy. The lowering in activation energy is to the same extent for the forward as well as for the backward reaction.

(3) Catalysts are highly specific in nature. A catalyst which can catalyse one reaction may have no effect on another reaction even, if that reaction is very similar.

(4) The catalyst does not change ΔE (or ΔH) of the reaction.

Half Life Period of a Reaction

Half life period of a reaction is defined as the time during which the concentration of a reactant is reduced to half of its initial concentration.

or

The time in which half of a reaction is completed. It is generally denoted as t½

The half life period of a first order reaction may be calculated as given below:

The first order rate equation for the reaction

A → Products

$$kt = 2.303 \log \frac{[A]_0}{[A]}$$

$$t = \frac{2.303}{k} = \log \frac{[A]_0}{[A]}$$

Half life period of a reaction

Now, half life period corresponds to time during which the initial concentration, [A]0 is reduced to half i.e.

[A] = [A]0 /2   at t= t½

Then half life period, t½ becomes

$$t_{1/2} = \frac{2.303}{k} \log \frac{[A]_0}{[A]_0/2} = \frac{2.303}{k} \log 2$$

$$t_{1/2} = \frac{2.303 \times 0.3010}{k} = \frac{0.693}{k}$$

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

Half life period of a reaction

Thus, half life period of a first order reaction is independent of the initial concentration of the reactant. Half life period for the first order reaction is inversely proportional to the rate constant.

For example,

(i) time required to complete 1/3 of the reaction will be given as:

[A]o = a , [A] = a – a/3=2/3a

$$t_{1/3} = \frac{2.303}{k} \log \frac{a}{1/3a} = \frac{2.303}{k} \log \frac{3}{2}$$

time required to complete 1/3 of the reaction

(ii) time required to complete 3/4 of the reaction will be

[A]o = a , [A] = a – 3/4 a = 1/4 a

time required to complete 3/4 of the reaction

$$t_{3/4} = \frac{2.303}{k} \log \frac{a}{1/4a} = \frac{2.303}{k} \log 4$$

Half Life period of zero order and second order reactions

The integrated rate equation is ,

$$kt = [A]o - [A]$$

For half life period, t½ , [A] = [A]0/2

$$t½ = [A]0 /2k$$

Similarly for second order reaction,

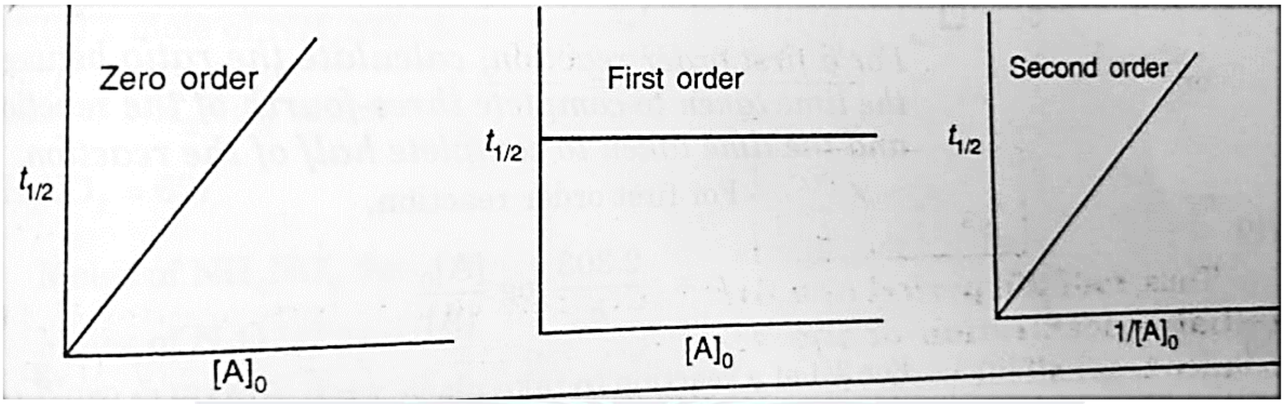
$$kt = \frac{1}{[A]} - \frac{1}{[A]_0}$$

For half life period, $t_{1/2} = [A] = [A]_0 / 2$

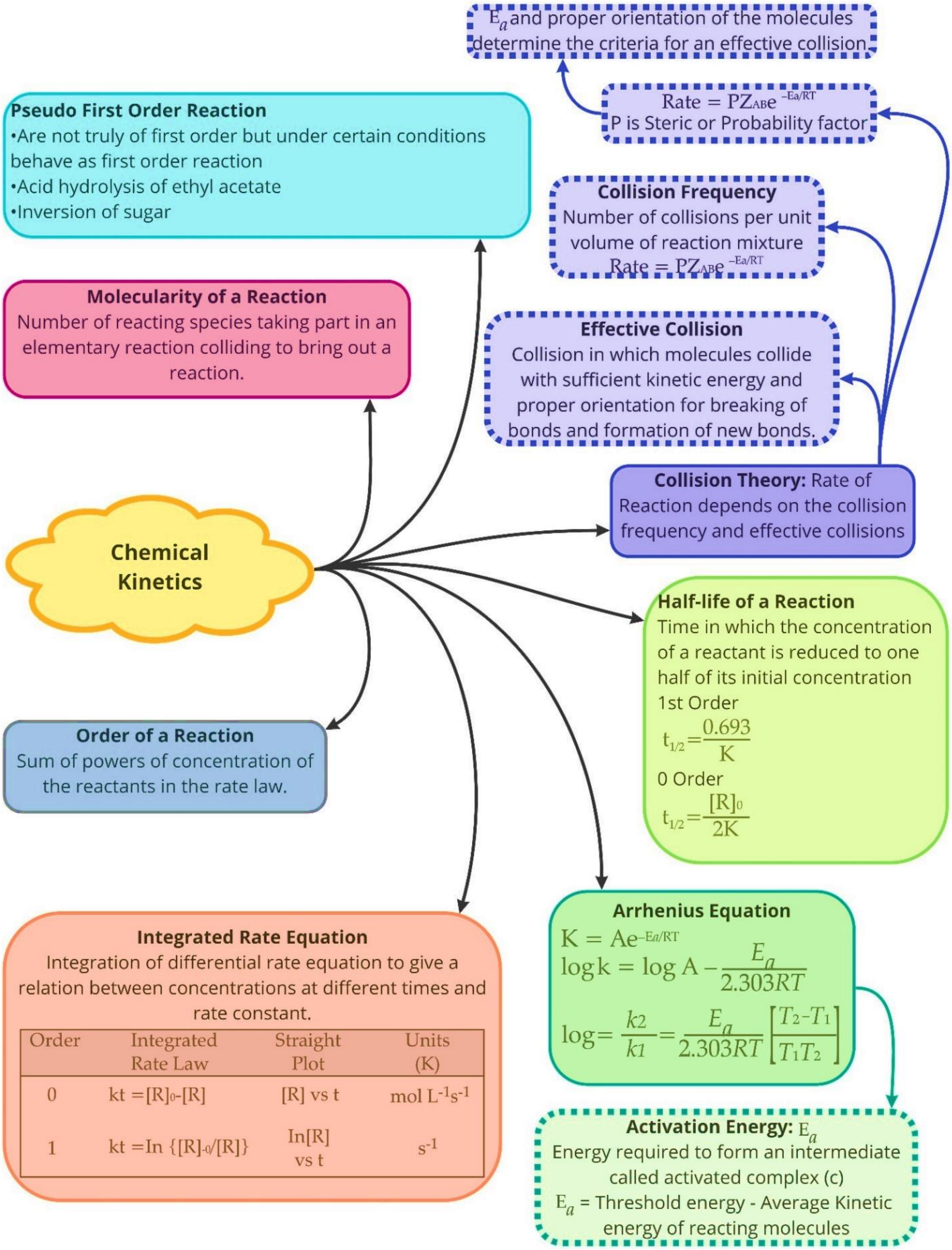
$$\therefore \quad kt_{1/2} = \frac{2}{[A]_0} - \frac{1}{[A]_0} = \frac{1}{[A]_0}$$

$$\therefore \quad t_{1/2} = \frac{1}{k[A]_0}$$

Type of reaction	**Rate equation**	$t_{1/2}$
Zero order	Rate = $k[A]^\circ$	$\frac{[A]_0}{2k}$
First order	Rate = $k[A]$	$\frac{0.693}{k}$
Second order	Rate = $k[A]^2$	$\frac{1}{k[A]_0}$



Class : 12th Chemistry
Chapter-4 : Chemical Kinetics (Part_1)



Chemical Kinetics

Pseudo First Order Reaction

- Are not truly of first order but under certain conditions behave as first order reaction
- Acid hydrolysis of ethyl acetate
- Inversion of sugar

Molecularity of a Reaction

Number of reacting species taking part in an elementary reaction colliding to bring out a reaction.

Order of a Reaction

Sum of powers of concentration of the reactants in the rate law.

Integrated Rate Equation

Integration of differential rate equation to give a relation between concentrations at different times and rate constant.

Order	Integrated Rate Law	Straight Plot	Units (K)
0	$kt = [R]_0 - [R]$	[R] vs t	mol $L^{-1}s^{-1}$
1	$kt = In\ \{[R]_{-0}/[R]\}$	In[R] vs t	s^{-1}

Arrhenius Equation

$$K = Ae^{-Ea/RT}$$

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

$$\log = \frac{k2}{k1} = \frac{E_a}{2.303RT}\left[\frac{T_2 - T_1}{T_1 T_2}\right]$$

Activation Energy: E_a

Energy required to form an intermediate called activated complex (c)

E_a = Threshold energy - Average Kinetic energy of reacting molecules

Half-life of a Reaction

Time in which the concentration of a reactant is reduced to one half of its initial concentration

1st Order

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

0 Order

$$t_{1/2} = \frac{[R]_0}{2K}$$

Collision Theory: Rate of Reaction depends on the collision frequency and effective collisions

Effective Collision

Collision in which molecules collide with sufficient kinetic energy and proper orientation for breaking of bonds and formation of new bonds.

Collision Frequency

Number of collisions per unit volume of reaction mixture

$Rate = PZ_{AB}e^{-Ea/RT}$

$Rate = PZ_{AB}e^{-Ea/RT}$

P is Steric or Probability factor

E_a and proper orientation of the molecules determine the criteria for an effective collision.

Class : 12th Chemistry
Chapter-4 : Chemical Kinetics (Part_2)

Rate of disappearance of R

$$= \frac{\text{Decease in concentration of R}}{\text{Time taken}} = \frac{-\triangle[R]}{\triangle t}$$

Rate of appearance of P

$$= \frac{\text{Increase in concentration of P}}{\text{Time taken}} = \frac{+\triangle[P]}{\triangle t}$$

R → P

Average Rate

Appearance of products or disappearance of reactants over a long time interval.

$$r_{av} = \frac{d\,[P]}{dt} = \text{slope}$$

$$r_{av} = \frac{-d\,[R]}{dt} = -\text{slope}$$

Instantaneous Rate

Rate of change in concentration of reactant/product at a particular time

$$r_{inst} = \frac{-d[R]}{dt} = \frac{+d[P]}{dt}$$

Chemical Kinetics →

Rate of Chemical Reaction

Change in concentration of reactants or products in unit time;

Unit : mol $L^{-1}s^{-1}$ or atm s^{-1}

Rate Law

Expression in which reaction rate in given in terms of molar concentration of reactants with each term raised to power which may or may not be same as stoichiometric coefficient of reactants in a balanced chemical equation. aA + bB - cC + dD

$$\text{Rate} = K\,[A]^X\,[B]^y = \frac{d\,[R]}{dt}$$

Rate Constant: Rate of a reaction when concentration of each of the reactant in unity

Order	Unit
0	$molL^{-1}s^{-1}$
1	s^{-1}
2	$mol^{-1}Ls^{-1}$

Factor Influencing

Concentration: Higher the concentration of reactants, faster is the rate of reaction.

Temperature: Increases with increase in temperature. becomes almost double with 10°C rise.

Presence of Catalyst: Increases with a catalyst.

Surface Area: Greater is the surface area, faster is the rate of reaction.

Activation Energy: Lower the activation energy, faster is the reaction.

Important Questions

Multiple Choice Questions-

1. A first order reaction has a half life period of 34.65 seconds. Its rate constant is
   (a) 2×10^{-2} s^{-1}
   (b) 4×10^{-4} s^{-1}
   (c) 20 s^{-1}
   (d) 2×10^{-4} s^{-1}
2. If a graph is plotted between In k and 1/T for the first order reaction, the slope of the straight line so obtained is given by
   (a) $-\frac{E_a}{R}$
   (b) $\frac{E_a}{2.303R}$
   (c) $\frac{2.303}{E_a \cdot R}$
   (d) $\frac{E_a}{2.303}$
3. The unit of rate constant for a zero order reaction is
   (a) mol L^{-1}s^{-1}
   (b) s^{-1}
   (c) L mol^{-1}s^{-1}
   (d) L2mol^{-2}s^{-1}
4. A catalyst increases the speed of a chemical reaction by
   (a) increasing activation energy
   (b) decreasing activation energy
   (c) increasing reactant energy
   (d) decreasing threshold energy
5. The units of the rate constant for the second order reaction are:
   (a) mol^{-1} litre s^{-1}
   (b) mol litre^{-2} s^{-1}
   (c) s^{-1}
   (d) mol litre^{-1} s^{-1}
6. The value of k for a reaction is 2.96×10^{-30} s$^{-1.}$ What is the order of the reaction?
   (a) Zero
   (b) 3
   (c) 2
   (d) 1
7. A reaction is found to be of second order with respect to concentration of carbon monoxide. If concentration of carbon monoxide is doubled, the rate of reaction will
   (a) triple
   (b) increase by a factor of 4
   (c) double
   (d) remain unchanged
8. If the concentrations are expressed in mol litre-1 and time in s, then the units of rate constant for the first-order reactions are
   (a) mol litre^{-1} s^{-1}
   (b) mol^{-1} litre s^{-1}
   (c) s^{-1}
   (d) mol^{2} litre^{-2} s^{-1}
9. The half life of a first order reaction having rate constant 200 s-^{1} is
   (a) 3.465×10^{-2} s
   (b) 3.465×10^{-3} s
   (c) 1.150×10^{-2} S
   (d) 1.150×10^{-3} S
10. The rate of a reaction is 1.209×10^{-4}L^{2} mol^{-2}s^{-1}. The order of the reaction is:
    (a) zero
    (b) first
    (c) second
    (d) third

Very Short Question:

1. Is rate of reaction always constant?
2. Can order of reaction be zero? Give example.
3. What do you understand by rate law expression?
4. Is it possible to determine or predict the rate law theoretically by merely looking at the equation?
5. Define the term chemical kinetics?
6. Define – Rate of reaction and the factors affecting the rate of reaction.
7. What is average rate of a reaction? How is it determined?
8. What are the units of rate of a reaction?

9. Identify the reaction order for from each of the following rate constant –

(a) $k = 2.3 \times 10^{-5}\ L\ mol^{-1}\ s^{-1}$

(b) $k = 3.1 \times 10^{-4}\ s^{-1}$

10. Consider the equation

$$2NO(q)+2H_2(g)\rightarrow N_2(g)+2H_2O(g)$$

The rate law for this equation is first order with respect to H_2 and second order with respect to NO. write the rate law for this reaction.

Short Questions:

1 For the reaction A+B → C+D, the rate of reaction doubles when the concentration of A doubles, provided the concentration of B is constant. To what order does A enter into the rate expression?

2. A chemical reaction $2A \Leftrightarrow 4B+C$ in gas phase occurs in a closed vessel. The concentration of B is found to be increased by $5 \times 10^{-3}\ mole\ L^{-1}$ in 10 second. Calculate (i) the rate of appearance of B (ii) the rate of disappearance of A?

3. For the following reactions, write the rate of reaction expression in terms of reactants and products?

(i) $4NH_3(g)+5O_2(g)\,4\rightarrow NO(g)+6H_2O(g)$

(ii) $2N_2O_5\ 2NO_2 + O_2$

4. The reaction $2N_2O_5(g) \rightarrow 2NO_2(g) + O_2(g)$ was studied and the following data were collected:

S.No.	$[N_2O_5]$ mol L−1	Rate of disappearance of $[N_2O_5]$ (mol/L/min)
1.	1.13×10^{-2}	34×10^{-5}
2.	0.84×10^{-2}	25×10^{-5}
3.	0.62×10^{-2}	18×10^{-5}

Determine

i) The order

ii) The rate law.

iii) Rate constant for the reaction.

5. The following experimental data was collected for the reaction:

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

Trial	Intial conc. of Cl_2 (mol/L)	NO mol/L	Initial Rate (mol/L/s)
1	0.10	0.010	1.2×10^{-4}
2	0.10	0.030	10.8×10^{-4}
3	0.20	0.030	21.6×10^{-4}

Construct the rate equation for the reaction.

6. Draw a graph for

a) Concentration of reactant against time for a zero order reaction.

b) Log Ro/ R against time for a first order reaction.

7. In general it is observed that the rate of a chemical reaction doubles with every 10° rise in temperature. If this generalization holds for a reaction in the temperature range295K to 305K, what would be the activation energy for this reaction? (R = $8.314\ Jk^{-1}\ mol^{-1}$)

8. The rate constant for a reaction is $1.5 \times 10^{7}\ s^{-1}$ at 50°C and $4.5 \times 10^{7}\ s^{-1}$ at 100°C. Calculate the value of activation energy for the reaction (R = $8.314\ Jk^{-1}\ mol^{-1}$)?

9. Plot a graph showing variation of potential energy with reaction. coordinate?

10. The conversion of molecules X to Y follows second order kinetics. If concentration of X is increased to three times how will it affect the rate of formation of Y?

Long Questions:

1. The rate of the chemical reaction doubles for an increase of 10 K in absolute temperature from 298 K. Calculate E_a.

2. The activation energy for the reaction $2HI(g) \rightarrow H_2 + I_2(g)$ is $209.5\ kJ\ mol^{-1}$ at 581K. Calculate the fraction of molecules of reactants having energy equal to or greater than activation energy?

3. From the rate expression for the following reactions, determine their order of reaction and the dimensions of the rate constants.

(i) $3NO(g) \rightarrow N_2O(g)$ Rate = $k[NO]^2$

(ii) $H_2O_2(aq)+3I^-(aq)+H^+ \rightarrow 2H_2O(I)+I_3^-$

$$Rate = k[H_2O_2][I^-]$$

(iii) $CH_3CHO(g) \rightarrow CH4(g) + CO(g)$

$$Rate = k[CH_3CHO]^{3/2}$$

(iv) $C_2H_5Cl(g) \rightarrow C_2H_2(g) + HCl(g)$

Rate = $k[C_2H_5Cl]$

4. The decomposition of NH_3 on platinum surface is zero order reaction. What are the rates of production of N_2 and H_2 if $k = 2.5 \times 10^{-4}$ mol^{-1} L s^{-1}?

5. The decomposition of dimethyl ether leads to the formation of CH_4, H_2 and CO and the reaction rate is given by Rate = $k[CH_3OCH_3]^{3/2}$. The rate of reaction is followed by increase in pressure in a closed vessel, so the rate can also be expressed in terms of the partial pressure of dimethyl ether, i.e., $\text{Rate} = k\left(P_{CH_cOCH_3}\right)^{3/2}$. If the pressure is measured in bar and time in minutes, then what are the units of rate and rate constants?

Assertion and Reason Questions:

1. In these questions, a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following choices.

a) Assertion and reason both are correct statements and reason is correct explanation for assertion.

b) Assertion and reason both are correct statements but reason is not correct explanation for assertion.

c) Assertion is correct statement but reason is wrong statement.

d) Assertion is wrong statement but reason is correct statement.

Assertion: The rate ofreaction is always negative.

Reason: Minus sign used in expressing the rate shows that concentration of product is decreasing.

2. In these questions, a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following choices.

a) Assertion and reason both are correct statements and reason is correct explanation for assertion.

b) Assertion and reason both are correct statements but reason is not correct explanation for assertionss.

c) Assertion is correct statement but reason is wrong statement.

d) Assertion is wrong statement but reason is correct statement.

Assertion: Kinetics explains the reaction mechanism.

Reason: Kinetics explains the formation of products.

Case Study Questions:

1. ln a reaction, the rates of disappearance of different reactants or rates of formation of different products may not be equal but rate of reaction at any instant of time has the same value expressed in terms of any reactant or product. Further, the rate of reaction may not depend upon the stoichiometric coefficients of the balanced chemical equation. The exact powers of molar concentrations of reactants on which rate depends are found experimentally and expressed in terms of 'order of reaction'. Each reaction has a characteristic rate constant depends upon temperature. The units of the rate constant depend upon the order of reaction.

The following questions are multiple choice questions. Choose the most appropriate answer:

(i) The rate constant of a reaction is found to be 3×10^{-3} mol^{-2} L^2 sec^{-1}. The order of the reaction is:

a) 0.5

b) 2

c) 3

d) 1

(ii) ln the reaction, $A + 3B \rightarrow 2C$, the rate of formation of C is:

a) The same as rate of consumption of A.

b) The same as the rate of consumption of B.

c) Twice the rate of consumption of A.

d) 3232 times the rate of consumption of B.

(iii) Rate of a reaction can be expressed by following rate expression, Rate = $k[A]^2[B]$, if concentration of A is increased by 3 times and concentration of B is increased by 2 times, how many times rate of reaction increases?

a) 9 times

b) 27 times

c) 18 times

d) 8 times

(iv) The rate of a certain reaction is given by, rate = $k[H^+]^n$.The rate increases 100 times when the pH changes from 3 to 1. The order (n) of the reaction is:

a) 2

b) 0

c) 1

d) 1.5

(v) In a chemical reaction A + 2B → products, when concentration of A is doubled, rate of the reaction increases 4 times and when concentration of B alone is doubled rate continues to be the same. The order of the reaction is:

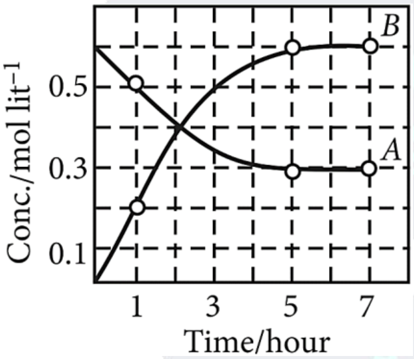
a) 1

b) 2

c) 3

d) 4

2. The progress of the reaction, $A \rightleftharpoons nB$ with time is represented in the following figure:



The following questions are multiple choice questions. Choose the most appropriate answer:

(i) What is the value of n?

a) 1

b) 2

c) 3

d) 4

(ii) Find the value of the equilibrium constant.

a) 0.6M

b) 1.2M

c) 0.3M

d) 2.4M

(iii) The initial rate of conversion of A will be:

a) 0.1 mol $L^{-1}hr^{-1}$

b) 0.2 mol $L^{-1}hr^{-1}$

c) 0.4 mol $L^{-1}hr^{-1}$

d) 0.8 mol $L^{-1}hr^{-1}$

(iv) For the reaction, if $\frac{d[B]}{dt} = 2 \times 10^{-4}$, value of $\frac{d[A]}{dt}$ will be:

a) 2×10^{-4}

b) 10^{-4}

c) 4×10^{-4}

d) 0.5×10^{-4}

(v) Which factor has no effect on rate of reaction?

a) Temperature.

b) Nature of reactant.

c) Concentration of reactant.

d) Molecularity.

Answers key

MCQ Answer:

1. **Answer:** (a) 2×10^{-2} s^{-1}
2. **Answer:** (a) $-\frac{E_a}{R}$
3. **Answer:** (a) mol $L^{-1}s^{-1}$
4. **Answer:** (b) decreasing activation energy
5. **Answer:** (a) mol^{-1} litre s^{-1}
6. **Answer:** (d) 1
7. **Answer:** (b) increase by a factor of 4
8. **Answer:** (c) s^{-1}
9. **Answer:** (b) 3.465×10^{-3} s
10. **Answer:** (d) third

Very Short Answers:

1. **Answer:** No. rate of a reaction is not always constant. It depends on many factors such as concentration, temperature etc.
2. **Answer:** Yes, decomposition of ammonia on a hot platinum surface is a zero order of reaction at high pressure
3. **Answer:** The rate law is the expression in which rate is given in terms of molar concentration of reactants with each term raised to some power, which may or may not be same as the

stoichiometric coefficient of the reacting species in a balanced chemical equation.

4. **Answer:** No, the rate law cannot be predicted by merely looking at the balanced chemical equation but must be determined experimentally.

5. **Answer:** The branch of chemistry that deals with the study of reaction rates and their mechanisms is called chemical Kinetics.

6. **Answer:** Rate of reaction can be defined as the change in concentration of a reactant or product per unit time. Factors affecting the rate of reaction are temperature, concentration of reactants and catalyst.

7. **Answer:** Average rate of a reaction is defined as the change in concentration of a reactant or a product per unit time. It can be determined by dividing the change in concentration of reactant or product by the time interval

   For the reaction: $A \rightarrow B R_{av}$

   $$= \frac{\Delta[A]}{\Delta t} = \frac{\Delta[B]}{\Delta t}$$

8. The units of rate of a reaction are Mol L^{-1} S^{-1} . In gaseous reaction the unit of rate of reaction is atom.

9. a) Since the units of rate constant are $Lmoll^{-1}s^{-1}$. The reactions is of second order.

   b) Since the units of rate constant are S^{-1}, The reaction is of first order

10. The rate law will be R = K $[NO]^2$ $[H_2]$

Short Answers:

1. **Answer**

   . A+B → C+D

   Rate $[A]^x$

   Rate = 1 when A = 1 ———- 1)

   Rate = 2 when A = 2———-2)

   Dividing equation 2) by 1)

   $$\frac{2}{1} \alpha \frac{(2)^x}{1^x}$$

   2^1 α $(2)^x$

   $\therefore x = 1$

   The reaction is first order reaction.

2. **Answer:**

   2A → 4B

   $$-\frac{1}{2}\frac{d[A]}{dt} = \frac{1}{4}\frac{d[B]}{dt} = \frac{d[C]}{dt}$$

   i) Rate of disappearance of B

   $$= \frac{5\times10^{-3}}{10^{5}} mol/L^{-1}$$

   $= 5 \times 10^{-4}$ $mol\ L^{-1}\ s^{-1}$

   $$= \frac{d[A]}{dt} = \frac{2}{4}\frac{d[B]}{dt} = \frac{1}{2}\frac{d[B]}{dt}$$

   ii) $$= \frac{1}{2}\times 5\times10^{-4}\ mol\ L^{-1}\ s^{-1}$$

   $$= 2.5\times10^{4}\ mol\ L^{-1}\ s^{-1}$$

3. **Answer:**

In terms of reactant	In terms of products
(i) $R_1 = \frac{-1}{4}\frac{\Delta[NH_3]}{\Delta t}$	$R_3 = \frac{1}{4}\frac{\Delta[NO]}{\Delta t}$
$R_2 = \frac{-1}{5}\frac{\Delta[O_2]}{\Delta t}$	$R_4 = \frac{1}{6}\frac{\Delta[H_2O]}{\Delta t}$

$$\frac{1}{4}R_1 = \frac{1}{5}R_2 = \frac{1}{4}R_3 = \frac{1}{6}R_4$$

$$-\frac{1}{4}\frac{\Delta[NH_3]}{\Delta t} = -\frac{1}{5}\frac{\Delta[O_2]}{\Delta t}$$

$$= \frac{1}{4}\frac{\Delta[NO]}{\Delta t} = \frac{1}{6}\frac{\Delta[H_2O]}{\Delta t}$$

In terms of reactant	In terms of products
(ii) $R_1 = \frac{\Delta[N_2O_5]}{\Delta t}$	$R_2 = \frac{\Delta[NO_2]}{\Delta t}$
	$R_3 = \frac{\Delta[O_2]}{\Delta t}$

$$\frac{1}{4}R_1 = \frac{1}{5}R_2 = R_3$$

$$\frac{\Delta[N_2O_5]}{\Delta t} = \frac{1}{2}\frac{\Delta[NO_2]}{\Delta t} = \frac{\Delta[O_2]}{\Delta t}$$

4. **Answer:**

   Let the order of reaction be x

   $Rate = K\,[N_2O_5]^x$

   i) From the data –

   $$34\times10^{-5} = \left(1.13\times10^{-2}\right)^x \quad ....(1)$$

   $$25\times10^{-5} = \left(0.84\times10^{-2}\right)^x \quad ....(2)$$

   $$18\times10^{-5} = \left(0.62\times10^{-2}\right)^x \quad ....(3)$$

   Dividing 1) by 2)

$$\frac{34\times10^{-5}}{25\times10^{-5}}=\left(\frac{1.13\times10^{-2}}{0.84\times10^{-2}}\right)^{x}$$

$(1.36) = (1.35)^x$

$X = 1$

The order of reaction with respect with respect to N_2O_5 is 1

ii) Rate law $R = K[N_2O_5]^x$

iii) Rate constant , K

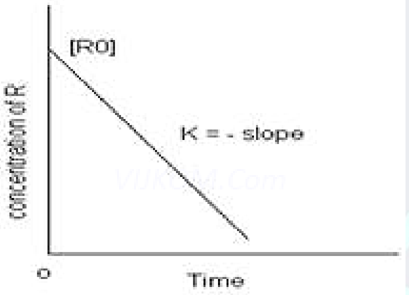
$$=\frac{Rate}{[N_2O_5]}=\frac{18\times10^{-5}\ mol/L/\min}{0.62\times10^{-2}\ mol/L}=0.29\min^{-1}$$

5. **Answer :**

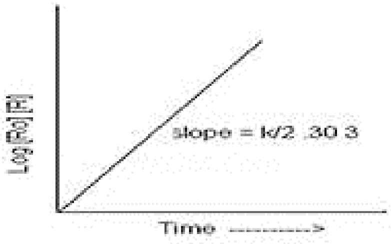
Order of NO is 2

Rate law = $K[Cl_2]\ [NO]^2$

6. **Answer**



(a)



(b)

7. **Answer:**

$T_1=295K\quad T_2=305K$

$$E_a=2.303\,R\left[\frac{T_2T_1}{T_2-T_1}\right]\left[\log\frac{k_2}{k_1}\right]$$

$K_2 = 2k_1$

$$E_a=2.303\times8.314\times\left[\frac{305\times295}{305-295}\right]\log\frac{2k_1}{k_1}$$

$=2.303\times8.314\times8997.5\,K\log2$

$= 51855.2\ J/mol$ $(\log2 = 0.3010)$

8. **Answer:**

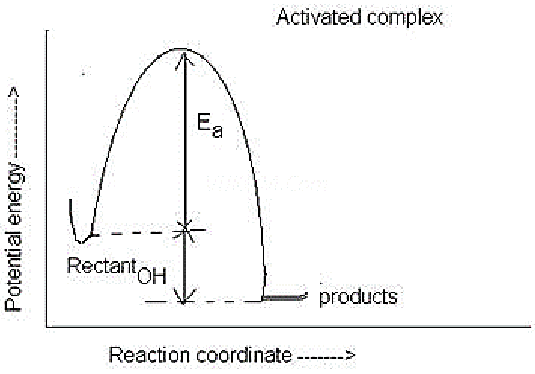
$$\log\frac{4.5\times10^{7}}{1.5\times10^{7}}=\frac{E_a}{2.303\times3.314}\left(\frac{373-323}{373\times323}\right)$$

$$\log1.5=\frac{E_a}{2.303\times3.314}\left(\frac{50}{373\times323}\right)$$

$$E_a=\left(\frac{2.303\times3.314\times373\times323}{50}\right)\times\log1.5$$

$=22\ KJ/mol$

10. **Answer :**



11. **Answer :**

The reaction X → Y follows second order kinetics. Therefore, the rate equation for this reaction will be:

Rate = $k\ [X]^2$ ....(1)

Let $X = a\ mol^{-1}$ mol^{-1} , then equation (1) can be written as:

$Rate_1 = k.(a)_2$

$= ka_2$

If the concentration of X is increased to three times, then $X = 3a\ mol\ L^{-1}$

Now, the rate equation will be:

$Rate = k(3a)_2$

$=9(ka^2)$

Hence, the rate of formation will increase by 9 times.

Long Answers:

1. **Answer:**

It is given that T_1 = 298 K

Therefore, $T_2 = (298 + 10)\ K = 308\ K$

We also know that the rate of the reaction doubles when temperature is increased by 10°.

Therefore, let us take the value of $k_1 = k$ and that of $k_2 = 2k$

Also, R = 8.314 $JK^{-1}\ mol^{-1}$

Now, substituting these values in the equation:

$$\log\frac{k_2}{k_1}=\frac{E_a}{2.303R}\left[\frac{T_2-T_1}{T_1T_2}\right]$$

We get:

$$\log\frac{2k}{k}=\frac{E_a}{2.303\times8.314}\left[\frac{10}{298\times308}\right]$$

$$\log2=\frac{E_a}{2.303\times8.314}\left[\frac{10}{298\times308}\right]$$

$$E_a=\frac{2.303\times8.314\times298\times308\times\log2}{10}$$

= 52897.78 J mol^{-1}

= 52.9 k J mol^{-1}

2. **Answer:**

In the given case:

$$E_a=209.5\,kJ\ mol^{-1}=209500\ J\ mol^{-1}$$

T = 581 K

R = 8.314 $JK^{-1}\ mol^{-1}$

Now, the fraction of molecules of reactants having energy equal to or greater than activation energy is given as:

$$X=e^{-Ea/RT}$$

In $x=-E_a/RT$

$$\log x=\frac{E_a}{2.303\,RT}$$

$$\log x=\frac{209500\ J\ mol^{-1}}{2.303\times8.314\ JK^{-1}mol^{-1}\times581}$$

=18.8323

Now, x = Anti log (18.8323)

= Anti log $\overline{19}.1677$ = 1.471 × 10^{-19}

3. **Answer:**

(i) Given rate = $k[NO]^2$

Therefore, order of the reaction = 2

$$\text{Dimension of } k=\frac{Rate}{[NO]^2}$$

$$=\frac{mol\ L^{-1}s^{-1}}{(mol\ L^{-1})^2}$$

$$=\frac{mol\ L^{-1}s^{-1}}{mol^2L^{-2}}$$

$= L\ mol^{-1}s^{-1}$

(ii) Given rate = $k[H_2O_2][I^-]$

Therefore, order of the reaction = 2

$$\text{Dimension of } k=\frac{Rate}{[H_2O_2][I^-]}$$

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

(iii) Given rate = $k[CH_3CHO]^{3/2}$

Therefore, order of reaction = $\frac{3}{2}$

$$\text{Dimension of } k=\frac{Rate}{[CH_3CHO]^{3/2}}$$

$$=\frac{mol\ L^{-1}s^{-1}}{(mol\ L^{-1})^{3/2}}$$

$$=\frac{mol\ L^{-1}s^{-1}}{mol^{3/2}L^{-3/2}}$$

$= L^{3/2}\ mol^{-1/2}s^{-1}$

(iv) Given rate = $k[C_2H_5Cl]$

Therefore, order of the reaction = 1

$$\text{Dimension of } k=\frac{Rate}{[C_2H_5Cl]}$$

$$=\frac{mol\ L^{-1}s^{-1}}{mol\ L^{-1}}=s^{-1}$$

4. **Answer:**

The decomposition of NH_3 on platinum surface is represented by the following equation.

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

Therefore,

$$Rate=-\frac{1}{2}\frac{d[NH_3]}{dt}=\frac{d[N_2]}{dt}=\frac{1}{3}\frac{d[H_2]}{dt}$$

However, it is given that the reaction is of zero order.

$$-\frac{1}{2}\frac{d[NH_3]}{dt}=\frac{d[N_2]}{dt}=\frac{1}{3}\frac{d[H_2]}{dt}=k$$

Therefore, = 2.5 × 10^{-4} mol $L^{-1}s^{-1}$

Therefore, the rate of production of N_2 is

$$\frac{d[N_2]}{dt}=2.5\times10^{-4}\ mol\ L^{-1}s^{-1}$$

And, the rate of production of H_2 is

$$\frac{d[H_2]}{dt} = 3 \times 2.5 \times 10^{-4}\ mol\ L^{-1} s^{-1}$$

$$= 7.5 \times 10^{-4}\ mol\ L^{-1} s^{-1}$$

5. **Answer:**

If pressure is measured in bar and time in minutes, then

Unit of rate = b ar min^{-1}

$$Rate = k\left(P_{CH_3OCH_3}\right)^{3/2}$$

$$k = \frac{Rate}{\left(P_{CH_3OCH_3}\right)^{3/2}}$$

Therefore, unit of rate constants

$$(k) = \frac{bar\ \text{min}^{-1}}{bar^{3/2}}$$

= $\text{bar}^{-1/2}\ \text{min}^{-1}$

Assertion and Reason Answers:

1. (d) Assertion is wrong statement but reason is correct statement.

Explanation:

The rate reaction is never negative. Minus sign used in expressing the rate only shows that the concentration of the reactant is decreasing.

2. (a) Assertion and reason both are correct statements and reason is correct explanation for assertion.

Explanation:

Kinetics deals with the reaction mechanism i.e., how the atoms rearrange themselves in the reactant molecules in a single step or a number of steps, finally leading to the product molecules.

Case Study Answers:

1. **Answer:**

(i) (c) 3

Explanation:

Unit of *k* for nth order = $(\text{mol L}^{-1})^{1-n}\ \text{sec}^{-1}$

Here, *k* = $3 \times 10^{-3}\ \text{mol}^{-2}\ \text{L}^2\ \text{sec}^{-1}$

Unit of *k* = $\text{mol}^{-2}\ \text{L}^2\ \text{sec}^{-1} \Rightarrow (\text{mol L}^{-1})\ \text{sec}^{-1}$

Comparing (i) and (ii) we get, 1 – n = –2

⇒ n = 3

(ii) (c) twice the rate of consumption of A.

Explanation:

$$Rate = \frac{d[A]}{dt} = -\frac{1}{3}\frac{d[B]}{dt} = \frac{1}{2}\frac{d[C]}{dt}$$

(iii) (c) 18 times

Explanation:

Given, $R_1 = k[A]^2\ [B]$

According to question, $R_2 = k[3A]^2\ [2B]$

$= k \times 9[A]^2 \times 2[B] = 18 \times k[A]^2\ [B] = 18\ R_1$

(iv) (c) 1

Explanation:

Rate (r) = $k[H^+]^n$

When pH = 3; $[H^+] = 10^{-3}$

and when pH = 1; $[H^+] = 10^{-1}$

$$\therefore \frac{r_1}{r_2} = \frac{k(10^{-3})^n}{k(10^{-1})^n}$$

$$\Rightarrow \frac{1}{100} = \left(\frac{10^{-3}}{10^{-1}}\right)^n \quad (\because r_2 = 100\, r_1)$$

$$\Rightarrow (10^{-2})^1 = (10^{-2})^n \ \Rightarrow n = 1$$

(v) (b) 2

Explanation:

Let the order of reaction *w.r.t.* A is *x* and *w.r.t.* B is *y*.

$$r_1 = k[A]^x [B]^y$$

$$r_2 = k[2A]^x [B]^y$$

$$r_3 = k[A]^x [2B]^y$$

$$\frac{r_1}{r_2} = \frac{k[A]^x [B]^y}{k[2A]^x [B]^y}$$

$$\Rightarrow \frac{1}{4} = \left(\frac{1}{2}\right)^x \Rightarrow \left(\frac{1}{2}\right)^2 = \left(\frac{1}{2}\right)^x \Rightarrow x = 2$$

Similarly, $\dfrac{r_1}{r_3} = \dfrac{k[A]^x [B]^y}{k[A]^x [2B]^y}$

$$\Rightarrow 1 = \left(\frac{1}{2}\right)^y \Rightarrow \left(\frac{1}{2}\right)^0 = \left(\frac{1}{2}\right)^y \Rightarrow y = 0$$

Hence the rate law equation is

Rate = $k[A]^2\ [B]^0 \Rightarrow$ Order of reaction = 2

2. **Answer :**

(i) (b) 2

Explanation:

According to the figure,

In the given time of 4 hours (1 to 5) concentration of A falls from 0.5 to 0.3 M, while in the same time concentration of B increases from 0.2 to 0.6 M.

Decrease in concentration of A in 4 hours

= 0.5 – 0.3 = 0.2 M

Thus, increase in concentration of B in a given time is twice the decrease in concentration of A. Thus, n = 2.

(ii) (b) 1.2 M

Explanation:

$$K = \frac{[B]^2}{[A]} = \frac{(0.6)^2}{0.3} = 1.2\,\text{M}$$

(iii) (a) 0.1 mol $L^{-1}hr^{-1}$

Explanation:

From $t = 0$ to $t = 1$hr,

For A, $dx = 0.6 - 0.5 = 0.1$ mol L^{-1}

$$\therefore \text{Initial rate of conversion of A} = \frac{dx}{dt}$$

$$= \frac{0.1\,\text{mol L}^{-1}}{1\text{hr}} = 0.1\,\text{mol L}^{-1}\text{hr}^{-1}$$

(iv) (b) 10^{-4}

Explanation:

$$A \rightleftharpoons 2B$$

$$-\frac{d[A]}{dt} = +\frac{1}{2}\frac{d[B]}{dt}$$

$$= \frac{1}{2} \times 2 \times 10^{-4} = 10^{-4}$$

(v) (d) Molecularity

Explanation:

The number of reacting species (atoms, ions or molecules) taking part in an elementary reaction is called molecularity and it has no influence on the rate of reaction.

❖❖

The p-Block Elements 4

Sulphur and its Compounds

Allotropic Forms of Sulphur

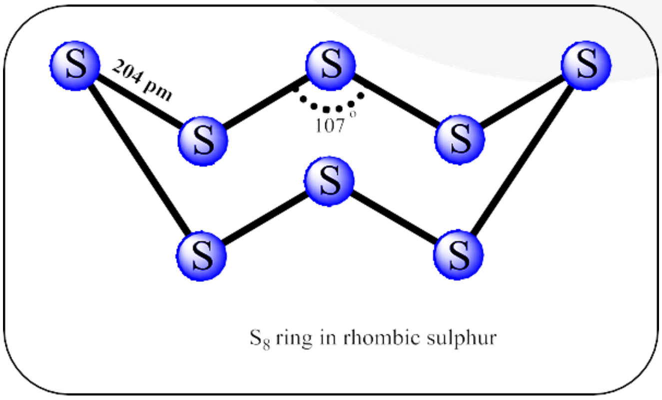
Sulphur forms a variety of allotropes. The most common allotropes are yellow rhombic and monoclinic sulphur. Rhombic sulphur is more stable at room temperature. It gets transformed to monoclinic sulphurwhen heated above 369 K.

Rhombic Sulphur

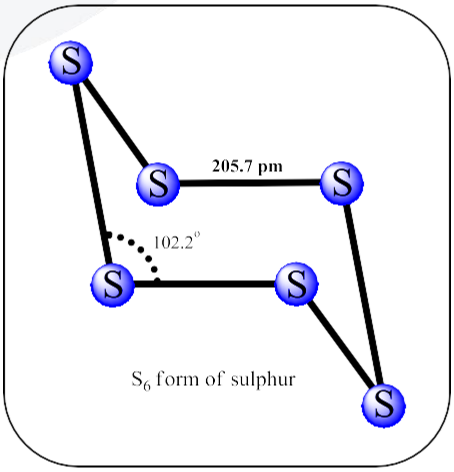
- This allotrope is yellow in colour. Its melting point is about 385.8 K and specific gravity is 2.06.
- Rhombic sulphur crystals are formed when the solution of roll sulphur in CS_2 is evaporated.
- It is insoluble in water but dissolves to some extent in benzene, alcohol and ether. It is more solublein CS_2.

Monoclinic Sulphur

- Its melting point is 393 K and its specific gravity is 1.98. It is soluble in CS_2.
- This form of sulphur is prepared by melting rhombic sulphur in a dish and cooling, till a crust isformed.
- Two holes are made in the crust and the remaining liquid is poured out. After removing the crust,colourless needle-shaped crystals of sulphur are formed.
- It is stable above 369 K and transforms into sulphur below 369 K.
- Also, we can say that the sulphur is stable below 369 K and transforms into sulphur above this. At369 K, both forms are stable. This temperature is called transition temperature.
- Rhombic and monoclinic sulphur have S_8 molecules. These S_8 molecules are packed to givedifferent crystal structures. The S_8 ring in both forms is puckered and has a crown shape.



In the cyclo-S_6 form, the molecule is in the chair shape.



At very high temperatures (~1000 K); S_2 is paramagnetic like O_2.

Sulphur Dioxide

Preparation

It can be prepared in the laboratory with the action of metallic sulphate on a dilute acid.

$$Na_2SO_3 + H_2SO_4 \rightarrow Na_3SO_4 + H_2O + SO_2$$

Sulphur dioxide is formed together with a trace amount of sulphur trioxide (6–8%) when sulphur isburnt in air or oxygen:

$$S(s) + O_2(g) \rightarrow SO_2$$

- In the laboratory, sulphite is treated with dilute sulphuric acid to give sulphur dioxide.

$$SO_3^{2-}(aq) + 2H^+(aq) \longrightarrow H_2O(l) + SO_2(g)$$

- It is also produced as a by-product of the roasting of sulphide ores.

$$4FeS_2(s) + 110(g) \longrightarrow 2Fe_2O_3(s) + 8SO_2(g)$$

- The gas is first dried and is liquefied under pressure and stored in steel cylinders.

Properties

Physical Properties

- Sulphur dioxide is one of the gases which can be easily liquefied.

  Sulphur dioxide is a colourless gas with pungent smell and is highly soluble in water.
- It liquefies at room temperature under a pressure of 2 atmospheres and boils at 263 K.
- When sulphur dioxide is passed through water, it forms a solution of sulphurous acid.

Chemical Properties

It reacts with sodium hydroxide solution to give sodium sulphite, which then reacts with excess ofsulphur dioxide to form sodium hydrogen sulphite.

$$2NaOH + SO_2 \rightarrow Na_2SO_3 + H_2O$$

$$Na_2SO_3 + H_2O + SO_2 \rightarrow 2NaHSO_3$$

- When sulphur dioxide reacts with water or alkali, its behaviour is similar to that of carbon dioxide.

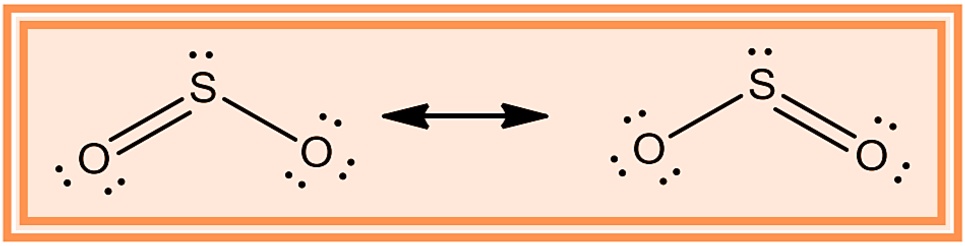
  Sulphur dioxide reacts with chlorine in the presence of charcoal (which acts as a catalyst) to givesulphuryl chloride SO_2Cl_2.

  It is oxidised to sulphur trioxide by oxygen in the presence of vanadium (V) oxide catalyst.

$$SO_2\ g + Cl_2\ g \rightarrow SO_2Cl_2\ l$$

$$2SO_2\ g + O_2\ g \rightarrow SO_3\ g$$

- Under moist conditions, sulphur dioxide behaves as a reducing agent. For example, it converts iron (III) ions to iron (II) ions and decolourises acidified potassium permanganate (VII) solution.
- The molecule of SO_2 is angular. It is a resonance hybrid of the two canonical forms:



Uses

- As a bleaching agent
- In refining petroleum and sugar
- In bleaching wool and silk
- As an anti-chlor, disinfectant and preservative
- In the manufacture of sulphuric acid, sodium hydrogen sulphite and calcium hydrogen sulphite (industrial chemicals)
- Liquid SO_2 is used as a solvent to dissolve several organic and inorganic chemical

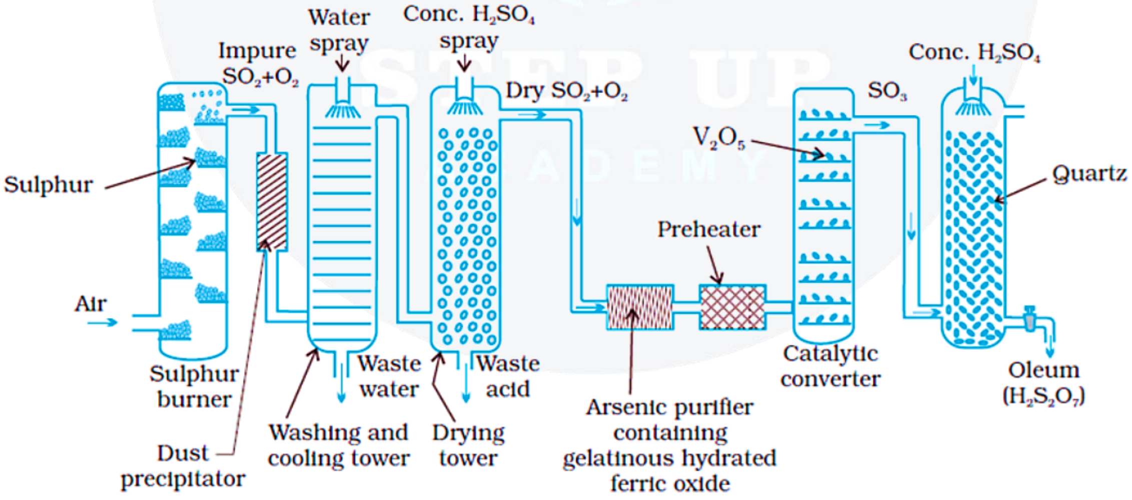
Oxoacids of Sulphur

- Sulphur dioxide is a strong oxidising agent.
- Sulphur forms several oxoacids such as H_2SO_3, $H_2S_2O_3$, $H_2S_2O_4$, $H_2S_2O_5$, $H_2S_xO_6$ (x = 2–5), H_2SO_4, $H_2S_2O_7$, H_2SO_5 and $H_2S_2O_8$.
- Some of these acids are unstable and cannot be isolated.
- They commonly occur in the form of an aqueous solution or in the form of their salts.

Sulphuric Acid

Preparation

- Sulphuric acid is one of the most important industrial chemicals.
- Sulphuric acid is manufactured by the contact process which involves three steps:
  - Burning of sulphur or sulphide ores in air to generate SO_2
  - Conversion of SO_2 to SO_3 by the reaction with oxygen in the presence of a catalyst (V_2O_5)
  - Absorption of SO_3 in H_2SO_4 to give oleum ($H_2S_2O_7$)



Flow diagram for the manufacture of sulphuric acid

- SO_2 produced by this process is purified by removing dust and other impurities such as arseniccompounds.
- The major step in the manufacture of H_2SO_4 is the catalytic oxidation of SO_2 with O_2 to give SO_3 inthe presence of V_2O_5 (catalyst).
- The reaction is exothermic and reversible. The forward reaction leads to a decrease in volume.

$$2SO_2\ (g) + O_2\ (g) \xrightarrow{V_2O_5} 2SO_3\ (g)\ \Delta_r H^\ominus = -196.6\ kJmol^{-1}$$

- Low temperature and high pressure are favourable conditions for maximum yield.

- But the temperature should not be very low; otherwise the rate of reaction will become slow.
- In actual practice, the plant is operated at a pressure of 2 bar and 720 K.
- SO_3 gas from the catalytic converter is absorbed in concentrated H_2SO_4 to produce oleum. Dilutionof oleum with water gives H_2SO_4 of the required concentration.
- In the industry, two steps are carried out simultaneously to make the process a continuous one andto reduce the cost.

$$SO_3 + H_2SO_4 \rightarrow \underset{\text{Oleum}}{H_2S_2O_7}$$

- Sulphuric acid obtained by the contact process is 96–98% pure.

Properties

- Sulphuric acid is a colourless, dense, oily liquid with a specific gravity of 1.84 at 298 K.
- The acid freezes at 283 K and boils at 611 K.
- It is highly exothermic in the presence of water. It dissolves in water with the evolution of a large quantity of heat.
- Hence, care must be taken while preparing sulphuric acid solution from concentrated sulphuric acid.
- The concentrated acid must be added slowly into water with constant stirring.
- Chemical reactions of sulphuric acid are as a result of the following characteristics:
- In an aqueous solution, sulphuric acid ionises in two steps.

$$H_2SO_4\ aq + H_2O\ l \rightarrow H_3O^+\ aq + HSO_4^-\ aq\ ;\ K_{a_1} = \text{very large}\quad K_{a_1} > 10$$

$$HSO_4^-\ aq + H_2O\ l \rightarrow H_3O^+\ aq + SO_4^{2-}\ aq\ ;\ K_{a_2} = 1.2 \times 10^{-2}$$

- The larger value of K_{a1} ($K_{a1} > 10$) means that H_2SO_4 is largely dissociated into H^+ and HSO_4.
- Greater the value of the dissociation constant (Ka), the stronger is the acid.
- The acid forms two series of salts—normal sulphates (sodium sulphate and copper sulphate) andacid sulphates (sodium hydrogen sulphate).
- Sulphuric acid can be used to manufacture more volatile acids from their corresponding saltsbecause of its low volatility.
- Concentrated sulphuric acid is a strong dehydrating agent.

$$2MX + H_2SO_4 \rightarrow 2HX + M_2SO_4\ (X = F,\ Cl,\ NO_3)$$

Low

Strong acidic

Strong affinity for

Ability to act as an oxidising

- Many wet gases can be dried by passing them through sulphuric acid, provided the gases do notreact with the acid.

- Sulphuric acid removes water from organic compounds; it is evident by its charring action on carbohydrates.
- Hot concentrated sulphuric acid is a moderately strong oxidising agent.

$$C_{12}H_{22}O_{11} \xrightarrow{H_2SO_4} 12\,C + 11\,H_2O$$

- In this respect, it is intermediate between phosphoric acid and nitric acid.
- Both metals and non-metals are oxidised by concentrated sulphuric acid, which is reduced to SO_2.

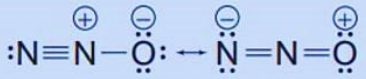
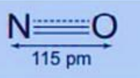
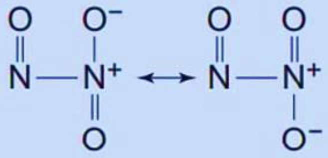
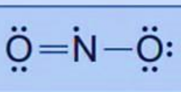
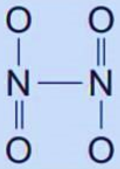
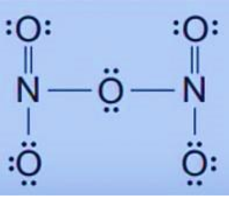
Uses

- Sulphuric acid is a very important industrial chemical as many other chemicals can be prepared from it.

$$Cu + 2\,H_2SO_4\ \text{conc.} \rightarrow CuSO_4 + SO_2 + 2\,H_2O$$
$$S + 2\,H_2SO_4\ \text{conc.} \rightarrow 3\,SO_2 + 2\,H_2O$$
$$C + 2\,H_2SO_4\ \text{conc.} \rightarrow CO_2 + 2\,SO_2 + 2\,H_2O$$

- Primary use of sulphuric acid is in the synthesis of fertilisers.
- The industrial strength can be judged by the quantity of sulphuric acid it produces and consumes.
- It is needed for the manufacture of hundreds of other compounds and in many industrial processes.
- Bulk of sulphuric acid produced is used in the manufacture of fertilisers (ammonium sulphate and superphosphate).

Oxides of Nitrogen

Nitrous oxide	N_2O	
Nitric oxide	NO	
Dinitrogen trioxide (or) Nitrogen sesquoxide	N_2O_3	
Nitrogen dioxide	NO_2	
Nitrogen tetraoxide	N_2O_4	
Nitrogen pentoxide	N_2O_5	

Nitrogen combines with oxygen under different conditions to form a number of binary oxides which differ with respect to the oxidation state of the nitrogen atom. They range from N^2O (oxidation state of N +1) through NO (+2), N_2O_3 (+3), N_2O_4 (+4) to N_2O_5(5). The tendency to form pπ - pπ multiple bonds dictates the structures of oxides.

(1) Nitrous Oxide (N_2O)

(a) It is prepared by heating ammonium nitrate.

$NH_4NO_3 \longrightarrow N_2O + 2H_20$

(b) It is a colourless unreactive gas having faint pleasant smell. It is also known as laughing gas because it causes hysterical laughter when inhaled in minor quantities.

(c) It is a neutral oxide and reacts with sodamide to form sodium azide.

$N_2O + 2NaNH_2 \longrightarrow NaN_3 + NH_3 + NaOH$

Sodamide Sodium azide

(d) In small amounts, it acts as an anaesthetic for minor operations.

(e) It decomposes into nitrogen and oxygen at 873 K.

$2N_2O \longrightarrow 2N_2 + O_2$

Therefore, it supports the combustion acting as a source of oxygen.

(2) Nitric Oxide (NO)

(a) It is prepared by the catalytic oxidation of ammonia at 1100 K in the presence of platinum.

$4NH_3 + 5O_2 \longrightarrow 4NO + 6H_2O$

(b) It can also prepared by the reaction of nitric acid on copper as :

$3Cu + 8HNO_3 \longrightarrow 3Cu(NO_3)_2 + 2NO + 4H_2O$

(c) It can also be prepared by the reduction of sodium nitrite with ferrous sulphate in the presence of sulphuric acid.

$2NaNO_2 + 2FeSO_4 + 3H_2SO_4 \longrightarrow Fe2(SO_4)_3 + 2NaHSO_4 + 2H_2O + 2NO$

(d) It is a neutral oxide

(e) It is a colourless gas. It has odd number of electrons (11 valence electrons) and therefore, it is paramagnetic in the gaseous state. However, in the liquid and solid states, it forms a loose dimer in such a way that the magnetic effects of two unpaired electrons are cancelled out. The molecule is diamagnetic.

(f) Nitric oxide readily reacts with oxygen to give brown fumes of nitrogen dioxide.

$2NO\,(g) + O_2(g) \longrightarrow 2NO_2\,(g)$

(g) Nitric oxide readily forms complexes with transition metals.

For example: Fe^{2+} combines with NO to form the complex $[Fe(H_2O)_5NO]^{2+}$ which is responsible for brown ring test for nitrates.

(h) It is thermodynamically unstable and decomposes into elements at high temperatures (1373 K 1473 K)

$2NO\,(g) \longrightarrow N2\,(g) + O2\,(g)$

Dinitrogen Trioxide (N_2O_3)

(1) It is prepared by cooling equimolar quantities of nitric oxide and nitrogen dioxide to below 253 K.

$NO(g) + NO_2(g) \Leftrightarrow N_2O_3$

(2) It can also be prepared by reacting nitric oxide and dinitrogen tetraoxide at 250 K.

$2NO + N_2O_4 \longrightarrow 2N_2O_3$

Properties of Dinitrogen Trioxide

(1) It is a blue solid and is acidic in nature. It is anhydride of nitrous acid (HNO_2).

$N_2O_3 + H_2O \longrightarrow 2HNO_2$

(2) It exists in the pure form only in the solid state at very low temperatures.Above its melting point (273 K) it dissociates to NO and NO_2.

$N_2O_3 \longrightarrow NO + NO_2$

Nitrogen Dioxide (NO_2)

It is prepared by heating dried lead nitrate in a steel reaction vessel.

$$2Pb(NO_3)_2 \longrightarrow 2PbO + 4NO_2 + O_2$$

It is also an odd electron molecule and in the gas phase, it exists in equilibrium with N_2O_4 as :

$$N_2O_4 \Leftrightarrow 2\,NO_2$$

Above 415 K it contains mainly NO_2 and at 250 K, it consists of mainly N_2O_4

$$2\,NO_2 \Leftrightarrow N_2O_4$$

Dinitrogen Pentoxide (N_2O_5)

(1) It is prepared by dehydrating the concentrated nitric acid with phosphorus pentoxide.

$4HNO_3 + P_4O_{10} \longrightarrow 2N_2O_5 + HPO_3$

(2) N_2O_5 exists as colourless solid below 273K. As the temperature rises, the colour changes to yellow due to the partial decomposition of colourless N_2O_5 to brown NO_2.

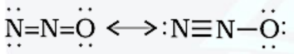
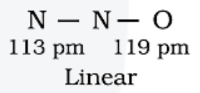
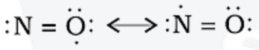
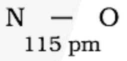
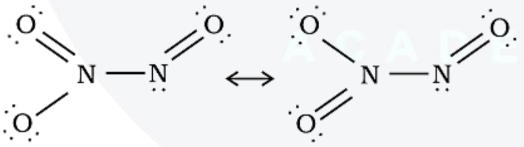
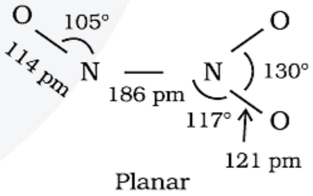
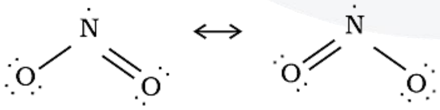
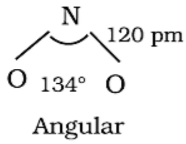
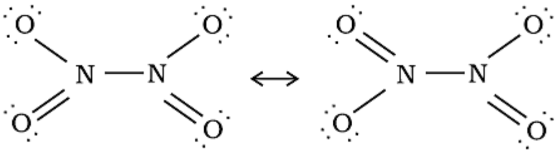
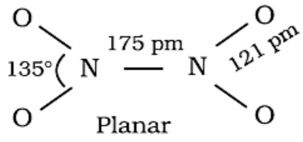
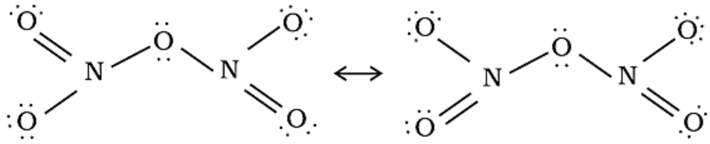
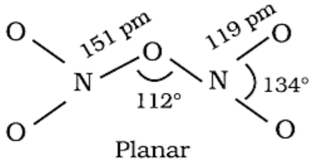
$2\,N_2O_5 \longrightarrow 4NO_2 + O_2$

(3) At 303K, the crystals melt giving a yellow liquid which decomposes at 313K to give NO2.

(4) N_2O_5 acts as a strong oxidising agent and oxidises iodine to I_2O_5

NO and NO_2 are used in the manufacture of nitric acid and nitrate fertilizers Liquid N_2O_4 is also used as an oxidiser for the rocket fuels in missiles and space vehicles.

(5) NO causes a pollution problem in atmosphere due to its poisonous nature. Its vapours are emitted in the atmosphere during the burning of oil and coal.

Formula	Resonance Structures	Bond Parameters
N_2O		
NO		
N_2O_3		
NO_2		
N_2O_4		
N_2O_5		

Nitric Acid (HNO_3)

The common oxoacids of nitrogen are given below :

Name	Formula	Oxidation State of N	Nature
Hyponitrous acid	$H_2N_2O_2$	+2	weak acid known as its salts
Nitroxylic acid	$H_4N_2O_4$	+2	highly explosive difficult to get in pure state
Nitrous acid	HNO_2	+3	weak acid and unstable
Nitric acid	HNO_3	+5	weak acid and stable
Peroxonitric acid	HNO_4	+5	unstable and explosive

Nitric acid is a very strong oxidising agent. Nitrogen shown an oxidation state of +5 in nitric acid.

Laboratory Preparation of Nitric Acid

In the laboratory, nitric acid can be prepared by heating sodium or potassium nitrate with concentrated sulphuric acid to about 423-475 K.

$$NaNO_3 + H_2SO_4 \longrightarrow NaHSO_4 + HNO_3$$

Anhydrous nitric acid can be obtained by distillation of concentrated aqueous nitric acid with P_4O_{10}.

Manufacture of Nitric Acid

Nitric acid is commonly manufactured by Ostwald process in which it is prepared by the catalytic oxidation of ammonia by atmospheric oxygen. The reaction is carried out at about 500 K and 9 x 10^5 Pa (9 bar) pressure in the presence of Pt or Rh gauge as catalyst.

$$4NH_3(g) + 5O_2(g) \longrightarrow 4NO(g) + 6H_2O(g) \quad \Delta H = -\ 90.2\ kJ$$

Pt/Rh gauge, 500K, 9 bar

Nitric oxide thus formed combines with oxygen to form nitrogen dioxide.

$$2NO(g) + O_2\ (g) \longrightarrow 2\ NO_2\ (g)$$

Nitrogen dioxide so formed, dissolves in water to give nitric acid.

$$3NO_2\ (g) + H_2O(l) \longrightarrow 2HNO_3(aq) + NO(g)$$

Dilute nitric acid is further concentrated by dehydration with concentrated sulphuric acid to get about 98% acid.

Properties of Nitric Acid

Physical Properties

1) Pure nitric acid is a colourless liquid.
2) It has boiling point 355.6 K and freezing point 231.4 K.
3) Laboratory grade nitric acid contains about 68% of HNO_3 by mass and has a specific gravity of 1.504.
4) The impure acid is generally yellow due to the presence of nitrogen dioxide as impurity. Nitric acid containing dissolved nitrogen dioxide is known as fuming nitric acid.
5) It has a corrosive action on skin and produces painful blisters.

Chemical Properties

(1) **Acidic character:** It is one of the strongest acids because it is highly ionised in aqueous solution giving hydronium and nitrate ions.

$2HNO_3(aq) + H_2O\ (l) \longrightarrow H_3O^+ + NO_3^-(aq)$

It turns blue litmus red. It forms salts with alkalies, carbonates and bicarbonates.

$NaOH + HNO_3 \longrightarrow NaNO_3 + H_2O$

$Na_2CO_3 + HNO_3 \longrightarrow 2NaNO_3 + H_2O + CO_2$

$NaHCO_3 + HNO_3 \longrightarrow NaNO3 + H_2O + CO_2$

(2) Action on metals: With the exception of gold and platinum, nitric acid attacks all metals forming a variety of products. The product depends upon the nature of metal, the concentration of acid and temperature.

(A) Metals that are more electropositive than hydrogen (Mg, Al, Mn, Zn, Fe, Pb, etc.). In this case nascent hydrogen is liberated which further reduces nitric acid.

$M + 2HNO_3$ ——> $M(NO_3)_2 + 2H$

$HNO_3 + H$ —-> Reduction product + H_2O

The principal product is NO_2, with conc. HNO_3, N_2O with dil. HNO_3, and ammonium nitrate with very dil. HNO_3.

For example: Zn reacts as:

(a) Using concentrated nitric acid (forms nitrogen dioxide)

$Zn + 2HNO_3$ —–> $Zn\ (NO_3)_2 + 2H$

$HNO_3 + H$ —–> $NO_2 + H_2O]$ x 2

——————————————————————-

$Zn + 4HNO_3$ —-> $Zn\ (NO_3)_2 + 2NO_2 + 2H_2O$

(b) Using dilute nitric acid (forms nitrous oxide)

$Zn + 2HNO_3$ —–> $Zn(NO_3)\quad + 2H\ ]$ × 4

2 HNO3 + 8 H —–> NO2 + 5 H2O

——————————————————————-

$Zn + 10HNO_3$ —-> $4Zn\ (NO_3)_2 + NO_2 + 5H_2O$

(c) Using very dilute nitric acid (forms ammonium nitrate)

$Zn + 2HNO_3$ —–> $Zn\ (NO_3)_2 + 2H]$ × 4

$HNO_3 + 8H$ —–> $NH_3 + 3\ H_2O$

$NH_3 + HNO_3$ ——–> NH_4NO_3

——————————————————————-

$4Zn + 10\ HNO_3$ —–> $4Zn\ (NO_3)_2 + NH_4NO_3 + 3\ H_2O$

(B) Metals which are less electropositive than hydrogen (Cu, Bi, Hg, Ag). In this case nascent hydrogen is not liberated.

$HNO_3 \rightarrow$ Reduction product + H_2O + [0]

Metal + (O) + $HNO_3 \rightarrow$ Metal nitrate + H_2O

The principal product is NO_2 with conc. HNO_3 and NO with dil. HNO_3

For example: Cu reacts as

(a) Using concentrated nitric acid

$2HNO_3$ ——> $2NO_2 + H_2O + [O]$

$Cu + O + 2HNO_3$ ——–> $Cu\ (NO_3)_2 + H_2O$

——————————————————————-

$Cu + 4HNO_3 \rightarrow Cu\ (NO_3)_2 + 2NO_2 + 2H_2O$

(b) Using dilute nitric acid

$2HNO_3$ —–> $2NO + H_2O + 3[O]$

$Cu + O + 2HNO_3$ –> $Cu\ (NO_3)_2 + H_2O]$ x 3

————————————————————————-

$3Cu + 8HNO_3$ ——-> $Cu\ (NO_3)_2 + 2NO + 4H_2O$

$Hg + 4HNO_3$ —–> $Hg\ (NO_3)_2 + 2NO_2 + 2H_2O$

$6Hg + 8HNO_3$ —–> $3Hg_2(NO_3)2 + 2NO + 4H_2O$

$Ag + 4HNO_3$ —–> $AgNO_3 + NO_2 + 2H_2O$

$3\ Ag + 4\ HNO_3$ —–> $3\ AgNO_3 + NO + 2H_2O$

(c) Action on noble metals

Noble metals like gold and platinum are not attacked by nitric acid. However, these metals are attacked by aqua regia (3 parts conc. HCl and 1 part conc. HNO_3) forming their chlorides.

$NaOH + HNO_3 \longrightarrow NaNO_3 + H_2O$

$HNO_3 + 3\,HCl \longrightarrow NOCl + 2\,H_2O + 2\,Cl$

Nitrosyl chloride

$Au + 3Cl \longrightarrow AuCl_3$

$Pt + 4Cl \longrightarrow PtCl_4$

(3) Oxidising nature -Oxidation of non-metals and compounds.

Nitric acid behaves as a strong oxidising agent. It has a tendency to give nascent oxygen as:

$2HNO_3 \longrightarrow 2NO_2 + H_2O + O$

(conc.)

$2HNO_3 \longrightarrow 2NO + H_2O + 3\,[O]$

Therefore, nitric acid oxidises many non-metals and compounds.

(A) Oxidation of non-metals: Dilute nitric acid has no action on non-metals like carbon, sulphur, phosphorus, etc. However, concentrated nitric acid oxidises many non-metals.

For example:

(i) Nitric acid oxidises sulphur to sulphuric acid

$2HNO_3 \longrightarrow 2NO_2 + H_2O + O] \times 3$

$1/8\, S_8 + H_2O + 3O \longrightarrow H_2SO_4$

————————————————————————

$1/8\, S_8 + 6HNO_3 \longrightarrow H_2SO_4 + 6NO_2 + 2H_2O$

————————————————————

$S_8 + 48HNO_3 \longrightarrow 8\,H_2SO_4 + 48NO_2 + 12H_2O$

————————————————————-

(ii) Nitric acid oxidises carbon to carbonic acid

$2HNO_3 \longrightarrow 2NO_2 + H_2O + O] \times 2$

$C + H_2O + 2O \longrightarrow H_2CO_3$

——————————————————

$C + 4HNO_3 \longrightarrow H_2CO_3 + 4NO_2 + 2H_2O$

——————————————————

(iii) Nitric acid oxidises phosphorus to phosphoric acid

$2HNO_3 \longrightarrow 2NO_2 + H_2O + O] \times 5$

$2P + 3H_2O + 5O \longrightarrow 2\,H_3PO_4$

———————————————

$2P + 10HNO_3 \longrightarrow 2\,H_3PO_4 + 10\,NO_2 + 2\,H_2O$

$p + 5\,HNO_3 \longrightarrow H_3PO_4 + 5\,NO_2 + H_2O$

$P_4 + 20\,HNO_3 \longrightarrow H_3PO_3 + 20\,NO_2 + 4\,H_2O$

(iv) It oxidises iodine to iodic acid.

$2HNO_3 \longrightarrow 2NO_2 + H_2O + O] \times 5$

$I2 + H_2O + 5O \longrightarrow HIO_3$

————————————————————

$I_2 + 10HNO_3 \longrightarrow 2\,HIO_3 + 10\,NO_2 + 4\,H_2O$

————————————————————

(v) Nitric acid oxidises arsenic to arsenic acid.

$2HNO_3 \longrightarrow 2NO_2 + H_2O + O] \times 5$

$2As + 3H_2O + 5O \longrightarrow 2H_3AsO_4$

————————————————————————-

$2As + 10HNO_3 \longrightarrow 10NO_2 + 2H_3AsO_4 + 2H_2O$

$As + 5HNO_3 \longrightarrow 5NO_2 + H_3AsO_4 + H_2O$

(B) Oxidation of compounds

Dilute as well as concentrated nitric acid oxidises a number of compounds.

(1) Nitric acid oxidises hydrogen sulphide to sulphur.

dil HNO_3:

$3H_2S + 2\ HNO_3 \longrightarrow 2\ NO + 4\ H_2O + 3S$

Conc HNO_3

$3H_2S + 2\ HNO_3 \longrightarrow 2\ NO_2 + 4\ H_2O + S$

(2) Nitric acid oxidises sulphur dioxide to sulphuric acid

dil HNO_3

$3SO_2 + 2HNO_3 + 2H_2O \longrightarrow 3\ H_2SO_4 + 2\ NO$

conc. HNO_3

$SO_2 + 2\ HNO_3 \longrightarrow H_2SO_4 + 2\ NO_2$

(3) Nitric acid oxidises ferrous sulphate to ferric sulphate

dil HNO_3

$6FeSO_4 + 2HNO_3 + 3H_2SO_4 \longrightarrow 3Fe_2(SO_4)_3 + 2NO + 4\ H_2O$

conc. HNO_3

$2FeSO_4 + 2HNO_3 + 3H_2SO_4 \longrightarrow 3Fe_2(SO_4)_3 + 2NO_2 + 4\ H_2O$

(4) Action on organic compounds

Nitric acid also reacts with organic compounds.

For example: sucrose (cane sugar) is oxidised to oxalic acid by nitric acid.

$C_{12}H_{22}O_{11} + 36\ HNO_3 \rightarrow 6\ (COOH)_2 + 36NO_2 + 23\ H_2O$

In the presence of sulphuric acid, nitric acid reacts with aromatic compounds forming nitro compounds. This process is called nitration.

For example: it reacts with benzene to form nitrobenzene.

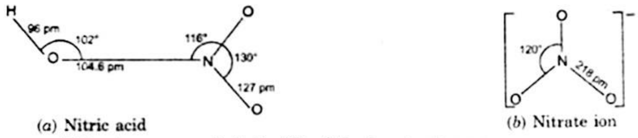
$C_6H_6 + HNO_3 \longrightarrow C_6H_5NO_2 + H_2O$

Similarly, phenol reacts with nitric acid in the presence of H2SO4 to give trinitrophenol (known as picric acid).

Nitric acid attacks proteins giving a yellow nitro compound known as xantho protein. Therefore, nitric acid stains skin and renders wool yellow.

Structure

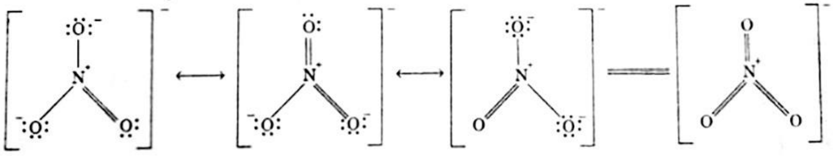
Gaseous nitric acid has planar structure. Nitrate ion, NO_3^- has also planar symmetrical structure



(a) Nitric acid

(b) Nitrate ion

The structure of NO_3^- is resonance hybrid of the following structures :



Brown Ring test for NO_3^- ion

Nitrates give brown ring test with Fe2+ ions in the presence of conc. H_2SO_4.This is based upon the tendency of Fe2+ to reduce nitrates to nitric oxide which reacts with Fe2+ to form a brown coloured complex.

The test is usually performed by adding dilute $FeSO_4$ solution to an aqueous solution containing NO_3^- ion and then adding conc. H_2SO_4 slowly along the sides of the test tube. A brown ring at the interface between the solution and sulphuric acid indicates the presence of NO_3^- ion.

$$3Fe^{2+} + NO_3^- + 4\,H^+ \longrightarrow NO + 3Fe^{3+} + 2H^2O$$

$$Fe^{3+} + NO + 5\,H^2O \longrightarrow [Fe\,(H^2O)^5\,NO]^{2+}$$

Pentaaquanitrosyl iron (II) ion

Uses of Nitric Acid

(i) It is used in the manufacture of ammonium nitrate for fertilizers.

(ii) It is used in the manufacture of sulphuric acid by lead chamber process.

(iii) It is used in the manufacture of explosives such as trinitro toluene (TNT), nitroglycerine, picric acid, etc.

(iv) It is used in the manufacture of dyes, perfumes and silk.

(v) It is used for the manufacture of nitrates for use in explosive and pyrotechnics.

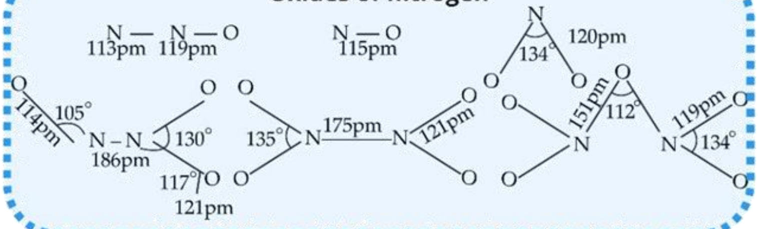
(vi) It is used in picking of stainless steel and etching of metals.

(vii) It is also used as an oxidiser in rocket fuels.

(viii) It is used in the purification of gold and silver as aqua regia.

Class : 12th Chemistry
Chapter-7 : The P- Block Elements (Part_1)

Oxides of nitrogen



Physical properties

Polyatomic, metallic character increases down the group. N and P are non-metals, As and Sb metalloids and Bi metal. B.P increases top to bottom and M.P. increases upto As and then decreases upto Bi. Except Ni all show allotropy

Dinitrogen preparation

- **In laboratory:**

$NH_4Cl + NaNO_2 \longrightarrow N_2 + 2H_2O + NaCl$

- **Thermal decomposition:**

$(NH_4)_2Cr_2O_7 \xrightarrow{\text{Heat}} N_2 + 4H_2O + Cr_2O_3$

$Ba(N_3)_2 \longrightarrow Ba + 3N_2$

- **Properties:**

$6Li + N_2 \xrightarrow{\Delta} 2Li_3N$

$3Mg + N_2 \xrightarrow{\Delta} Mg_3N_2$

$N_2 + 3H_2 \xrightarrow{773\,K} 2NH_3 \Delta_fH^\circ = 46.1\ KJ\ mol^{-1}$

$N_2 + O_2 \xrightarrow{\Delta} 2NO$

Ammonia Preparation

$NH_4CO\,NH_2 + 2H_2O \longrightarrow (NH_4)_2CO_3 \rightleftharpoons 2NH_3 + H_2O + CO_2$

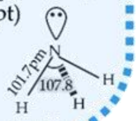
$N_2 + 3H_2 \rightleftharpoons 2NH_3\ \Delta_fH^\circ = -46.1\ kJ\ mol^{-1}$

Properties: Colourless with pungent odour, soluble in water

$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$

$ZnSO_4 + 2NH_4OH \longrightarrow Zn(OH)_2 + (NH_4)SO_4$
(white ppt)

$FeCl_3 + NH_4OH \longrightarrow Fe_2O_3.xH_2O + NH_4Cl$
(Brown ppt)



The P- Block Elements

Group 15 Elements

Electronic Configration
ns^2np^3

Elements
$_7N$, $_{15}P$, $_{33}As$, $_{51}Sb$, $_{83}Bi$

Ionization enthalpy
Decreases down the group due to gradual increase in atomic size.

Chemical properties
Common O.N : –3, +3 and +5. Nitrogen shows anomalous behaviour.

Electro-negativity
Decreases down the group with increasing atomic size.

Atomic and Ionic radii
Increase in size down the group.

Group 16 Elements

Electronic configuration : ns^2np^4

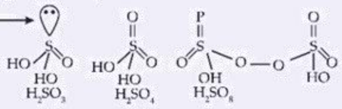
Atomic and ionic radii : Increase down the group

- IE : Decreases down the group
- Electron Gain enthalpy : O hass less–ve than S.
- Electro-negativity : Decreases with increase in atomic number
- Physical properties : O and S are non metals, Se and Te metalloids whereas Po is a metal. All exhibit allotropy
- M.P. and B.P. : Increases down the group
- Chemical properties : variable

  Reactivity with hydrogen : stable hydrides

  Reactivity with halogens : $F^- > Cl^- > Br^- > I^-$

- Oxoacids of S :⟶



- Dioxygen (O_2) :

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

Properties : Colourless and odourless gas

$2Ca + O_2 \longrightarrow 2CaO;\ 4Al + 3O_2 \longrightarrow 2AlO_3$

$2SO_2 + O_2 \xrightarrow{V_2O_5} 2SO_3;\ 4HCl + O_2 \xrightarrow{CuCl} 2Cl + 2H_2O$

Class : 12th Chemistry
Chapter-7 : The P- Block Elements (Part_2)

The P- Block Elements

Group 18 Elements

- Occurrence: All except radon occur in atmosphere
- Electronic configuration: $ns^2\ np^6$ except He
- IE : High
- Atomic radii: Increases down group
- Electron gain enthalpy: Largely positive
- Physical properties: Monoatmic, colourless, odorless and tasteless. Sparingly soluble in water.
- Chemical properties: Least reactive xenone-fluorine compound: XeF_2, XeF_4 and XeF_6
- Xenone oxygen compounds: XeO_3, $XeOF_2$, $XeOF_4$

Group 17 Elements

Chemical properties

Allexhibit – 1oxidation state Cl, Br andIexhibit+1, +3,+5and + 7.O.N

Reactivity towards hydrogen : H – F > H – Cl > H – Br > H – I

Reactivity towards oxygen : F form OF_2(stable) and O_2F_2

Reactivity towards metals : MF > MCl > MBr > MI

Reactivity towards other halogens: Forms XX', XX'_3, XX'_5 and XX'_7.

Occurrence

F and Cl are fairly abundant while Br and I less so

Electronic configuration

ns^2np^5

Atomic Ionic radii

Smallest in periods but increases from F to I

Chlorine

Preparation: $MnO_2 + 4HCl \longrightarrow MnCl_2 + Cl_2 + 2H_2O$

Deacon's process: $4HCl + O_2 \xrightarrow[CuCl_2]{} 2Cl_2 + 2H_2O$

Properties : Greenish yellow gas with pungent and suffocating odour.

Heavier than air

$2Al + 3Cl_2 \longrightarrow 2AlCl_3$

$H_2 + Cl_2 \longrightarrow 2HCl$

$H_2S + Cl_2 \longrightarrow 2HCl + S$

$8NH_3 + 3Cl_2 \longrightarrow 6NH_4Cl + N_2$

$2NaOH + Cl_2 \longrightarrow NaCl + NaOCl + H_2O$
(cold and dilute)

$2Ca(OH)_2 + 2Cl_2 \longrightarrow Ca(OCl)_2 + CaCl_2 + 2H_2O$

$CH_4 + Cl_2 \xrightarrow{uv} CH_3Cl + HCl$

$C_2H_4 + Cl_2 \xrightarrow{RT} C_2H_4Cl_2$

$2FeSO_4 + H_2SO_4 + Cl_2 \longrightarrow Fe_2(SO_4)_3 + 2HCl$

Electron gain enthalpy

Less –ve down the group

Electro-negativity

High, decreases down the group

Physical properties

F and Cl are gases, Br is liquid and I solid

M.P. and B.P.

Increases with atomic number

IE

Decreases down the group

Important Questions

Multiple Choice Questions

1. H_2S is more acidic than H_2O because
   (a) oxygen is more electronegative than sulphur.
   (b) atomic number of sulphur is higher than oxygen.
   (c) H—S bond dissociation energy is less as compared to H—O bond.
   (d) H—O bond dissociation energy is less also compared to H — S bond.
2. The boiling points of hydrides of group 16 are in the order
   (a) $H_2O > H_2Te > H_2S > H_2Se$
   (b) $H_2O > H_2S > H_2Se > H_2Te$
   (c) $H_2O > H_2Te > H_2Se > H_2S$
   (d) None of these
3. In the manufacture of sulphuric acid by contact process Tyndall box is used to
   (a) convert SO_2 and SO_3
   (b) test the presence of dust particles
   (c) filter dust particles
   (d) remove impurities
4. Fluorine differs from rest of the halogens in some of its properties. This is due to
   (a) its smaller size and high electronegativity.
   (b) lack of d-orbitals.
   (c) low bond dissociation energy.
   (d) All of the these.
5. The set with correct order of acidity is
   (a) $HClO < HClO_2 < HClO_3 < HClO_4$
   (b) $HClO_4 < HClO_3 < HClO_2 < HClO$
   (c) $HClO < HClO_4 < HClO_3 < HClO_2$
   (d) $HClO_4 < HClO_2 < HClO_3 < HClO$
6. When chlorine reacts with cold and dilute solution of sodium hydroxide, it forms
   (a) Cl^- and ClO^-
   (b) Cl^- and ClO_2^-
   (c) Cl^- and ClO_3^-
   (d) Cl^- and ClO_4^-
7. The formation of $O_2^+ [PtF_6]^-$ is the basis for the formation of first xenon compound. This is because
   (a) O_2 and Xe have different sizes.
   (b) both O_2 and Xe are gases.
   (c) O_2 and Xe have comparable electro-negativities.
   (d) O_2 and Xe have comparable ionisation enthalpies.
8. Partial hydrolysis of XeF_4 gives
   (a) XeO_3
   (b) $XeOF_2$
   (c) $XeOF_4$
   (d) XeF_2
9. Helium is preferred to be used in balloons instead of hydrogen because it is
   (a) incombustible
   (b) lighter than hydrogen
   (c) more abundant than hydrogen
   (d) non polarizable
10. The increasing order of reducing power of the halogen acids is
   (a) HF < HCl < HBr < HI
   (b) HI < HBr < HCl < HF
   (c) HBr < HCl < HF < HI
   (d) HCl < HBr < HF < HI

Very Short Questions-

1. Write the elements of group 15?
2. Write chemical name & formulae of
   a) Chile saltpetre
   b) Indian saltpetre
3. What is special about the valence configuration of Group 15?
4. The atomic radii increases considerably from N to P but very little increase is observed from As to Bi. why?
5. Give reason for the following- the first ionization enthalpy of 15th group elements is higher than 16th group elements?

6. How does metallic character vary down the 15 group & why?
7. What are the common oxidation states of this group?
8. What is the maximum covalence shown by N
9. Bi (v) is a stronger oxidizing agent than Bi (III). Why?
10. Give an example showing disproportionation of oxidation state of nitrogen?

Short Questions

1. Write the various steps for preparation of sulphuric acid by contact process?
2. Name different sulphates formed by sulphuric acid?
3. Why are pentahalides more covalent than trihalides?
4. Why is BiH_3 the strongest reducing agent amongst all the hydrides of Group 15 elements?
5. Why is N_2 less reactive at room temperature?
6. How does ammonia react with a solution of Cu^{2+}?
7. What is the covalence of nitrogen in N_2O_5?
8. What happens when white phosphorus is heated with concentrated NaOH solution in an inert atmosphere of CO_2?
9. Write a balanced equation for the hydrolytic reaction of PCl_5 in heavy water.
10. What happens when PCl_5 is heated?

Long Questions

1. Give reasons: -
   (a) Oxygen molecule is diatomic whereas sulphur molecule is polyatomic.
   (b) The most common oxidation state of oxygen is -2.
   (c) H_2O is liquid whereas H_2S is gas at room temperature.
   (d) The increasing order of acidic character in 16th group hydrides is $H_2O < H_2Se < H_2Te$.
   (e) SF_6 is exceptionally stable, SH_6 does not exist.
2. Discuss the different types of oxides.
3. Bond angle in PH_4^+ is higher than that in PH_3. Why?
4. Comment on the nature of two S-O bonds formed in SO_2 molecule. Are the two S-O bonds in this molecule equal?
5. Discuss the general characteristics of Group 15 elements with reference to their electronic configuration, oxidation state, atomic size, ionisation enthalpy and electronegativity.
6. Discuss the trends in chemical reactivity of group 15 elements.
7. Write main differences between the properties of white phosphorus and red phosphorus.
8. Describe the manufacture of H_2SO_4 by contact process?
9. How is SO_2 an air pollutant?

Assertion and Reason Questions-

1. In these questions, a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following choices.

a) Assertion and reason both are correct statements and reason is correct explanation for assertion.
b) Assertion and reason both are correct statements but reason is not correct explanation for assertion.
c) Assertion is correct statement but reason is wrong statement.
d) Assertion is wrong statement but reason is correct statement.

Assertion: Caro's acid has S atom in +6 oxidation state.

Reason: Caro's acid contains one peroxo O_2^2 – group.

2. In these questions, a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following choices.

a) Assertion and reason both are correct statements and reason is correct explanation for assertion.
b) Assertion and reason both are correct statements but reason is not correct explanation for assertion.
c) Assertion is correct statement but reason is wrong statement.
d) Assertion is wrong statement but reason is correct statement.

Assertion: HOF bond angle in HFO is higher than HOCl bond angle in HClO.

Reason: Oxygen is more electronegative than all halogens except fluorine.

Case Study Questions-

1. Read the passage given below and answer the following questions:

Chlorine is a greenish yellow gas with pungent and suffocating odour. With dry slaked lime, it gives bleaching powder. Bleaching powder is a mixture of calcium hypochlorite and basic calcium chloride:

$[Ca(OCl)_2 \cdot CaCl_2 \cdot Ca(OH)_2 \cdot 2H_2O]$.

The amount of chlorine obtained from a sample of bleaching powder by the treatment with excess of dilute acids or CO_2 is called available chlorine. Chlorine is a powerful bleaching agent. Bleaching effect of chlorine is permanent.

The following questions are multiple choice questions. Choose the most appropriate answer:

(i) Chlorine gas reacts with ____ to form bleaching powder.

a) $Ca(OH)_2$

b) $CaCl_2$

c) $CaSO_4$

d) dry CaO

(ii) Chlorine reacts with cold and dilute alkali to form:

a) Chloride

b) Hypochlorite

c) Chlorate

d) Both (a) and (b)

(iii) Which of the following is produced on the reaction of bleaching powder with a few drops of cone. HCl?

a) Hypochlorous acid

b) Oxygen

c) Chlorine

d) Calcium oxide

(iv) Chlorine is used as a bleaching agent. The bleaching action is due to.

a) Oxidation

b) Chlorination

c) Hydrogenation

d) Reduction

(v) Bleaching powder contains a salt of an oxoacid as one of its components. The anhydride of that oxoacid is:

a) Cl_2O

b) Cl_2O_7

c) ClO_2

d) Cl_2O_6

2. Read the passage given below and answer the following questions:

Noble gases are inert gases with general electronic configuration of ns^2np^6. These are monoatomic, colourless, odourless and tasteless gases. The first compound of noble gases was obtained by the reaction of Xe with PtF_6. A large number of compounds of Xe and fluorine have been prepared till now. The structure of these compounds can be explained on the basis of VSEPR theory as well as concept of hybridisation. The compounds of krypton are fewer. Only the difluoride of krypton (KrF_2) has been studied in detail. Compounds of radon have not isolated but only identified by radio tracer technique. However, no true compounds of helium, neon or argon are yet known.

The following questions are multiple choice questions. Choose the most appropriate answer:

(i) The formula of the compound when Xe and PtF_6 are mixed, is:

a) XeF_6

b) XeF_4

c) Xe_2PtF_6

d) $Xe^+[PtF_6]^-$

(ii) The shape and hybridisation of some xenon oxy-fluoride and fluoride compounds are given below. Find the incorrect one.

a) $XeOF_2$ - T-shape - sy^3d

b) $XeOF_4$ - square pyramidal - sp^3d^2

c) XeF_2 - linear - sp^3d

d) XeF_6 - square planar - dsp^2

(iii) Which of the following is not formed by Xe?

a) XeF_5

b) XeF

c) XeF_3

d) All of these.

(iv) The number oflone pairs and bond pairs of electrons around Xe in $XeOF_4$ respectively are,
  a) 0 and 5
  b) 1 and 5
  c) 1 and 4
  d) 2 and 3

(v) Which of the following compounds has more than one lone pair of electrons around central atom?
  a) XeO_3
  b) XeF_2
  c) $XeOF_4$
  d) XeO_2F_2

Answer Key

MCQ Answers-

1. Answer: b
2. Answer: b
3. Answer: b
4. Answer: b
5. Answer: b
6. Answer: a
7. Answer: d
8. Answer: a
9. Answer: a

Very Short Answers-

1. **Ans.** The elements of group 15 are Nitrogen (N), Phosphorous (P) , Arsenic (As) ,

   Antimony (Sb) and Bismuth (Bi).

2. **Ans.** (a) Chile saltpetre – Sodium nitrate – $NaNO_3$
   (b) Indian saltpetre – Potassium nitrate – KNO_3

3. **Ans.** The valence configuration of 15 group is ns^2np^3 the s-orbital is completely filled, and p-orbital is half filled. This half-filled orbital gives extra stability to elements of this group.

4. **Ans.** There is a considerable increase in size from N to P as expected but due to the presence of completely filled d- orbitals which have very poor shielding effects, the increase in size is very little from As to Bi.

5. **Ans.** Due to extra stability of half-filled configuration, the first Ionisation enthalpy of 15th group elements is higher than 16th group configuration ns^2np^3 .

6. **Ans.** The metallic character increases down the group due to decrease in ionization enthalpy and increase in size of atom.

7. **Ans.** The common oxidation states of the group are -3, +3 & +5.

8. **Ans.** Nitrogen shows a maximum covalence of +4 because only four orbitals, one S and three P-orbitals are available for bonding in Nitrogen.

9. **Ans.** Bi is more stable in +3 oxidation state in comparison to +5 due to inert pair effect therefore Bi (v) has a strong tendency to act as oxidizing agent.

10. **Ans.**

$$\underset{+3}{3HNO_2} \rightarrow \underset{+5}{HNO_3} + H_2O + \underset{+2}{2NO}$$

Here Nitrogen is getting oxidized to a higher oxidation state as well as reduced to a lower oxidation state.

Short Answers-

1. Contact process for sulphuric acid: -

   Step 1: Burning of sulphur in air to give SO_2. $S + O_2SO_2$.

   Step 2: Conversion of SO_2 to SO_3 by reacting it with oxygen in presence of V_2O_5.

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

   Step 3: Absorption of SO_3 in H_2SO_4 to give of oleum ($H_2S_2O_7$)

$$SO_3 + H_2SO_4 \rightarrow H_2S_2O_7\,(oleum)$$

   Step 4: Dilution of oleum with water to get H_2SO_4 of desired concentration.

$$H_2S_2O_7 + H_2O \rightarrow 2H_2SO_4$$

2. The two type of sulphates are –

   (i) Normal sulphate eg. Na_2SO_4, $CuSO_4$

   (ii) acid sulphate eg. Na_2HSO_4.

3. In pentahalides, the oxidation state is +5 and in trihalides, the oxidation state is +3. Since the metal ion with a high charge has more polarizing power, pentahalides are more covalent than trihalides.

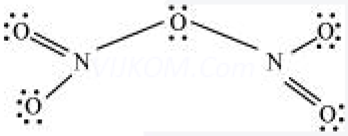
4. As we move down a group, the atomic size increases and the stability of the hydrides of group 15 elements decreases. Since the stability of hydrides decreases on moving from NH_3 to BiH_3, the reducing character of the hydrides increases on moving from NH_3 to BiH_3.

5. The two N atoms in N_2 are bonded to each other by very strong triple covalent bonds. The bond dissociation energy of this bond is very high. As a result, N_2 is less reactive at room temperature.

6. NH_3 acts as a Lewis base. It donates its electron pair and forms a linkage with metal ion.

$$\underset{\text{Blue}}{Cu^{2+}_{(aq)}} + 4NH_{3(aq)} \leftrightarrow \underset{\text{Deep Blue}}{\left[Cu(NH_3)_4\right]^{2+}_{(aq)}}$$

7.



From the structure of N_2O_5, it is evident that the covalence of nitrogen is 4.

8. White phosphorous dissolves in boiling NaOH solution (in a CO_2 atmosphere) to give phosphine, PH_3.

$$PH_3 . P_4 + 3NaOH + 3H_2O \rightarrow \underset{\text{Phosphine}}{PH_3} + \underset{\text{Sodium hypophosphite}}{3NaH_2PO_2}$$

9. All the bonds that are present in PCl_5 are not similar. It has three equatorial and two axial bonds. The equatorial bonds are stronger are stronger than the axial ones. Therefore, when PCl_5 is heated strongly, it decomposes to form PCl_5.

10. $PCl_5 + D_2O \rightarrow POCl_3 + 2DCl_2$

$POCl_3 + 3D_2O \rightarrow D_3PO_4 + 3DCl$

Therefore, the net reaction can be written as $PCl_5 + 4D_2O \rightarrow D_3PO_4 + 5DCl$

Long Answers

1. (a) Oxygen being small in size forms effective and strong p^{π}-p^{π} bonds with other oxygen atom. Therefore, oxygen molecule is diatomic and discrete whereas Sulphur due to its larger size, its orbitals cannot overlap effectively to form p^{π}-p^{π} bonds & completes valency by forming σ bonds with many sulphur, atom. Therefore, sulphur molecule is polyatomic solid.

(b) Since oxygen is highly electronegative, it has little tendency to give electrons. Therefore, its most common oxidation state is -2.

(c) H_2O is liquid at room temperature due to presence of intermolecular Hydrogen bonding which is absent in H_2S.

(d) As we move down the group, the size of atom increases this make the bond of the element with hydrogen weak. Due to weaker bonds, the bond dissociation enthalpy decreases making the molecule more acidic. Therefore, the order of acidic strength is.

$H_2O < H_2S < H_2Se < H_2Te$

(e) SF_6 is exceptionally stable due to steric reasons. Hydrogen being electropositive or less electronegative than fluorine cannot make the s- electrons of sulphur to participate in bonding. Therefore SF_6 does not exist.

2. A binary compound of oxygen with another element is called oxide. Oxides can be simple or mixed. Simple oxides can be classified as acidic, basic Amphoteric or neutral.

An oxide that combines with water to give an acid is termed acidic oxide e.g. CO_2, SO_2 etc.

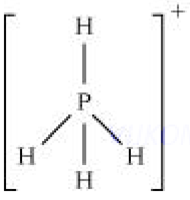
An oxide that combines with water to give a base is called basic oxide e.g. Na_2O, CaO, BaO etc.

An **oxide** that shows characteristics of both acids and bases is Amphoteric oxide e.g. Al_2O_3.

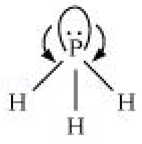
An oxide that shows characteristic of neither acid nor base is called neutral oxide e.g. CO, NO and N_2O.

3. In PH_3, P is sp_3 hybridized. Three orbitals are involved in bonding with three hydrogen atoms and the fourth one contains a lone pair. As lone pair-bond pair repulsion is stronger than bond pair-bond pair repulsion, the tetrahedral shape associated with *sp*3bonding is changed to pyramidal. PH_3 combines with a proton to form PH^+_4 in which the lone pair is absent. Due to the absence of lone pair in PH^+_4, there is no lone pair-

bond pair repulsion. Hence, the bond angle in PH^+_4 is higher than the bond angle in PH_3.



PH_4^+

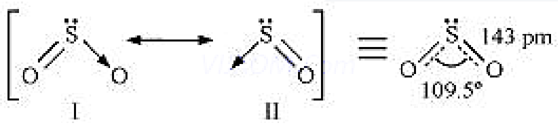


PH_3

Concept insite: the long pair-bond pair repulsion is more than bond pair-bond pair repulsion.

4. The electronic configuration of S is $1s^2 2s^2 2p^6 3s^2 3p^4$.

During the formation of



SO_2, one electron from 3*p* orbital goes to the 3*d* orbital and S undergoes sp^2 hybridization. Two of these orbitals form sigma bonds with two oxygen atoms and the third contains a lone pair. *p*-orbital and *d*-orbital contain an unpaired electron each. One of these electrons forms $p^\pi - p^\pi$ bond with one oxygen atom and the other forms $p^\pi : p^\pi$ bond with the other oxygen. This is the reason SO_2 has a bent structure. Also, it is a resonance hybrid of structures I and II. Both S-O bonds are equal in length (143 pm) and have a multiple bond character.

5. General trends in group15 elements

(i) **Electronic configuration**: All the elements in group 15 have 5 valence electrons. Their general electronic configuration is $ns^2 np^3$.

(ii) **Oxidation states:** All these elements have 5 valence electrons and require three more electrons to complete their octets. However, gaining electrons is very difficult as the nucleus will have to attract three more electrons. This can take place only with nitrogen as it is the smallest in size and the distance between the nucleus and the valence shell is relatively small. The remaining elements of this group show a formal oxidation state of -3 in their covalent compounds. In addition to the -3 state, N and P also show -1 and -2 oxidation states. All the elements present in this group show +3 and +5 oxidation states. However, the stability of +5 oxidation state decreases down a group, whereas the stability of +3 oxidation state increases. This happens because of the inert pair effect.

(iii) **Ionization energy and electronegativity** First ionization decreases on moving down a group. This is because of increasing atomic sizes. As we move down a group, electronegativity decreases, owing to an increase in size.

(iv) **Atomic size:** On moving down a group, the atomic size increases. This increase in the atomic size is attributed to an increase in the number of shells.

6. **General trends in chemical properties of group – 15**

(i) **Reactivity towards hydrogen:** The elements of group 15 react with hydrogen to form hydrides of type EH_3, where E = N, P, As, Sb, or Bi. The stability of hydrides decreases on moving down from NH_3 to BiH_3 .

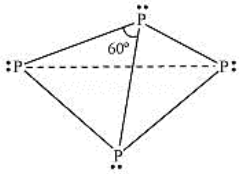
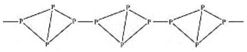
(ii) **Reactivity towards oxygen:** The elements of group 15 form two types of oxides: E_2O_3 and E_2O_5, where E = N, P, As, Sb, or Bi. The oxide with the element in the higher oxidation state is more acidic than the other. However, the acidic character decreases on moving down a group.

(iii) **Reactivity towards halogens:** The group 15 elements react with halogens to form two series of salts: EX_3 and EX_5. However, nitrogen does not form NX_5 as it lacks the *d*-orbital. All trihalides (except NX_3) are stable.

(iv) **Reactivity towards metals:** The group 15 elements react with metals to form binary compounds in which metals exhibit -3 oxidation states.

7.

White phosphorus	**Red Phosphorus**
It is a soft and waxy solid. It possesses a garlic smell.	It is a hard and crystalline solid, without any smell.
It is poisonous.	It is non-poisonous.

It is insoluble in water but soluble in carbon disulphide.	It is insoluble in both water and carbon disulphide.
It undergoes spontaneous combustion in air.	It is relatively less reactive.
In both solid and vapour states, it exists as a P4 molecule.  	It exists as a chain of tetrahedral P4 units. 

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

The elements of group 16 are collectively called chalcogens.

(i) Elements of group 16 have six valence electrons each. The general electronic configuration of these elements is $ns^2\ np^4$, where n varies from 2 to 6.

(ii) **Oxidation state:** As these elements have six valence electrons ($ns^2\ np^4$), they should display an oxidation state of -2. However, only oxygen predominantly shows the oxidation state of -2 owing to its high electronegativity. It also exhibits the oxidation state of -1 (H_2O_2), zero (O_2) and +2 (OF_2). However, the stability of the -2 oxidation state decreases on moving down a group due to a decrease in the electronegativity of the elements. The heavier elements of the group show an oxidation state of +2, +4, and +6 due to the availability of *d*-orbitals.

(iii) **Formation of hydrides:** These elements form hydrides of formula H_2E, where E = O, S, Se, Te, PO. Oxygen and sulphur also form hydrides of type H_2E_2. These hydrides are quite volatile in nature.

9. Sulphuric acid is manufactured by the contact process. It involves the following steps:

Step (i): Sulphur or sulphide ores are burnt in air to form SO_2.

Step (ii): By a reaction with oxygen, SO_2 is converted into SO_3 in the presence of V_2O_5 as a catalyst.

$$2SO_{2(g)} + O_2 \xrightarrow{V_2O_5} 2SO_{3(g)}$$

Step (iii): SO_3 produced is absorbed on H_2SO_4 to give $H_2S_2O_7$ (oleum).

$$SO_3 + H_2SO_4 \rightarrow H_2S_2O_7$$

This oleum is then diluted to obtain H_2SO_4 of the desired concentration.

In practice, the plant is operated at 2 bar (pressure) and 720 K (temperature). The sulphuric acid thus obtained is 96-98% pure.

10. Sulphur dioxide causes harm to the environment in many ways:

1. It combines with water vapour present in the atmosphere to form sulphuric acid. This causes acid rain. Acid rain damages soil, plants, and buildings, especially those made of marble.

2. Even in very low concentrations, SO_2 causes irritation in the respiratory tract. It causes throat and eye irritation and can also affect the larynx to cause breathlessness.

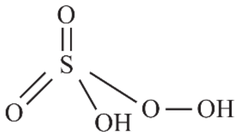
3. It is extremely harmful to plants. Plants exposed to sulphur dioxide for a long time lose colour from their leaves. This condition is known as chlorosis. This happens because the formation of chlorophyll is affected by the presence of sulphur dioxide.

Assertion and Reason Answers-

1. (a) Assertion and reason both are correct statements and reason is correct explanation for assertion.

Explanation:

This can be explained through structure of caro's acid (peroxomonosulphuric acid).



Oxidation no. of S = x, oxidation no. of H = +1,

Oxidation no. of O in peroxo linkage = -1 (each),

Oxidation no. of other oxygen atoms = -2 (each).

2 + x - 6 - 2 = 0 or x = +6.

2. (d) Assertion is wrong statement but reason is correct statement.

Explanation:

HOF bond angle in HFO is lesser than that of HOCl bond angle in HClO. Oxygen is more electronegative than all halogens except fluorine.

Case Study Answers-

1. Answer :

(i) (a) $Ca(OH)_2$

(ii) (d) Both (a) and (b)

Explanation:

In cold, chlorine reacts with dilute alkalies to form chlorides and hypochlorites.

(iii) (c) Chlorine

(iv) (a) Oxidation

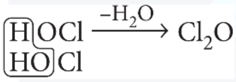
Explanation:

$Cl_2 + H_2O \rightarrow 2HCl + [O]$

(v) (a) Cl_2O

Explanation:

Bleaching powder contains OCl^- ion, hence the oxoacid is HOCl. Anhydride of HOCl is Cl_2O.



$$\begin{matrix}\boxed{H}OCl \\ \boxed{HO}Cl\end{matrix} \xrightarrow{-H_2O} Cl_2O$$

2. Answer :

(i) (d) $Xe^+[PtF_6]^-$

(ii) (d) XeF_6 - square planar - dsp^2

Explanation:

XeF_6 has sp^3d^3 hybridisation and distorted octahedral shape.

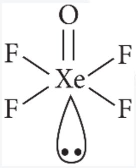
(iii) (d) All of these.

Explanation:

Xe has completely filled 5p-orbital. As a result, when it undergoes bonding with an odd number (1, 3 or 5) of fluorine atoms, it leaves behind one unpaired electron. This causes the molecule to become unstable. As a result, XeF, XeF_3 and XeF_5 do not exist.

(iv) (b) 1 and 5

Explanation:



(v) (b) XeF_2

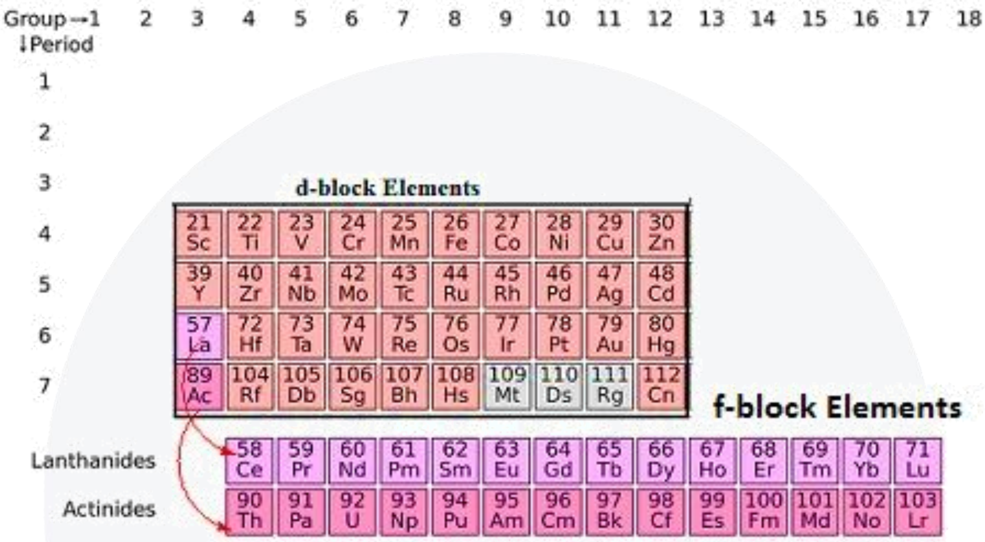
Explanation: XeF_2 has 3 lone pairs on Xe atom.

◆ ◆

The d and f-Block Elements

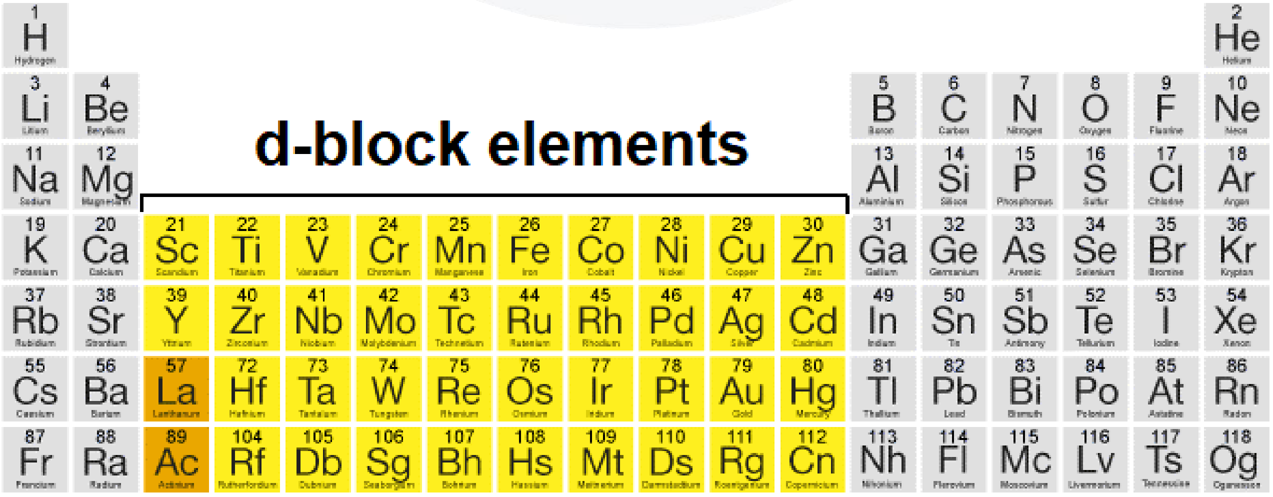
5

Introduction to d-Blocl Elements



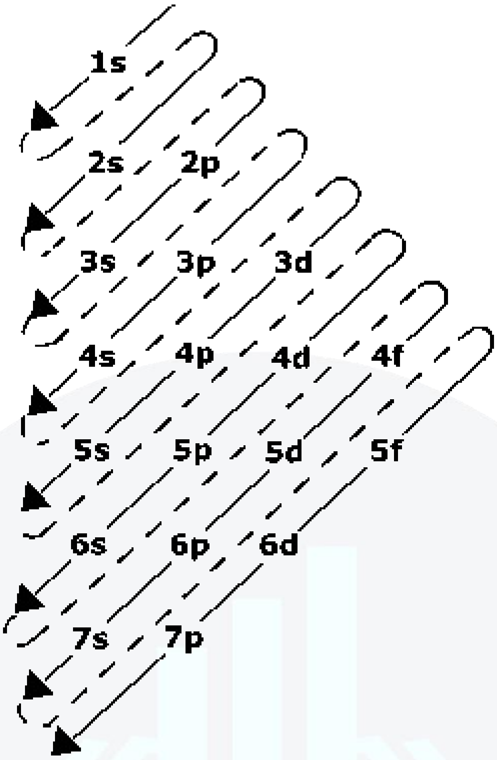
- In the periodic table the d block consist of the elements of group 3 to 12.
- The d orbital of the d-block elements in four periods are filled.
- The three series of the transitionmetals are 3d series from Sc to Zn, 4d series from Y to Cd and 5dseries from La
- to Hg.
- The fourth 6dseries begins from Ac and is incomplete till now.

Position of d-block in periodic table



- The d-block elements are found in the middle section of s- and p- block elements in the periodic elements.
- This lead to its name ‘transition’ due to its position between s- and p- block elements.

Electronic Configurations of the d-Block Elements

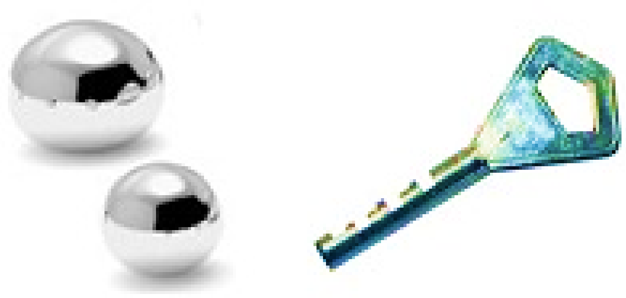


- The electronic configuration of d-block elements is$(n-1)\ d^{1-10}\ ns^{1-2}$. They have two incomplete outershells.
- Where (n–1) = Inner d orbitals having electrons from 1-10.
- ns = Outermost orbital may have one or two
- $(n-1)\ d^{10}\ n\ s^2$ represents the electronic configurations of Zn, Cd and Hg.
- They exhibit variable valency that differ by units of one.

Element	Symbol	Electronic Configuration
Scandium	Sc	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^1\ 4s^2$
Titanium	Ti	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^2\ 4s^2$
Vanadium	V	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^3\ 4s^2$
Chromium	Cr	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^5\ 4s^2$
Manganese	Mn	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^5\ 4s^2$
Iron	Fe	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^6\ 4s^2$
Cobalt	Co	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^7\ 4s^2$
Nickel	Ni	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^8\ 4s^2$
Copper	Cu	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^1$
Zinc	Zn	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^2$

Physical Properties

- The transition metals are hard and tough. They have low volatility butZn, Cd and Hg are an exception.



- They have high melting and boilingpoints due to the greaterquantity of electrons from (n-1) d along with the ns electrons metallic

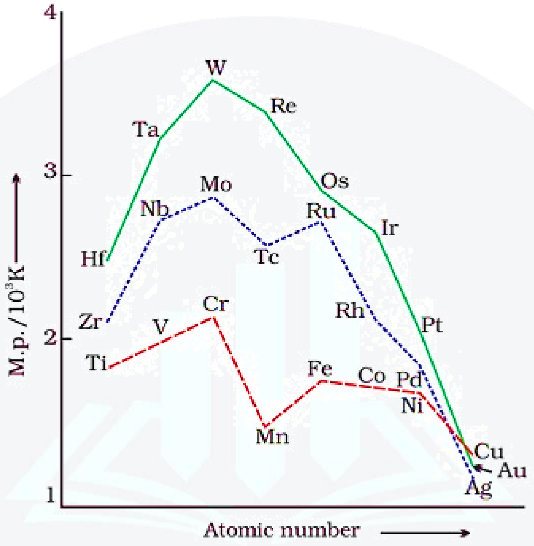


Fig. The trends in melting point of d-block elements.

- Metals possessing high boiling point are noble in their
- The metals belonging to second and third series have greater enthalpies of atomisation than the elements belonging to first series.

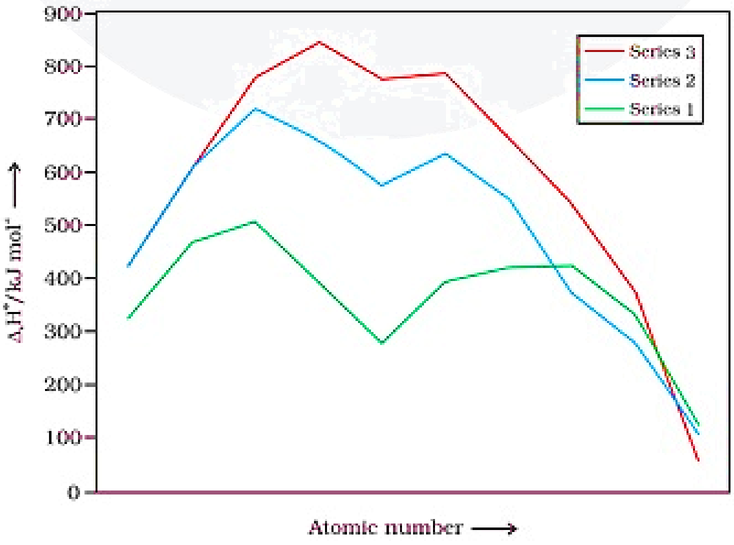


Fig. Enthalpies of atomisation

Metallic characteristics:

- All transition metals exhibit metallic character.

- They are good conductors of heat and electricity.

Fig. Metal is used at the tip of the plug that is inserted into the socket

- They are hard and tough.
- Being metal they exhibit the property of malleability, ductility and sonorousity.

Fig. Aluminium is beaten into thin sheets to make aluminium foil used to pack food (Malleability)

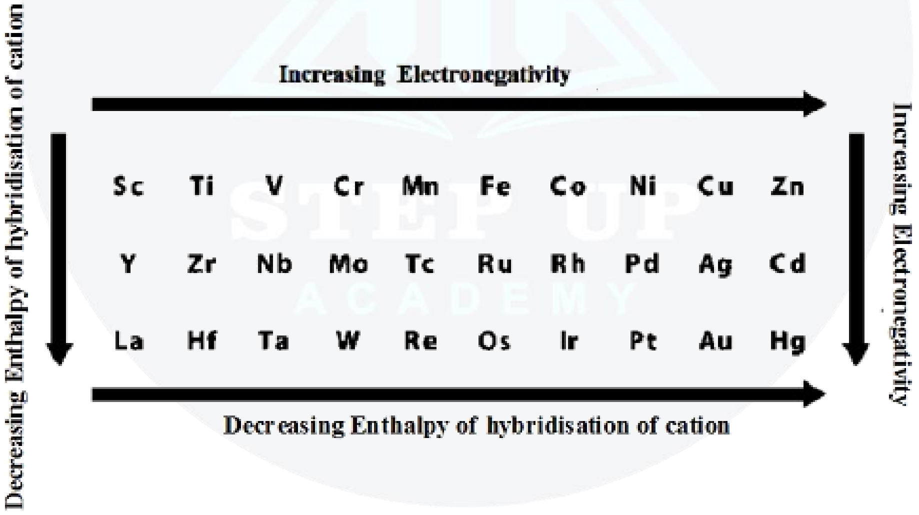
Fig. bells in temples are made of metal that when struck against hard surface produces sound (Sonorousity)

Fig. Metals are drawn into wires (Ductility)

- They form alloys by combining with some other metals.
- They are found to exist in face- centered cubic (fcc) structure, hexagonal close-packed (hcp) structure and body-centered cubic (bcc) structure.
- The transition elements exhibit covalent as well as metallic bonding within the atoms.

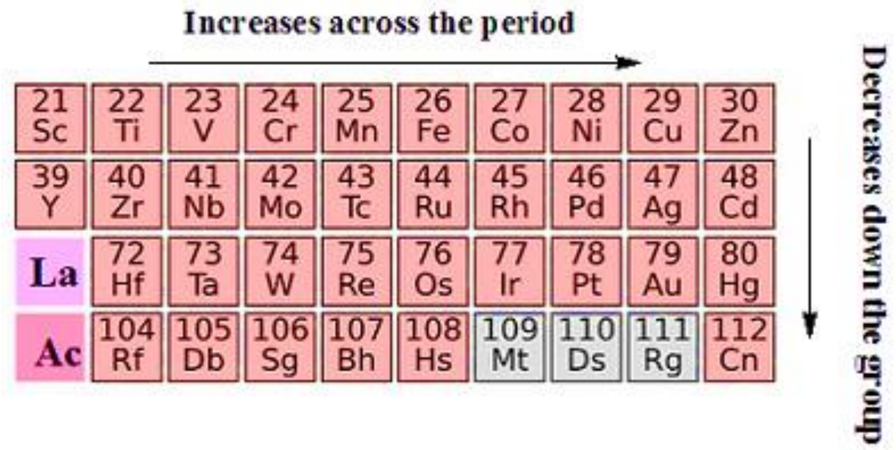
Atomic radii

- The atomic radii of the elements of 3d-series decreases as the atomic number increases.
- The atomic radii increase from 3d to 4d, the atomic radii of the 4d and 5d transition series are very close due to lanthanoid contraction. For example, Zirconium and Hafnium.
- This decrease in the metallic radius due to increase in the atomic mass leads to an increase in the density of elements. Consequently the density increases from titanium to copper.



Ionisation Enthalpies

- Transition elements have small size which results in high ionization energy.
- They exhibit less electro positivity than the s-block elements due to their ionization potentials lying between S and P block elements.
- They form covalent compounds.
- The d-block elements exhibit an increase in the ionization potentials from left to right due to the screening effect of the new electrons added into the (n-1) d subshell.
- The first transition series exhibit an increase in the second ionisation energies with the increase in atomic number due to stable electronic configuration.
- Ionization energy decreases down the group.
- Ionization energy increases across the period.



21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn
39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd
La	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg
Ac	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Cn

Oxidation States

- The number allotted to an element in a compound representing the number of electrons lost or gained by an atom of the element of the compound is called oxidation state.

  For example, the electron configuration of copper is [Ar] $3d^{10}$ $4s^1$. It attains noble gas configuration by losing one electron. The energy required to lose one more electron is very less and hence copper loses 2 electrons and forms Cu^{2+} ion. Therefore copper exhibits +1 and +2 oxidation state. But +2 oxidation states are more common.

  It forms compounds like $CuCl_2$ and also with oxygen like CuO. In both the cases the oxidation state of Cu is +2.
- Transition elements exhibit varying oxidation states due to the minor energy difference between ns and (n - 1) d orbitals.
- Along with ns electrons, (n -1) d electrons takes part in bonding. But due to the availability of few electrons for bonding Scandium does not show variable oxidation states.
- Due to presence of more d electrons, zinc has less orbital available for bonding and hence does not exhibit varying oxidation state.
- Among d-block elements the elements belonging to 8th group exhibit maximum oxidation state.
- Among the elements of 3d –series Manganese belonging to 7th group exhibits maximum oxidation state.
- Among the elements of 4d-Series Ruthenium belonging to 8th group exhibits maximum oxidation state.
- Among the elements of 5d-Series Osmium belonging to 8th group exhibits maximum oxidation state.
- The oxidation number of a free element is always 0.
- Oxidation number of (group I) elements like Li, Na, K, Rb, Cs is +1.
- Oxidation number of (group II) elements like Be, Mg, Ca, Sr, Ba is +2.
- Oxidation number of oxygen is -2.
- For example, oxidation state of Phosphorous in the compound HPO32- can be calculated by the following method:

  Oxidation state of H = +1

  Oxidation state of O = -2

  Oxidation state of O_3 = 3(-2) [Since it has 3 atoms of oxygen.]

  Overall oxidation state of the compound = -2

  Let P represent the oxidation state of Phosphorous.

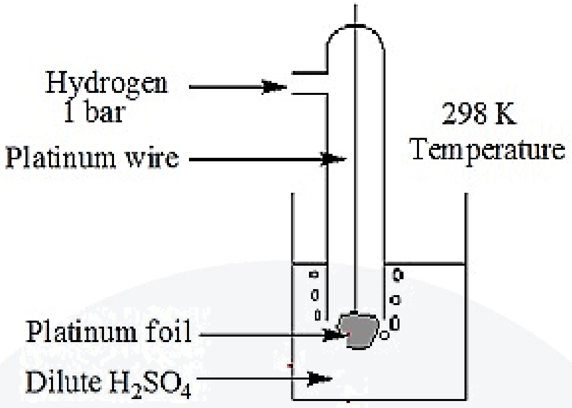
  Therefore,

  HPO_3^{2-} = +1+P+3(-2) = -2
- P = +3

Standard hydrogen electrode

- The electrode is connected to a standard hydrogen electrode (SHE) to constitute a cell
- It consists of a platinum electrodecoated with a layer of platinum black.

$$H^+ (aq) + e^- \rightarrow \frac{1}{2} H_2(g)$$



- The electrode is immersed in an acidicsolution and the pure hydrogen gas is bubbled through it.
- Theconcentration of the reduced form and the oxidized form of hydrogen issustained at unity with following conditions:
- Pressure of hydrogen gas = 1 bar
- Concentration of hydrogen ion in the solution = 1 molar

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

  $E_{cell} = E_{cathode} - 0 = E_{cathode}$
- The measured Emf of the cell:

  Pt| H_2 (1 bar)| H^+ (1M) || Cu^{2+} (1M)| Cu is 0.34 V.

  The positive value of the standard electrode potential signifies the easy reduction of Cu^{2+} ions than H^+ ions.
- The measured Emf of the cell

  Pt| H_2 (1 bar)| H^+ (1M) || Zn^{2+} (1M)| Zn is -0.76 V.

  The negative value of the standard electrode potential signifies that the hydrogen ions oxidizes the zinc (or it can be said that zinc can reduce hydrogen ions).
- An electrode with standard electrode potential greater than zero is stable in its reduced form compared tohydrogen gas.
- Whereas an electrode with negative standard electrode potential is less stable in its reduced form compared to hydrogen gas.
- This decreases the standard electrodepotential which in turn decreases the oxidizing power ofthe specific electrode on the left and increases the reducing power of the electrodeto the right of the reaction.

Magnetic Properties

Substances, depending on their behaviour in an external magnetic field, are classified into 2 types:

Paramagnetic

- They are weakly attracted on application of magnetic field due to presence of one or more unpaired electrons that gets attracted by the magnetic field.
- Application of a magnetic field magnetizes the paramagnetic substances in the same direction but lose their magnetism in the absence of magnetic field.
- O_2, Cu^{2+}, Fe^{3+}, Cr^{3+} are some examples of such substances.

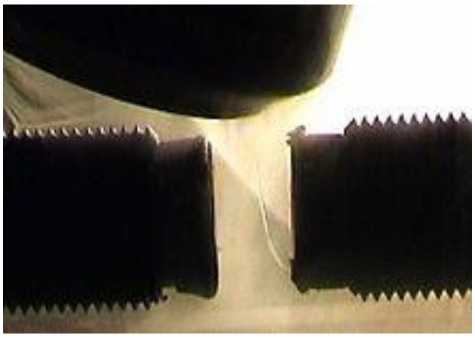
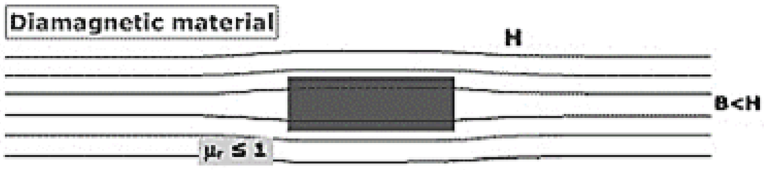


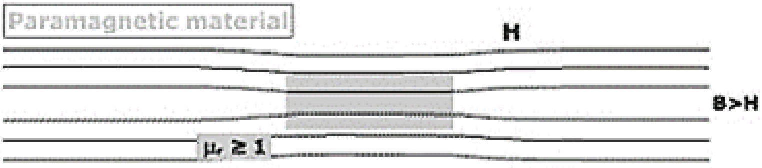
Fig. A trickle of liquid oxygen is deflected by a magnetic field, illustrating its paramagnetism.

Diamagnetic

- They are weakly repelled by a magnetic field due to the absence of unpaired electrons.
- They are weakly magnetized on application of magnetic field in opposite direction.
- Pairing of electrons cancels out their magnetic moments and they lose their magnetic character.
- For example, H_2O, NaCl and C_6H_6 are some examples of such substances.

In 3d series the orbital angular momentum of the electrons of the elements is less due to which they exhibit less contribution.





The magnetic moment for these elements is calculated using the spin only formula

$$\mu = \sqrt{(n(n+2))}$$

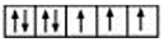
Where n = number of unpaired electrons

μ = magnetic moment in units of Bohr Magneton (BM).

PROBLEM: Calculate the 'spin only' magnetic moment of M2+(aq) ion (Z = 27).

SOLUTION: Z = 27 = [Ar] $3d^7\ 4s^2$

M^{2+} = [Ar] $3d^7$

$3d^7 =$ 

This means that it has 3 unpaired electrons.

$$n = 3$$

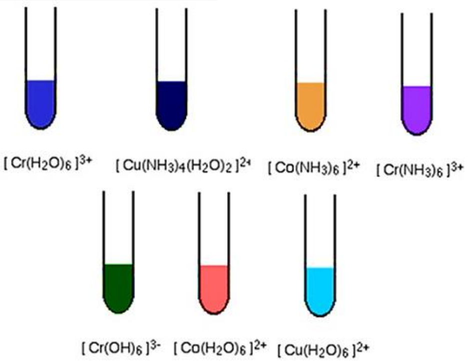
$$\Rightarrow \sqrt{n(n+2)} = \mu$$

$$\Rightarrow \sqrt{3(3+2)} = \mu$$

$$\Rightarrow \sqrt{15} = \mu$$

$$\mu \approx 4\,BM$$

Formation of Coloured Ions

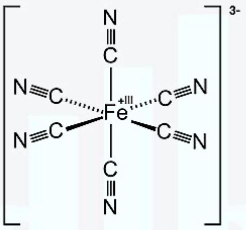


- An electron from a lower energy d orbital is excited to a higher energy d orbital, the energy of excitation corresponds to the frequency of light absorbed.
- This frequency generally lies in the visible
- The colour of the transition metal ions is due to the presence of unpaired or incomplete d-orbitals.
- The absorption of visible light and hence coloured nature of the transition metal cations is due to the promotion of one or more unpaired d-electron from a lower to a higher level within the same d-subshell. This promotion requires small amount of energy available in the visible light.
- Sc^{3+}, Ti^{4+}, Cu^{+} and Zn^{2+} have either entirely empty or entirely filled 3d-orbital, i.e. they do not have any unpaired d-electron, and hence appear colourless.

Configuration	Example	Colour
$3d^0$	Sc^{3+}	colourless
$3d^0$	Ti^{4+}	colourless
$3d^1$	Ti^{3+}	purple
$3d^1$	V^{4+}	blue
$3d^2$	V^{3+}	green
$3d^3$	V^{2+}	violet
$3d^3$	Cr^{3+}	violet
$3d^4$	Mn^{3+}	violet
$3d^4$	Cr^{2+}	blue
$3d^5$	Mn^{2+}	pink
$3d^5$	Fe^{3+}	yellow
$3d^6$	Fe^{2+}	green
$3d^6 3d^7$	$Co^{3+}Co^{2+}$	bluepink
$3d^8$	Ni^{2+}	green
$3d^9$	Cu^{2+}	blue
$3d^{10}$	Zn^{2+}	colourless

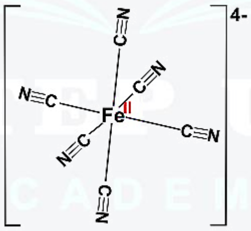
Formation of Complex Compounds

- The cations of transition metals have great tendency to form complexes with several molecules or ions called ligands.
- The bonds involved in the formation of complexes are coordinate and hence the complexes are called coordinate complexes.
- The structure of these complex ions is linear, square, planar, tetrahedral, octahedral depending upon nature of hybridization of metal ions.
- The weak ligand like CO, NO forms complexes only when transition metals are in zero due to the availability of vacant orbitals in the donor atom of the ligand in addition to lone pair.
- The highly electronegative and basic ligand like F-, Cl- can form complexes with transition metals even though there are in high oxidation states due to the presence of small, highly charged or neutral ligands with lone pair of electrons that can form strong sigma bond by donating a lone pair of electrons.
- In a transition series the stability of complexes increases with the rise in atomic number.
- The transition metal atom reveals multiple oxidation state; the higher valent ion forms more stable complexes.
- A few examples are:
- $[Fe\ (CN)6]^{3-}$



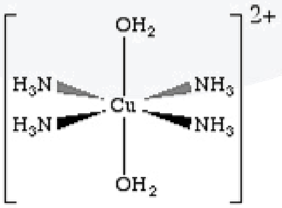
Octahedral Geometry

- $[Fe(CN)6]^{4-}$



Octahedral Geometry

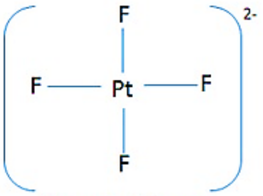
- $[Cu(NH3)4]^{2+}$



Square Planar

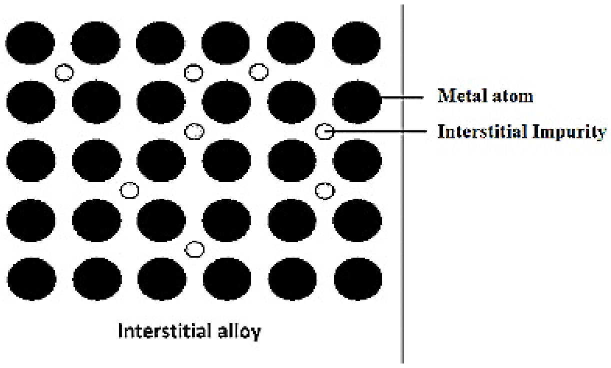
- $[PtCl4]^{2-}$

$[PtF_4]^{2-}$



Square Planar

Formation of Interstitial Compounds



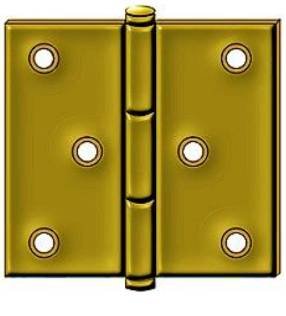
Interstitial alloy

- Transition elements in combination with small atoms like H, B, C, N etc. leads to the formation of interstitial compounds that are non-stoichiometric in composition.

  E.g.: $TiH_{1.3}$, $VH_{0.54}$
- The interstitial compounds so formed are chemically inert having higher melting points as compared to pure metals. These compounds are hard and tough and keeps metallic conductivity.

Alloy Formation

- Alloys are homogeneous mixtures of more than one metal that can displace another metal from the crystal lattice due to their comparable sizes. This leads to the formation of alloys.
- The alloys so formed are hard with high melting points. For example, chromium, vanadium, tungsten, manganese, molybdenum are the ferrous alloys.
- Some other examples are brass (alloy of copper + zinc), stainless steel, bronze (alloy of copper + tin), etc.

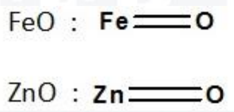


Hinges made of bronze

Medal made of Brass

Non-stoichiometric Compounds

- The compounds in which the there is no conformity in chemical composition with the ideal chemical formula are called non-stoichiometric compounds.
- These compounds are formed due to variable valency in transition metals and also due to the defects arising in solid state.
- The compounds formed with O, S, Se, Te, Fe, Zn etc. are the examples of such compounds.



Preparation of $K_2Cr_2O_7$

Potassium dichromate, ($K_2Cr_2O_7$) is an orange-ish inorganic chemical reagent. In different laboratory or industry it is basically used as an oxidizing agent usually for alcohols.

It can be prepared through the following process:

- At first the fusion of chromite ore $FeCr_2O_4$ with sodium or potassium carbonate in the presence of access of air.

  $4FeCr_2O_4 + 8Na_2CO_3 + 7O_2 \rightarrow 8Na_2CrO_4 + 2FeO_3 + 8CO_2$
- Solution of sodium chromate is first filtered and then acidified with a solution of sulfuric acid which results in an orange sodium dichromate solution $Na_2Cr_2O_7\ 2H_2O$ can be crystallized.

  $2Na_2CrO_4 + 2H^+ \rightarrow Na_2Cr_2O_7 + 2Na^+ + H_2O$
- Sodium dichromate is more soluble than potassium dichromate and therefore it is fused with KCl that leads to the formation of orange crystals of potassium dichromate.

  $Na_2Cr_2O_7 + 2KCl \rightarrow K_2Cr_2O_7 + 2NaCl$
- At pH equal to 4 the dichromates and chromates exists in equilibrium and can be inter convertible.

  $2CrO_4{}^{2-} + 2H^{2+} \rightarrow Cr_2O_7{}^{2-} + H_2O$

  $Cr_2O_7{}^{2-} + 2OH- \rightarrow 2CrO_4{}^{2-} + H_2O$

- The yellow colour of chromate changes to orange coloured dichromate in the presence of acidic medium whereas the dichromate changes into chromate in the presence of basic medium.

  $2CrO_4^{2-} + 2H^+$ --> $2HCrO_4^-$ (Hydrogen chromate)

  $2HCrO^{4-}$ --> $Cr_2O_7^{2-} + H_2O$ Dichromate (orange)
- The chromate ion is tetrahedral and the dichromate ion consists of two tetrahedral sharing at one corner, with Cr-O-Cr bond angle 126 degree.

Properties of Potassium dichromate ($K_2Cr_2O_7$)

Oxidizing properties

Potassium dichromate is a powerful oxidizing-agent in an acidic medium.

$Cr_2O_7{}^{2-} + 14H^+ + 6$ electron --> $2Cr^{3+} + 7H_2O$

It oxidizes iodides to iodine.

$Cr_2O7{}^{2-} + 14H^+ + 6I^-$ --> $2Cr^{3+} + 7H_2O + 3I_2$

It oxidizes ferrous salts to ferric salts.

$Cr_2O_7{}^{2-} + 14H^+ + 6\ Fe2+$ --> $2Cr^{3+} + 7H_2O + 6Fe^{3+}$

It oxidizes stannous salts to stannic salts.

$Cr_2O_7{}^{2-} + 14H^+ + 3Sn^{2+}$ --> $2Cr^{3+} + 7H_2O + 3Sn^{4+}$

It oxidizes H2S to sulphur.

$Cr_2O_7{}^{2-} + 8H^+ + 3H_2S$ --> $2Cr^{3+} + 7H_2O + 3S$

Action of heat

Application of heat leads to the decomposition of Potassium dichromate leading to the formation of potassium chromate, chromic oxide and oxygen.

$4K_2Cr_2O_7$ -Heat-> $4K_2CrO_4 + 2CrO_3 + 3O_2$

Preparation of Pottassium Permanganate ($KMnO_4$)

Pottassium Permanganate ($KMnO_4$) is a dark purple solid consisting of two ions: a potassium ion (K^+) and a permanganate ion ($MnO^{-\ 4}$). It is a strong oxidizing agent and also possess medication properties due to which it is extensively used to clean wounds and in dermatitis.

- Fusion of powdered **Pyrolusite ore** (**MnO_2**) with an alkali metal hydroxide like KOH in the presence of air or an oxidizing agent like KNO_3 leads to the formation of dark green **potassium Manganate** (**K_2MnO_4**) which disproportionate either in a neutral or acidic medium and results in the formation of **potassium permanganate**.

  $2\ MnO_2 + 4\ KOH + O_2$ --> $2K_2MnO_4 + 2H_2O$

  $3\ MnO_4^{2-} + 4H^+$ --> $2MnO_4^- + MnO_2 + 2H_2O$
- Potassium permanganate is commercially prepared by an alkaline oxidative fusion of Pyrolusite ore (MnO_2) and again by the electrolytic oxidation of manganate (4) ion.

  $2\ MnO_2 + 4KOH + O_2$ --> $2K_2MnO_4 + 2H_2O$

  MnO_4^{2-} + (electrolytic oxidation) --> $MnO_4^- + e^-$

Introduction to f-Block Elements

- These elements are also called inner transition elements because the last electron enters (n−2) f-orbital, i.e. inner to the penultimate energy level and forms a transition series.
- The general electronic configuration of these elements can be given as

  Hence, they have three incomplete shells, viz. (n−2), (n−1) and nth.

Classification of f-block elements

- ✓ **Lanthanoids:**
  - They are called Lanthanoids because they come immediately after Lanthanum.
  - They are also called 4f-block elements or first inner transition series elements or lanthanides or lanthanons.

✓ **Actinoids:**

- They are called Actinoids because they come immediately after Actinium.
- They are also called 5f-block elements or second inner transition series elements oractinides or actinons.

Important Points

Though Lanthanum is a d-block element, it is included in the lanthanoid series because it closely resembles lanthanoids.

Like Lanthanum, Actinium is also included in the actinoid series.

Study of lanthanoids is comparatively easier because they show only one stable oxidation state.

Chemistry of actinoids is more complicated because they show a wide range of oxidation states and most of them are radioactive.

✓ **The Lanthanoids:**

❖ **Electronic Configuration:**

Name of the element	Symbol (Ln)	Atomic No. (Z)	Electronic configuration	Oxidation state	E.C. outside [Xe] core		
					Ln2+	Ln3+	Ln4+
Lanthanum	La	57	[Xe] 5d1 6s2	+3	5d1	4f0	
Cerium	Ce	58	[Xe] 4f2 5d0 6s2	+3, +4	4f2	4f1	4f0
Praseodymium	Pr	59	[Xe] 4f3 5d0 6s2	+3,+4	4f3	4f2	4f1
Neodymium	Nd	60	[Xe] 4f4 5d0 6s2	+2, +3, +4	4f4	4f3	4f2
Promethium	Pm	61	[Xe] 4f5 5d0 6s2	+3	4f5	4f4	
Samarium	Sm	62	[Xe] 4f6 5d0 6s2	+2, +3	4f6	4f5	
Europium	Eu	63	[Xe] 4f7 5d0 6s2	+2, +3	4f7	4f6	
Gadolinium	Gd	64	[Xe] 4f7 5d1 6s2	+3	4f7 5d1	4f7	
Terbium	Tb	65	[Xe] 4f9 5d0 6s2	+3, +4	4f9	4f8	4f7
Dysprosium	Dy	66	[Xe] 4f10 5d1 6s2	+3, +4	4f10	4f9	4f8
Holmium	Ho	67	[Xe] 4f11 5d1 6s2	+3	4f11	4f10	
Erbium	Er	68	[Xe] 4f12 5d1 6s2	+3	4f12	4f11	
Thulium	Tm	69	[Xe] 4f13 5d1 6s2	+2, +3	4f13	4f12	
Ytterbium	Yb	70	[Xe] 4f14 5d0 6s2	+2, +3	4f14	4f13	
Lutetium	Lu	71	[Xe] 4f14 5d1 6s2	+3	4f13 5d1	4f14	

- Lanthanoids have the common electronic configuration of 6s2 and electrons occupying 4f levelvariably. The electronic configuration of all the tripositive ions are of the form 4fn (n = 1 –14) with increasing atomic number.
- The electronic configuration of Europium (Z = 63) is 4f7 6s2 and that of Gadolinium (Z = 64) is 4f7 5d1 6s2. This can be explained on the basis of extra stability of the half-filled orbitals in theircores.

- The electronic configuration of Ytterbium (Z = 70) is 4f14 6s2 and that of Lutetium (Z = 71) is4f14 5d1 6s2. This is also explained on the basis of extra stability of the filled orbitals in theircores.

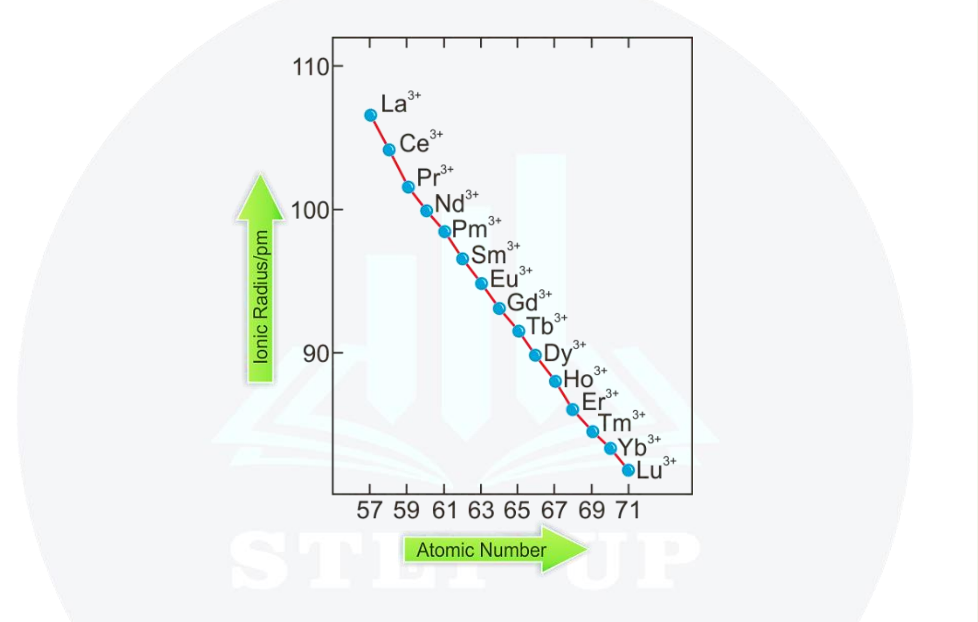
❖ **Oxidation states:**

- The common oxidation state of the lanthanoids is +3.
- The +2 and +4 oxidation states are very less common. These are exhibited by those elementswhich attain a stable electronic configuration of f0, f7 or f14 by losing 2 or 4 electrons.
- Here, each element tries to attain the stable oxidation state by losing or gaining electrons, i.e.

  +3. Hence, Sm2+, Eu2+ and Yb2+ ions in solutions are good reducing agents and aqueoussolutions of Ce4+ and Tb4+ are good oxidising agents.

❖ **Atomic and ionic radii of Lanthanoids:**

- In lanthanoids, if the atomic number increases, atomic and ionic radii decrease from La3+ toLu3+.



Variation of ionic radii of trivalent lanthanoids

- ***Causes of lanthanoid contraction:***
  1. When we move from left to right along the lanthanoid series, the nuclear charge increasesby one unit at each neighbouring element. The new electron is added to the same subshell. So, the attractive force between the electron and nucleus increases, and hence,the size decreases.
  2. When a new electron is added to the f-subshell, the shielding effect of one electron by another is not perfect due to the shape of f-orbitals. Such a shielding cannot balance theeffect of increased nuclear charge. Hence, contraction occurs.
- ***Consequences of lanthanoid contraction:***

  (a) Difficulty in separation of lanthanoids:
    1. Because of the slight difference in ionic radii of lanthanoids, their chemical propertiesare similar. This makes separation of lanthanoids more difficult.
    2. Also, due to the difference in the size of lanthanoids, properties such as solubility,complex ion formation and hydration show differences. This helps separate the individual lanthanoids by the ion exchange method.

(b) Similarity in the size of elements belonging to the same group of the second and third transition series:

1. The size of elements belonging to the second transition series is always greater than that of the elements belonging to the same group of the first transition series. Also, the size of the atom of the third transition series, i.e. after lanthanum, is nearly the same as that of the atom of the element belonging to the same group of the second transition series.
2. Similarity in size of the atoms of the elements belonging to the same group of the 2nd and 3rd transition series is due to the effect of lanthanoid contraction.

(c) Effect on the basic strength of hydroxides:

Because the size of lanthanoid ions decreases from La3+ to Lu3+, the covalent character of the hydroxides increases, and hence, the basic strength decreases. Therefore, La(OH)3 is more basic, while Lu(OH)3 is weakly basic.

❖ **Characteristics of Lanthanoids:**

(a) Silvery appearance and softness:

All lanthanoids are silvery white soft metals and tarnish easily in air. As the atomic number increases, their hardness also increases.

(b) Melting point:

They have a very high-melting point in the range 1000–1200 K except samarium, which has a high melting point of about 1623 K.

(c) Electrical and thermal conductivity:

They have metallic characteristics, and hence, they are good conductors of heat and electricity.

(d) Density:

They have high densities in the range of 6.77–9.74 gcm^{-3}. Density and other properties differ smoothly with increasing atomic number except in Eu and Yb.

(e) Colour:

They are silvery white. Most of the trivalent ions are coloured in solid and in aqueous solution. This is due to f–f transition.

(f) Magnetic behaviour:

All the lanthanoids except La^{3+} and Lu^{3+} show paramagnetism. This property is due to the presence of unpaired electrons in the incomplete 4f subshell.

(g) Ionisation enthalpies:

The first ionisation enthalpies of lanthanoids are about 600 kJ mol^{-1} and the second is about 1200 kJ mol^{-1}. The third ionisation enthalpy is low if it leads to a stable electronic configuration,

i.e. empty, half-filled or completely filled.

(h) Electropositive character:

They are highly electropositive because they possess low ionisation enthalpy.

(i) Standard electrode potential:

The value of their standard electrode potential, i.e. Eo for half-reaction, $M^{3+}(aq) + 3e^- \rightarrow M(s)$, lies in the range −2.2 to −2.4 V. Europium is an exception because its Eo value is −2.0 V.

(j) Reducing agents:

They easily lose electrons; hence, they are good reducing agents.

(k) Complex formation:

Because of their large size and low charge density, they do not have much tendency to form complexes. This tendency of complex formation increases with increasing atomic number.

(l) Chemical behaviour:

The first few elements of the series are more reactive like calcium. As the atomic numberincreases, their behaviour becomes similar to that of aluminium. They show the followingproperties:

- They combine with hydrogen on heating.
- They form carbides when heated with carbon.
- They form halides when burnt with halogens.
- They react with dilute acids to liberate hydrogen gas.
- They form oxides and hydroxides.

❖ **Uses of lanthanoids:**

1. It is mainly used in the production of alloy steels to improve the strength of steel. A well-knownalloy is mischmetal which has the following composition:

   - ✓ Lanthanoid metal = 95%
   - ✓ (about 50% Ce, 40% La and the rest other lanthanoids)
   - ✓ Iron = 5%
   - ✓ S, C, Ca and Al = traces

   The mischmetal is mostly used in making a magnesium-based alloy. It is pyrophoric alloy, i.e.an alloy which emits sparks when struck. It is used in making bullets, shells and lighter flints.
2. Their oxides are used in the glass industry—for polishing glass and to make optical glass.
3. Mixed oxides of lanthanoids are used as catalysts in petroleum cracking.
4. Ceric sulphate is a well-known oxidising agent used in volumetric analysis.

Actinoids

❖ **Electronic Configuration:**

Name of the element	Symbol (M)	Atomic No. (Z)	Electronic configuration	Oxidation state	E.C. outside [Rn] core M3+	M4+
Actinium	Ac	89	[Rn] 6d1 7s2	+3	5f0	
Thorium	Th	90	[Rn] 6d2 7s2	+3, +4	5f1	5f0
Protactinium	Pa	91	[Rn] 5f2 6d1 7s2	+3, +4, +5	5f3	5f1
Uranium	U	92	[Rn] 5f3 6d1 7s2	+3, +4, +5, +6	5f3	5f1

Neptunium	Np	93	[Rn] 5f4 6d1 7s2	+3, +4, +5, +6, +7	5f4	5f3
Plutonium	Pu	94	[Rn] 5f6 6d0 7s2	+3, +4, +5, +6, +7	5f5	5f4
Americium	Am	95	[Rn] 5f7 6d0 7s2	+3, +4, +5, +6	5f6	5f5
Curium	Cm	96	[Rn] 5f7 6d1 7s2	+3, +4	5f7	5f6
Berkelium	Bk	97	[Rn] 5f9 6d0 7s2	+3, +4	5f7	5f7
Californium	Cf	98	[Rn] 5f10 6d0 7s2	+3	5f9	5f8
Einsteinium	Es	99	[Rn] 5f11 6d0 7s2	+3	5f10	5f9
Fermium	Fm	100	[Rn] 5f12 6d0 7s2	+3	5f11	5f10
Mendelevium	Md	101	[Rn] 5f13 6d0 7s2	+3	5f12	5f11
Nobelium	No	102	[Rn] 5f14 6d0 7s2	+3	5f13	5f12
Lawrencium	Lr	103	[Rn] 5f14 6d1 7s2	+3	5f14	5f13

- All the actinoids have common 7s2 configuration, and filling of the 5f and 6d subshells isvariable.
- The 14 electrons are being added to 5f, except in thorium (Z = 90), but this filling of the 5fsubshell continues further after thorium till 5f orbitals are complete at Z = 103.
- Irregularities in the electronic configurations of actinoids are concerned with the stabilities of f0,f7 and f14 configurations.
- Although the 4f and 5f orbitals have similar shapes, 5f is less deeply buried than 4f. Hence, 5felectrons can participate in bonding.

❖ **Oxidation state:**

- The common oxidation state of all actinoids is +3.
- Actinoids also possess the oxidation state of +4. Some of them show higher oxidation state. The oxidation state gradually increases from the extreme left to the middle of the series and then decreases.
- The compounds of actinoids with +3 and +4 oxidation states undergo hydrolysis.

❖ **Ionic radii and actinoid contraction:**

- Like lanthanoids, actinoids also show contraction due to the poor shielding effect of the 5f-electrons.
- So, the radii of the atoms or ions of actinoids decrease gradually along the series.
- This contraction is greater from element to element in a series because 5f orbitals extend in thespace beyond 6s and 6p orbitals.

❖ **Characteristics of Actinoids:**

(a) Silvery appearance:

Actinoids are metals with silvery appearance.

(b) Structural variability:

They have much more regularities in their metallic radii; hence, they show great structural variability.

(c) Colour:

They are silvery white metals. Their cations are generally coloured. The colour of these cationsdepends on the number of 5f-electrons.

The cations containing zero 5f electrons or seven 5f electrons are colourless. The cationscontaining 2–6 5f electrons are coloured.

This colour mainly arises because of f–f transition.

(d) Melting and boiling points:

Actinoids have high melting and boiling points. They do not show any gradual change even with increasing atomic number.

(e) Density:

With the exception of thorium and americium, all actinoids have high densities.

(f) Ionisation enthalpies:

They have low ionisation enthalpies than lanthanoids. This is because 5f is less penetrating than 4f and hence is more effective in shielding from nuclear charge.

(g) Electropositive character:

They are highly electropositive.

(h) Magnetic behaviour:

They are strongly paramagnetic. The change in magnetic susceptibility of actinoids with increasing number of unpaired electrons is the same as lanthanoids, but the values are higher for actinoids.

(i) Reducing agents:

All the actinoids are strong reducing agents.

(j) Radioactivity:

All the actinoids are radioactive. The first few members of the series have long half-lives. The remaining have half lives ranging from very few days to few minutes.

(k) Chemical behaviour:

They are highly reactive in the crushed form. They show the following properties:

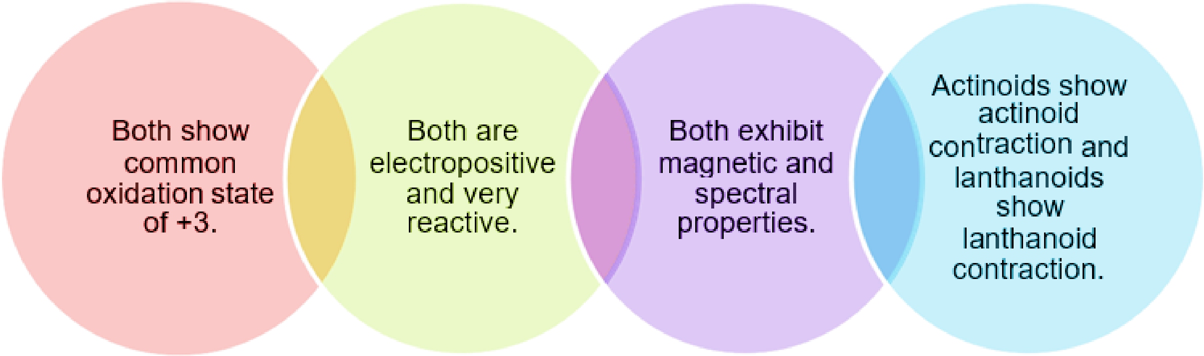
- They react with boiling water to give a mixture of oxide and hydride.
- They combine with most of the non-metals at moderate temperature.
- They react readily with HCl but the reaction with HNO_3 is less effective because it forms a protective oxide layer on the surface.
- Alkalies have no action on them.

❖ **Uses of actinoids:**

Uses of thorium	Uses of uranium	Uses of plutonium
•It is used in atomic reactors and in treatment of cancer. •Its salts are used in making incandescent gas mantles.	•It is used as nuclear fuel. •Its salts are used in glass, textile, ceramic industries and in medicines.	•It is used as a fuel for atomic reactors. •It is also used for making bombs.

Comparison of Lanthanoids and Actinoids

- **Similarities:**



Both show common oxidation state of +3.

Both are electropositive and very reactive.

Both exhibit magnetic and spectral properties.

Actinoids show actinoid contraction and lanthanoids show lanthanoid contraction.

- **Differences:**

LANTHANOIDS	ACTINOIDS
They also show +2 and +4 oxidation states in few cases.	They also show higher oxidation states such as +4, +5, +6 and +7.
Most of their ions are colourless.	Their ions are coloured.
They have low tendency towards complex formation.	They have high tendency towards complex formation.
Their compounds are weakly basic.	Their compounds are strongly basic.
They are non-radioactive (except Promethium).	They are radioactive.
Their magnetic properties can be explained easily.	Their magnetic properties cannot be explained easily.

Comparison of Actinoids with Lanthanoids

General Characteristics and Comparison of Actinoids with Lanthanoids

(i) Electronic configuration

The general electronic configuration for actinoids is [Rn]^{86} 5f$^{1-14}$ 6d0^{-1} 7s^{2} and for lanthanoids is [Xe]^{54} 4f$^{0-14}$ 5d$^{0-1}$ 6s^{2}.

(ii) Atomic and Ionic sizes

Like lanthanoids the ionic radii of actinoids gradually decrease across the series due to the poor screening effect of nuclear charge exerted by the f electrons.

(iii) Oxidation states

The lanthanoids exhibit +3 oxidation states. Some elements may exhibit +2 and +4 oxidation states due to extra stability of fully - filled and half - filled orbitals.

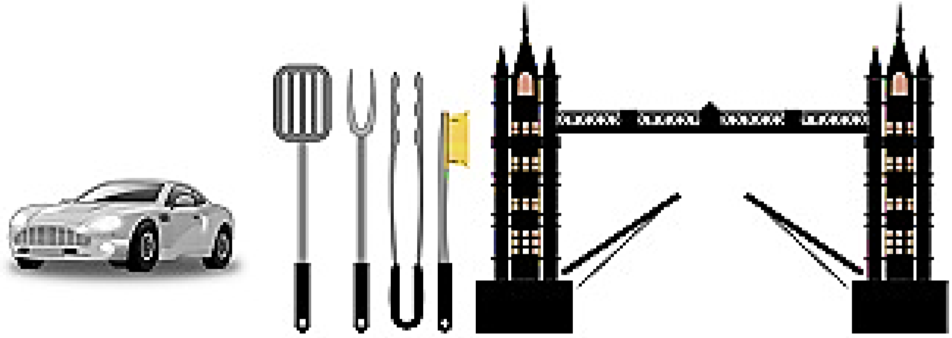
On the other hand Actinoids also exhibit +3 oxidation state. They also exhibit varying oxidation states due to the comparable energies of 5f, 6d, and 7s.

(iv) Chemical reactivity

- Earlier members of the lanthanide series are more reactive and are comparable to CSolution: They resemble Al with increasing atomic number.
- Finely divided Actinoids are highly reactive metals and when added to boiling water gives a mixture of oxide and hydride.
- At moderate temperatures Actinoids combine with most of the non-metallic elements.
- Actinoids remain unaffected by the action of alkalies but gets slightly affected by nitric acid due to the formation of a protective oxide layer.

Applications of d- and f-Block elements

Iron and steels are used for making tools, utensils, vehicles, bridges and much more.



TiO for the pigment industry and MnO_2 for use in dry battery cells.

Zn and Ni/Cd is also used for battery industry.

Elements of Group 11 called the coinage metals.

V_2O_5 catalyses the oxidation of SO_2 in the manufacture ofsulphuric acid.

$TiCl_4$ with $A1(CH_3)_3$ forms the basis of the Ziegler catalystsused to manufacture polyethylene (polythene).

Iron catalysts are used inthe Haber process for the production of ammonia from N_2/H_2 mixtures.

Nickel catalysts enable the hydrogenation of fats

Wackerprocess the oxidation of ethyne to ethanal is catalysed by $PdCl_2$.

Nickel useful in the polymerisation of alkynes and other organiccompounds such as benzene.

The photographic industry relies on thespecial light-sensitive properties of AgBr.

Problem: Write down the electronic configuration of:

(i) Cr^{3+} (iii)Cu^{+} (v)Co^{2+} (vii)Mn^{2+}

(ii) Pm^{3+} (iv)Ce^{4+} (vi) Lu^{2+} (viii)Th^{4+}

Solution:

(i) Cr^{3+}: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^3$

Or, $[Ar]^{18}3d^3$

(ii) Pm^{3+}: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^2\ 4p^6\ 4d^{10}\ 5s^2\ 5p^6\ 4f^4$

Or, $[Xe]^{54}\ 3d^3$

(iii) Cu^+: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}$

Or, $[Ar]^{18}\ 3d^{10}$

(iv) Ce^{4+}: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^2\ 4p^6\ 4d^{10}\ 5s^2\ 5p^6$

Or, $[Xe]^{54}$

(v) CO^{2+}: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^7$

Or, $[Ar]^{18}3d^7$

(vi) Lu^{2+}: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^2\ 4p^6\ 4d^{10}\ 5s^2\ 5p^6\ 4f^{14}\ 5d^1$

Or, $[Xe]^{54}2f^{14}3d^3$

(vii) Mn^{2+}: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^5$

Or, $[Ar]^{18}\ 3d^5$

Class : 12th Chemistry
Chapter-8 : The D And F Block Elements (Part_1)

The D And F Block Elements

Uses

- Helps in production of iron and steels.
- TiO in pigment industry
- MnO_2 in dry battery cells.
- As catalysts in industry.
- Ni complexes useful in the polymerization of alkynes and other organic compounds such as benzene.
- Ag Br in photographic industry.

Lanthanoid contraction in progressive decrease in atomic/ionic radii from La^{3+} and Lu^{3+}

f– Block transition elements

Lanthanoids

- Electronic: configuration $4f^{1-14}\ 5d^{0-1}\ 6s^2$
- Atomic and ionic sizes: Decreases from La to Lu
- Oxidation states: Most common is +3.Some elements exhibit+2 and+4.
- **General characteristics**

–Silvery while soft metals and tarnish rapidly in air.
–Hardness increases with increasing atomic number.
–Metallic structure and good conductors of heat and electricity.
–Variable density
–Trivalent Lanthanoid ions are coloured.

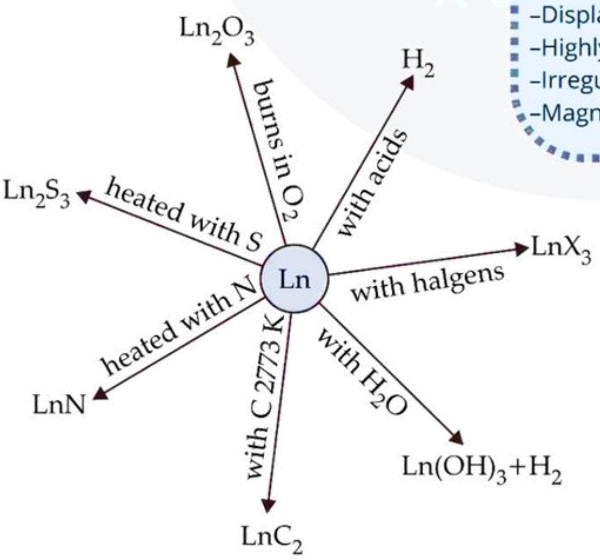
- **Ionisation Enthalpies:** Low third ionisation enthalpies

Actinoids

- **Electronic:** configuration $[Rn]5f^{1-14}\ 6d^{0-2}\ 7s^2$
- **Ionic sizes:** Gradual decrease along the series
- **Oxidation states:** Mostcommonis+3.They show ON of +4,+5, +6 and+7.
- **General characteristics:**

–Silvery in appearance
–Display variety of structures
–Highly reactive metals
–Irregularities in metallic radii, greater than in Lanthanoids.
–Magnetic properties more complex than lanthanoids.

Chemical Properties



Class : 12th Chemistry
Chapter-8 : The D And F Block Elements (Part_2)

The D And F Block Elements

d– Block transition elements groups 3–12

- **Position:** Between s–and p–blocks
- Electronic configuration: (n–1) $d^{1-10}ns^{1-2}$
- Physical properties: Show typical metallic properties, melting and boiling point are high; High enthalpies of atomization
- Decrease in radius with increasing atomic number. Lanthanoid contraction is due to imperfect shielding of one e by another in same set of orbitals.
- Ionisation enthalpies: Increases from left to right
- Oxidation states: Variable ;higher ON stable
- Trends in M^{2+}/M E°:E° for Mn,Ni and Zn are more negative than expected.
- Trends in M^{3+}/M^{2+} E°:variable
- Chemical reactivity and E° values : Variable ;Ti^{2+}, V^{2+} and Cr^{2+} are strong reducing agents.
- Magnetic properties : Diamagnetism and paramagnetism. Magnetic moment increases with increasing atomic number.
- Formation of coloured ions: Form coloured compounds due to d–d transitions
- Formation of complex compounds :Form a large number of complex compounds
- Catalytic properties : Due to variable oxidation states and ability to form complexes.
- Forms interstitial compounds :Non - stoichiometric and are neither ionic nor covalent.
- Alloy formation: Due to similar atomic sizes.

Oxides and oxoanions of metals

- Potassium dichromate $K_2Cr_2O_7$

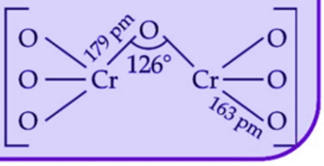
  Preparation : $4FeCr_2O_4 + 8Na_2CO_3 + 7O_2 \rightarrow 8Na_2CrO_4 + 2Fe_2O_3 + 8CO_2$

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

  $Na_2Cr_2O_7 + 2KCl \rightarrow K_2Cr_2O_7 + 2NaCl$

  Properties : $Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$

  Oxidises iodides to iodine, H_2S to S, SO_3^{2-} to SO_4^{2-}, NO_2^- to NO_3^-



- Potassium permanganate $KMnO_4$

  Preparation : $2MnO_2 + 4KOH + O_2 \rightarrow 2KMnO_4 + 2H_2O$

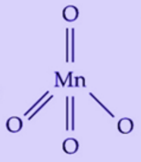
  $3MnO_4^{2-} + 4H^+ \rightarrow 2MnO_4^- + MnO_2 + 2H_2O^+$

  $2Mn^{2+} + 5S_2O_3 \quad + 8H_2O \rightarrow 2MnO_4^- + 10SO_4^{2-} + 16H^+$

  Properties : Intense colour, weak temperature dependent paramagnetism

  $MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$

  Oxidizes I^- to I_2, Fe^{2+} to Fe^{3+}, $C_2O_4^{2-}$ to CO_2, S^{2-} to S, SO_3^{2-} to SO_4^{2-}, NO_2^- to NO_3^-



Important Questions

Multiple Choice questions-

1. Which transition metal can show highest oxidation state?
   (a) Sc
   (b) Ti
   (c) Os
   (d) In
2. Which of the following is not an actinoid?
   (a) Thorium
   (b) Californium
   (c) Uranium
   (d) Terbium
3. Which of the following would be diamagnetic?
   (a) Cu^{2+}
   (b) Ni^{2+}
   (c) Cd^{2+}
   (d) Ti^{3+}
4. Misch metal is an alloy of
   (a) La
   (b) Th
   (c) Ac
   (d) none of these
5. Maximum magnetic moment is shown by
   (a) $3d^8$
   (b) $3d^7$
   (c) $3d^9$
   (d) $3d^5$
6. Maximum oxidation number of manganese is in
   (a) K_2MnO_4
   (b) MnO_2
   (c) $KMnO_4$
   (d) Mn_2O_4
7. Electronic configuration of Fez+ ion is
   (a) [Ar] $4s^2 3d^4$
   (b) [Ar] $4s^1 3d^5$
   (c) [Ar] $3d^6$
   (d) [Ar] $3d^8$
8. Electronic configuration of Cr (Z = 24) is
   (a) $3d^4\ 4s^2$
   (b) $3d^6\ 4s^0$
   (c) $3d^5\ 4s^1$
   (d) none of these
9. Increasing order of paramagnetism is
   (a) Cu^{2+} CO^{2+}, Mn^{2+}, Ni^{2+}
   (b) CO^{2+}, Cu^{2+}, Mn^{2+}, Ni^{2+}
   (c) Cu^{2+}, Ni^{2+}, CO^{2+}, Mn^{2+}
   (d) Mn^{2+}, CO^{2+}, Ni^{2+}, Cu^{2+}
10. Copper sulphate dissolves in excess of KCN to give:
   (a) $[CU(CN)_4]^{3-}$
   (b) $[CU(CN)_4]^{2-}$
   (c) CuCN
   (d) $[Cu(CN_2]$.

Very Short Questions-

1. Zinc, cadmium and mercury are not considered as transition metals. Why?
2. Write the general configuration of d- block elements.
3. What are the factors that decide the ionization potential?
4. What are interstitial compounds. Give two examples
5. What is the ore of $K_2Cr_2O_7$ and $KMnO_4$?
6. What is the effect of adding a base to potassium dichromate?
7. Draw the structure of chromate and dichromate ions?
8. Draw the structure of manganate and permanganate ions?
9. Complete and balance: -
   1. $5Fe^{2+} + MnO_4^- + 8H^+ \rightarrow$
   2. $5NO_2^- + 2MnO_4^- + 6H^+ \rightarrow$
   3. $2MnO_4^- + H_2O + I^- \rightarrow$
   4. $8MnO_4^- + 3S_2O_8^{2-} + H_2O \rightarrow$
   5. $Cr_2O_7^2 + 14H^+ + 6Fe^{2+} \rightarrow$
   6. $Cr_2O_7^{2-} + Sn^{2+} + 14H^+ \rightarrow$

10. Name the two series of f-block.
11. The chemistry of actinoids is more complicated than lanthanoids. Why?
12. What is the general valance configuration of f-block elements?
13. What is the most common oxidation state of lanthanoids and actinoids?
14. Actinoid contraction is more than lanthanoid contraction. Give reason.
15. What is the composition of mischmetal? Give its one use.
16. Actinoids show larger number of oxidation states than lanthanoids. Why?

Short Questions-

1. Give an explanation for the catalytic properties shown by transition metals.
2. Write some characteristics of interstitial compounds.
3. Describe the steps of preparation of $KMnO_4$?
4. Give some of the uses of $KMnO_4$?
5. What happens when

   (a) A lanthanoid reacts with dill- acid

   (b) A lanthanoid reacts with water.
6. Transition metals generally form coloured ions. Why? Which of the following will be coloured?

   Sc^{3+}, V^{2+}, Mn^{2+}, Cu^{+}, Ni^{2+}
7. Explain the steps of preparation of potassium dichromate?
8. What is the lanthanoid contraction? What are its causes and consequences?

Long Questions-

1. Give reasons-
   - (i) Transition metals have high melting points.
   - (ii) Second and third transition series have similar radii.
   - (iii) Second ionization is difficult from Cu and Cr whereas it is easy for Zn.
   - (iv) Most of the transition elements are paramagnetic.
   - (v) Transition elements form alloys.
2. Silver atom has completely filled *d* orbitals ($4d^{10}$) in its ground state. How can you say that it is a transition element?
3. In the series Sc ($Z = 21$) to Zn ($Z = 30$), the enthalpy of atomization of zinc is the lowest, i.e., 126kJmol^{-1}. Why?
4. Which of the $3d$ series of the transition metals exhibits the largest number of oxidation states and why?
5. The $E^{\theta}(M^{2+}/M)$ value for copper is positive (+0.34V). What is possibly the reason for this? (Hint: consider its high Δ_aH^{θ} and low $\Delta_{hyd}H^{\theta}$)
6. How would you account for the irregular variation of ionization enthalpies (first and second) in the first series of the transition elements?
7. Why is the highest oxidation state of a metal exhibited in its oxide or fluoride only?
8. Which is a stronger reducing agent Cr^{2+} or Fe^{2+} and why?

Assertion and Reason Questions-

1. In these questions, a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following choices.

   a) Assertion and reason both are correct statements and reason is correct explanation for assertion.

   b) Assertion and reason both are correct statements but reason is not correct explanation for assertion.

   c) Assertion is correct statement but reason is wrong statement.

   d) Assertion is wrong statement but reason is correct statement.

   Assertion: Co (IV) is known but Ni (IV) is not.

   Reason: Ni (IV) has d^6 electronic configuration.

2. In these questions, a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following choices.

   a) Assertion and reason both are correct statements and reason is correct explanation for assertion.

   b) Assertion and reason both are correct statements but reason is not correct explanation for assertion.

c) Assertion is correct statement but reason is wrong statement.

d) Assertion is wrong statement but reason is correct statement.

Assertion: Transition metals form substitutional alloys.

Reason: Alloys are made to develop some useful properties which are absent in the constituent elements.

Case Study Questions-

1. Read the passage given below and answer the following questions:

The f-block elements are those in which the differentiating electron enters the (n -2)f orbital. There are two series of F-block elements corresponding to filling of 4f and 5f-orbitals. The series of 4f-orbitals is called lanthanides. Lanthanides show different oxidation states depending upon stability of f^0, f^7 and F^{14} configurations, though the most conunon oxidation states is +3. There is a regular decrease in size oflanthanides ions with increase in atomic number which is known as lanthanide contraction.

The following questions are multiple choice questions. Choose the most appropriate answer:

(i) The atomic numbers of three lanthanide elements X, Y and Z are 65, 68 and 70 respectively, their Ln^{3+} electronic configuration is:

a) $4f^8$, $4f^{11}$, $4f^{13}$

b) $4f^{11}$, $4f^8$, $4f^{13}$

c) $4f^0$, $4f^2$, $4f^{11}$

d) $4f^3$, $4f^7$, $4f^9$

(ii) Lanthanide contraction is observed in:

a) Gd

b) At

c) Xe

d) Te

(iii) Which of the following is not the configuration of lanthanoid?

a) $[Xe]4f^{10}6s^2$

b) $[Xe]4f^15d^16s^2$

c) $[Xe]4d^{14}5d^{10}6s^2$

d) $[Xe]4f^75d^16s^2$

(iv) Name a member of the lanthanoid series which is well known to exhibit +4 oxidation state.

a) Cerium (Z = 58)

b) Europium (Z = 63)

c) Lanthanum (Z = 57)

d) Gadolinium (Z = 64

(v) Identify the incorrect statement among the following.

a) Lanthanoid contraction is the accumulation of successive shrinkages.

b) The different radii of Zr and Hf due to consequence of the lanthanoid contraction.

c) Shielding power of 4f electrons is quite weak.

d) There is a decrease in the radii of the atoms or ions as one proceeds from La to Lu.

2. Read the passage given below and answer the following questions:

The transition elements have incompletely filled d-subshells in their ground state or in any of their oxidation states. The transition elements occupy position in betweens- and p-blocks in groups 3-12 of the Periodic table. Starting from fourth period, transition elements consists of four complete series : Sc to Zn, Y to Cd and La, Hf to Hg and Ac, Rf to Cn. In general, the electronic configuration of outer orbitals of these elements is $(n-1)d^{1-10}\ n^{1-2}$. The electronic configurations of outer orbitals of Zn, Cd, Hg and Cn are represented by the general formula $(n-1)d^{10}ns^2$. All the transition elements have typical metallic properties such as high tensile strength, ductility, malleability. Except mercury, which is liquid at room temperature, other transition elements have typical metallic structures. The transition metals and their compounds also exhibit catalytic property and paramagnetic behaviour. Transition metal also forms alloys. An alloy is a blend of metals prepared by mixing the components. Alloys may be homogeneous solid solutions in which the atoms of one metal are distributed randomly among the atoms of the other.

The following questions are multiple choice questions. Choose the most appropriate answer:

(i) Which of the following characteristics of transition metals is associated with higher catalytic activity?

a) High enthalpy of atomisation.

b) Variable oxidation states.

c) Paramagnetic behaviour.

d) Colour of hydrated ions.

(ii) Transition elements form alloys easily because they have.

a) Same atomic number.

b) Same electronic configuration.

c) Nearly same atomic size.

d) Same oxidation states.

(iii) The electronic configuration of tantalum (Ta) is:

a) $[Xe]4f^05d^16s^2$

b) $[Xe]4f^{14}5d^26s^2$

c) $[Xe]4f^{14}5d^36s^2$

d) $[Xe]4f^{14}5d^46s^2$

(iv) Which one of the following outer orbital configurations may exhibit the largest number of oxidation states?

a) $3d^54s^1$

b) $3d^54s^2$

c) $3d^24s^2$

d) $3d^34s^2$

(v) The correct statement(s) among the following is/ are:

I. All d and f-block elements are metals.

II. All d and f-block elements form coloured ions.

III. All d and f-block elements are paramagnetic.

a) (I) only

b) (I) and (II) only

c) (II) and (III) only

d) (I), (II) and (III)

Answer Key

MCQ Answers-

1. **Answer:** (c) Os
2. **Answer:** (d) Terbium
3. **Answer:** (c) Cd^{2+}
4. **Answer:** (a) La
5. **Answer:** (d) $3d^5$
6. **Answer:** (c) $KMnO_4$
7. **Answer:** (c) [Ar] $3d^6$
8. **Answer:** (c) $3d^5\ 4s^1$
9. **Answer:** (c) Cu^{2+}, Ni^{2+}, CO^{2+}, Mn^{2+}
10. **Answer:** (a) $[CU(CN)_4]^{3-}$

Very Short Answers-

1. Zinc, cadmium and mercury have fully filled d^{10} configuration. Therefore, they are not considered as transition metal.

2. General electronic configuration of d- block elements is $(n-1)\ d^{1-10}ns^{1-2}$.

3. The ionization potential values are governed by various ionization enthalpy values, bond enthalpy values and hydration enthalpy values.

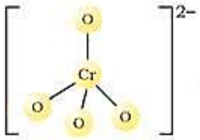
4. Compounds formed by trapping small atoms like H, C, or N inside the crystal lattices of metals eg. TiC, Mn_4N etc.

5. Potassium dichromate $\rightarrow$ chromite ore $(FeCr_2O_4)$ Potassium Permanganate $\rightarrow MnO_2$ pyrolusite.

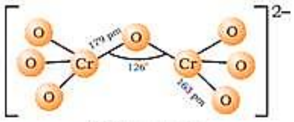
6. When a base is added to orange coloured potassium dichromate its colour changes to yellow due to formation of potassium chromate.

$$Cr_2O_7^{2-} + 2OH^- \rightarrow 2CrO_4^{2-} + H_2O$$

7.

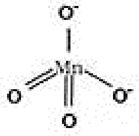


Chromate ion

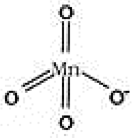


Dichromate ion

8.



Tetrahedral manganate (green) ion



Tetrahedral permanganate (purple) ion

9.
1. $5Fe^{2+} + MnO_4^- + 8H^+ \rightarrow Mn^{2+} + 4H_2O + 5Fe^{3+}$
2. $5NO_2^- + 2MnO_4^- + 6H^+ \rightarrow 2Mn^{2+} + 5NO_3^- + 3H_2O$
3. $2MnO_4^- + H_2O + I^- \rightarrow 2MnO_2 + 2OH^- + IO_3^-$
4. $8MnO_4^- + 3S_2O_3^{2-} + H_2O \rightarrow 8MnO_2 + 6SO_4^{2-} + 2OH^-$
5. $Cr_2O_7^2 + 14H^+ + 6Fe^{2+} \rightarrow 2Cr^{3+} + 6Fe^{3+} + 7H_2O$
6. $Cr_2O_7^{2-} + Sn^2 + 14H^+ \rightarrow Sn^{4+} + 2Cr^{3+} + 7H_2O$

10. The two series are-

i) 4f series or Lanthanoids

ii) 5f series or actinoids.

11. The complications in the actinoid series is due to

i) Existence of a wide range of oxidation states.

ii) Their radioactivity.

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

13. The common oxidation states of

(1) 4f series is +3

(2) 5f series is +3, +4, +5, +6 & +7

14. The actinoid contraction is more than Lanthanoid contraction as the shielding Power of 5f orbitals is poorer than 4f orbitals.

15. Mischmetal is an alloy of a Lanthanoid metal and iron and traces of S, C, Ca & Al. It is used in Magnesium based alloy to produce bullets, shell and lighter Flint.

16. Actinoids can show many oxidation states as in actinoids 5f orbitals are filled which are not as buried as Lanthanoids and can also participate in bonding to a greater extent besides 6d and 7s electrons.

Short Answers-

1. Catalytic properties shown by transition metals can be explained due to

(i) Presence of variable valency and ability of elements to form complexes.

(ii) Surface of metals where the reaction can occur.

2. Some characteristics of interstitial compounds are

(i) They have high melting points.

(ii) They are very hard.

(iii) They retain metallic lustre.

(iv) They are chemically inert.

3. Potassium Permanganate is prepared in two steps:

Step 1: Fusion of MnO_2 with KOH and oxidizing agent to give dark green K_2MnO_4.

$2MnO_2 + 4KOH + O_2 \rightarrow 2K_2MnO_4 + 2H_2O$

Step 2: Disproportionation of manganate ions to give permanganate ions.

$3MnO_4^{2-} + 4H+ \rightarrow 2MnO_4^- + MnO_2 + 2H_2O$

4. Uses of potassium permanganate –

(a) As an oxidizing agent.

(b) For bleaching of wool, cotton & silk.

(c) For decolourisation of oils.

5. (i) When a Lanthanoid reacts with dilute- acid, it liberates hydrogen gas.

$Ln + dil.HCL \rightarrow Ln\ Cl_3 + H_2$

(ii) When a Lanthanoid reacts with water, it forms hydroxide.

$Ln + H_2O \rightarrow Ln\ (OH)_3 + H_2$

6. Transition metals form coloured ions due to d-d transition. Coloured ions will be those which have unpaired electrons.

Sc^{3+}	$3d^0$	Colourless
V^{2+}	$3d^3$	Coloured
Mn^{2+}	$3d^5$	Coloured
Cu^+	$3d^{10}$	Colourless
Ni^{2+}	$3d^8$	Coloured.

7. Preparation of potassium dichromate takes place in three steps.

Step 1: Fusion of chromite ore with sodium or potassium carbonate in free excess of air.

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

Step 2: Conversion of Sodium Chromate to Sodium Dichromate by acidifying it.

$2NaCrO_4 + 2H^+ \rightarrow Na_2Cr_2O_7 + H_2O + 2Na^+$

Step 3: Conversion of sodium dichromate to potassium dichromate by reaching it with KCl.

$Na_2Cr_2O_7 + KCl \rightarrow K_2Cr_2O_7 + NaCl$

8. Lanthanoid contractions – The cumulative effect of the regular decrease in size or radii of Lanthanoid with increase in atomic number is called Lanthanoid contraction.

Causes – The shape of f orbitals is diffused. They have poor shielding effect due to which the effective nuclear charge increase with increase in atomic number. This causes a decrease in atomic radii

Consequences – Due to Lanthanoid contraction

1. Radii of the members of the third transition series is similar to those of second transition series.
2. It becomes difficult to separate Lanthanoids.

Long Answers-

1. (i) In transition metals besides ns electrons, (n-1)d electrons can also participate in bonding making stronger metallic bonds. This increases their melting points.

(ii) Due to lanthanoid contraction, there is a decrease in size of 5d series. This makes their sizes same as sizes of elements of 4d series.

(iii) In Cr the electronic configuration is $3d^5 4s^1$ and for Cu, it is $3d^{10} 4s^1$. In these after first ionization, which removes the electron from 4s, second ionization requires disturbance in half filled or fully filled configuration which requires high enthalpy whereas the configuration of Zn is $3d^{10} 4s^2$. Here after second ionization, the configuration of Zn is completely filled. Therefore, second ionization is easier for Zn but difficult for Cr and Cu.

(iv) Para magnetism in transition elements arises due to presence of one or more unpaired electrons in atomic orbitals.

(v) Due to similarity in their sizes, transition metals can take each others position in their crystal lattice. Therefore they are able to form alloys.

2. Ag has a completely filled 4*d* orbital ($4d^{10} 5s^1$) in its ground state. Now, silver displays two oxidation states (+1 and +2). In the +1-oxidation state, an electron is removed from the *s*-orbital. However, in the +2-oxidation state, an electron is removed from the *d*-orbital. Thus, the *d*-orbital now becomes incomplete ($4d^9$). Hence, it is a transition element.

3. The extent of metallic bonding an element undergoes decides the enthalpy of atomization. The more extensive the metallic bonding of an element, the more will be its enthalpy of atomization. In all transition metals (except Zn, electronic configuration: $3d^{10} 4s^2$), there are some unpaired electrons that account for their stronger metallic bonding. Due to the absence of these unpaired electrons, the inter-atomic electronic bonding is the weakest in Zn and as a result, it has the least enthalpy of atomization.

4. Mn (Z = 25) = $3d^5 4s^2$ Mn has the maximum number of unpaired electrons present in the *d*-subshell (5 electrons). Hence, Mn exhibits the largest number of oxidation states, ranging from +2 to +7.

5. The $E^0(M^{2+}/M)$ value of a metal depends on the energy changes involved in the following:

1. **Sublimation:** The energy required for converting one mole of an atom from the solid state to the gaseous state.

$M_{(s)} \rightarrow M_{(g)} \qquad \Delta_S H$ (Sublimation energy)

2. **Ionization:** The energy required to take out electrons from one mole of atoms in the gaseous state.

$M_{(g)} \rightarrow M^{2+}{}_{(g)} \qquad \Delta_i H$ (Ionization energy)

3. **Hydration:** The energy released when one mole of ions are hydrated.

$M^{2+}{}_{(g)} \rightarrow M^{2+}{}_{(aq)} \qquad \Delta_{hyd} H$ (Hydration energy)

Now, copper has a high energy of atomization and low hydration energy. Hence, the $E^0(M^{2+}/M)$ value for copper is positive.

6. Ionization enthalpies are found to increase in the given series due to a continuous filling of the inner *d*-orbitals. The irregular variations of ionization enthalpies can be attributed to the extra stability of configurations such as d^0, d^5, d^{10}. Since these states are exceptionally stable, their ionization enthalpies are very high.

In case of first ionization energy, Cr has low ionization energy. This is because after losing one electron, it attains the stable configuration ($3d^5$). On the other hand, Zn has exceptionally high first ionization energy as an electron has to be removed from stable and fully-filled orbitals ($3d^{10} 4s^2$).

Second ionization energies are higher than the first since it becomes difficult to remove an electron when an electron has already been taken out. Also, elements like Cr and Cu have exceptionally high second ionization energies as after losing the first electron, they have attained the stable configuration (Cr^{+}:$3d^{5}$ and Cu^{+}:$3d^{10}$). Hence, taking out one electron more from this stable configuration will require a lot of energy.

7. Both oxide and fluoride ions are highly electronegative and have a very small size. Due to these properties, they are able to oxidize the metal to its highest oxidation state.

8. The following reactions are involved when Cr^{2+} and Fe^{2+} act as reducing agents.

$$Cr^{2+} \rightarrow Cr3Fe^{2} \rightarrow Fe^{3+}$$

The $E^\circ_{Cr^{3+}/Cr^{2+}}$ value is −0.41 V and $E^\circ_{Fe^{3+}/Fe^{2+}}$ is +0.77 V. This means that Cr^{2+} can be easily oxidized to Cr^{3+}, but Fe^{2+} does not get oxidized to Fe^{3+} easily. Therefore, Cr^{2+} is a better reducing agent that Fe^{3+}.

Assertion and Reason Answers-

1. (d) Assertion is wrong statement but reason is correct statement.

Explanation:

Both Co and Ni have (IV) oxidation state. Ni (IV) has $3d^{6}$ electronic configuration.

Metals	Outer electronic configuration	Oxi. states
Co	$3d^{7}4s^{2}$	+2, +3, +4
Ni	$3d^{8}4s^{2}$	+2, +3, +4

2. (b) Assertion and reason both are correct statements but reason is not correct explanation for assertion.

Explanation:

Transition metals form substitutional alloys since they have nearly the same size, they can substitute one another in the crystal lattice.

Case Study Answers-

1. **Answer :**

(i) (a) $4f^{8}$, $4f^{11}$, $4f^{13}$

Explanation:

Terbium (65), $4f^{8}$; Dysprosium (Dy), $4f^{9}$; Ytterbium (Yb), $4f^{13}$.

(ii) (a) Gd

(iii) (c) $[Xe]4d^{14}5d^{10}6s^{2}$

(iv) (a) Cerium (Z = 58)

(v) (b) The different radii of Zr and Hf due to consequence of the lanthanoid contraction.

Explanation:

The almost identical radii of Zr (160pm) and Hf (159pm), a consequence of lanthanoid contraction.

2. **Answer :**

(i) (b) Variable oxidation states.

Explanation:

The transition metals and their compounds are known for their catalytic activity. This activity is ascribed to their ability to adopt multiple oxidation states to form complexes.

(ii) (c) Nearly same atomic size.

Explanation:

Because of similar radii and other characteristics of transition metals, alloys are readily formed by these metals.

(iii) (c) $[Xe]4f^{14}5d^{3}6s^{2}$

(iv) (b) $3d^{5}4s^{2}$

Explanation:

Greater the number of valence electrons, more will be the number of oxidation states exhibited by the element.

(v) (a) (i) only

Explanation:

All the d-block elements are metals, they exhibit most properties of metals like lustre, malleability, ductility, high density, high melting and boiling point, hardness, conduction of heat and electricity, etc. All the f-block elements are also metals but they are not good conductors of heat and electricity.

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Coordination Compounds 6

Coordination compounds are a special class of compounds in which the central metal atom is surrounded by ions or molecules beyond their normal valency. These are also referred to as complex compounds. These compounds are called Coordination compounds.

Many biologically important compounds are coordination compounds in which complicated organic species are bound to metal ions. The common examples are : haemoglobin which is a coordination compound of iron, chlorophyll which is a coordination compound of magnesium, vitamin B12 which is a coordination compound of cobalt etc.

The coordination compounds contain a central metal atom or ion surrounded by a number of oppositely charged ions or neutral molecules more than its normal valency.

For example: When aqueous ammonia is added to green solution of nickel chloride, $NiCl_2$, the colour changes to purple. The Ni2+ ions almost disappear from the solution. The solution on evaporation, yields purple crystals corresponding to the formula $[Ni(NH_3)_6]Cl_2$. Such a compound is called coordination (or complex) compound. The properties of the complex compound are completely different from those of Ni^{2+} ions or ammonia molecules.

$$NiCl_2 + 6NH_3 \rightarrow \underset{\text{Coordination compound}}{[Ni(NH3)_6]Cl_2}$$

When the compound is dissolved in water, it ionises to give a new species $(Ni(NH_3)_6]_2+$. Such an ion is called complex ion.

$$[Ni(NH3)_6]Cl_2 \rightarrow [Ni(NH_3)_6]_2+ + 2Cl^-$$

At this stage, it may be noted that the species in the square brackets does not ionise. It remains as single entity. It is known as complex entity.

Double Salts

Double salts are addition or molecular compounds which are formed by two apparently saturated compounds but they lose their identity when dissolved in water.

The common double salts are:

Mohr's salt : $FeSO_4$. $(NH_4)2SO_4.6H_2O$

Potash alum : $K_2SO_4.Al_2(SO_4)3.24H_2O$

Carnallite : $KCl.MgCl_2.6H_2O$

For example: Mohr's salt dissolves in water and gives the characteristic properties of Fe2+, NH4+, and SO42- ions. Thus, double salts are stable in solid state but break up into constituents when dissolved in water.

$$FeSO_4.(NH_4)2SO_4 \rightarrow Fe^{2+} + (aq) + 2NH^{4+}\,(aq) + 2SO_4^{2-}(aq)$$

On the other hand, the coordination compounds retain their identities in the solid state as well as when dissolved in water or any other solvent. Their properties are completely different from the constituents (metal and ions or molecules).

For example, $[Ni(NH_3)_6]Cl_2$ does not show the properties of $NiCl_2$ or ammonia. Similarly, complex ion such as $[Fe(CN)_6]^{4-}$ of $K_4[Fe(CN)_6]$ does not dissociate into Fe^{2+} and CN^- ions.

Werner’s Coordination Theory

Alfred Werner a Swiss chemist, in 1892 prepared a large number of coordination compounds and studied their physical, chemical and isomeric behaviour by simple experimental techniques. He isolated cobalt compounds from the reaction of cobalt chloride and ammonia.

The earlier studies of cobalt complexes were precipitation reactions, conductance measurements and isomeric behaviour.

(1) Precipitation Studies

The number of ions furnished by a complex in a solution can be determined by precipitation reactions.

For example:

(a) The number of Cl^- ions in a solution of various amines were determined by the treatment with silver nitrate solution. From the amount of white precipitate of AgCl formed per mole of the compound, the number of Cl^- ions can be calculated.

(b) When the compound $CoCl_3.6NH_3$ is treated with excess of $AgNO_3$, 3 mol of AgCl are obtained from 1 mol of the compound i.e. all the three Cl^- ions are precipitated.

(c) When the compound $CoCl_3.5NH_3$ is treated with excess of $AgNO_3$, 2 mol of AgCl are obtained i.e., only two Cl^- ions are precipitated. This means that the compound $CoCl_3.5NH_3$ has three ionizable chloride ions whereas in the compound $CoCl_3.5NH_3$ only two chlorine atoms are ionizable as Cl^- ions.

$CoCl_3.6NH_3 \rightarrow 3\ AgCl$ (corresponding to 3 Cl^- ions)

$CoCl_3.5NH_3 \rightarrow 2\ AgCl$ (corresponding to 2 Cl^- ions)

Similarly, the number of chloride ions precipitated in the case of the compounds $CoCl_3.4NH_3$ and $CoCl_3.3NH_3$ have been found to be 1 and none.

(2) Conductance measurements

The measurement of molar conductances (^m) of solutions of coordination compounds helps to estimate the number of ions furnished by the compound in solution.

By comparing the molar conductance of the compounds with those of some known electrolytes, Werner was able to predict the number of ions present in the solution.

For example: The complex $CoCl_3.6NH_3$ behaved as 1:3 electrolyte, $CoCl_3.5NH_3$ as 1:2 electrolyte, $CoCl_3.4NH_3$ as 1:1 electrolyte.

(3) Isomers of compounds

Werner attempted to assign structures of different coordination compounds by comparison of the number of known isomers and the number of theoretically possible structures.

Postulates of Werner’s Coordination Theory

(1) In co-ordination compounds, metal atoms exhibit two types of valencies namely, the primary valency and the secondary valency. The primary valency is ionizable whereas the secondary valency is non ionizable. The primary valency corresponds to oxidation state and the secondary valency corresponds to coordination number.

(2) Every metal atom has a fixed number of secondary valencies i.e., it he fixed coordination number.

(3) The metal atom tends to satisfy both its primary as well as secondary valencies. Primary valencies are satisfied by negative ions whereas secondary valencies are satisfied either by negative ions or by neutral molecules. In certain cases, a negative ion may satisfy both types of valencies.

(4) The secondary valencies are always directed towards the fixed position in space and this leads to definite geometry of the coordination compound. Secondary valencies have characteristic spatial arrangements corresponding to different coordination numbers. Spatial arrangements are called coordination polyhedra.

For example: If a metal ion has six secondary valencies, these are arranged octahedrally around the central metal ion. If the metal ion has four secondary valencies, these are arranged in either tetrahedral or square planar arrangement around the central metal ion. The secondary valencies, thus, determine the stereochemistry of the complex.

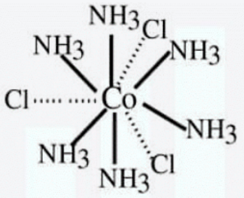
Thus, a metal atom exhibits primary valencies in the formation of its salts (e.g., CoCl3 , AgNO3) while the metal atom exhibits its secondary valencies in the formation of its complex ions

e.g.: [Co(NH3)6]3+ , [Ag(NH3)2]+

Structures of Coordination Compounds on the Basis of Werner's Theory

(1) **$CoCl_3.6NH_3$:** Cobalt has primary valency (oxidation state) of three and secondary valency (coordination number) six. Secondary valencies are represented by thick lines (—) and primary valencies are shown by dotted lines (….). In the complex, all the 6 secondary valencies are occupied by six NH_3 molecules. The Cl^- ions are bonded to Co by three primary valencies. These chloride ions are ionisable and therefore can be precipitated on the addition of silver nitrate. The central metal ion and the neutral molecules or ions (ligands) satisfying secondary valencies are written in a square bracket while writing the formula of the complex compound.

Thus, the coordination compound may be formulated as $[Co(NH_3)6]Cl_3$.



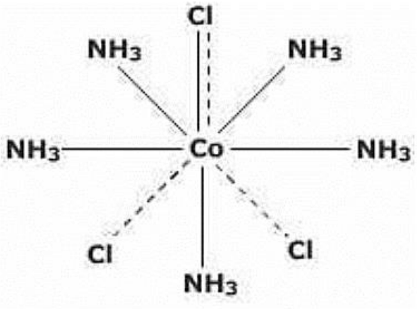
The primary valencies are ionizable and therefore, all the chloride ions would get precipitated on the addition of silver nitrate.

The species within the square brackets are also called coordination entities (or complexes). The ions outside the square brackets are called counter ions. Thus, in the coordination compound [Co(NH_3)6Cl]3, $[Co(NH_3)6]^{3+}$ represents coordination entity and $3Cl^-$ ions represent counter ions

The ionisation of the coordination compound is written as:

$$[Co(NH_3)6Cl]_3 \Leftrightarrow [Co(NH_3)_6]^{3+} + 3Cl^-$$

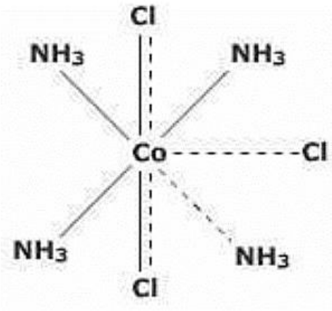
(2) **$CoCl_3.5NH_3$:** In this compound, the coordination number of cobalt is 6 but now five positions are occupied by NH3 molecules and the sixth position by one of the chloride ions.This chloride ion has dual character as it satisfies secondary as well as a primary valency as indicated by a full line as well as a dotted line.The two Cl^- ions satisfy the remaining two primary valencies of cobalt. This satisfies 6 secondary and 3 primary valencies of cobalt. However, on ionisation, only two Cl^- ions will be precipitated because one Cl- ion which also satisfied secondary valency, will not be precipitated.



Thus, the coordination compound may be formulated as $[CoCl(NH_3)5]Cl_2$ which has $[CoCl(NH_3)_5]2+$ complex entity and $2Cl^-$ ions as counter ions. The ionisation of the coordination compound may be written as:

$$[CoCl(NH_3)_5]Cl_2 \Leftrightarrow [CoCl(NH_3)5]^{2+} + 2Cl^-$$

(3) **$CoCl_3.4NH_3$:** In the compound $CoCl_3.4NH_3$, two chloride ions exhibit dual character of satisfying both primary and secondary valencies. It will give precipitate with silver nitrate corresponding to only one Cl^- ion and the number of ions in this case is 2.



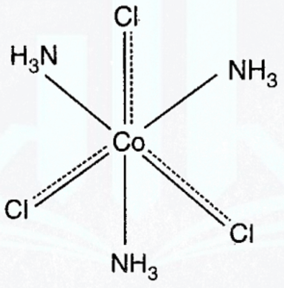
It may be formulated as

$$[CoCl_2(NH_3)_4]Cl \Leftrightarrow [CoCl_2(NH_3)_4]^+ + Cl^-$$

(4) **$CoCl_3.NH_3$:** In the compound $CoCl_3.3NH_3$,three chloride ions satisfy primary and secondary valencies. All the chloride ions are non-ionisable and will not be precipitated by the addition of $AgNO_3$. Therefore, the coordination compound behaves as neutral non- conducting molecule.

It may be formulated as $[CoCl_3(NH_3)3]$ and does not ionise.

$[CoCl_3(NH_3)3] \Leftrightarrow$ Does not ionize



$[CoCl_3(NH_3)_3]$

Differences between coordination compound and double bond

Coordination compound	Double salt
A coordination compound contains a central metal atom or ion surroundedby several oppositely charged ions orneutral molecules. These ions or molecules re-bonded to the metal atom or ion by a coordinate bond.	When two salts in stoichiometric ratioare crystallised together from their saturated solution, they are called double salts.
Example: $K_4[Fe(CN)_6]$	**Example:** $FeSO_4.(NH_4)_2SO_4.6H_2O$ (Mohr's salt)
They do not dissociate into simpleions when dissolved in water.	They dissociate into simple ions when dissolved in water.

- **Coordination entity:** A coordination entity constitutes a central metal atom or ion bonded to a fixednumber of ions or molecules. Example: In $K_4[Fe(CN)_6]$, $[Fe(CN)_6]^{4-}$ represents a coordination entity.
- **Central atom or ion:** In a coordination entity, the atom/ion to which a fixed number of ions/groups are bound in a definite geometrical arrangement is called the central atom or ion. Example: In $K_4[Fe(CN)_6]$,Fe^{2+} is the central metal ion.

- **Ligands:** A molecule, ion or group which is bonded to the metal atom or ion in a complex or coordination compound by a coordinate bond is called a ligand. It may be neutral, positively ornegatively charged. Examples: H_2O, CN^-, NO^+ etc.
- **Donor atom:** An atom of the ligand attached directly to the metal is called the donor atom. Example:In the complex $K_4[Fe(CN)_6]$, carbon is a donor atom.
- **Coordination number:** The coordination number (CN) of a metal ion in a complex can be defined asthe number of ligand donor atoms to which the metal is directly bonded. Example: In the complex $K_4[Fe(CN)_6]$, the coordination number of Fe is 6.
- **Coordination sphere**: The central atom/ion and the ligands attached to it are enclosed in squarebracket and is collectively termed the coordination sphere. Example: In the complex $K_4[Fe(CN)_6]$, $[Fe(CN)_6]^{4-}$ is the coordination sphere.
- **Counter ions:** The ions present outside the coordination sphere are called counter ions. Example: Inthe complex $K_4[Fe(CN)_6]$, K^+ is the counter ion.
- **Coordination polyhedron:** The spatial arrangement of the ligand atoms which are directly attached tothe central atom/ion defines a coordination polyhedron about the central atom. The most common coordination polyhedra are octahedral, square planar and tetrahedral. Examples: $[PtCl_4]^{2-}$ is square planar, $Ni(CO)_4$ is tetrahedral and $[Cu(NH_3)_6]^{3+}$ is octahedral.
- **Charge on the complex ion:** The charge on the complex ion is equal to the algebraic sum of thecharges on all the ligands coordinated to the central metal ion.
- **Denticity:** The number of ligating (linking) atoms present in a ligand is called denticity.
- **Unidentate ligands:** The ligands whose only donor atom is bonded to a metal atom are calledunidentate ligands. Examples: H_2O, NH_3, CO, CN^-
- **Didentate ligands:** The ligands which contain two donor atoms or ions through which they are bonded to the metal ion. Example: Ethylene diamine ($H_2NCH_2CH_2NH_2$) has two nitrogen atoms, and oxalate ion $\left(\begin{array}{l}COO^-\\ |\\ COO^-\end{array}\right)$ has two oxygen atoms which can bind with the metal atom.
- **Polydentate ligand:** When several donor atoms are present in a single ligand, the ligand is called a polydentate ligand. Example: In $N(CH_2CH_2NH_2)_3$, the ligand is said to be polydentate. Ethylenediaminetetraacetate ion ($EDTA^{4-}$) is an important hexadentate ligand. It can bind through two nitrogen and four oxygen atoms to a central metal ion.
- **Chelate:** An inorganic metal complex in which there is a close ring of atoms caused by attachment ofa ligand to a metal atom at two points. An example is the complex ion formed between ethylene diamine and cupric ion $[Cu(NH_2CH_2NH_2)_2]^{2+}$.
- **Ambidentate ligands:** Ligands which can ligate (link) through two different atoms present in it are called ambidentate ligands. Examples: NO^- and SCN^-. NO^- can link through N as well as O, while SCN^- can link through S as well as N.
- **Werner's coordination theory:** Werner was able to explain the nature of bonding in complexes. The postulates of Werner's theory are:
    - Metal shows two kinds of valencies—primary valence and secondary valence.

Primary valence	Secondary valence
This valence is normallyionisable.	This valence is non-ionisable.
It is equal to the positive chargeon the central metal atom.	The secondary valency equals to the number of ligand atoms coordinated to the metal. It is also called the coordination number of the metal.

These valencies are satisfied by negatively charged ions.	It is commonly satisfied by neutral and negatively charged, sometimes by positively charged ligands.
Example: In $CrCl_3$, the primaryvalency is three. It is equal to the oxidation state of the central metal ion.	

  - The ions/groups bound by secondary linkages to the metal have characteristic spatialarrangements corresponding to different coordination numbers.
  - The most common geometrical shapes in coordination compounds are octahedral, square planarand tetrahedral.
- **Oxidation number of the central atom:** The oxidation number of the central atom in a complex is defined as the charge it would carry if all the ligands are removed along with the electron pairs whichare shared with the central atom.
- **Homoleptic complexes:** Those complexes in which metal or ion is coordinately bonded to only onekind of donor atom. Example: $[Co(NH_3)_6]^{3+}$
- **Heteroleptic complexes:** Those complexes in which metal or ion is coordinately bonded to more thanone kind of donor atom. Example: $[CoCl_2(NH_3)_4]^+$, $[Co(NH_3)_5Br]^{2+}$
- **Isomers:** Two or more compounds which have the same chemical formula but different arrangementof atoms are called isomers.

Types of isomerism

- Structural isomerism
  - Linkage isomerism
  - Solvate isomerism or hydrate isomerism
  - Ionisation isomerism
  - Coordination isomerism
- Stereoisomerism
  - Geometrical isomerism
  - Optical isomerism

- **Structural isomerism:** This type of isomerism arises due to the difference in structures of coordination compounds. Structural isomerism, or constitutional isomerism, is a form of isomerism inwhich molecules with the same molecular formula have atoms bonded together in different orders.
  - **Ionisation isomerism:** This form of isomerism arises when the counter ion in a complex salt isitself a potential ligand and can displace a ligand which can then become the counter ion.

    Examples: $[Co(NH_3)_5Br]\ SO_4$ and $[Co(NH_3)_5\ SO_4]\ Br$
  - **Solvate isomerism:** It is isomerism in which the solvent is involved as the ligand. If the solvent iswater, then it is called hydrate isomerism. Example: $[Cr(H_2O)_6]Cl_3$ and $[Crcl_2(H_2O)_4]\ Cl_2.2H_2O$
  - **Linkage isomerism:** Linkage isomerism arises in a coordination compound containing an ambidentate ligand. In the isomerism, a ligand can form linkage with metal through different atoms.

    Examples: $[Co(NH_3)_5ONO]Cl_2$ and $[Co(NH_3)_5NO_2]Cl_2$
  - **Coordination isomerism:** This type of isomerism arises from the interchange of ligands between cationic and anionic entities of different metal ions present in a complex. Examples: $[Co(NH_3)_6][Cr(C_2O_4)_3]$ and $[Cr(NH_3)_6][Co(C_2O_4)_3]$

- **Stereoisomerism:** This type of isomerism arises because of different spatial arrangement.
    - **Geometrical isomerism:** It arises in heteroleptic complexes due to different possible geometrical arrangements of ligands.
    - **Optical isomerism:** Optical isomers are those isomers which are non-superimposable mirrorimages.

Isomerism in Coordination Compounds

Isomerism

Two or more compounds having the same molecular formula but different arrangement of atoms are called isomers and the phenomenon is called isomerism. Because of different arrangement of atoms, isomers differ in one or more physical or chemical properties.

Isomers can be broadly classified into two major categories :

(A) Structural isomers

(B) Stereoisomers

Structural isomers

1. Ionisation isomerism
2. Hydrate isomerism
3. Coordination isomerism
4. Linkage isomerism

Stereoisomers

1. Geometrical isomerism
2. Optical isomerism

(A) Structural isomerism

The isomers which have same molecular formula but different structural arrangement of atoms or groups of atoms around the central metal ion are called structural isomers.

(1) Ionisation isomerism

The compounds which have same molecular formula but give different ions in solution are called ionisation isomers. In this type of isomerism, the difference arises from the interchange of groups within or outside the coordination entity. This type of isomerism occurs when the counter ion in a coordination compound is itself a potential ligand.

For example: There are two isomers of the compound of the formula $Co(NH_3)_5BrSO_4$

(a) One of these is red-violet and forms a precipitate with $BaCl_2$ indicating that sulphate ion is outside the coordination entity.

(b) The second one is red and does not form precipitate with $BaCl_2$ but forms a precipitate of AgBr with silver nitrate indicating that bromide ion is outside the coordination entity.

The structures of the two compounds and their mode of ionisation are :

$[CoBr(NH_3)_5]SO_4 \rightarrow [CoBr(NH_3)_5]^{2+} + SO_4^{2-}$

Pentaamminebromido –

cobalt (III) sulphate   Gives test SO_4^{2-} ions

Structure (Red-violet)

$[CoSO_4(NH_3)_5]SO_4 \rightarrow [Co\ SO_4(NH_3)_5]^+ + Br^-$

Pentaamminebromido –

cobalt (III) bromide Gives test Br^- ions

(Red)

Other compounds showing this type of isomerism are:

(i) $[CoCl_2(NH_3)_4]NO_2$ and $[CoCl(NO_2)(NH_3)_4]Cl$

(ii) $[Co(NO_3)(NH_3)]SO_4$ and $[Co(SO_4)(NH_3)_5]NO_3$

(iii) $[PtCl_2(NH_3)_4]Br_2$ and $[PtBr_2(NH_3)_4]Cl_2$

(iv) $[CoCl(NO_2)(NH_3)_4]Cl$ and $[CoCl_2(NH_3)_4]NO_2$

(2) Solvate or Hydrate isomerism

The compounds which have the same molecular formula but differ by whether or not a solvent molecule is directly bonded to the metal ion or merely present as free solvent molecules in the crystal lattice are called solvate isomers.

It is also known as hydrate isomerism where water is involved as a solvent.Thus, hydrate isomers differ in the number of water molecules present as ligands or as molecules of hydration.

In type of isomerism water molecules may occur inside and outside the coordination sphere as a coordinated group or a water of hydration.

For example, there are three isomers having the molecular formula $CrCl_3 \cdot 6H_2O$.

These are :

$(CrCl_3(H_2O)_3]$, $[CrCl(H_2O)_5]Cl_2 \cdot H_2O$ and $[CrCl_2(H_2O)_4]Cl \cdot 2H_2O$

(i) [Cr(H2O)6]Cl3 : It does not lose water when treated with conc. H2SO4 and three chloride ions are precipitated with AgNO3.

(ii) $[CrCl(H_2O)_5]Cl_2 \cdot H_2O$

Blue green

It loses one water molecule when treated with conc. H_2SO_4 and $2Cl^-$ ions are precipitated with $AgNO_3$

(iii) $(CrCl_2(H_2O)4]Cl.2H_2O$: It loses two water molecules on treatment with conc. H_2SO_4 dark green and one Cl^- ion is precipitated with $AgNO_3$.

Similarly, the following two isomers are hydrate isomers :

$[CoCl(en)_2(H_2O)]Cl_2$ and $[CoCl_2(en)_2]Cl.H_2O$

$[CoCl(H_2O)(NH_3)_4]Cl_2$ and $[CoCl_2(NH_3)_4]Cl.H_2O$

$[CrCl_2(C_2H_5N)_2(H_2O)_2]Cl$ and $[CrCl_3(C_2H_5N_5)_2H_2O].H_2O$

(3) Coordination isomerism

The type of isomerism occurs in compounds containing both cationic and anionic entities and the isomers differ in the distribution of ligands in the coordination entity of cationic and anionic parts. This type of isomerism arises from the interchange of ligands between cationic and anionic entities of different metal ions present in the complex.

The examples are:

(i) $[Co(NH_3)_6][Cr(CN)_6]$ and $[Cr(NH_3)_6]$ $[Co(CN)_6]$

(ii) $[Cu(NH_3)_4[PtCl_4]$ and $[Pt(NH_3)_4][CuCl_4]$

This type of isomerism is also shown by compounds in which the metal ion is the same in both cationic and anionic complexes.

For example :

(i) $[Cr(NH_3)6][Cr(CN)6]$ and $[Cr(CN)_2(NH_3)_4][Cr(CN)_4(NH_3)_2]$

(ii) $[(Pt(NH_3)4]$ $[PtCl_4]$ and $[PtCl(NH_3)3][PtCl_3(NH_3)]$

(4) Linkage isomerism

The compounds which have the same molecular formula but differ in the mode of attachment of a ligand to the metal atom or ion are called linkage isomers.

For example: In $NO2^-$ ion, the nitrogen atom as well as the oxygen atom can donate their lone pairs. This gives rise to isomerism.

If nitrogen donates its lone pair, one particular compound will be formed.

If oxygen donates its lone pair, a different compound (although having the same molecular formula) is obtained. If the bonding is through N, the ligand is named as nitrito-N(or nitro) and if it is through O, it is named as nitrito-O (or nitrito).

$NO2^-$ nitrito-N (or nitro)

ONO^- nitrito-O (or nitrito)

For example: Jorgensen discovered such behaviour in the complex $[(Co(NH_3)_5(NO_2)]Cl$. He prepared two different pentaamminecobalt(II) chloride each containing the NO_2 group in the complex ion. These are:

The unidentate ligands which can bind to the central atom through two donor atoms are also called ambidentate ligands.

Other examples of ligands are:

CN Cyano (through C)

NC Isocyano (through N)

SCN Thiocyanato (through S)

NCS Isothiocyanato (through N)

(B) Stereoisomers

Stereoisomers are those isomers which have the same position of atoms or groups but they differ in the spatial arrangements around the central atom. Two types of isomerism viz., geometrical isomerism and optical isomerism.

(1) Geometrical isomerism

Geometrical isomerism arises in heteroleptic complexes due to ligands occupying different positions around the central ion. The ligands occupy positions either adjacent to one another or opposite to one another. These are referred to as cis- form (ligands occupy adjacent positions) and trans- form (ligands occupy opposite positions). This type of isomerism is, therefore, also referred to as cis-trans isomerism.

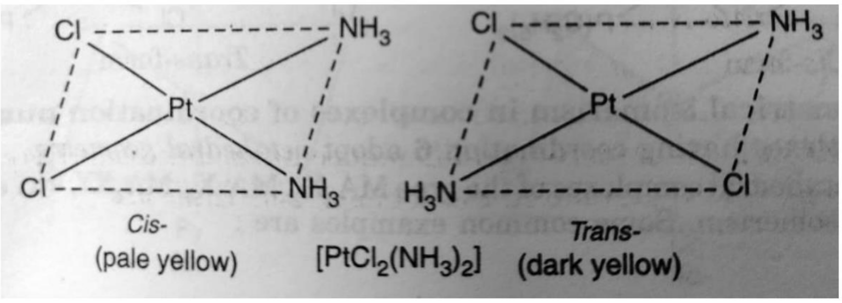
(a) Geometrical isomerism in complexes of coordination number 4

The complexes having coordination number 4 adopt tetrahedral or square planar geometry. The geometrical isomerism is not possible in tetrahedral complexes. This is because in tetrahedral geometry all the positions adjacent to one another in these complexes.

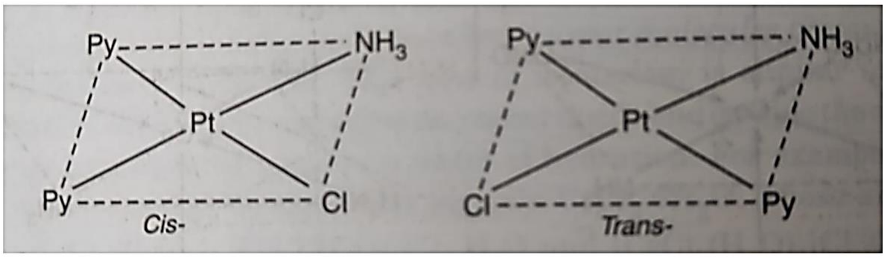
However, square planar complexes show geometrical isomerism.

(1) Square planar complexes of the type MA2X2 , MA2XY, MABX2, MABXY can exist as geometrical isomers (Here A and B are neutral ligands such as H2O, NH_3, CO, NO, C_5H_5N whereas X and Y are anionic ligands such as Cl^-, $NO2^-$, CN^-, SCN^- etc.)

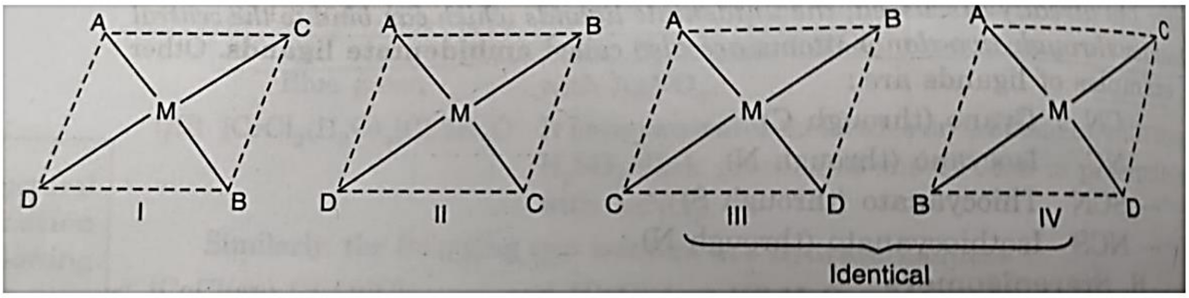
Example:



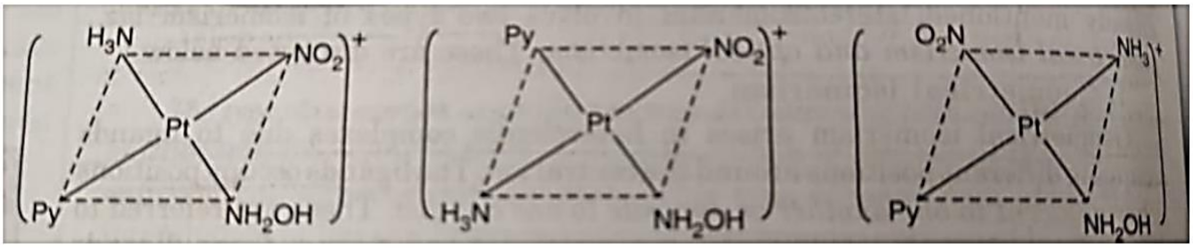
(ii) $[PtCl(C_5H_5N)_2(NH_3)]$ exists in cis and trans form as:



(iii) Square planar complexes of the type MABCD show three isomers. The structures of these isomers can be written by fixing the position of one ligand (say A) and placing the other ligands B, C and D trans to it.

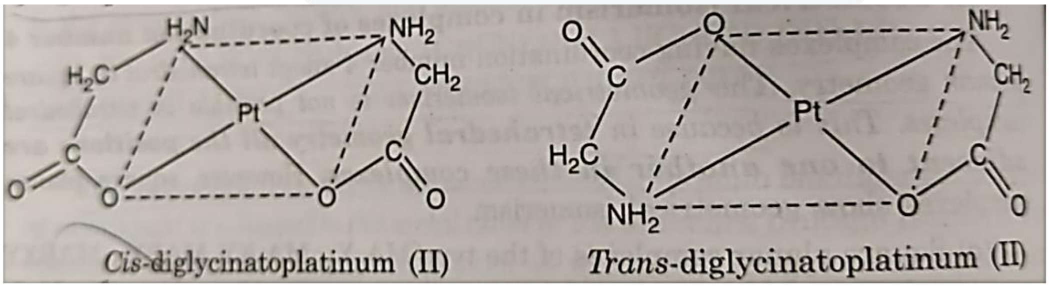


The complex $[Pt(NO_2)(py)(NH_2OH)(NH_3)]^+$ exists in three geometrical isomers as represented below:



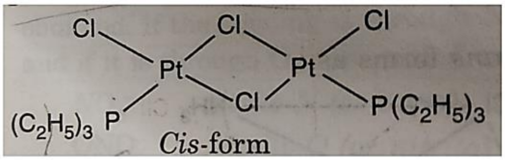
(iv) Geometrical isomerism cannot occur in complexes of the type MA_4, MA_3B or MAB_3 because all possible spatial arrangements for any of these complexes will be exactly equivalent.

(v) The square planar complexes containing unsymmetrical bidentate ligands such as $[M(AB)_2]$ also show geometrical isomerism. For example, the complex $[Pt(gly)_2]$ where gly = $NH_2CH_2COO^-$ exists in cis and trans form :

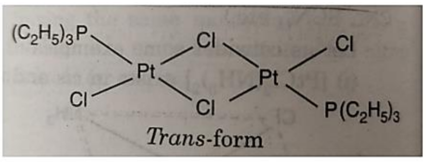


Cis-diglycinatoplatinum (II) *Trans*-diglycinatoplatinum (II)

(vi) Geometrical isomerism is also shown by bridged binuclear complexes of the type $M_2A_2X_4$. For example: the complex $[PtCl_2P(C_2H_5)_3]_2$ exhibits geometrical isomers as :



Cis-form



Trans-form

IUPAC Nomenclature of Coordination Compounds

Rules for Writing Formula

The formula of a compound is a shorthand method used to provide basic information about the constitution of a compound in a concise and convenient manner.

(1) The formula of the cation whether simple or complex is written first followed by that of the anion.

(2) The coordination entity is written in square brackets.

(3) The sequence of symbols within the coordination entity is : first the symbol of the central metal atom followed by ligands in alphabetical order.

The ligands in coordination entity are arranged as:

(a) The different ligands are arranged alphabetically according to the first symbol of their formulae. For example, H_2O , NH_3, NO_3^-, SO_4^{2-} and OH^- etc. are cited at H, N, N, O, S and O.

(b) When the two ligands have same defining atom, the ligand with fewer such atoms is cited first followed by the ligand having more atoms. For example, NH_3 precedes N_2

(c) If the numbers of defining atoms are equal, subsequent symbol decides the sequence.

For example NH_2^- precedes NO_2^- because H comes before O.

(d) Polydentate ligands are also listed alphabetically. In case of abbreviated ligand, the first letter of the abbreviation is used to determine the position of the ligand in alphabetical order.

(e) The formula for the co-ordination entity, whether charged or not, is enclosed in square brackets. Polyatomic ligands are enclosed in parentheses (), but all ligands are written without any separation in between.

(f) There should be no space between the representations of ionic species within the formula.

(g) Sometimes abbreviations are used for formulae of the ligands. These abbreviations should be in lower case and enclosed in parenthesis.

For example, py is used for pyridine and en is used for ethane-1, 2-diamine or ethylene diamine.

(h) The number of cations or anions to be written in the formula is calculated on the basis that total positive charge must be equal to total negative charge.

(i) When the formula of the charged coordination entity is written without the formula of the counter ion, the charge is indicated outside the square brackets as a right superscript with the number before the sign (+ or -).

For example,

$[Ni(NH_3)_6]^{2+}$, $[Co(CN)_6]^{3-}$, $[CoCl(NH_3)_5]^{2+}$, etc.

Some common examples are :

$K_3[Fe(CN)_6]$

$[CoCl_2(NH_3)_4]Cl$ Cl is cited first than NH_3

$[Co(H_2O)_2(NH_3)_4]Cl_2$ H is cited before N

$[Pt\ Cl_2(C_5H_5N)NH_3]$ Among neutral ligands C_5H_5N and NH_3, C_5H_5N precedes NH_3

Rules for naming the coordination compounds

(1) Order of naming ions

In ionic complexes, the cation is named first and then the anion.

NaCl : sodium chloride

Non-ionic complexes are given a one word name.

(2) Naming the coordination entity

In naming the coordination entity, the ligands are named first and then the central metal ion.

(3) Names of ligands

The names of anionic ligands (organic or inorganic) end in o-. In general, if the anionic ligand name ends in -ide, -ite or -ate, the final 'e' is replaced by 'o' giving-ido,-ito and-ato respectively. For inorganic anionic ligands containing numerical prefixes such as triphosphate enclosing marks () are added. The names of positive ligands end in -ium. The neutral ligands are named as such.

For example :

(i) Negative ligands end in -o :

F - fluorido
Cl - chlorido
Br^- - bromido
$NO2^-$ - nitrito-N
ONO^- - nitrito-O
SO_4^{2-} - sulphato
OH- - hydroxo
$C_2O_4^{2-}$ - oxalato
CN^- - cyano
CH_3COO^- - acetato
SCN- - thiocyanato
O_2^{2-} - peroxo
O^{2-} - oxo
N^{3-} - nitrido
P^{3-} - phosphido
N_3^- - azido
NCS^- - isothiocyanato
H^- - hydrido
CO_3^{2-} - carbonato
NO_3^- - nitrato
$NH2^-$ - amido
NH^{2-} - imido
$ClO3^-$ - Chlorato
$S_2O_3^{2-}$ - thiosulphato

(ii) positive ligands end in -ium

NO^+ - nitrosonium
$NH_2NH_3^+$ - hydrazinium
NO_2^+ - nitronium

(iii) neutral ligands are named as such

$NH_2CH_2CH_2NH_2$ ethane-1,2-diamine or ethylenediamine
C_6H_5N - pyridine (py)
$(C_6H_5)_3P$ - triphenylphosphine
PH_3 - phosphine
CS - thiocarbonyl
H_2NCSNH_2 - thiourea (tu) dipyridyl (dipy)

However, there are a few exceptions in naming neutral ligands. For example,

H_2O - aqua

NH_3 - ammine

NO - nitrosyl

CO - carbonyl

(4) Order of naming ligands

When more than one type of ligands are present, they are named in alphabetical order of preference without any consideration of charge.

For example : In the complex $[CoCl(NO_2)(NH_3)_4]^+$, the ligands are named in the order :

ammine, chlorido and nitrito-N. Similarly, in the complex $K_3[Fe(CN)_5NO]$, the ligands are named as cyano and nitrosyl.

(5) Numerical prefixes to indicate number of ligands

When more than one ligands of a particular kind are present in the complex, the di-, tri-, tetra-, penta-, hexa-, etc. are used to indicate their number: two, three, four, five and six respectively.

When the name of the ligand, includes the numerical prefix (di, tri, tetra), the prefixes bis, tris, tetrakis are used for two, three, four ligands, respectively. Such ligands are called complexligands.

For example: to indicate two simple ligands such as chloro, bromo, ammine, oxalato, etc., we use the prefix di but to indicate two complex ligands such as ethylenediamine we use the prefix bis (ethylenediamine) or bis (1,2-ethanediamine).

The name of the complex ligand is given in brackets.

For example :

$[Co(en)_3]^{3+}$ - tris(ethane-1,2,-diamine)cobalt(III) ion

$[NiCl_2(PPh_3)_2]$ - dichloridobis (triphenylphosphine)nickel(II)

(6) Ending of names

When the complex is anionic, the name of the central metal atom ends in -ate. For cationic and neutral complexes, the name of the metal is written without any characteristic ending.

For example, the cationic complex $[Co(NH_3)_6]Cl_3$ is named without characteristic ending of the name of the metal as :

$[Co(NH_3)_6]Cl_3$ hexaamminecobalt (III) chloride

The coordination compound, $K[PtCl_5(NH_3)]$ which contains the anionic complex $[PtCl_5(NH_3)]^-$ is named with ending of the name of the metal as -ate.

$K[PtCl_5(NH_3)]$ - potassium amminepentachloridoplatinate (IV)

Similarly, the anionic complex $Ca_2[Fe(CN)_6]$ is named as calcium hexacyanoferrate (II).

$[Co(SCN)_4]^{2-}$ - tetrathiocyanatocobaltate(II) ion.

For anionic complexes the Latin names of certain metals are commonly used.

For example: ferrate for Fe, cuperate for Cu, argentate for Ag, aurate for Au, stannate for

Sn, etc.

However, if the complex is cationic or neutral the name of the metal is given as such e.g., iron for Fe, silver for Ag, gold for Au, copper for Cu, etc.

For example:

K3[Fe(CN)6] Potassium hexacyanoferrate (III)

[Fe(CO)5] Pentacarbonyliron (0)

(7) Oxidation state of central metal ion

The oxidation state of the central metal ion is designated by a Roman numeral (such as II, III, IV) in the brackets at the end of the name of the complex without a gap between the two. Let us discuss some examples:

(i) $CoCl(NH_3)_5]Cl_2$

In this case the ligands are chloro and ammine. The complex is cation and chloride is anion. The oxidation state of cobalt is III as

$x + 5(0) - 1 - 2 = 0$

or

$x = +3$.

Its name is pentaamminechloridocobalt(III) chloride

(ii) $K_3[Fe(CN)_6]$

In this case, the ligands are cyano. The complex is anionic. The oxidation state of iron is +3 as $3(+1) + x + 6(-1) = 0$

The name of the complex is potassium hexacyanoferrate(III). If the complex containing the central ion, Fe^{3+} is anionic, the Latin name of metal is used i.e. ferrate.

(iii) $[Co(H_2NCH_2CH_2NH_2)_3](SO_4)_3$

In this case, ligands are ethane-1, 2-diamine (or ethylenediamine). The complex is cationic. The oxidation state of cobalt is +3 as

$[x + 3 \times 0]2 + 3(-2) = 0$ or

$2x = +6$ or

$x = +3$

The name of the complex is tris (ethane-1, 2-diamine) cobalt(II) sulphate.

tris is used because the ligand is complex ligand.

(iv) $[Ag(NH_3)_2][Ag(CN)_2]$

Both cation and anion are complexes. The oxidation state of silver in both cationic and anionic complexes is +1. The name of the complex is diamminesilver (I) dicyanoargentate (I)

(8) Point of attachment

When a ligand can coordinate through more than one atom, then the point of attachment of the ligand is indicated by putting the symbol of the atom through which coordination occurs after the name of the ligand. For example: NO_2^- can coordinate through -N or -O. If it coordinates through N, it is called nitrito -N (or simply as nitro). If it coordinates through O, -ONO, it is called nitrito -O or simply as nitrito.

NO_2^- (through N)

$-ONO^-$ (through O)

Nitrito – N

Nitrito – O

SCN^- (through S) thiocyanato

NCS (through N) isothiocyanato

For example,

$[Co(NO_2)_3(NH_3)_3]$ triamminetrinitrito-N-cobalt(III)

$[Co(ONO)(NH_3)_5]SO_4$ pentaamminenitrito-O-cobalt(III) sulphate

(9) Naming geometrical isomers

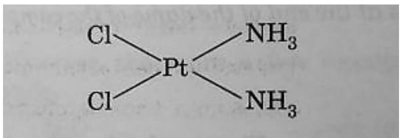
Geometrical isomers are named by the use of the terms cis-to designate adjacent positions and trans- to designate opposite positions.

For example: in square planar complexes shown below

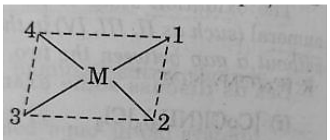
(a) the positions 1, 4 ; 1, 2 ; 2, 3 and 3, 4 are **cis-**

(b) 1,3 and 2, 4 are **trans**

In naming these complexes, cis or trans is written before the names of these compounds. Similarly, for octahedral complexes, cis- and trans are used in isomerism in coordination compounds.



cis-diamminedichloridoplatinum



Square planar complex

(10) Naming optical isomers

Optically active compounds are designated by the symbols (+) or d -for dextrorotatory and (-) or l- for laevorotatory.

For example : d- $K_3[Cr(C_2O_4)_3]$ Potassium (+) trioxalatochromate (III)

Valence bond theory:

According to this theory, the metal atom or ion under the influence of ligands can use its (n − 1)d, ns, np or ns, np or nd orbitals for hybridization to yield a set of equivalent orbitals of definite geometry such as octahedral, tetrahedral and square planar.These hybridised orbitals are allowed to overlap with ligand orbitals which can donate electron pairs for bonding.

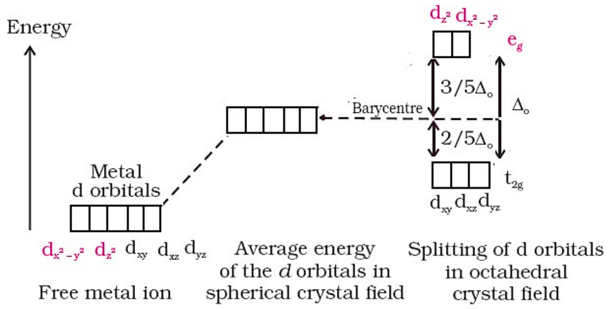
Coordination number	Type of hybridisation	Distribution of hybrid orbitals in space
4	sp^3	Tetrahedral
4	dsp^2	Square planar
5	sp^3d	Trigonal bipyramidal
6	sp^3d^2 (nd orbitals are involved; outer orbital complex or high-spin or spin-free complex)	Octahedral
7	d^2sp^3 [(n − 1)d orbitals are involved; inner orbital complex or low-spin or spin-paired complex]	Octahedral

- **Magnetic properties of coordination compounds:** A coordination compound is paramagnetic in nature if it has unpaired electrons and diamagnetic if all the electrons in the coordination compoundare paired.

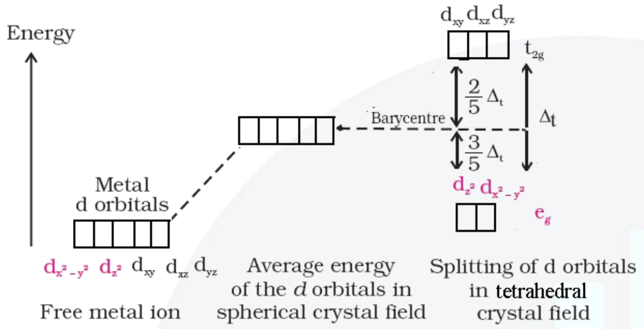
  Magnetic moment $\mu = \sqrt{n(n+2)}$ where n is the number of unpaired electrons.

- **Crystal Field Theory:** It assumes the ligands to be point charges and there is an electrostatic force of attraction between ligands and the metal atom or ion. It is a theoretical assumption.

- **Crystal field splitting in octahedral coordination complexes**



- **Crystal field splitting in tetrahedral coordination complexes**



- For the same metal, the same ligands and metal–ligand distances, the difference in energy between $e_g$and t_{2g} level is

$$\Delta_t = \frac{4}{9}\Delta_0$$

- **Metal carbonyls:** Metal carbonyls are homoleptic complexes in which carbon monoxide (CO) acts asthe ligand. Example: $Ni(CO)_4$

  The metal–carbon bond in metal carbonyls possesses both σ and π characters. The metal–carbon bond in metal carbonyls possess both *s* and *p* characters. The M–C σ bond is formed by the donation of a lone pair of electrons from the carbonyl carbon into a vacant orbital of the metal. The M–C π bond is formed by the donation of a pair of electrons from a filled *d* orbital of metal into the vacant anti-bonding π* orbital of carbon monoxide. The metal to ligand bonding creates a synergic effect which strengthensthe bond between CO and the metal.

Class : 12th Chemistry
Chapter-9 : Coordination Compounds (Part_1)

Werner's Theory: Postulates

- In coordination compounds metals show primary and secondary linkages (valances)
- Primary valences are ionisable and are satisfied by negative ions.
- Secondary valences are non-ionisable and are satisfied by neutral molecules or negative ions.
- Ions/groups bound by secondary linkages to metal have characteristic spatial arrangements corresponding to different coordination numbers.

Crystal field theory

Ligands are point charges and there is electrostatic force of attraction between ligands and metal atom/ion. Degeneracy of d orbitals is lighted causing splitting of d orbitals. Δ0 depends upon the field produced by the ligand and charge on metal ion.

Colour

Caused by d-d transition; the colour is complementary to wavelength absorbed

Coordination Compounds

Bonding

In metal carbonyls

Metal–carbon bond possess both σ and π character

Valance bond theory

Metal atom/ion under the influence of ligands can use its (n–1)d, ns, np or ns, np, nd orbitals for hybridisation; sp^3(Tetrahedral), dsp^2(square) planar, sp^3d (Trigonal pyramidal), sp^3d^2 and d^2sp^3 (Octahedral); Magnetic moment = $\sqrt{n(n+2)}$ BM

Uses

- In qualitative and quantitative chemical analysis.
- Estimation of hardness of water.
- In extraction metals.
- In purification of metals.
- In biological systems.
- As catalysts for industrial processes.
- In black and white photography.
- In medicinal chemistry.

Isomerism

Structural: different bonds

Ionisation counter ion is a potential ligand and can displace a ligand
$[Co(NH_3)_5SO_4]Br$
$[CO(NH_3)_5Br]SO_4$

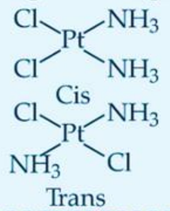
Coordination interchange of ligands between catonic and anionic entities of different metal ions
$[CO(NH_3)_6]$ $[Cr(CN)_6]$
$[Cr(NH_3)_6]$ $[CO(CN)_6]$

Solvate differ in number of water molecules attached to metal atom/ion
$[Cr(H_2O)_6]Cl_3$
$[Cr(H_2O)_5Cl]Cl_2.H_2O$

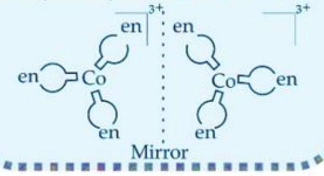
Linkage occurs in ambidentate ligand
$[CO(NO_2)(NH_3)_5]Cl$
$[CO(ONO)(NH_3)_5]Cl$

Stereoisomerism: different spatial arrangements

Geometrical: different arrangements Ligand



Optical: images which cannot be superimposed $[Co(en)_3]^{3+}$



Class : 12th Chemistry
Chapter-9 : Coordination Compounds (Part_2)

Formulas of monomuclear
- Central atom is listed first
- Ligands in alphabetical order.
- Formula is enclosed in square bracket.
- Polyatomic ligands in parenthesis.
- No space between ligand and metal.
- Charge is indicated outside brackets.
- Charge of cation(s) balanced by charge of anion(s)

Naming of monomuclear
- Cation is named first.
- Naming of ligands in alphabetical order.
- Anionic ligands end in–o, neutral and cationic are same
- Prefixes mono, di, tri etc. are used.
- Followed by roman numeral in parentheses.

Complex compound: do not dissociate into simple ions when dissolved in water $(K_4[Fe(Cn)]_6)$

Coordination Compounds

Stability: expressed by equilibrium constant
$Br = K_1 \times K_2 \times K_3 ....K_n$

Double salt: Dissociate completely into simple ions when dissolved in water.
(Mohr's salt $FeSO_4.\ (NH_4)2SO_4.6H_2O$)

Compounds in which a central metal atom or ion is linked to a fixed number of ions or molecules through coordinate bonds.

Terms
- Coordination entity : A central metal atom/ion bonded to fixed number of ions or molecules. $[Ni(CO)_4]$
- Central atom/ion : Atom/ion to which a fixed number of ions/groups are bound in a definite geometrical arrangement.
- Ligands : Ions or molecules bound to central atom/ion types :
  Unidentate – single donor, Didentate –two donors
  Polydentate – several donors,
  Chelating – Di-or polydentate which forms more than one coordinate bonds.
  Ambidentate : Can ligate through two different atoms.
- Coordination number : No. of ligand donor atoms to which metal is directly bonded
- Coordination sphere : Central atom/ion and the ligands attached to it and enclosed in square bracket.
- Oxidation number : Charge of central atom if all ligands are removed along with e– pairs shared with central atom.
- Homoleptic complex : Metal is bound to one type of donor groups. $[Co(NH_3)_6]_{3+}$
- Heteroleptic complex: Metal is bound to more than one type of donor groups

Important Questions

Multiple Choice questions-

1. IUPAC name of $[Pt(NH_3)_3 Br (NO_2) Cl] Cl$ isw
   (a) triamminechlorodibromidoplatinum (IV) chloride
   (b) triamminechloridobromidonitrochloride-platinum (IV) chloride
   (c) triamminebromidochloridonitroplatinum (IV) chloride
   (d) triamminenitrochlorobromoplatinum (IV) chloride
2. Trunbull's blue is
   (a) Ferricyanide
   (b) Ferrous ferricyanide
   (c) Ferrous cyanide
   (d) $Fe_3[Fe(CN)_6]_4$
3. Primary and secondary valency of Pt in $[Pt(en)_2Cl_2]$ are
   (a) 4, 4
   (b) 4, 6
   (c) 6, 4
   (d) 2, 6
4. The complex ions $[Co(NH_3)_5(NO_2)]^{2+}$ and $[Co(NH_3)_5 (ONO)]^{2+}$ are called
   (a) Ionization isomers
   (b) Linkage isomers
   (c) Co-ordination isomers
   (d) Geometrical isomers
5. Which of the following has square planar structure?
   (a) $[NiCl_4]^{2-}$
   (b) $[Ni(CO)_4]$
   (c) $[Ni(CN)_4]^{2-}$
   (d) None of these
6. Which of the following has magnesium?
   (a) Chlorophll
   (b) Haemocyanin
   (c) Carbonic anhydrate
   (d) Vitamin B_{12}
7. Mohr's salt is
   (a) $Fe_2(SO_4)$ 3 . $(NH_4)_2SO_4$. $6H_2O$
   (b) $FeSO_4$. $(NH_4)_2$. SO_4 . $6H_2O$
   (c) $MgSO_4$. $7H_2O$
   (d) $FeSO_4$. $7H_2O$
8. Which of the following shall form an octahedral complex?
   (a) d^4 (low spin)
   (b) d^8 (high spin)
   (c) d^6 (low spin)
   (d) All of these
9. EDTA is used for the estimation of
   (a) Na^+ and K^+ ions
   (b) Cl^- and Br^- ions
   (c) Cu^{2+} and Cs^+ ions
   (d) Ca^{2+} and Mg^{2+} ions
10. The solution of the complex $[Cu(NH_3)_4]$ SO_4 in water will
    (a) give the tests of Cu^{2+} ion
    (b) give the tests of NH_3
    (c) give the tests of SO_4^{2-} ions
    (d) not give the tests of any of the above

Very Short Questions-

1. What is the shape of $[Fe(CO)_5]$?
2. What do you understand by stability of a complex and instability constant of coordination compounds?
3. How is EDTA used in estimation of hardness of water?
4. Explain the role of complexes in metallurgy with an example.
5. How is excess of copper and iron removed from body?
6. Define – isomerism.
7. Indicate the types of isomerisms shown by the complex –$K[Fe(H_2O)_2 (en)_2 Cl_2]$?
8. Give an example of coordination isomerism?
9. What are complex compounds?
10. Give some examples of coordination compounds.

Short Questions-

1. Explain the synergic bonding in metal carbonyls.
2. Give some examples showing importance of complexes in biological system?
3. Give examples of complexes in
   a) Chemical analysis
   b) Industries

4. Distinguish between homoleptic and heteroleptic ligands.
5. What are the different shapes or coordination polyhedral in the complexes?
6. What is the difference between a double salt and a complex? Explain with an example.
7. Predict the number of unpaired electrons in the square planar $[Pt(CN)_4]^{2-}$ ion.
8. Write all the geometrical isomers of $[Pt(NH_3)(Br)(Cl)(py)]$ and how many of these will exhibit optical isomers?
9. What is spectrochemical series? Explain the difference between a weak field ligand and a strong field ligand.
10. A solution of $[Ni(H_2O)_6]^{2+}$ is green but a solution of $[Ni(CN)_4]^{2-}$ is colourless. Explain.

Long Questions-

1. What are ligands? Explain different types of ligands.
2. Write the formulas for the following coordination compounds:
   (i) Tetraamminediaquacobalt (III) chloride
   (ii) Potassium tetracyanonickelate (II)
   (iii) Tris(ethane-1,2-diamine) chromium (III) chloride
   (iv) Amminebromidochloridonitrito-N-platinate (II)
   (v) Dichloridobis (ethane-1,2-diamine)platinum(IV) nitrate
   (vi) Iron (III) hexacyanoferrate (II)
3. Write the IUPAC names of the following coordination compounds:
   (i) $[Co(NH_3)6]Cl_3$
   (ii) $[Co(NH_3)_5Cl]Cl_2$
   (iii) $K_3[Fe(CN)_6]$
   (iv) $K_3[Fe(C_2O_4)_3]$
   (v) $K_2[PdCl_4]$
   (vi) $[Pt(NH_3)_2Cl(NH_2CH_3)]Cl$
4. Indicate the types of isomerism exhibited by the following complexes and draw the structures for these isomers:
   (i) $K[Cr(H_2O)_2(C_2O_4)_2]$
   (ii) $[Co(en)_3]Cl_3$
   (iii) $[Co(NH_3)_5(NO_2)(NO_3)_2]$
   (iv) $[Pt(NH_3)(H_2O)Cl_2]$
5. Explain on the basis of valence bond theory that $[Ni(CN)_4]^{2-}$ ion with square planar structure is diamagnetic and the $[NiCl_4]^{2-}$ ion with tetrahedral geometry is paramagnetic.
6. $[NiCl_4]^{2-}$ is paramagnetic while $[Ni(CN)_4]$ is diamagnetic though both are tetrahedral. Why?
7. $[Fe(H_2O)_6]^{3+}$ is strongly paramagnetic whereas $[Fe(CN)_6]^{3}$ is weakly paramagnetic. Explain.
8. Explain $[Co(NH_3)_6]^{3+}$ is an inner orbital complex whereas $[Ni(NH_3)_6]^{2+}$ is an outer orbital complex.

Assertion and Reason Questions-

1. In these questions, a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following choices.
   a) Assertion and reason both are correct statements and reason is correct explanation for assertion.
   b) Assertion and reason both are correct statements but reason is not correct explanation for assertion.
   c) Assertion is correct statement but reason is wrong statement.
   d) Assertion is wrong statement but reason is correct statement.

   Assertion: Zeise's salt is a ππ-bonded organometallic compound.

   Reason: The oxidation number of platinum in Zeise's salt is +2.

2. In these questions, a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following choices.
   a) Assertion and reason both are correct statements and reason is correct explanation for assertion.

b) Assertion and reason both are correct statements but reason is not correct explanation for assertion.

c) Assertion is correct statement but reason is wrong statement.

d) Assertion is wrong statement but reason is correct statement.

Assertion: The second and third transition series elements have lesser tendency to fonn low spin complex as compared to the first transition series.

Reason: The CFSE (Δ_0) is more for 5d and 4d.

Case Study Questions-

1. Read the passage given below and answer the following questions:

Metal carbonyl is an example of coordination compounds in which carbon monoxide (CO) acts as ligand. These are also called homoleptic carbonyls. These compounds contain both **σ** and **π** character. Some carbonyls have metal-metal bonds. The reactivity of metal carbonyls is due to (i) the metal centre and (ii) the CO ligands. CO is capable of accepting an appreciable amount of electron density from the metal atom into their empty **π** or **π**−orbital. These types of ligands are called **π**−accepter or **π**−acid ligands. These interactions increases the Δ_0 value.

The following questions are multiple choice questions. Choose the most appropriate answer:

(i) What is the oxidation state of metal in $[Mn_2(CO)_{10}]$?

a) +1

b) -1

c) +2

d) 0

(ii) Among the following metal carbonyls, the C-O bond order is lowest in:

a) $[Mn(CO)_6]^+$

b) $[Fe(CO)_5]$

c) $[Cr(CO)_6]$

d) $[V(CO)_6]^-$

(iii) Which of the following can be reduced easily?

a. $V(CO)_6$

b. $Mo(CO)_6$

c. $[Co(CO)_4]^-$

d. $Fe(CO)_5$

(iv) The oxidation state of cobalt in $K[Co(CO)_4]$ is:

a. +1

b. +3

c. -1

d. 0

(v) Structure of decacarbonyl manganese is:

a. Trigonal bipyramidial

b. Octahedral

c. Tetrahedral

d. Square pyramidal

2. Read the passage given below and answer the following questions:

Coordination compounds are formulated and named according to the IUPAC system.

Few rules for naming coordination compounds are:

I. In ionic complex, the cation is named first and then the anion.

II. In the coordination entity, the ligands are named first and then the central metal ion.

III. When more than one type of ligands are present, they are named in alphabetical order of preference without any consideration of charge.

The following questions are multiple choice questions. Choose the most appropriate answer:

(i) The IUPAC name of the complex $[Pt(NH_3)_3Br(NO_2)Cl]Cl$ is:

a) Triamminechlorobromonitroplatinum (IV) chloride.

b) Triamminebromonitrochloroplatinum (IV) chloride.

c) Triamminebromidochloridonitroplatinum (IV) chloride.

d) Triamminenitrochlorobromoplatinum (IV) chloride.

(ii) The IUPAC name of $[Ni(CO)_4]$ is:

- a) Tetracarbonylnickel (II).
- b) Tetracarbonylnickel (0).
- c) Tetracarbonylnickelate (II).
- d) Tetracarbonylnickelate (0).

(iii) As per IUPAC nomenclature, the name of the complex $[Co(H_2O)_4(NH_3)_2]Cl_3$ is:

- a) Tetraaquadiamminecobalt (II) chloride.
- b) Tetraaquadiamminecobalt (III) chloride.
- c) Diamminetetraaquacobalt (II) chloride.
- d) Diamminetetraaquacobalt (III) chloride.

(iv) Which of the following represents correct formula of dichloridobis(ethane -1, 2-diamine)cobalt (III) ion?

- a) $[CoCl_2(en)]^{2+}$
- b) $[CoCl_2(en)_2]^{2+}$
- c) $[CoCl_2(en)]^{+}$
- d) $[CoCl_2(en)_2]^{+}$

(v) Correct formula of pentaamminenitro-O-cobalt (III) sulphate is:

- a) $[Co(NO_2)(NH_3)_5]SO_4$
- b) $[Co(ONO)(NH_3)_5]SO_4$
- c) $[Co(NO_2)(NH_3)_4](SO_4)_2$
- d) $[Co(ONO)(NH_3)_4](SO_4)_2$

Answer Key

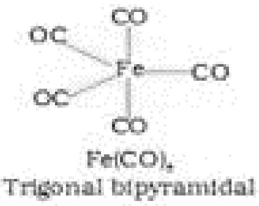
MCQ Answers-

1. Answer: c
2. Answer: b
3. Answer: d
4. Answer: b
5. Answer: c
6. Answer: a
7. Answer: b
8. Answer: b
9. Answer: d
10. Answer: c

Very Short Answers-

1. $[Fe(CO)_5]$

Geometry = Trigonal bipyramidal/span>



2. The stability of a complex in solution is the degree of association between the two species involved in the state of equilibrium. The instability constant is reciprocal of the formation constant. It is also called dissociation constant.

3. Hard water is titrated with Na_2 –EDTA complex for estimation of its hardness. During the process, the Ca^{2+} and Mg^{2+} ions form complex with EDTA replacing Na^+. The method is based on the difference in the stability constant of calcium and magnesium complexes.

4. Some extraction processes make use of complex formation e.g. during metallurgy of Gold, it combines with cyanide in the presence of oxygen and water to form the complex $[Au(CN)_2]^-$ in aqueous solution by addition of zinc.

5. Excess of copper and iron are removed by chelating Ligands D – penicillamine and deferoxamine B through the formation of coordination compounds.

6. Isomerism is the phenomenon of existence of two or more compounds with same chemical formula but a different arrangement of atoms.

7. Both geometrical and optical isomerisms will be present.

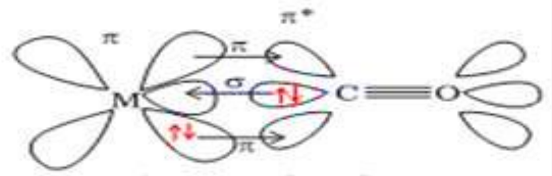
8. Example of coordination isomerism is $[Cr(NH_3)_6][Co(CN)_6]$ and $[Co(NH_3)_6][Cr(CN)_6]$

9. Complex compounds or coordination compounds are those compounds in which the metal atoms are bound to a number of anions or neutral molecules.

10. Examples of coordination compounds are chlorophyll, haemoglobin, and vitamin B_{12}

Short Answers-

1. The metal – carbon bond in metal carbonyls has both s & P- character. The M – Cσ bond is formed by donation of lone pair of electrons of carbonyl carbon into a vacant orbital of metal. The M – Cπ bond is formed by the donation of a pair of electrons from a filled d- orbital of metal to the vacant π orbital of carbon monoxide. The metal to ligand bonding creates a synergic effect that strengthens the bond.



Synergic bonding

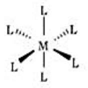
2. Examples of complexes in biological system:
   1. Chlorophyll is a complex of Mg.
   2. Haemoglobin is a complex of iron.
   3. Cyanocobalamin, Vit B_{12}, is a complex of cobalt.

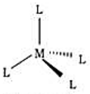
3. **(a) Chemical analysis** – Qualitative and Quantitative analysis methods involve use of Ligands like EDTA, DMG etc.

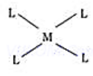
   (b) Industries - Hydrogenation of alkenes is done by using a sodium complex called Wilkinson catalyst. In black and white photography, silver complexes are used.

4. Homoleptic complexes are those in which only one type of ligand or donor group is present e.g. $[Pt(NH_3)_6]^{3+}$ has only NH_3 as ligand. Whereas heteroleptic complexes are those in which different types of ligands are present eg. $[Pt(NH_3)_4Cl_2]^{3+}$ has two type of ligands- NH_3 and Cl^-.

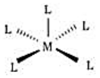
5. The various coordination polyhedra are –


Octahedral


Tetrahedral

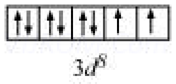

Square planar


Trigonal bipyramidal


Square pyramidal

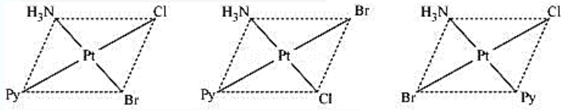
6. Double salts dissociate completely into simple ions when dissolved in water e.g., Mohr salt, $FeSO_4(NH_4)_2SO_4, 6H_2O$ will dissolve in water and give ferrous, ammonium and sulphate ions. On the other hand, the complex ions do not completely dissociate into all constituent ions e.g. $K_4[Fe(CN)_6]$ will dissociate to give potassium ions and $[Fe(CN)_6]^{4-}$ ions only.

7. $[Pt(CN_4)]^{2-}$ In this complex, Pt is in the +2 state. It forms a square planar structure. This means that it undergoes dsp^2 hybridization. Now, the electronic configuration of Pd(+2) is $5d^8$.



CN^- being a strong field ligand causes the pairing of unpaired electrons. Hence, there are no unpaired electrons in $[Pt(CN)_4]^{2-}$.

8. $[Pt(NH_3)(Br)(Cl)(py)]$



From the above isomers, none will exhibit optical isomers. Tetrahedral complexes rarely show optical isomerization. They do so only in the presence of unsymmetrical chelating agents.

9. A spectrochemical series is the arrangement of common ligands in the increasing order of their crystal-field splitting energy (CFSE) values. The ligands present on the R.H.S of the series are strong field ligands while that on the L.H.S are weak field ligands. Also, strong field ligands cause higher splitting in the *d* orbitals than weak field ligands.

$$I- < Br^- < S^{2-} < SCN^- < Cl^- < N_3 < F^- < OH^- < C_2O_4^{2-}$$

$$\sim H_2O < NCS^- \sim H^- < CN^- < NH_3 < en$$

$$\sim SO_3^{2-} < NO_2^- < phen < CO$$

10. In $[Ni(H_2O)_6]^{2+}$, $H_2\ddot{O}$, is a weak field ligand. Therefore, there are unpaired electrons in Ni^{2+}. In this complex, the *d* electrons from the lower energy level can be excited to the higher energy level i.e., the possibility of *d* – *d* transition is present. Hence, $[Ni(H_2O)_6]^{2+}$ is coloured.

In $[Ni(CN)_4]^{2-}$, the electrons are all paired as CN^- is a strong field ligand. Therefore, *d*-

d transition is not possible in $[Ni(CN)_4]^{2-}$. Hence, it is colourless.

Long Answers-

1. The ions or molecules bound to central atom or ion in the coordination entity are ligands e.g. $[Fe(CN)_6]^{4-}$ has six CN^- ligands.

Types:

(1) On the basis of charges on them ligands can be negative, positive (e.g. H_3O^+, NH_4^+ etc.) or neutral (e.g. CO, NH_3, H_2O^+).

(2) On the basis of their donor atoms ligands can be monodentate or unidentate (one donor atom) e.g. H_2O, NH_3, Cl^- etc., or didentate ligands (two donor atoms) $H_2NCH_2CH_2NH_2$ or $C_2O_4^{2-}$ etc. or polydentate (several donor atoms) e.g. $[EDTA]^{4-}$ is a hexadentate ligand.

(3) Ligands which can ligate through two different atoms are called ambidentate ligands eg. NO_2^- and SCN^- ions. Whereas when a di⁻ or polydentate ligand uses its two or more donor atoms to bind a single metal ion, it is called chelate ligand.

2. **(i)** $\left[CO(H_2O)_2(NH_3)_4\right]Cl_3$

(ii) $K_2\left[Ni(CN)_4\right]$

(iii) $\left[Cr(en)_3\right]Cl_3$

(vi) $\left[Pt(NH)_3BrCl(NO_2)\right]^-$

(v) $\left[PtCl_2(en)_2\right](NO_3)_2$

(vi) $Fe_4\left[Fe(CN)_6\right]_3$

3. **(i)** Hexaamminecobalt(III) chloride

(ii) Pentaamminechloridocobalt(III) chloride

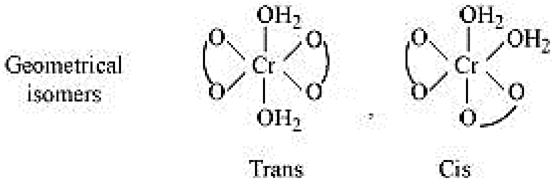
(iii) Potassium hexacyanoferrate(III)

(iv) Potassium trioxalatoferrate(III)

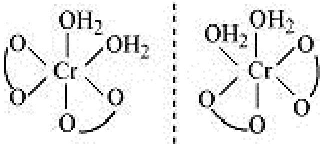
(v) Potassium tetrachloridopalladate(II)

(vi) Diamminechlorido(methylamine) platinum(II) chloride

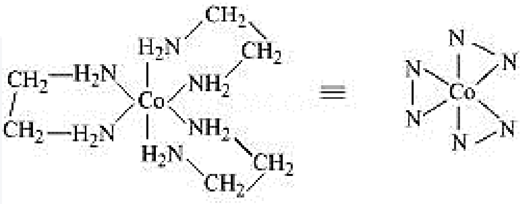
4. Both geometrical (*cis*-, *trans*-) isomers for $K[Cr(H_2O)_2(C_2O_4)_2]$ can exist. Also, optical isomers for cis isomer exist.



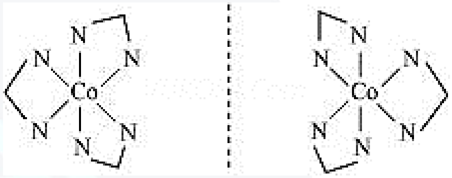
Trans-isomer is optically inactive. On the other hand, cis isomer is optically active.



(ii) Two optical isomers for $[CO(en)_3]Cl_3$ exist.

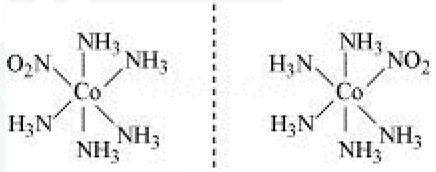


Two optical isomers are possible for this structure.



(iii) $\left[CO(NH_3)_5(NO_2)\right](NO_3)_2$

A pair of optical isomers:



It can also show linkage isomerism.

$\left[CO(NH_3)_5(NO_2)\right](NO_3)_2$ and

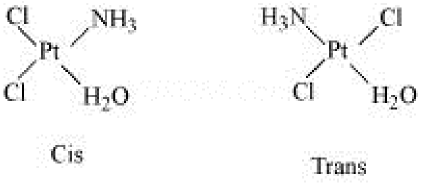
$\left[CO(NH_3)_5(ONO)\right](NO_3)_2$

It can also show ionization isomerism.

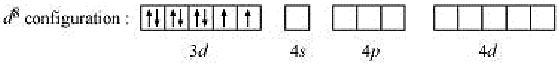
$\left[Co(NH_3)_5(NO_2)\right](NO_3)_2$

$\left[CO(NH_3)_5(NO_3)\right](NO_3)(NO_2)$

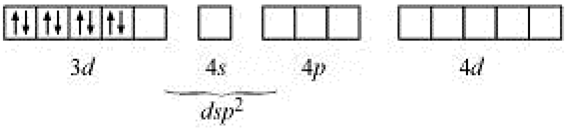
(iv) Geometrical (*cis*-, *trans*-) isomers of $[Pt(NH_3)(H_2O)Cl_2]$ can exist.



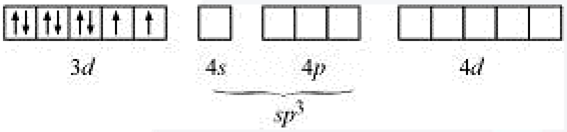
5. Ni is in the +2-oxidation state i.e., in d^8 configuration.



There are $4CN^-$ ions. Thus, it can either have a tetrahedral geometry or square planar geometry. Since CN^- ion is a strong field ligand, it causes the pairing of unpaired 3*d* electrons.

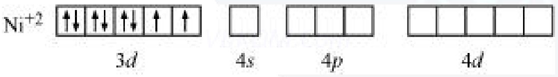


It now undergoes dsp^2 hybridization. Since all electrons are paired, it is diamagnetic. In case of $[NiCl_4]^{2-}$, CN^- ion is a weak field ligand. Therefore, it does not lead to the pairing of unpaired 3*d* electrons. Therefore, it undergoes sp^3 hybridization.

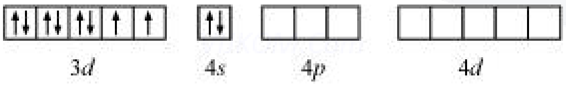


Since there are 2 unpaired electrons in this case, it is paramagnetic in nature.

6. Though both $[NiCl_4]^{2-}$ and $[Ni(CO)_4]$ are tetrahedral, their magnetic characters are different. This is due to a difference in the nature of ligands. CN^- is a weak field ligand and it does not cause the pairing of unpaired 3*d* electrons. Hence, $[NiCl_4]^{2-}$ is paramagnetic.

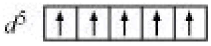


In $Ni(CO)_4$, Ni is in the zero-oxidation state i.e., it has a configuration of $3d^8\ 4s^2$.

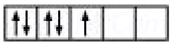


But CO is a strong field ligand. Therefore, it causes the pairing of unpaired 3*d* electrons. Also, it causes the 4s electrons to shift to the 3d orbital, thereby giving rise to sp^3 hybridization. Since no unpaired electrons are present in this case, $[Ni(CO)_4]$ is diamagnetic.

7. In both $[Fe(H_2O)_6]^{3+}$ and $[Fe(CN)_6]^{3-}$, Fe exists in the +3-oxidation state i.e., in d^5 configuration.



Since CN^- is a strong field ligand, it causes the pairing of unpaired electrons. Therefore, there is only one unpaired electron left in the *d*-orbital.



Therefore,

$$\mu = \sqrt{n(n+2)}$$

$$= \sqrt{1(1+2)}$$

$$= \sqrt{3}$$

$$= 1.732 \text{ BM}$$

On the other hand, H_2O is a weak field ligand. Therefore, it cannot cause the pairing of electrons. This means that the number of unpaired electrons is 5.

Therefore,

$$\mu = \sqrt{n(n+2)}$$

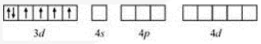
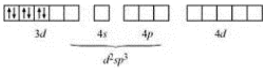
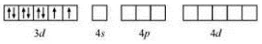
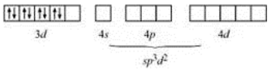
$$= \sqrt{5(5+2)}$$

$$= \sqrt{35}$$

$$= 6 \text{ BM}$$

Thus, it is evident that $[Fe(H_2O)_6]^{3+}$ is strongly paramagnetic, while $[Fe(CN)_6]^3$ is weakly paramagnetic.

8.

$[Co(NH_3)_6]^{3+}$	$[Ni(NH_3)_6]^{2+}$
Oxidation state of cobalt = +3	Oxidation state of Ni = +2
Electronic configuration of cobalt = d^6	Electronic configuration of nickel = d^8
 NH_3 being a strong field ligand causes the pairing. Therefore, Cobalt can undergo d^2sp^3 hybridization.  Hence, it is an inner orbital complex.	 If NH_3 causes the pairing, then only one 3*d* orbital is empty. Thus, it cannot undergo d^2sp^3 hybridization. Therefore, it undergoes sp^3d^2 hybridization.  Hence, it forms an outer orbital complex.

Assertion and Reason Answers-

1. (b) Assertion and reason both are correct statements but reason is not correct explanation for assertion.

Explanation:

In these complexes, the metal and ligand fonn a bond that involves the ππ-electrons of the ligand and so it is a ππ-bonded organometallic compound.

2. (d) Assertion is wrong statement but reason is correct statement.

Explanation:

4d and 5d elements have greater tendency to form low spin complex (allows better pairing of electrons) in comparison to 3d because the difference in energy of t_{2g} and e_g (CFSE, Δ_0) increases in 4d and 5d.

Case Study Answers-

1. Answer :

(i) (d) 0

Explanation:

Oxidation state of Mn in $[Mn_2(CO)_{10}]$ is zero.

(ii) (d) $[V(CO)_6]^-$

Explanation:

In $[V(CO)_6]^-$, the anionic carbonyl complex can delocalise more electron density to antibonding **π**–orbital (**dπ–pπ** back bonding) of CO and thus lowers the bond order.

(iii) (a) $V(CO)_6$

Explanation:

$V(CO)_6$ can be easily reduced to $[V(CO)_6]^-$. $V(CO)_6$ has a total of 17 bonding electrons, hence it is very reactive and unstable. $[V(CO)_6]^-$ on the other hand has complete set of 18 bonding electrons as an electron is added into the bonding orbital when $V(CO)_6$ gets reduced to $[V(CO)_6]^-$. All others have 18 bonding electrons.

(iv) (c) -1

Explanation:

$K[Co(CO)_4]$

$+1 + (x) + 4(0) = 0$ or $x = -1$

(v) (d) Square pyramidal.

Explanation:

$Mn_2(CO)_{10}$ is made up of two square pyramidal $Mn(CO)_5$ units joined by Mn-Mn bond.

2. Answer :

(i) (c) Triamminebromidochloridonitroplatinum (IV) chloride.

Explanation:

Ligands are named in alphabetical order irrespective of their charge.

(ii) (b) Tetracarbonylnickel (0).

(iii) (d) Diamminetetraaquacobalt (III) chloride.

(iv) (d) $[CoCl_2(en)_2]^+$

(v) (b) $[Co(ONO)(NH_3)_5]SO_4$

Explanation:

Ligand NO_2^- is ambidentate ligand as it can donate electrons through either nitrogen (NO_2) or oxygen (ONO).

❖ ❖

Haloalkanes and Haloarenes

7

Based on the structure i.e depending upon the number of halogen atoms in a compound, Alkyl/ Aryl halides are classified as mono, di, and polyhalogen. When compared to carbon, halogen atoms are more electronegative. Therefore

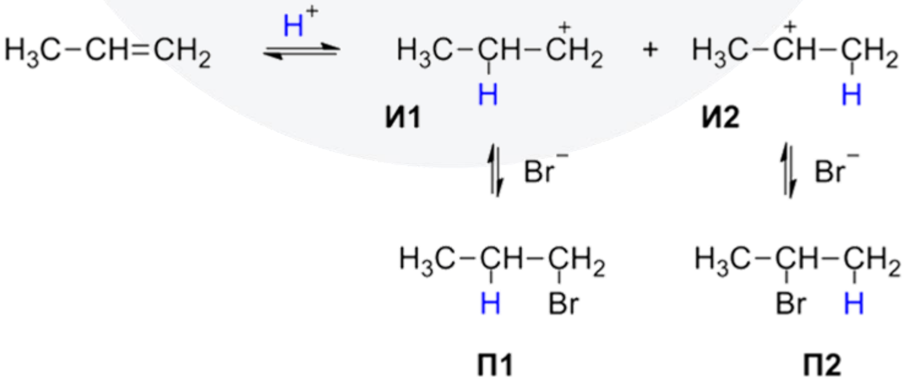
- The bond (carbon-halogen bond) of alkyl halide is polarised.
- Halogen atom carries a partial negative charge
- Carbon atom carries a partial positive

Preparation Of Alkyl Halides

Alkyl halides are produced by the free radical halogenation of alkanes:

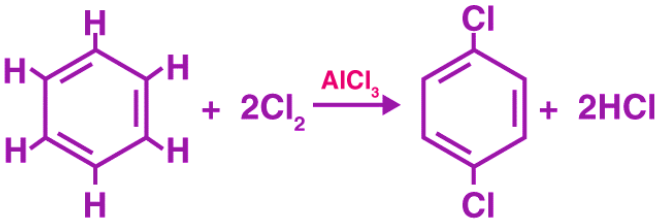
Step 1 – Adding halogen acids to alkenes

Step 2 – Replacing –OH group of alcohols by halogens with the use of phosphorus halides or halogen acids or thionyl chloride. Aryl halides are prepared with the help of electrophilic substitution to arenes. Iodides and Fluorides are prepared with halogen exchange method. Organohalogens have a higher boiling point when compared hydrocarbons due to strong van der Waals forces and dipole-dipole forces. They partial dissolve in water but completely dissolve in organic solvents. Organometallic compounds are formed by the nucleophilic substitution, elimination, and reaction with metal atoms which occurs due to the polarity of a carbon-halogen bond of alkyl halides. Based on the kinetic properties Nucleophilic substitution reactions are classified as S_N1 and S_N2. Chirality plays a very important in S_N2 reactions of understanding the reaction mechanisms of these reactions. S_N2 reactions are characterized by inversion configuration whereas SN1 reactions are characterised by racemisation.



Substitution Reaction

The substitution reaction is defined as a reaction in which the functional group of one chemical compound is substituted by another group or it is a reaction which involves the replacement of one atom or a molecule of a compound with another atom or molecule.



Substitution Reaction

Substitution Reaction Example

These type of reactions are said to possess primary importance in the field of organic chemistry. For example, when CH_3Cl is reacted with the hydroxyl ion (OH-), it will lead to the formation of the original molecule called methanol with that hydroxyl ion. The following reaction is as shown below-

$CH_3Cl + (OH^-) \rightarrow CH_3OH$ (methanol) $+ Cl^-$

One more example would be the reaction of Ethanol with the hydrogen iodide which forms iodoethane along with water. The reaction is as shown-

$CH_3CH_2OH + HI \rightarrow CH_3CH_2I + H_2O$

Substitution Reaction Conditions

In order to substitution reaction to occur there are certain conditions that have to be used. They are-

- Maintaining low temperatures such as room temperature.
- The strong base such as NaOH has to be in dilute form. Suppose if the base is of a higher concentration, there are chances of dehydrohalogenation taking place.
- The solution needs to be in an aqueous state such as water.

Substitution Reactions – Types

Substitution Reactions are of two types naming nucleophilic reaction and electrophilic reactions. These two types of reactions mainly differ in the kind of atom which is attached to its original molecule. In the nucleophilic reactions the atom is said to be electron-rich species, whereas, in the electrophilic reaction, the atom is an electron-deficient species. A brief explanation of the two types of reactions is as given below.

nucleophiles

Nucleophiles are those species in the form of an ion or a molecule which are strongly attached to the region of a positive charge. These are said to be fully charged or have negative ions present on a molecule. The common examples of nucleophiles are cyanide ions, water, hydroxide ions, and ammonia.

Nucleophilic substitution reaction

A Nucleophilic substitution reaction in organic chemistry is a type of reaction where a nucleophile gets attached to the positive charged atoms or molecules of the other substance.

Nomenclature Of Haloalkanes And Haloarenes

Initially, there was no proper system for the naming of compounds. Mostly there were trivial names that were used depending upon the country and region. These trivial names were based on the discoverer or the nature of the compound or its place of discovery.

The system of trivial names was not standard and led to much confusion, thus raising the need for a standard system for the naming of organic compounds. IUPAC came up with a set of rules that are used universally for the naming of organic compounds.

There are two names associated with every compound:

Common name – It is different from a trivial name in the sense that it also follows a rule for its nomenclature.

IUPAC name – The IUPAC (International Union of Pure and Applied Chemistry) naming system is the standard naming system that chemists generally use.

Rules of Nomenclature

- Find the longest carbon chain.
- Number the longest carbon chain such that the carbon atom(s) to which the halogen(s) is/are attached get the lowest number(s).
- Multiple halogen atoms are labelled with the Greek numerical prefixes such as di, tri, tetra, to denote the number of identical halogen atoms attached to a carbon atom. If more than one halogen atoms attached to the same carbon atom, the numeral is repeated that much time.
- In case, different types of halogens are attached, they are named alphabetically.
- The position of the halogen atom is indicated by writing the position and name of the halogen just before the name of the parent hydrocarbon.

The Methodology of Writing Name

- First, write the root word for the parent hydrocarbon (depending upon the no. of carbon atoms in the longest carbon chain).
- Secondly, calculate the number of halogen atoms present. If there are multiple halogen atoms present, then arrange the halogens alphabetically in the prefix, labelling them with their respective positions. But, if the same halogen atom is present more than once then use the prefixes di, tri, tetra, etc.

Nomenclature of Haloalkanes

Alkyl halides are named in two ways. In the common system, the alkyl group is named first followed by an appropriate word chloride, bromide, etc. The common name of an alkyl halide is always written as two separate words. In the IUPAC system, alkyl halides are named as haloalkanes. The other rules followed in naming compounds is that

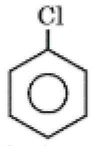
- Select the longest chain of carbon atoms containing the halogen atom.
- Number the chain to give the minimum number to the carbon carrying halogen atom.
- If multiple bonds (double or triple bond) is present, then it is given the preference in numbering the carbon chain.
- The IUPAC name of any halogen derivative is always written as one word.

Compound	**Common Name**	**IUPAC Name**
CH_3-Cl	Methyl Chloride	Chloromethane
CH_3-CH_2-Br	Ethyl bromide	Bromoethane
CH_3-$C(CH_3)_2$-Br	tert-Butyl bromide	2-Bromo-2-methylpropane
$CHCl_3$	Chloroform	Trichloromethane
CH_3-$CH(Br)_2$	Ethylidene bromide	1,1-Dibromoethane
CH_2=CH-CH_2-I	Allyl iodide	3-Iodoprop-1-ene

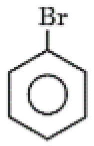
Nomenclature of Haloarenes

- Aryl halides are named by prefixing “halo” to the name of the parent aromatic hydrocarbon.
- If there is more than one substituent on the ring then the relative positions of the substituents are indicated by mathematical numerals.
- In the common system, the relative position of two groups is shown by prefixes ortho, meta or para.

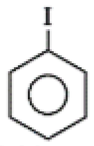
The common and IUPAC names of some representative haloarenes are given below.



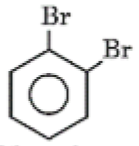
Chlorobenzene



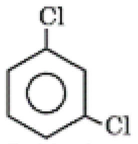
Bromobenzene



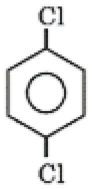
Iodobenzene



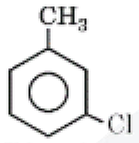
1,2-Dibromobenzene
(*ortho*-Dibromobenzene)



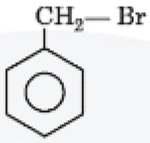
1, 3-Dichlorobenzene
(*meta*-Dichlorobenzene)



1,4-Dichlorobenzene
(*para*-Dichlorobenzene)



3-Chlorotoluene
(*meta*-Chlorotoluene)



Phenylbromomethane
(Benzyl bromide)

Haloarenes: Nature of C-X bond

Haloarenes are the chemical compounds containing arenes, where one or more hydrogen atoms bonded to an aromatic ring are replaced with halogens. The nature of C-X bond depends on both the nature of carbon in the aromatic ring and the halogen attached. Halogens are generally denoted by "X".

As we know halogens are group 17 elements having high electronegativity namely, fluorine (F), chlorine (Cl), bromine (Br), iodine (I) and astatine (At). Out of them, Fluorine has the highest electronegativity. The elements in this group are just one electron short of completing their nearest noble gas configuration.

Carbon in haloarenes is a 14th group element with comparatively lesser electronegativity in comparison to halogen molecules. This is due to the fact that electronegativity increase across a period from left to right.

Salient Points on the Nature of C-X Bond in Haloarenes are:

- The C-X bond in haloarenes is polarized, as halogens are more electronegative than carbon. Due to the high electronegativity of halogen, it attracts the electron cloud more towards itself and thus gains a slight negative charge, on the other hand, carbon obtains a slight positive charge.
- As halogens need only one electron to achieve their nearest noble gas configuration, only one sigma bond is formed between one carbon and one halogen atom.
- Due to the increase in atomic size from fluorine to astatine, the C-X bond length in haloarenes increases from fluorine to astatine and bond dissociation strength decreases.
- Dipole moment depends on the difference in electronegativity of carbon and halogens (group 17 trends properties) and as we know that the electronegativity of halogens decreases down the group, the dipole moment also decreases. There is an exception to C-Cl and C-F dipole moments. Though the electronegativity of Cl is less than F, the dipole moment of a C-Cl bond is more than C-F.

S_N1 and S_N2 Reaction of Haloalkanes

Haloalkanes are converted into alcohols using hydroxide ion in aqueous media through SN1 and SN2 Reactions. Alcohols can efficiently be prepared by substitution of haloalkanes and sulfonic esters with good leaving groups. The choice of reagents and reaction conditions for the hydrolysis is important because competitive elimination reactions are possible especially at high temperatures leading to alkenes.

The hydrolysis of haloalkanes depends on the structure of the haloalkanes, primary haloalkanes typically undergo S_N2 reactions whereas tertiary haloalkanes react an S_N1 mechanism for tertiary haloalkanes or tertiary alkyl halides. There are two kinds of reactions of haloalkanes naming S_N1 And S_N2 Reaction.

S_N1 Reaction

The S_N1 reaction is a substitution nucleophilic unimolecular reaction. It is a two-step reaction. In the first step, The carbon-halogen bond breaks heterolytically with the halogen retaining the previously shared pair of electrons. In the second step, the nucleophile reacts rapidly with the carbocation that was formed in the first step.

This reaction is carried out in polar protic solvents such as water, alcohol, acetic acid etc. This reaction follows first order kinetics. Hence, this is named as substitution nucleophilic unimolecular. This reaction takes place in two steps as described below.

Step-1:

- The bond between carbon and halogen breaks due to the presence of a nucleophile and formation of carbocation takes place.
- It is the slowest and the reversible step as a huge amount of energy is required to break the bond.
- The bond is broken by solvation of the compound in a protic solvent, thus this step is slowest of all.
- The rate of reaction depends only on haloalkane, not on nucleophile.

Step-2:

- The nucleophile attacks the carbocation formed in step 1 and the new compound is formed.
- Since, the rate defining step of the reaction is the formation of a carbocation, hence greater the stability of formation of an intermediate carbocation, more is the ease of the compound undergoing substitution nucleophilic unimolecular or S_N1 reaction.
- In the case of alkyl halides, 3° alkyl halides undergo S_N1 reaction very fast because of the high stability of 3° carbocations.
- Hence allylic and benzylic halides show high reactivity towards the S_N1 reaction.

S_N2 Reaction

This reaction follows second order kinetics and the rate of reaction depends upon both haloalkane and participating nucleophile. Hence, this reaction is known as substitution nucleophilic bimolecular reaction. In this reaction, the nucleophile attacks the positively charged carbon and the halogen leaves the group.

It is a one-step reaction. Both the formation of carbocation and exiting of halogen take place simultaneously. In this process, unlike the S_N1 mechanism, the inversion of configuration is observed. Since this reaction requires the approach of the nucleophile to the carbon bearing the leaving group, the presence of bulky substituents on or near the carbon atom has a dramatic inhibiting effect.

So opposite to S_N1 reaction mechanism, this is favoured mostly by primary carbon, then secondary carbon and then tertiary carbon. Nucleophilic substitution reaction depends on a number of factors. Some important factors include.

- Effect of the solvent
- Effect of the structure of the substrate
- Effect of the nucleophile
- Effect of leaving - group.

Comparing S_N1 and S_N2 Reactions

Related Concepts	S_N1 Reaction	S_N2 Reaction
Rate law	Unimolecular	Bimolecular
Haloalkane reactivity (electrophile)	$3^\circ > 2^\circ > 1^\circ$	$3^\circ < 2^\circ < 1^\circ$
Solvent	Polar solvent (protic solvent)	Polar aprotic solvent
Nucleophile	Weak nucleophile	Strong nucleophile
Stereochemistry	A mix of retention and inversion	Inversion

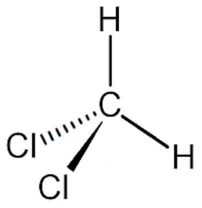
The solvent in which the nucleophilic substitution reaction is carried out also has an influence on whether an S_N2 or an S_N1 reaction will predominate. Before understanding how a solvent favours one reaction over another we must understand how solvents stabilize organic molecules.

Polyhalogen Compounds

Polyhalogen compounds: Carbon compounds containing more than one halogen atom permolecule.

Polyhalogen compounds are useful in various industries and in griculture. Some important polyhalogen compounds:

Dichloromethane (Methylene chloride)



Uses:

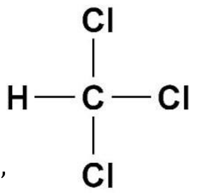
Dichloromethane (methylene chloride) is used as a:

1. Solvent for paint removers
2. Propellant in aerosols
3. Process solvent in the manufacture of drugs
4. Metal cleaning and finishing solvent

Harmful effects:

1. It endangers the human central nervous system.
2. Exposure to lower levels of methylene chloride in air can lead to slightly impaired hearing andvision.
3. High levels of methylene chloride in air cause dizziness, nausea, tingling and numbness in thefingers and toes.
4. In humans, direct skin contact with methylene chloride causes intense burning and mild rednessof the skin.
5. Direct contact with the eyes can burn the cornea.

Trichloromethane (Chloroform)



Uses:

1. Chemically, chloroform is used as a solvent for fats, alkaloids, iodine and other substances.
2. The major use of chloroform today is in the production of the freon refrigerant R-22.
3. It was once used as a general anaesthetic in surgery but has been replaced by less toxic, saferanaesthetics such as ether.

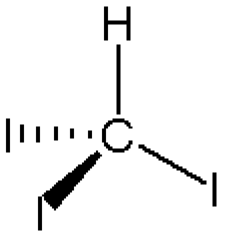
Harmful effects:

1. As might be expected from its use as an anaesthetic, inhaling chloroform vapour depresses the central nervous system.
2. Breathing about 900 parts of chloroform per million parts of air (900 ppm) for a short time can cause dizziness, fatigue and headache.
3. Chronic chloroform exposure may cause damage to the liver (where chloroform is metabolised to phosgene) and to the kidneys. Some people develop sores when the skin is immersed inchloroform.
4. Chloroform is slowly oxidised by air (oxygen) in the presence of light to an extremely poisonous gas, carbonyl chloride, also known as phosgene.

$$2CHCl_3 + O_2 \xrightarrow{\text{light}} \underset{\text{Phosgene}}{2COCl_2} + 2HCl$$

It is therefore stored in closed dark-coloured bottles which are completely filled so that air is keptout.

Triiodomethane (Iodoform)



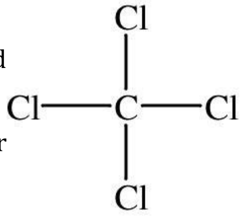
Uses:

- It was used earlier as an antiseptic, but the antiseptic properties are due to the liberation of freeiodine and not due to iodoform itself.

Drawback:

- Because of its objectionable smell, it has been replaced by other formulations containing iodine.

Tetrachloromethane (Carbon tetrachloride)



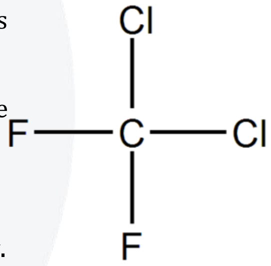
Uses:

1. It is produced in large quantities for use in the manufacture of refrigerants and propellants foraerosol cans.
2. It is also used as feedstock in the synthesis of chlorofluorocarbons and other chemicals, inpharmaceutical manufacturing and general solvent use.
3. Until the mid-1960s, it was also widely used as a cleaning fluid, both in industry, as a degreasingagent, and in the home, as a spot remover and fire extinguisher.

Harmful effects:

1. There is evidence that exposure to carbon tetrachloride causes liver cancer in humans.
2. The most common effects are dizziness, light headedness, nausea and vomiting, which cancause permanent damage to nerve cells.
3. In severe cases, these effects can lead rapidly to stupor, coma, unconsciousness or death. Exposure to CCl_4 can make the heart beat irregularly or stop.
4. The chemical may irritate the eyes on contact. When carbon tetrachloride is released into the air,it rises to the atmosphere and depletes the ozone layer.
5. Depletion of the ozone layer is believed to increase human exposure to ultraviolet rays, leading toincreased skin cancer, eye diseases and disorders, and possible disruption of the immunesystem.

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.
- They are manufactured from tetrachloromethane by Swarts reaction.
- By 1974, the total freon production in the world was about 2 billion pounds annually.

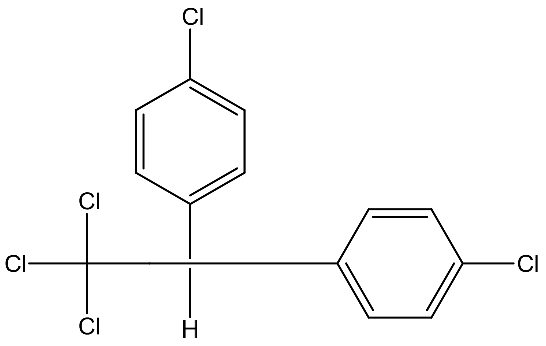
Uses:

1. These are usually produced for aerosol propellants, refrigeration and air conditioning purposes.
2. Freon 12 (CCl_2F_2) is one of the most common freons in industrial use.
3. Most freons, even those used in refrigeration, eventually make their way into the atmospherewhere it diffuses unchanged into the stratosphere.

Harmful Effect:

- In stratosphere, freons can initiate radical chain reactions which can upset the natural ozonebalance.

p,p′-Dichlorodiphenyltrichloroethane (DDT)



DDT, the first chlorinated organic insecticide, was originally prepared in 1873.

However, it was not until 1939 that Paul Muller of Geigy Pharmaceuticals in Switzerland discovered the effectiveness of DDT as an insecticide.

Paul Muller was awarded the Nobel Prize in Medicine and Physiology in 1948 for this discovery.

Paul Muller

Uses:

- The use of DDT increased enormously worldwide after World War II, primarily because of itseffectiveness against the mosquito which spreads malaria and lice which carry typhus.

Harmful Effects:

Problems related to extensive use of DDT began to appear in the late 1940s.

1. Many species of insects developed resistance to DDT.
2. It has a high toxicity towards fish.
3. The chemical stability of DDT and its fat solubility compounded the problem. DDT is not metabolised very rapidly by animals. Instead, it is deposited and stored in the fatty tissues. If ingestion continues at a steady rate, DDT builds up within the animal over time.

   The use of DDT was banned in the United States in 1973, although it is still in use in some other parts ofthe world.

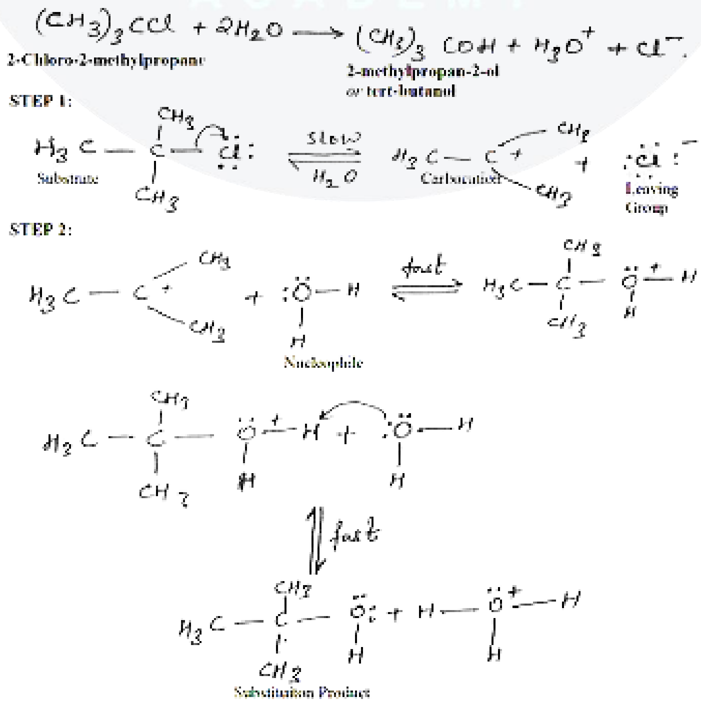
S_N1 mechanism

$$R-X \xrightarrow[\text{Slow}]{-\bar{X}} \overset{+}{R} \xrightarrow[\text{Fast}]{Nu^-} R-Nu$$

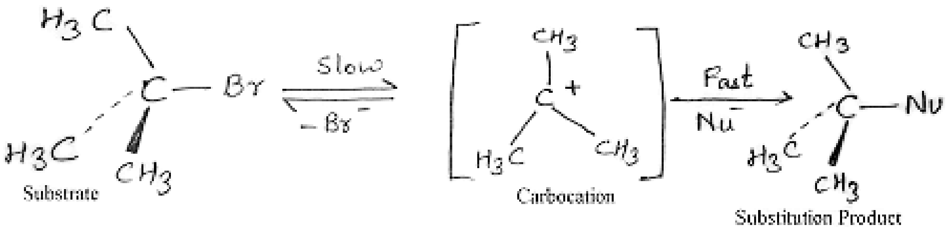
The tertiary alkyl halides react by S_N1 mechanism via formation of carbocation as intermediate. The reactivity order for S_N1 reaction is

Benzyl > Allyl > 3° > 2° > 1° > CH_3X.

A mechanism for the reaction of tert-butyl chloride with water apparently involves two steps:



Stereochemistry of S_N^1:



Key features:

More stable will be the carbocation intermediate; faster will be the SN^1 mechanism.

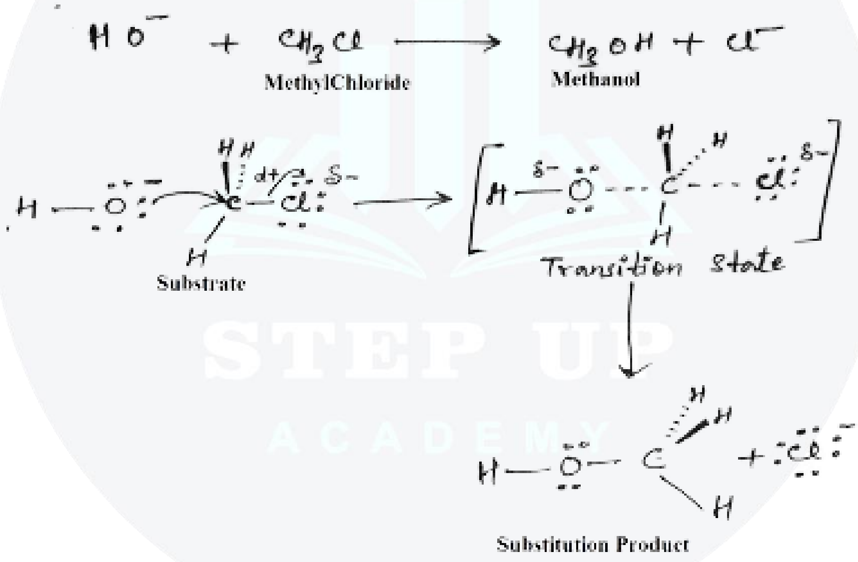
Polar solvents lead to polar transition state which in turn accelerates the SN^1 reaction.

If the initial compound is chiral then SN^1 reaction ends up with racemization of the product.

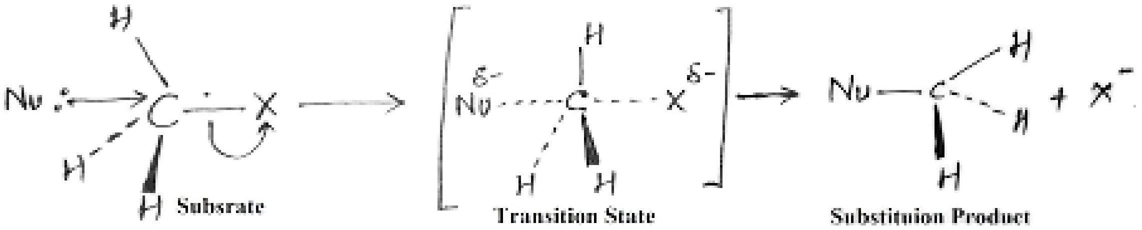
Weaker bases being leaving group favor SN^1 reaction.

S_N^2 mechanism

In case of S_N^2 reactions the halide ion leaves from the front side whereas the nucleophiles attacks from the back side; due to this reason S_N^2 reactions are always accompanied by the inversion of configuration. Thus formation of another enantiomer is lead by S_N^2 reaction of an optically active halide i.e. optical activity is retained but with opposite configuration.



Stereochemistry of SN^2:



Key features:

In SN^2 reaction the stereochemistry around carbon atom of the substrate undergoes inversion and is known as walden inversion.

The rate of reaction depends on the steric bulk of the alkyl group.

Increase in the length of alkyl group decreases the rate of reaction. Alkyl branching next to the leaving group decreases the rate drastically.

Under the following conditions S_N1 and S_N2 reactions take place:

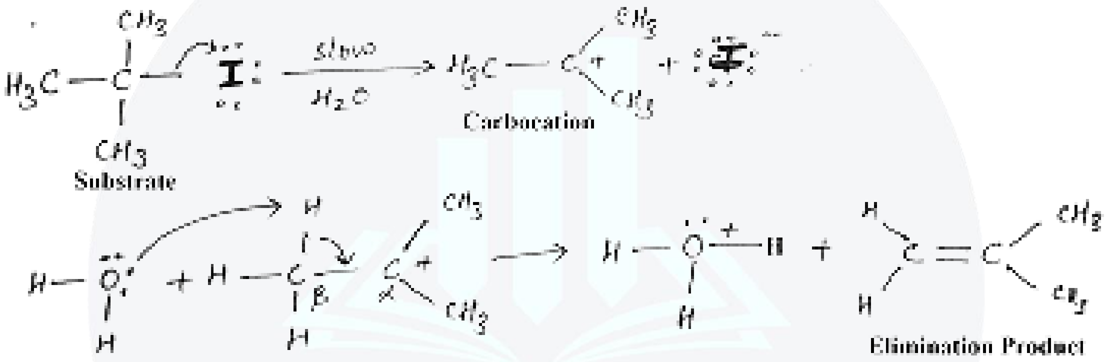
- The alkyl is secondary and tertiary.
- The solvent is Protic or Aprotic.
- To stabilize the intermediate stage..

E1 reaction

It is a unimolecular reaction. Rate determining step consist of formation of carbocation intermediate. Stability of carbocation intermediate determines the reactivity of E1 reaction.

Order of reactivity for E1 reaction is 30° > 20° > 10°. Both elimination and substitution reaction involves the use of (same reactive intermediate) carbocation. Therefore both the products are formed in comparable amount. This reaction is favored by entropy of reaction therefore increase in temperature favors the E1 reaction.

$(CH_3)_3CI + H_2O \rightarrow CH_2{=}C(CH_3)_2 + H_3O^+ + I^-$



Stereochemistry of E1 reaction:

E1 eliminations generally lead to the more stable stereochemistry.

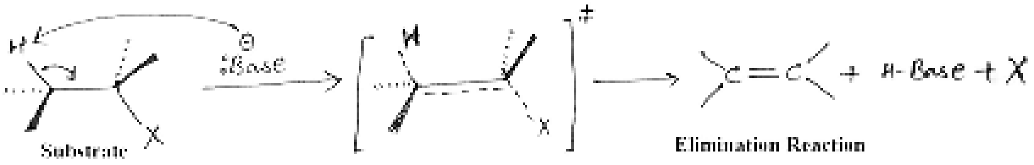
The rate of the E1 reaction depends only on the substrate, therefore more stable the carbocation is, faster will be the reaction. Slowest step is the formation of the carbocation. Alkenes formation doesn't require strong base, since there is no leaving group that needs to be displaced. So there is no requirement for the stereochemistry of the starting material;

E2 reaction

It's a biomolecular reaction. It is a single step reaction whose rate depends on the concentration of base and substrate. Reactivity depends on both strength of base and nature of alkyl halide. Order of reactivity for E1 reaction is 30° > 20° > 10°. This reaction proceeds at room temperature.

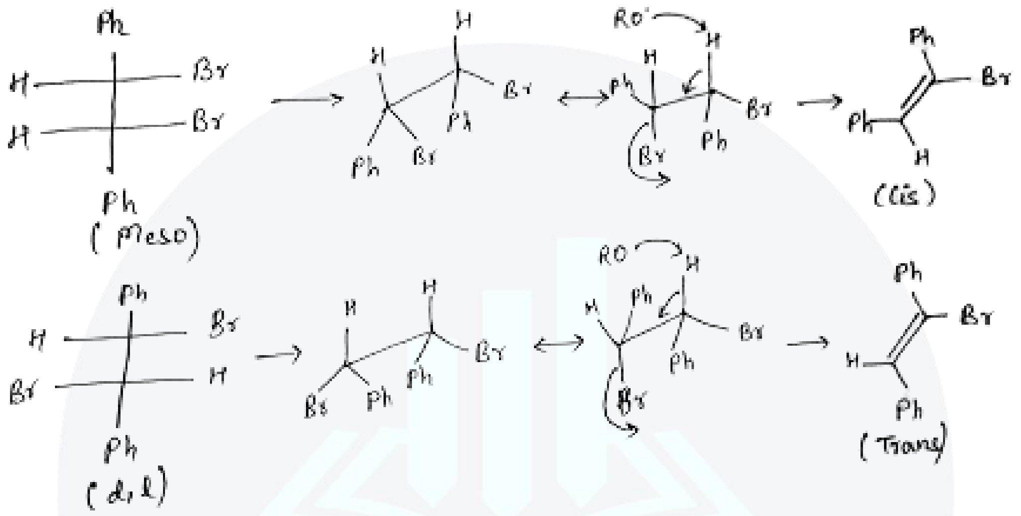
Example:

General mechanism:



Stereochemistry of E2 reaction:

E2 eliminations may or may not lead to the more stable stereochemistry. Initial material for this reaction has two sp^3 hybridized carbons which on rehybridization forms two sp^2 hybridized carbons. The C-X bond and the C-H bond lines up in the same plane and faces in anti directions to each other.



Class : 12th Chemistry
Chapter-10 : Haloalkanes And Haloarenes (Part_1)

Racemisation S_N1
- Chiral : Objects which are non-superimposable
- Achiral : objects which are superimposable

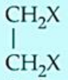
Haloalkanes and Haloarenes

Classification

- No. of halogen atoms

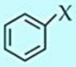
C_2H_5X

Monohaloalkane

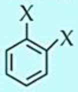


$$\begin{matrix} CH_2X \\ | \\ CH_2X \end{matrix}$$

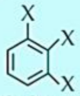
Dihaloalkane



Monohaloarene

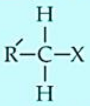


Dihaloarene

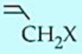


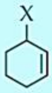
Trihaloarene

- Compounds containing sp^3 C–X bond
  - (a) Alkyl halides

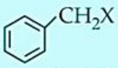


  - (b) Allylic halides

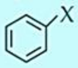




  - (c) Benzylic halides



- Compounds containing sp^2 C–X bond
  - (a) Vinylic halides
  - (b) Aryl halides

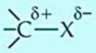


- Nomenclature

  Common name : alkyl group followed by halides. Dihalogen derivatives, prefixes o–, m–, p– are used.

  IUPAC name : numerals are used
- Nature of C –X bond

  : Carbon –halogen bond is polarized



Haloalkanes

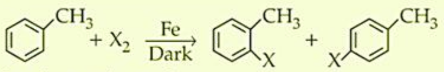
- Preparation
  - From alcohol :

$$R\text{–}OH + HCl \xrightarrow{ZnCl_2} R\text{–}Cl + H_2O$$
$$3R\text{–}OH + PX_3 \longrightarrow 3R\text{–}X + H_3PO_3$$
$$ROH + PCl_5 \longrightarrow R\text{–}Cl + POCl_3 + HCl$$

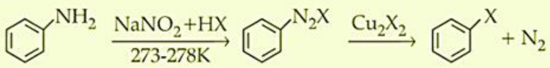
  - From hydrocarbons :
    - (a) By free radical halogenations

$$CH_3CH_2CH_2CH_3 \xrightarrow{Cl_2/UV} CH_3CH_2CH_2CH_2Cl + CH_3CH_2CHClCH_3$$

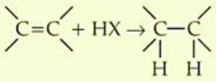
    - (b) By electrophilic substitution



    - (c) Sand meyer's reaction



    - (d) From alkenes



$$H_2C{=}CH_2 + Br_2 \xrightarrow{CCl_4} BrCH_2\text{–}CH_2Br$$

  - Halogen exchange :

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

- Properties
  - Physical : Colourless, volatile, sweet smell.

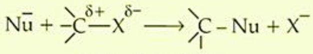
    Lower members are gases at room temperature while higher are solids.

    B.P : RI > R Br > RCl > RF.

    M.P : Para isomers have high m.p. than ortho and meta – isomers.

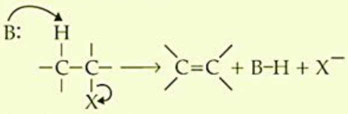
    Density : Increases with increase in number of C/X atoms and atomic masses of the X atoms.

    Solubility : Very slightly soluble in water.
  - Chemical :
    - (a) Nucleophilic substitution



$$\xrightarrow[\text{Tertiary, Secondary, Primary}]{\text{For } S_N2 \text{ reaction}}$$
$$\xleftarrow[\text{For } S_N1 \text{ reaction}]{}$$

    - (b) Elimination reaction



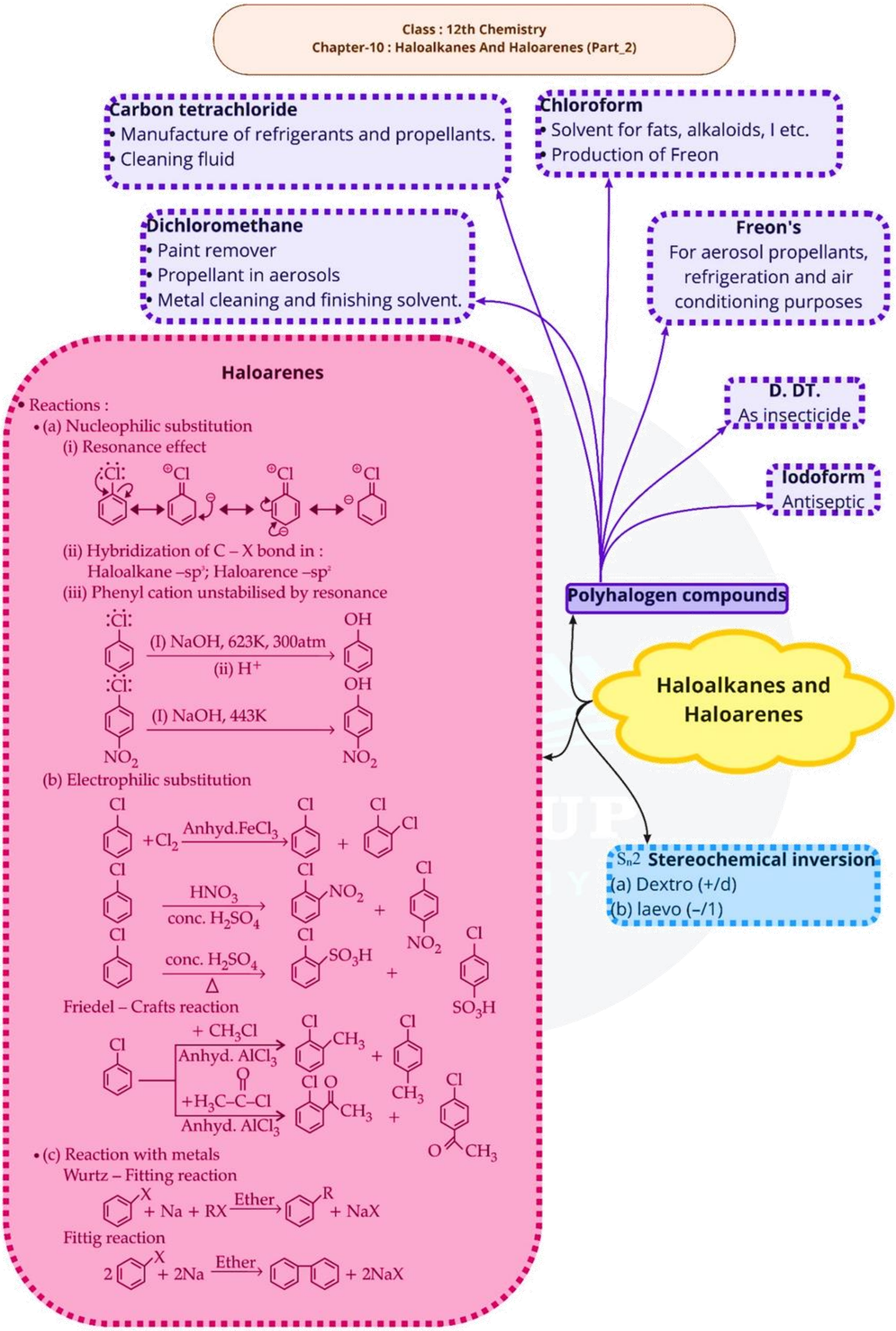
B = Base; X = Leaving group

    - (c) Reaction with metals

$$CH_2CH_2Br + M \longrightarrow CH_3CH_2MgBr$$

Wurtz reaction :

$$2RX + 2Na \xrightarrow{\text{Dry ether}} RR + 2NaX$$



Class : 12th Chemistry
Chapter-10 : Haloalkanes And Haloarenes (Part_2)

Haloalkanes and Haloarenes

Polyhalogen compounds

Carbon tetrachloride
- Manufacture of refrigerants and propellants.
- Cleaning fluid

Chloroform
- Solvent for fats, alkaloids, I etc.
- Production of Freon

Dichloromethane
- Paint remover
- Propellant in aerosols
- Metal cleaning and finishing solvent.

Freon's
For aerosol propellants, refrigeration and air conditioning purposes

D. DT.
As insecticide

Iodoform
Antiseptic

S_N2 Stereochemical inversion
(a) Dextro (+/d)
(b) laevo (–/1)

Haloarenes

- Reactions :
  - (a) Nucleophilic substitution
    (i) Resonance effect
    (ii) Hybridization of C – X bond in :
    Haloalkane –sp^3; Haloarence –sp^2
    (iii) Phenyl cation unstabilised by resonance
  - (b) Electrophilic substitution
    Friedel – Crafts reaction
  - (c) Reaction with metals
    Wurtz – Fitting reaction
    Fittig reaction

Important Questions

Multiple Choice questions-

1. S_N1 reaction of alkyl halides lead to
   (a) Retention of configuration
   (b) Racemisation
   (c) Inversion of configuration
   (d) None of these

2. p-djchlorobenzene has higher melting point than its o- and m- isomers because
   (a) p-dichlorobenzene is more polar than o- and m- isomer.
   (b) p-isomer has a symmetrical crystalline structure.
   (c) boiling point of p-isomer is more than o- and m-isomer.
   (d) All of these are correct reasons.

3. Chloropicrin is formed by the reaction of
   (a) steam on carbon tetrachloride.
   (b) nitric acid on chlorobenzene.
   (c) chlorine on picric acid.
   (d) nitric acid on chloroform.

4. Fitting reaction can be used to prepare
   (a) Toluene
   (b) Acetophenon
   (c) Diphenyl
   (d) Chlorobenzene

5. Identify the end product (C) in the following sequence:

   $$C_2H_5OH \xrightarrow[\text{Pyridine}]{SOCl_2} A \xrightarrow{KCN(alc.)} B \xrightarrow{2H_2O/H^+} C$$

   (a) $C_2H_5CH_2NH_2$
   (b) $C_2H_5CONH_2$
   (c) C_2H_5COOH
   (d) $C_2H_5NH_2$ + HCOOH

6. $CH_3CH_2CH_2Cl \xrightarrow{alc.KOH} B \xrightarrow{HBr} C \xrightarrow{Na/ether} D$

   In the above reaction, the product D is
   (a) Propane
   (b) 2, 3-Dimethylbutane
   (c) Hexane
   (d) Allyl bromide

7. Identify X and Y in the following sequence

   $$C_2H_5Br \xrightarrow{X} \text{Product} \xrightarrow{Y} C_3H_7NH_2$$

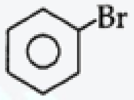
   (a) X = KCN, Y = $LiAlH_4$
   (b) X = KCN, Y = H_3O^+
   (c) X = CH_3Cl, Y = $AlCl_3$ HCl
   (d) X = CH_3NH_2, Y = HNO_2

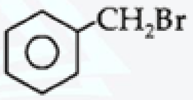
8. In the following sequence of reactions:

   $$C_2H_5Br \xrightarrow{AgCN} X \xrightarrow{\text{Reduction}} Y; \text{ Y is}$$

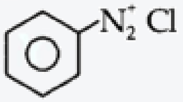
   (a) n-propylamine
   (b) isopropylamine
   (c) ethylamine
   (d) ethylmethylamine

9. $X \xrightarrow[HNO_3]{AgNO_3}$ Yellow or While ppt Which of the following cannot be X?

   (a) 

   (b) 

   (c) $(CH_3)_3$ Cl

   (d) 

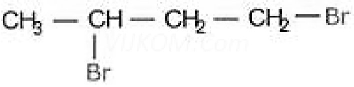
10. Identify Z in the series

    $$CH_2=CH_2 \xrightarrow{HBr} X \xrightarrow{aq.KOH} Y \xrightarrow[I_2\ excess]{Na_2CO_3} Z$$

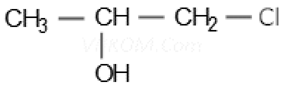
    (a) C_2H_5I
    (b) C_2H_5OH
    (c) CHI_3
    (d) CH_3CHO

Very Short Questions-

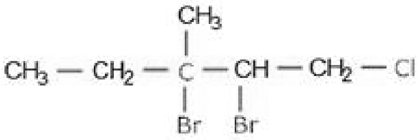
1. **Give IUPAC names of following compounds**

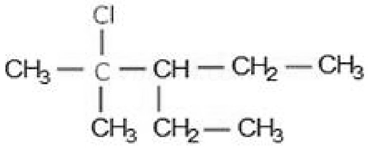
   (i) 

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

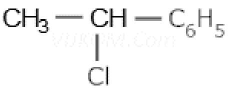
   (ii) 

   $CH_3-\underset{|\atop OH}{CH}-CH_2-Cl$

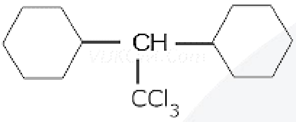
(iii)

$CH_3-CH_2-\underset{Br}{\overset{CH_3}{C}}-\underset{Br}{CH}-CH_2-Cl$

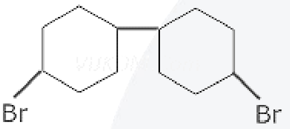
(iv)

$CH_3-\underset{CH_3}{\overset{Cl}{C}}-\underset{CH_2-CH_3}{CH}-CH_2-CH_3$

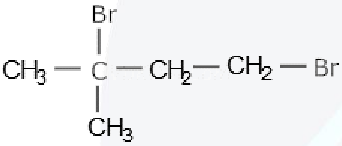
(v) $C_6H_5CH_2CH_2Cl$

(vi)

$CH_3-\underset{Cl}{CH}-C_6H_5$

(vii) $C_6H_6Cl_6$

(viii)


(ix)


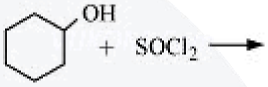
(x)

$CH_3-\underset{CH_3}{\overset{Br}{C}}-CH_2-CH_2-Br$

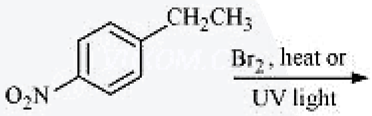
Short Questions

1. Thionyl chloride is preferred for converting alcohol to haloalkane.
2. Phenol cannot be converted to chlorobenzene by reacting with HCl.
3. HNO_3 is added during iodination of benzene.
4. p-dichlorobenzene has higher melting point than meta – dichlorobenzene.
5. The boiling points of isomeric haloalkenes decrease with increase in branching.
6. Hydrolysis of optically active 2- bromobutane forms optically inactive butan – 2 – ol.
7. Chlorobenzene is less reactive towards nucleophilic substitution reaction.
8. Chloroform is stored in dark coloured bottles.
9. The order of boiling points is $RCl < RBr < RI$.
10. Vinyl chloride is less reactive than allyl chloride.

Long Questions

1. Write structures of the following compounds:
   (i) 2-Chloro-3-methylpentane
   (ii) 1-Chloro-4-ethylcyclohexane
   (iii) 4-tert. Butyl-3-iodoheptane
   (iv) 1,4-Dibromobut-2-ene
   (v) 1-Bromo-4-sec. butyl-2-methylbenzene
2. Write structures of different dihalogen derivatives of propane.
3. Among the isomeric alkanes of molecular formula C_5H_{12}, identify the one that on photochemical chlorination yields
   (i) A single monochloride.
   (ii) Three isomeric monochlorides.
   (iii) Four isomeric monochlorides.
4. Draw the structures of major monohalo products in each of the following reactions:

(i)


(ii)


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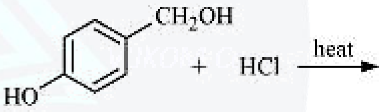

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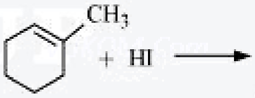
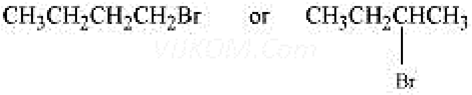
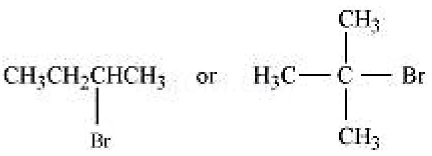


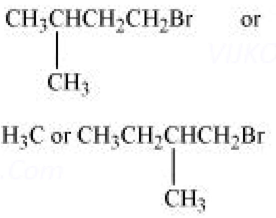
(v) $CH_3CH_2Br + NaI \longrightarrow$

(vi)

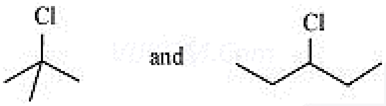

5. Arrange each set of compounds in order of increasing boiling points.
   (i) Bromomethane, Bromoform, Chloromethane, Dibromomethane.
   (ii) 1-Chloropropane, Isopropyl chloride, 1-Chlorobutane.
6. Which alkyl halide from the following pairs would you expect to react more rapidly by an S_N2 mechanism? Explain your answer.

(i)

$CH_3CH_2CH_2CH_2Br$ or $CH_3CH_2\underset{Br}{CH}CH_3$

(ii) 

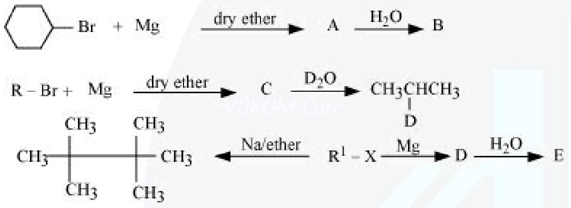
(iii) 

7. In the following pairs of halogen compounds, which compound undergoes faster S_N1 reaction?

(i) 

(ii) 

8. Identify A, B, C, D, E, R and R^1 in the following:



Assertion and Reason Questions

1. In these questions, a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following choices.

a) Assertion and reason both are correct statements and reason is correct explanation for assertion.

b) Assertion and reason both are correct statements but reason is not correct explanation for assertion.

c) Assertion is correct statement but reason is wrong statement.

d) Assertion is wrong statement but reason is correct statement.

Assertion: Isopropyl chloride is less reactive than CH3 Br in S_N2 reactions.

Reason: S_N2 reactions are always accompanied by inversion of configuration.

2. In these questions, a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following choices.

a) Assertion and reason both are correct statements and reason is correct explanation for assertion.

b) Assertion and reason both are correct statements but reason is not correct explanation for assertion.

c) Assertion is correct statement but reason is wrong statement.

d) Assertion is wrong statement but reason is correct statement.

Assertion: Lower members of alkyl halides are colourless gases.

Reason: Alkyl iodides in general turn black on exposure to air and light.

Case Study Questions

1. Read the passage given below and answer the following questions:

Haloarenes are less reactive than haloalkanes. The low reactivity of haloarenes can be attributed to:

- Resonance effect.
- sp^2 hybridisation of C - X bond.
- Polarity of C - X bond
- Instability of phenyl cation (formed by self-ionisation of haloarene).
- Repulsion between the electron rich attacking nucleophiles and electron rich arenes.

Reactivity of haloarenes can be increased or decreased by the presence of certain groups at certain positions for example, nitro ($-NO^2$) group at o/ p positions increases the reactivity of haloarenes towards nucleophilc substitution reactions.

The following questions are multiple choice questions Choose the most appropriate answer:

(i) Aryl halides are less reactive towards nucleophilic substitution reaction as compared to alkyl halides due to

a) The formation of less stable carbonium ion.

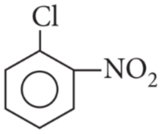
b) Resonance stabilisation.

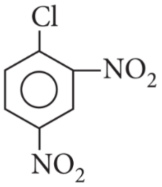
c) Larger carbon-halogen bond.

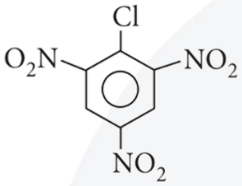
d) Inductive effect.

(ii) Which of the following aryl halides is the most reactive towards nucleophilic substitution?

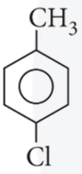
(a) 

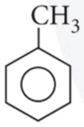
(b) 

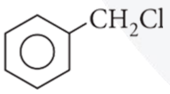
(c) 

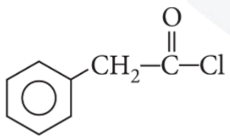
(d) 

(iii) Which one of the following will react fastest with aqueous NaOH?

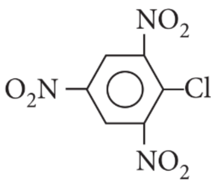
(a) 

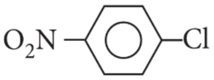
(b) 

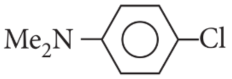
(c) 

(d) 

(iv) Which chloro derivative of benzene among the followings would undergo hydrolysis most readily with aqueous sodium hydroxide to furnish the corresponding hydroxy derivative?

(a) 

(b) 

(c) 

(d) C_6H_5Cl

(v) The reactivity of the compounds (i) MeBr, (ii) $PhCH_2Br$, (iii) MeCI, (iv) p-$MeOC_6H_4Br$ decreases as:

a) (i) > (ii) > (iii) > (iv)
b) (iv) > (ii) > (i) > (iii)
c) (iv) > (iii) > (i) > (ii)
d) (ii) > (i) > (iii) > (iv)

2. Read the passage given below and answer the following questions:

A chlorocompound (A) on reduction with Zn-Cu and ethanol gives the hydrocarbon (B) with five carbon atoms. When (A) is dissolved in dry ether and treated with sodium metal it gave 2, 2, 5, 5 - tetramethylhexane. The treatment of (A) with alcoholic KCN gives compound (C).

The following questions are multiple choice questions. Choose the most appropriate answer:

(i) The compound (A) is:

a) 1-chloro-2, 2-dimethylpropane.
b) 1-chloro-2, 2-dimethyl butane.
c) 1-chloro-2-methyl butane.
d) 2-chloro-2-methyl butane.

(ii) The reaction of (C) with Na, C_2H_5OH gives:

a) $(CH_3)_3C\ CH_2CONH_2$
b) $(CH_3)_3C\ NH_2$
c) $(CH_3)_3C\ CH_2CH_2NH_2$
d) $(CH_3)_2CHCH_2NH_2$

(iii) The reaction of (C) with Na, C_2H_5OH is called:

a) Gilman reaction.
b) Mendius reaction.
c) Grooves process.
d) Swart's reaction.

(iv) The reaction of (A) with aq. KOH will preferably favour:

a) S_N1 mechanism.
b) S_N2 mechanism.
c) E_1 mechanism.
d) E_2 mechanism.

(v) Compound (B) is:

a) N-pentane.
b) 2, 2-dimethylpropane.
c) 2-methylbutane.
d) None of these.

Answer Key

MCQ Answers-

1. Answer: b
2. Answer: b
3. Answer: d
4. Answer: c
5. Answer: c
6. Answer: b
7. Answer: a
8. Answer: d
9. Answer: a
10. Answer: c

Very Short Answers-

(i) 1, 3- Dibromobutane

(ii) 1- Cholopropan-2-ol

(iii) 2, 3 – Dibromo-1-chloro-3-methylpentane

(iv) 2-Choloro-3-ethyl-2-methyl pentane

(v) 1-Chloro-2-phenylethane

(vi) 1-Chloro-1-phenyl ethane

(vii) 1, 2, 3, 4, 5, 6- hexachlorocyclohexane

(viii) 2, 2- Dihexyl 1, 1, 1-Trichloro ethane

(ix) 4, 4-dibromobiphenyl

(x) 1, 3-Dibromo -3- methyl butane

Short Answers-

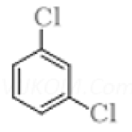
1. Thionyl chloride is preferred for converting alcohol to haloalkane because the bi- products formed are all gases which escape into the atmosphere.

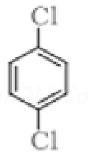
$R—OH + SOCl_2 \rightarrow RCl + SO_2 + HCl$

2. In phenol, due to resonance, the carbon –oxygen bond has a partial double bond character and is difficult to break being stronger than a single bond. Therefore, it can-not be converted to chlorobenzene by reacting with HCl.

3. When benzene is reacted with iodine, the reaction is reversible in nature. It leads to the formation of reactants back. Therefore, and oxidizing agent like HNO_3 oxidizes the HI formed in the reaction and keeps the reaction in forward direction.

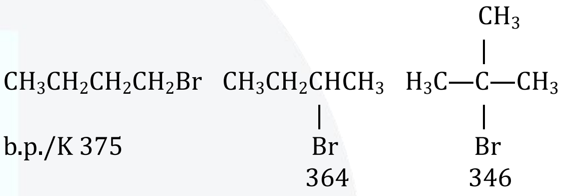
4.


m – dichlorobenzene


p - dichlorobenzene

p- dichlorobenzene is having symmetrical structure therefore it can fit better into the crystal lattice which increases its melting point.

5. The boiling points of isomeric haloalkanes decreases with branching due to decrease in surface areas with branching. As branching increasing the structure becomes more spherical and the surface area decreases. e.g. the boiling points of isomers of C_4H_9Br follows the order.



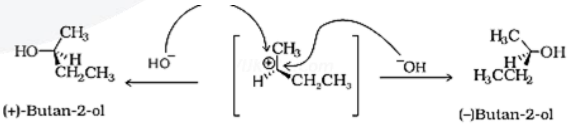
$CH_3CH_2CH_2CH_2Br$ $\quad CH_3CH_2\underset{Br}{\underset{|}{C}}HCH_3 \quad H_3C—\overset{CH_3}{\overset{|}{\underset{Br}{\underset{|}{C}}}}—CH_3$

b.p./K 375 364 346

6. $CH_3\,\underset{Br}{\underset{|}{C}H}—CH_2\,CH_3$ 2-Bromo butane

The compound undergoes hydrolysis by $S_N{}^1$ mechanism via the formation of carbocation which is planar.

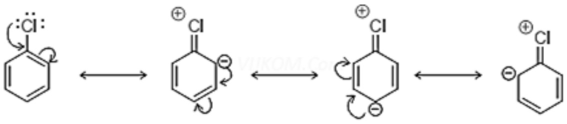
The attack of nucleophile can result in product which is a mixture of compounds both with same configuration and inverted configuration.



Therefore it results in the formation of racemic mixture which is optically inactive.

7. Chlorobenzene is less reactive towards nucleophilic substitution due to –

i. resonance, C- Cl bond acquires a double bond character and becomes stronger than a single bond.



ii. SP^2 hybridisation in C of C-X bond, the carbon becomes more electronegative and holds the electron pair of C-X bond more tightly decreasing the bond length.

iii. Instability of phenyl cation.

iv. Repulsion for incoming nucleophile from electron rich ring.

8. Chloroform gets oxidsed slowly by air in the presence of light to an extremely poisonous gas phosgene. Therefore, to avoid any exposure to air and sunlight, it is kept in dark coloured bottles.

$$2CHCl_3 + O_2 \xrightarrow[\text{light}]{} 2COCl_2 + 2HCl$$

9. The boiling points of alkyl halides depends on dipole and van-der-waal's interaction. These attractions get stronger as the molecules get bigger in size and have more electrons. As the size of halogens increases in the order –

Cl < Br < I

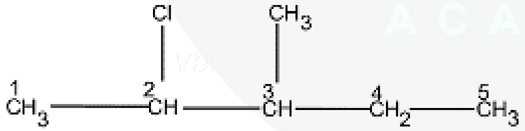
The boiling points also follow the order

RCl < RBr <RI

10. Due to resonance C- Cl bond gets double bond character and becomes stronger than a single bond, making vinyl chloride less reactive than allyl chloride.

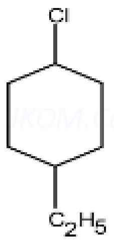
Long Answers-

1. (i) 2-Chloro-3-methyl pentane

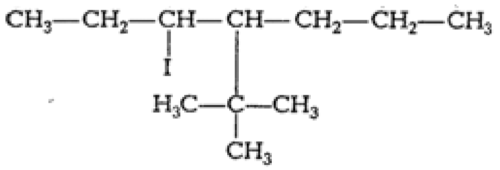


$$\overset{1}{C}H_3-\overset{2}{C}H(Cl)-\overset{3}{C}H(CH_3)-\overset{4}{C}H_2-\overset{5}{C}H_3$$

(ii) 1-Chloro-4-ethylcyclohexane



(iii) 4- tert-Butyl-3-iodoheptane



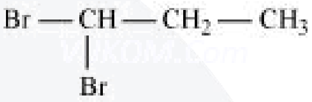
(iv) 1, 4-Dibromobut-2-ene

$$Br-\overset{1}{C}H_2-\overset{2}{C}H=\overset{3}{C}H-\overset{4}{C}H_2-Br$$

(v) 1-Bromo-4-sec-butyl-2-methylbenzene

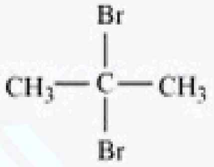
2. There are four different dihalogen derivatives of propane. The structures of these derivatives are shown below.

(i) 1, 1-Dibromopropane



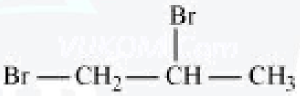
$$Br-CH(Br)-CH_2-CH_3$$

(ii) 2, 2-Dibromopropane



$$CH_3-CBr_2-CH_3$$

(iii) 1, 2-Dibromopropane

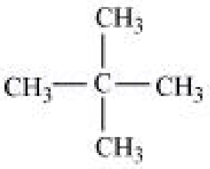


$$Br-CH_2-CH(Br)-CH_3$$

(iv) 1, 3-Dibromopropane

$$Br-CH_2-CH_2-CH_2-Br$$

3. (i) To have a single monochloride, there should be only one type of H-atom in the isomer of the alkane of the molecular formula C_5H_{12}. This is because, replacement of any H-atom leads to the formation of the same product. The isomer is neopentane.



$$C(CH_3)_4$$

Neopentane

(ii) To have three isomeric monochlorides, the isomer of the alkane of the molecular formula C_5H_{12} should contain three different types of H-atoms.

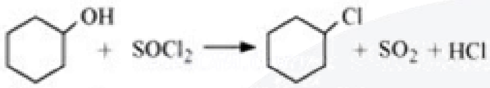
Therefore, the isomer is *n*-pentane. It can be observed that there are three types of H atoms labelled as *a*, *b* and *c* in *n*-pentane.

$$\overset{c}{C}H_3-\overset{b}{C}H_2-\overset{a}{C}H_2-\overset{b}{C}H_2-\overset{c}{C}H_3$$

n-Pentane

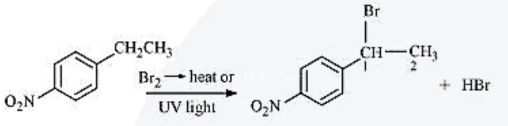
(iii) To have four isomeric monochlorides, the isomer of the alkane of the molecular formula C_5H_{12}should contain four different types of H-atoms. Therefore, the isomer is 2-methylbutane. It can be observed that there are four types of H-atoms labelled as *a*, *b*, *c*, and *d* in 2-methylbutane.

4\. (i)



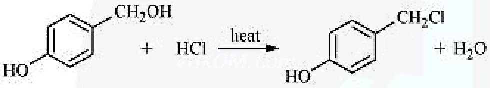
Cyclohexanol — Chlorocyclohexane

(ii)



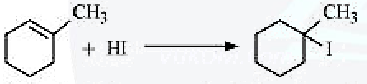
4 – Ethylnitrobenzene — 4 – (1 – Bromoethyl) nitrobenzene

(iii)



4 – Hydroxymethylphenol — 4 – Chloromethylphenol

(iv)

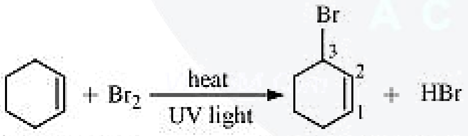


1 – Methylcyclohexene — 1 – Iodo – 1 – methylcyclohexane

(v) $CH_3CH_2Br + NaI \longrightarrow CH_3CH_2I + NaBr$

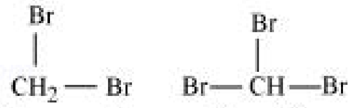
Bromoethane — Iodoethane

(vi)



Cyclohexene — 3 – Bromocyclohexene

5\. (i) $CH_3—Cl$ Chloromethane $CH_3—Br$ Bromomethane



$$\underset{\text{Dibromomethane}}{\overset{Br}{CH_2}—Br} \qquad Br—\overset{Br}{CH}—Br$$

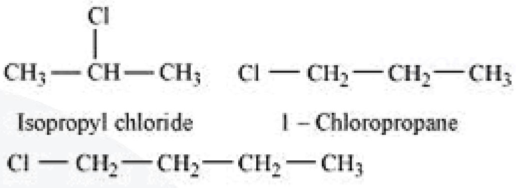
Dibromomethane   Bromoform

For alkyl halides containing the same alkyl group, the boiling point increases with an increase in the atomic mass of the halogen atom.

Since the atomic mass of Br is greater than that of Cl, the boiling point of bromomethane is higher than that of chloromethane. Further, for alkyl halides containing the same alkyl group, the boiling point increases with an increase in the number of halides. Therefore, the boiling point of Dibromomethane is higher than that of chloromethane and bromomethane, but lower than that of bromoform. Hence, the given set of compounds can be arranged in the order of their increasing boiling points as:

Chloromethane < Bromomethane < Dibromomethane < Bromoform.

(ii)



$$CH_3—\overset{Cl}{CH}—CH_3 \qquad Cl—CH_2—CH_2—CH_3$$

Isopropyl chloride   1 – Chloropropane

$Cl—CH_2—CH_2—CH_2—CH_3$

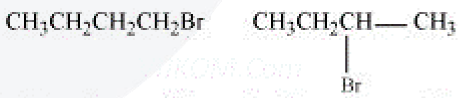
1 – Chlorobutane

For alkyl halides containing the same halide, the boiling point increases with an increase in the size of the alkyl group. Thus, the boiling point of 1-chlorobutane is higher than that of isopropyl chloride and 1-chloropropane. Further, the boiling point decreases with an increase in branching in the chain. Thus, the boiling point of isopropyl alcohol is lower than that of 1-chloropropane.

Hence, the given set of compounds can be arranged in the increasing order of their boiling points as:

Isopropyl chloride < 1-Chloropropane < 1-Chlorobutane

6\. (i)

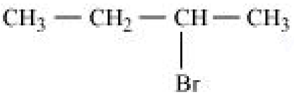


$$CH_3CH_2CH_2CH_2Br \qquad CH_3CH_2\underset{Br}{CH}—CH_3$$

1 – Bromobutane (1°)   2 – Bromobutane (2°)

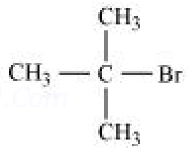
2-bromobutane is a 2° alkylhalide whereas 1-bromobutane is a 1° alkyl halide. The approaching of nucleophile is more hindered in 2-bromobutane than in 1-bromobutane. Therefore, 1-bromobutane reacts more rapidly than 2-bromobutane by an $S_N2$mechanism.

(ii)



$$CH_3—CH_2—\underset{Br}{CH}—CH_3$$

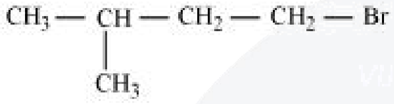
2 – Bromobutane (2°)



$$CH_3-\overset{CH_3}{\underset{CH_3}{C}}-Br$$

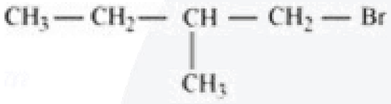
2 – Bromo – 2 – methylpropane (3°)

2-Bromobutane is 2° alkylhalide whereas 2-bromo-2-methylpropane is 3° alkyl halide. Therefore, greater numbers of substituents are present in 3° alkyl halide than in 2° alkyl halide to hinder the approaching nucleophile. Hence, 2-bromobutane reacts more rapidly than 2-bromo-2-methylpropane by an S_N2 mechanism.

(iii)


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

1 – Bromo – 3 – methylbutane (1°)



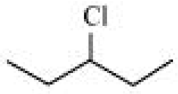
$$CH_3-CH_2-\underset{CH_3}{CH}-CH_2-Br$$

1 – Bromo – 2 – methylbutane (1°)

Both the alkyl halides are primary. However, the substituent $-CH_3$ is at a greater distance to the carbon atom linked to Br in 1-bromo-3-methylbutane than in 1-bromo-2-methylbutane. Therefore, the approaching nucleophile is less hindered in case of the former than in case of the latter. Hence, the former reacts faster than the latter by S_N2 mechanism.

7. (i)


2 – Chloro – 2 – methylpropane (3°)
(I)



3 – chloropentane (2°)
(II)

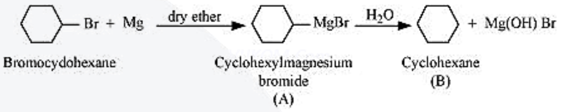
S_N1 reaction proceeds via the formation of carbocation. The alkyl halide (I) is 3° while (II) is 2°. Therefore, (I) forms 3° carbocation while (II) forms 2° carbocation. Greater the stability of the carbocation, faster is the rate of S_N1 reaction. Since 3° carbocation is more stable than 2° carbocation. (I), i.e. 2-chloro-2-methylpropane, undergoes faster S_N1 reaction than (II) i.e., 3-chloropentane.

(ii)

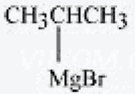

2 – chloroheptane (2°)
(I)

1 – chlorohexane (1°)
(II)

The alkyl halide (I) is 2° while (II) is 1°. 2° carbocation is more stable than 1° carbocation. Therefore, (I), 2-chloroheptane, undergoes faster S_N1 reaction than (II), 1-chlorohexane.

8.


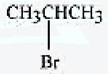
Since D of D_2O gets attached to the carbon atom to which MgBr is attached, C is



$$CH_3\underset{MgBr}{CH}CH_3$$

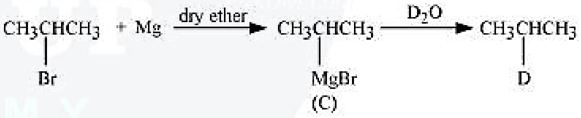
Isopropylmagnesium bromide

Therefore, the compound R – Br is

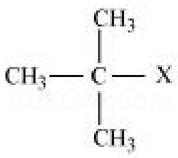


$$CH_3\underset{Br}{CH}CH_3$$

2 – Bromopropane



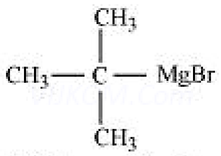
When an alkyl halide is treated with Na in the presence of ether, a hydrocarbon containing double the number of carbon atoms as present in the original halide is obtained as product. This is known as Wurtz reaction. Therefore, the halide, R^1–X, is



$$CH_3-\overset{CH_3}{\underset{CH_3}{C}}-X$$

tert – Butylhalide

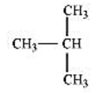
Therefore, compound D is



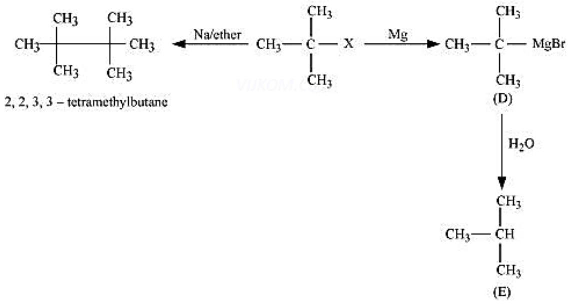
$$CH_3-\overset{CH_3}{\underset{CH_3}{C}}-MgBr$$

tert – Bulytmagnesiumbromide

And, compound E is



2 – Methylpropane



Assertion and Reason Answers

1. (b) Assertion and reason both are correct statements but reason is not correct explanation for assertion.

Explanation:

As the size of the alkyl groups increases, the S_N2 reactivity decreases, further C - Cl bond is stronger and more difficult to cleave than C - Br bond. So CH_3Br is more reactive than $(CH_3)_2CHCl$.

2. (c) Assertion is correct statement but reason is wrong statement.

Explanation:

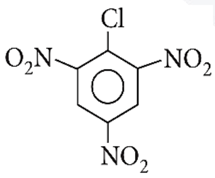
Alkyl iodides in general turn brown due to liberation of I^2 on decomposition by the action of air and light.

Case Study Answers-

1. Answer :

(i) (b) Resonance stabilisation.

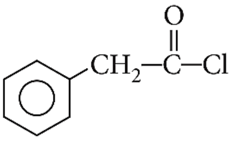
(ii) (d)



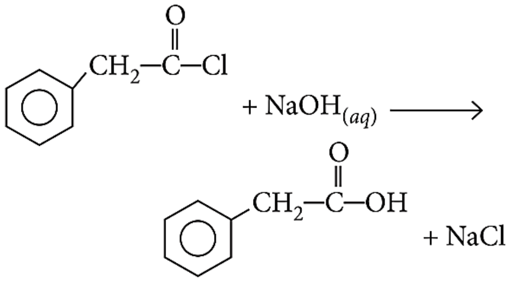
Explanation:

When in aryl halides the electron withdrawing groups are attached at ortho and para positions to the chlorine atom then the removal of chlorine atom as Cll- ion becomes easy, therefore, 2,4,6-trinitro chlorobenzene is the most reactive among given aryl halides.

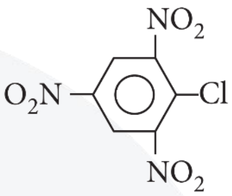
(iii) (d)



Explanation:



(iv) (a)



Explanation:

Cl in 2,4,6-trinitrochlorobenzene is activated by three NO_2 groups at o, and p-positions and hence undergoes hydrolysis most readily.

(v) (d) (ii) > (i) > (iii) > (iv)

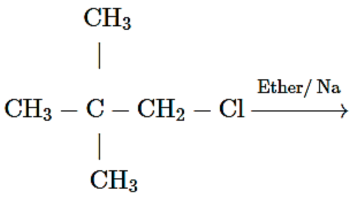
Explanation:

The order of reactivity follows the sequence: benzyl halides > alkyl halides> aryl halides. Out of chlorides and bromides, bromides are more reactive. Therefore, the correct order of reactivity is $PhCH_2Br$ (ii) > MeBr (i) > MeCl (iii) > p - $MeOC_6H_4Br$ (iv).

2. Answer :

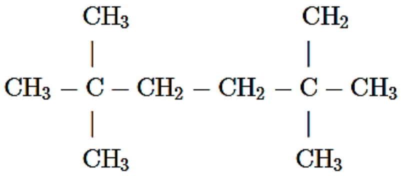
(i) (a) 1-chloro-2, 2-dimethylpropane.

Explanation:



$$CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_2-Cl\xrightarrow{\text{Ether/ Na}}$$

I -Chloro-2, 2-di methylpropane

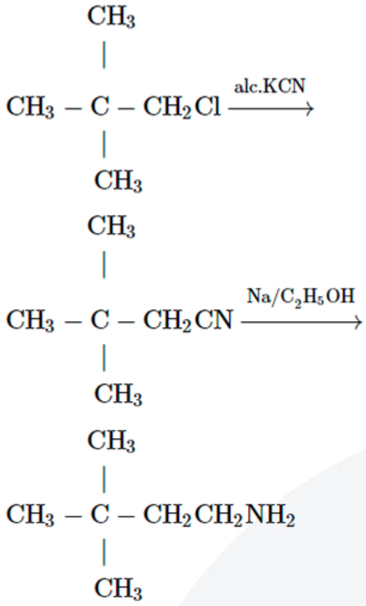


$$CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_2-CH_2-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_2}{|}}{C}}-CH_3$$

2, 2, 5, 5-Tetramethylhexane

(ii) (c) $(CH_3)_3C\ CH_2CH_2NH_2$

Explanation:



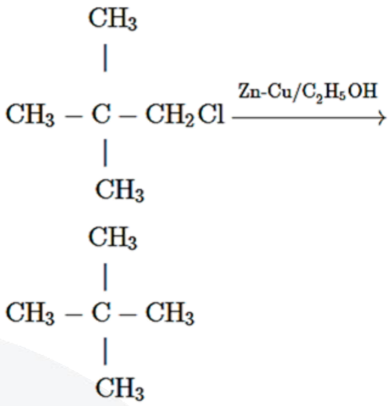
$$CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH_2Cl \xrightarrow{\text{alc.KCN}} CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH_2CN \xrightarrow{Na/C_2H_5OH} CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH_2CH_2NH_2$$

(iii) (b) Mendius reaction.

(iv) (a) S_N1 mechanism.

(v) (b) 2, 2-dimethylpropane.

Explanation:



$$CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH_2Cl \xrightarrow{Zn\text{-}Cu/C_2H_5OH} CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH_3$$

❖ ❖

Alcohols, Phenols and Ethers

8

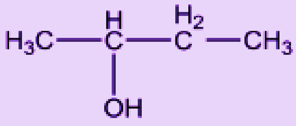
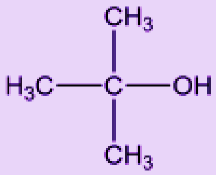
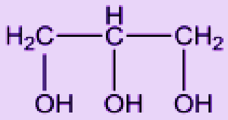
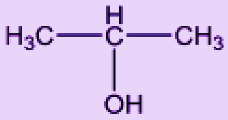
Introduction

- Alcohols and phenols are compounds formed when a hydrogen atom in a hydrocarbon is replaced by–OH group.
- An alcohol contains one or more hydroxyl (OH) group(s) directly attached to carbon atom(s) of analiphatic system.
- A phenol contains –OH group(s) directly attached to carbon atom(s) of an aromatic system (C_6H_5OH).
- The substitution of a hydrogen atom in a hydrocarbon by an alkoxy or aryloxy group (R-O/Ar-O) givesanother class of compounds known as ethers.

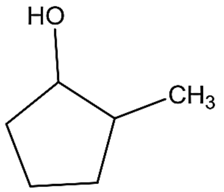
  For example: $C_2H_5-O-C_2H_5$ (Dimethyl ether)

Nomenclature

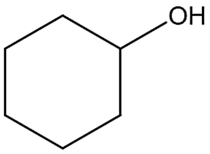
Alcohols

Compound	Common name	IUPAC name
 $H_3C-\underset{OH}{\overset{H}{C}}-\overset{H_2}{C}-CH_3$	*sec*-Butyl alcohol	Butan-2-ol
 $H_3C-\underset{CH_3}{\overset{CH_3}{C}}-OH$	*tert*-Butyl alcohol	2-Methylpropan-2-ol
 $\underset{OH}{H_2C}-\underset{OH}{\overset{H}{C}}-\underset{OH}{CH_2}$	Glycerol	Propane -1, 2, 3-triol
 $H_3C-\underset{OH}{\overset{H}{C}}-CH_3$	Isopropyl alcohol	Propan-2-ol
 $H_3C-\overset{H_2}{C}-\overset{H_2}{C}-OH$	*n*-Propyl alcohol	Propan-1-ol

In case of cyclic compounds, we use the prefix cyclo if the –OH group is attached to C-1.

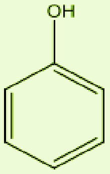
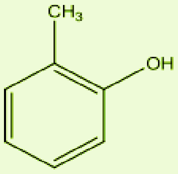
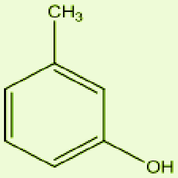
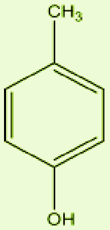
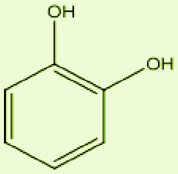
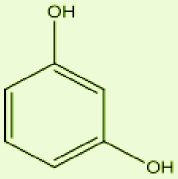
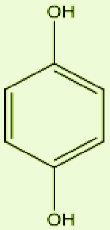


2-Methylcyclopentanol

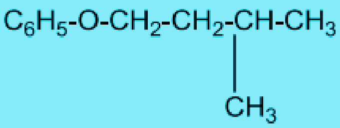
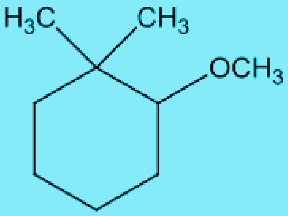


Cyclohexanol

Phenols

Compound	Common name	IUPAC name
	Phenol	Phenol
	*o*-Cresol	2-Methylphenol
	*m*-Cresol	3-Methylphenol
	*p*-Cresol	4-Methylphenol
	Catechol	Benzene-1,2-diol
	Resorcinol	Benzene-1,3-diol
	Hydroquinone or quinol	Benzene-1,4-diol

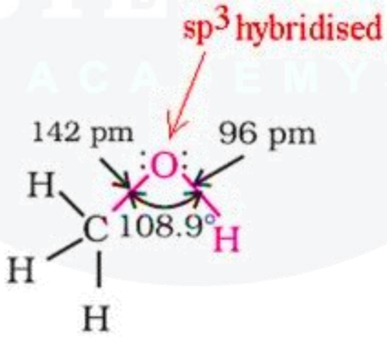
Ethers

Compound	Common name	IUPAC name
CH_3OCH_3	Dimethyl ether	Methoxymethane
$C_2H_5OC_2H_5$	Diethyl ether	Ethoxyethane
$C_6H_5O(CH_2)_6\text{-}CH_3$	Heptyl phenyl ether	1-Phenoxyheptane
 $C_6H_5\text{-}O\text{-}CH_2\text{-}CH_2\text{-}\underset{\Large CH_3}{\underset{\vert}{CH}}\text{-}CH_3$	Phenyl isopentyl ether	3- Methylbutoxybenzene
$CH_3\text{-}O\text{-}CH_2\text{-}CH_2\text{-}OCH_3$	----	1,2-Dimethoxyethane
	---	2-Ethoxy- -1,1-dimethylcyclohexane

Structures of Functional Groups

Alcohols

- For alcohols, the –OH group is linked to carbon by a sigma bond.
- The bond is formed by the overlap of sp^3 hybridised orbital of carbon with a sp^3 hybridised orbital ofoxygen.
- In alcohols, the bond angle is slightly less than the tetrahedral angle (109°-28’) due to therepulsion between the unshared electron pairs of oxygen.



Methanol

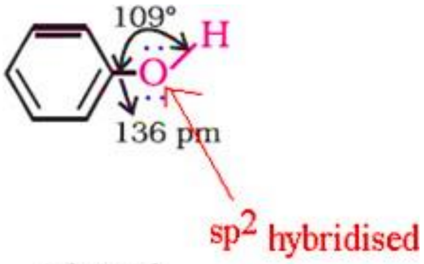
(Alcohol)

Phenols

- In phenols, the –OH group is linked to carbon by sp^2 hybridisation.
- The C-O bond length (136 pm) in phenol is slightly less than that in methanol.
- This arises due to:

➢ Partial double bond character on account of the conjugation of unshared electron pair of oxygenwith the aromatic ring.

- ➢ sp^2 hybridised carbon to which oxygen is linked.

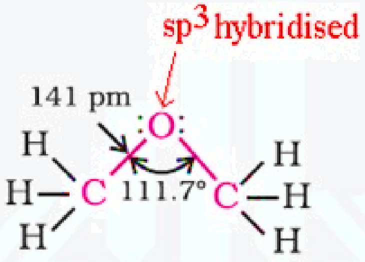


Phenol

(Phenol)

Ethers

- In ethers the two bond pairs and two lone pairs of electrons on oxygen form a tetrahedralarrangement.
- Due to the repulsive interaction between the two bulky (-R) groups the bond angle is slightlygreater than the tetrahedral angle.
- The C-O bond length is almost the same like alcohols.



Methoxymethane

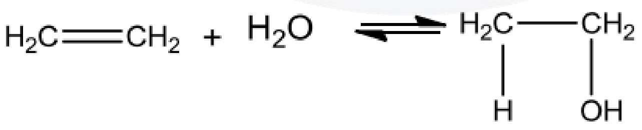
(Ether)

Preparation of Alcohols

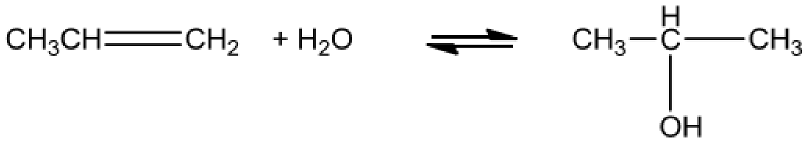
From Alkenes

- ➢ **Acid catalysed hydration:**

  Alcohols are prepared by treating alkenes with water in the presence of acid as catalyst.



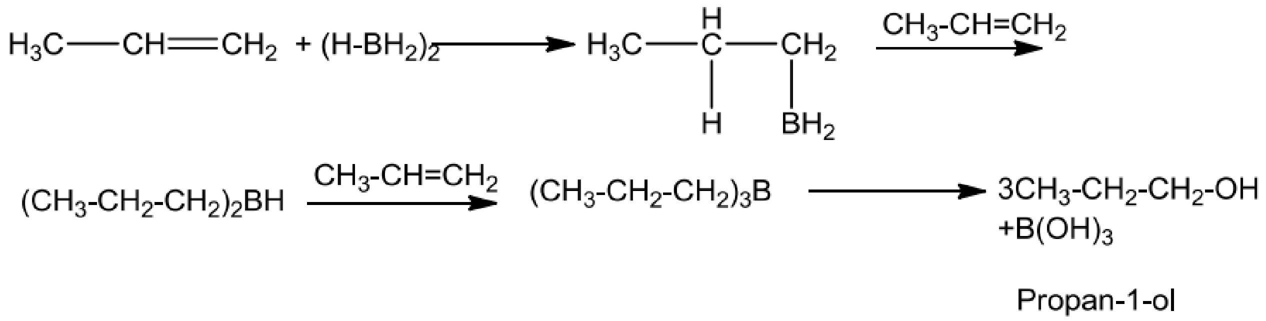
$$H_2C{=}CH_2 + H_2O \rightleftharpoons \underset{H}{\underset{|}{H_2C}}-\underset{OH}{\underset{|}{CH_2}}$$



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

- ➢ **Hydroboration-oxidation:**

  Alkenes on treatment with diborane give trialkyl boranes as addition product which is then oxidised toalcohol by hydrogen peroxide in the presence of aqueous sodium hydroxide.



$$H_3C-CH=CH_2 + (H\text{-}BH_2)_2 \longrightarrow H_3C-\overset{H}{\underset{H}{C}}-\underset{BH_2}{CH_2} \xrightarrow{CH_3\text{-}CH=CH_2}$$

$$(CH_3\text{-}CH_2\text{-}CH_2)_2BH \xrightarrow{CH_3\text{-}CH=CH_2} (CH_3\text{-}CH_2\text{-}CH_2)_3B \longrightarrow 3CH_3\text{-}CH_2\text{-}CH_2\text{-}OH + B(OH)_3$$

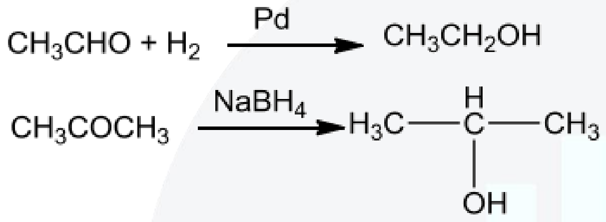
Propan-1-ol

The addition of borane to the double bond takes place in such a way that the boron gets added to thesp^2 carbon with more number of hydrogen atoms.

From Carbonyl Compounds

- **Reduction of Aldehydes & Ketones**

- Aldehydes yield primary alcohols whereas ketones give secondary alcohols.



$$CH_3CHO + H_2 \xrightarrow{Pd} CH_3CH_2OH$$

$$CH_3COCH_3 \xrightarrow{NaBH_4} H_3C-\overset{H}{\underset{OH}{C}}-CH_3$$

- **Reduction of Carboxylic acids and Esters**

- LiAlH4 is a strong reducing agent and reduces carboxylic acids to primary alcohols in excellent yields.

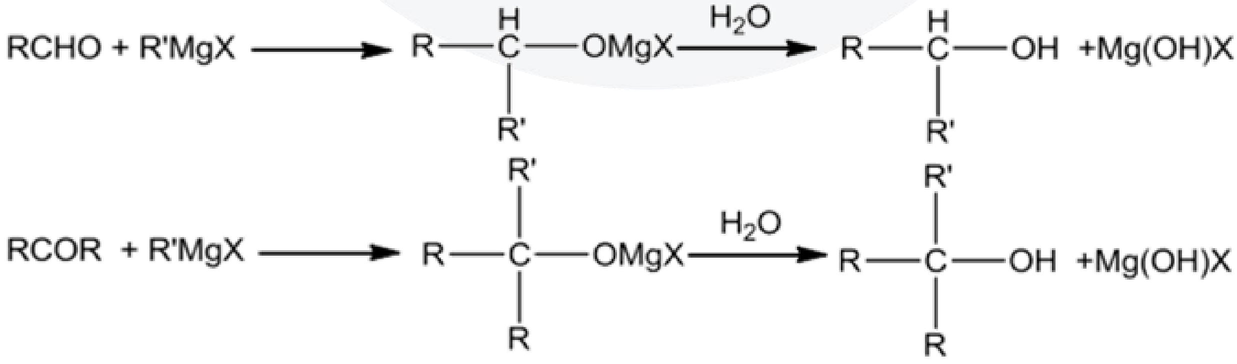
$$CH_3COOH \xrightarrow[\text{(ii)}\,H_2O]{\text{(i)}\,LiAlH_4} CH_3CH_2OH$$

- Alcohols are prepared on a commercial scale by converting acids to esters followed by reduction with hydrogen in the presence of catalyst.

$$CH_3COOH \xrightarrow{CH_3OH} CH_3COOCH_3 \xrightarrow[\text{Catalyst}]{H_2} CH_3CH_2OH + CH_3OH$$

From Grignard reagents

Grignard reagents on reacting with aldehydes and ketones yield alcohols.



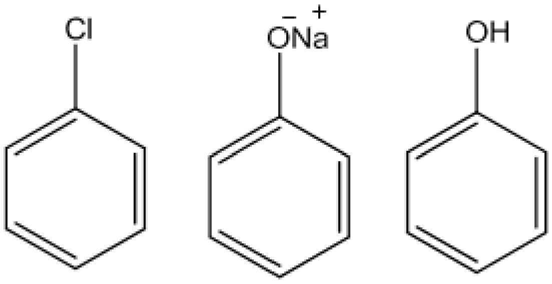
$$RCHO + R'MgX \longrightarrow R-\overset{H}{\underset{R'}{C}}-OMgX \xrightarrow{H_2O} R-\overset{H}{\underset{R'}{C}}-OH + Mg(OH)X$$

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

Preparation of Phenols

- **From Haloarenes**

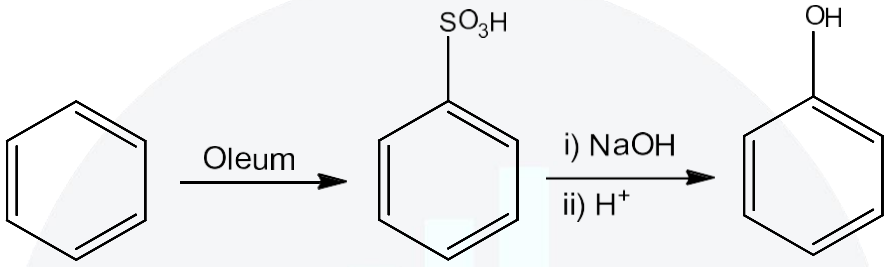
  Chlorobenzene on fusing with NaOH at 623 K and 320 atmospheric pressure gives sodium phenoxidewhich on acidification yields phenol.



$+NaOH \xrightarrow[300\,atm]{623K} \qquad \xrightarrow{HCl}$

- **From Benzenesulphonic Acid**

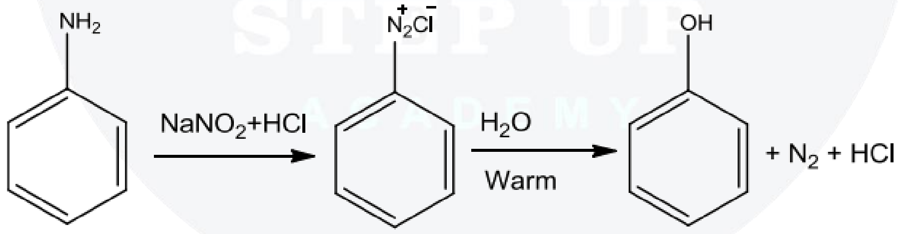
  Benzene on sulphonation with oleum gives benzene sulphonic acid which on heating with moltensodium hydroxide gives sodium phenoxide. Acidification of the sodium phenoxide gives phenol.



- **From Diazonium Salts**

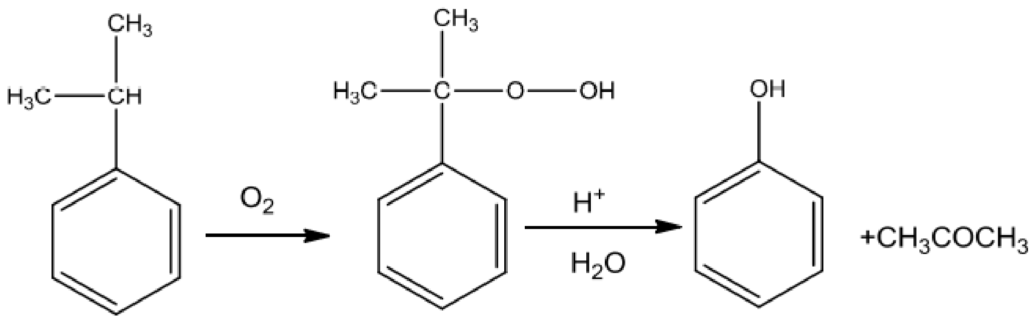
  Aniline on treatment with nitrous acid at 273-278K gives benzene diazonium chloride which onhydrolysis with warm water or treatment with dilute acids is converted to phenols.

- **From Cumene**



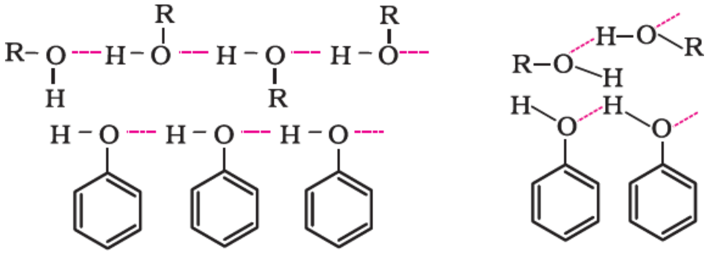
Benzene diazonium chloride

Cumene (isopropyl benzene) on oxidation with air gives cumene hydroperoxide which on treatment with dilute acid is converted to phenol.

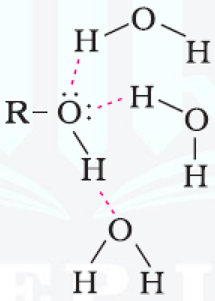


Physical Properties

- **Boiling points**
  - Boiling points of alcohols and phenols are higher in comparison to other classes of compounds, namely hydrocarbons, ethers, haloalkanes and haloarenes of comparable molecular masses. This isbecause the –OH group in alcohols and phenols is involved in intermolecular hydrogen bonding.



  - The boiling points of alcohols and phenols increase with increase in the number of carbon atoms. Thisis because of increase in van der Waals forces with increase in the surface area.
  - In alcohols, the boiling points decrease with increase in branching in the carbon chain. This is becauseof decrease in van der Waals forces with decrease in the surface area.
- **Solubility**
  - Alcohols and phenols are soluble in water due to their ability to form hydrogen bonds with water molecules.



  - The solubility of alcohols decreases with increase in the size of alkyl/aryl (hydrophobic) groups.

Chemical Properties

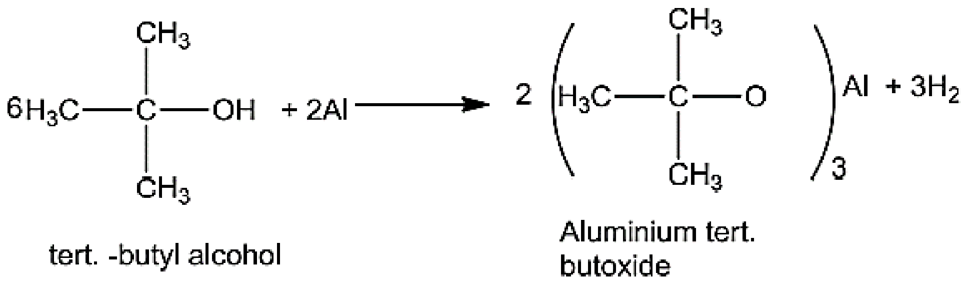
Alcohols react both as nucleophiles and electrophiles.

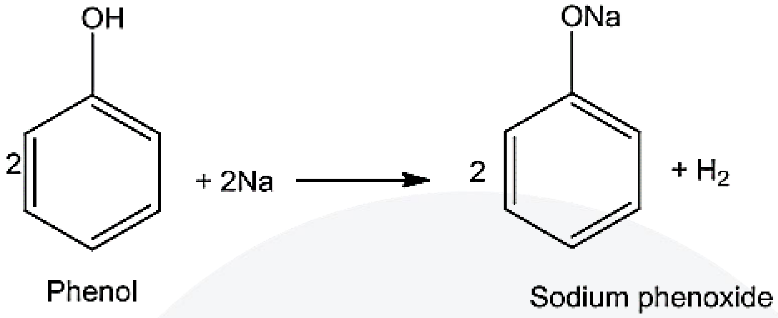
A) Reactions involving cleavage of O-H bond

(i) Reaction with Metals

Alcohols and phenols react with active metals like Na, K and Al to give corresponding alkoxides/phenoxides with the evolution of hydrogen.

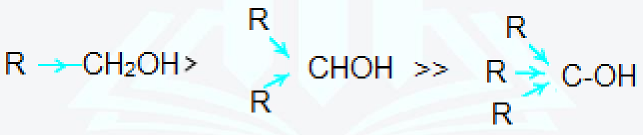
$2R\text{-}OH + 2Na \rightarrow 2R\text{-}O\text{-}Na + H_2$





(ii) Acidity of Alcohols

- The acidity of alcohols depends on the polar nature of O-H bond.
- The electron releasing groups (-CH_3, -C_2H_5) increases the electron density on oxygen and thus decrease the polarity of O-H bond which decreases the acid strength.
- The acid strength of alcohols decreases in the following order:



$$R\rightarrow CH_2OH > R_2CHOH >> R_3C\text{-}OH$$

- Alcohols are weaker acids than water which can be seen in the following reaction.

$$\underset{\text{Base}}{R-\ddot{\underset{\cdot\cdot}{O}}:^{-}} + \underset{\text{Acid}}{H-\ddot{\underset{\cdot\cdot}{O}}-H} \longrightarrow \underset{\text{Conjugate acid}}{R-O-H} + \underset{\text{Conjugate base}}{:\ddot{\underset{\cdot\cdot}{O}}H^{-}}$$

  In the reaction, water is a better proton donor (i.e., stronger acid) than alcohol. Over here the alkoxide ion is a better proton acceptor than hydroxide ion which suggests that alkoxides are stronger bases.

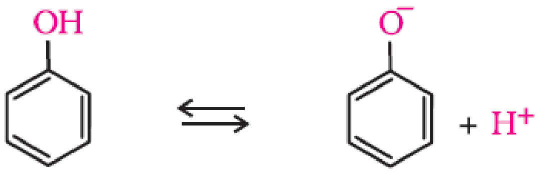
- Alcohols act as Bronsted bases as well due to the presence of unshared electron pairs on oxygen which makes them proton acceptors.

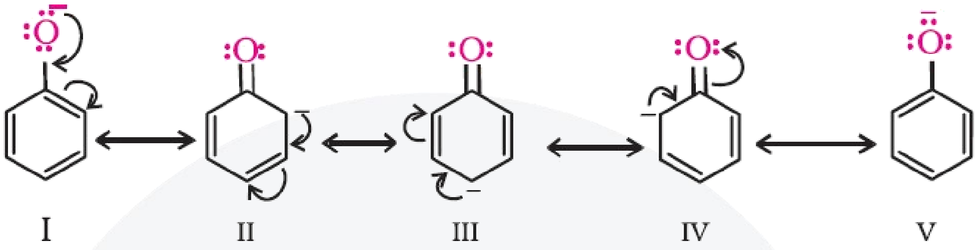
(iii) Acidity of Phenols

- In phenol, the hydroxyl group is directly attached to the *sp*^{2} hybridised carbon of the benzene ring which acts as an electron-withdrawing group. Whereas in alcohols, the hydroxyl group is attached to the alkyl group which has an electron-releasing inductive effect.
- In phenol, the hydroxyl group is directly attached to the *sp*^{2} hybridised carbon of the benzene ring. Whereas in alcohols, the hydroxyl group is attached to the *sp*^{3} hybridised carbon of the alkyl group. The *sp*^{2} hybridised carbon has higher electronegativity than the *sp*^{3} hybridised carbon. Thus, the polarity of the O–H bond of phenols is higher than that of alcohols. Hence, the ionisation of phenols is higher than that of alcohols.

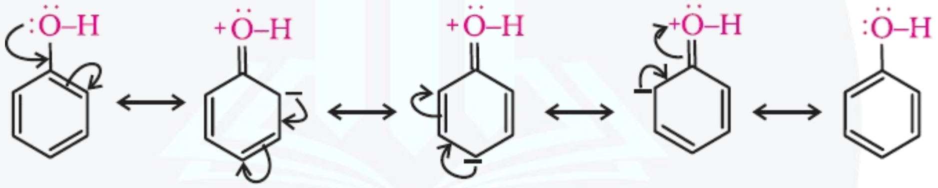
- The ionisation of an alcohol and a phenol occurs as follows:
- In alkoxide ion, the negative charge is localised on oxygen, while in phenoxide ion, thecharge is delocalised.

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





- The delocalisation of the negative charge makes the phenoxide ion more stable and favoursthe ionisation of phenol. Although there is charge delocalisation in phenol, its resonance structures have charge separation due to which the phenol molecule is less stable than the phenoxide ion.



- In substituted phenols, the presence of electron-withdrawing groups such as the nitro group enhances the acidic strength of phenol. On the other hand, electron-releasing groups, suchas alkyl groups, decrease the acidic strength. It is because electron-withdrawing groups lead to effective delocalisation of the negative charge in the phenoxide ion.

(iv) Esterification

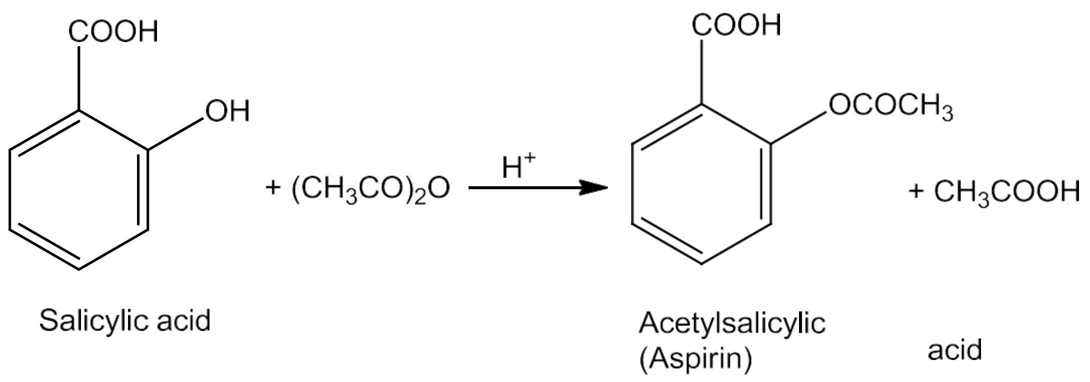
- Esters are formed when alcohols and phenols react with carboxylic acids, acid chloridesand acid anhydrides.

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

$$\text{Ar/RO-H} + (\text{R'CO})_2\text{O} \overset{H^+}{\rightleftharpoons} \text{Ar/ROCOR'} + \text{R'COOH}$$

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

- In case of acid chloride, the reaction is carried out in the presence of base called pyridine to neutralise the HCl formed and to shift the equilibrium to the right.



B) Reactions involving cleavage of Carbon-Oxygen(C-O) bond in alcohols

Only alcohols show reactions involving cleavage of C-O bond. Phenols exhibit this type of reactiononly with zinc.

i) Reaction with hydrogen halides

Alcohols on treatment with hydrogen halides form alkyl halides.

$ROH + HX \rightarrow R\text{-}X + H_2O$

How to distinguish between Primary, Secondary and Tertiary Alcohols?

Lucas reagent test

$$ROH + HCl \xrightarrow[\text{Lucas reagent}]{\text{conc.HCl} + ZnCl_2} RCl + H_2O$$

- If it is a primary alcohol, then no turbidity appears at room temperature. Turbidity appears onlyon heating.
- If it is a secondary alcohol, then turbidity appears in 5 minutes.
- If it is a tertiary alcohol, then turbidity appears immediately.

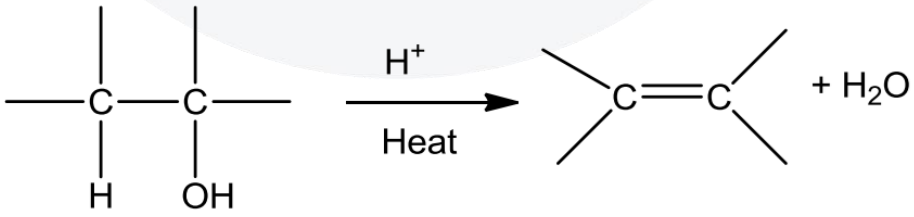
ii) Reaction with Phosphorus trihalides

Alcohols get converted into alkyl bromides on treatment with PBr_3.

$3R\text{-}OH + PBr_3 \rightarrow 3R\text{-}Br + H_3PO_3$

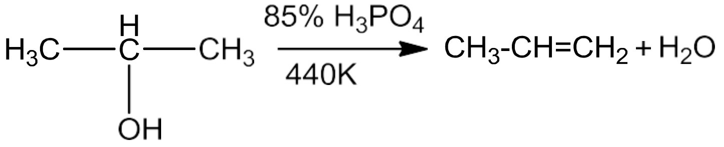
iii) Dehydration

- Alcohols undergo dehydration to form alkenes in the presence of conc. H_2SO_4 or H_3PO_3 orcatalysts such as anhydrous zinc chloride or alumina.

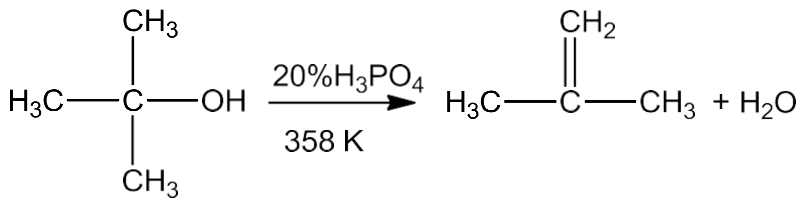


- Primary alcohol undergoes dehydration by heating it with conc. H_2SO_4 at 443K.
- Secondary and tertiary alcohols undergo dehydration in milder conditions.

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



$$H_3C-\underset{OH}{\overset{H}{C}}-CH_3 \xrightarrow[440K]{85\%\ H_3PO_4} CH_3\text{-}CH{=}CH_2 + H_2O$$

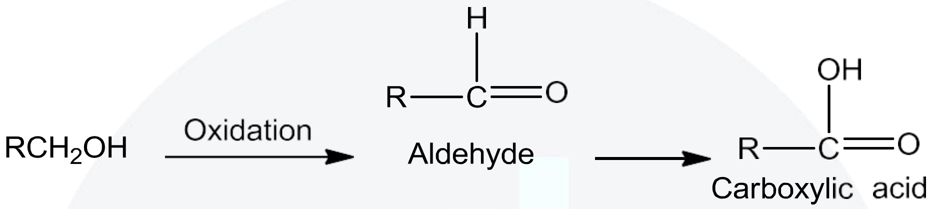


- Thus the ease of dehydration of alcohols follows the order:

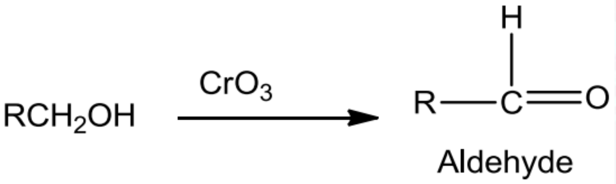
  Tertiary > Secondary > Primary

iv) Oxidation

- The oxidation of alcohols results in the formation of a carbon-oxygen double bond with the cleavage of an O-H and C-H bonds. The reaction is known as dehydrogenation reaction asit involves loss of dihydrogen from an alcohol molecule.



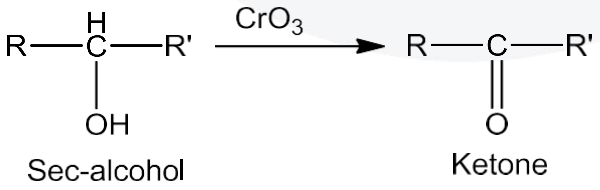
- Use of strong oxidising agents like acidified $KMnO_4$ is done to obtain carboxylic acids fromalcohols directly. CrO_3 in anhydrous medium is used for obtaining aldehydes.



- Pyridinium chlorochromate (PCC), a complex of chromium trioxide with pyridine and HCl isa better oxidizing agent for oxidation of primary alcohols to aldehydes in good yield.

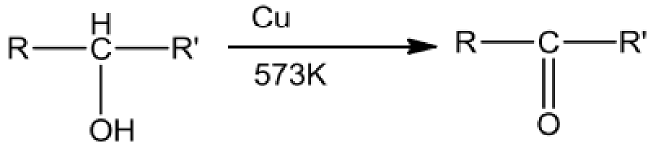
$$CH_3\text{-}CH{=}CH\text{-}CH_2OH \xrightarrow{PCC} CH_3\text{-}CH{=}CH\text{-}CHO$$

- CrO_3 is used to oxidize secondary alcohols to ketones.

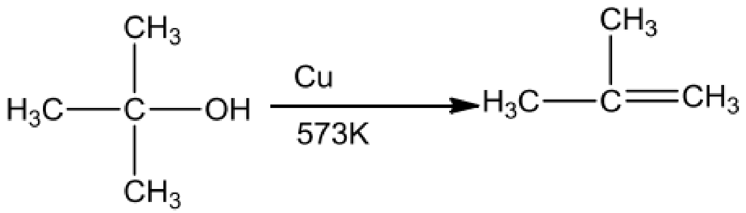


- Tertiary alcohols do not undergo oxidation reaction. In presence of strong oxidizing agents($KMnO_4$) and elevated temperatures, cleavage of C-C bonds takes place and a mixture of carboxylic acids containing lesser number of carbon atoms is formed.
- On passing vapours of a primary or a secondary alcohol over heated copper at 573K, dehydrogenation takes place and an aldehydes or a ketone is formed whereas tertiaryalcohols undergo dehydration.

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



$$R-CH(OH)-R' \xrightarrow[573K]{Cu} R-CO-R'$$



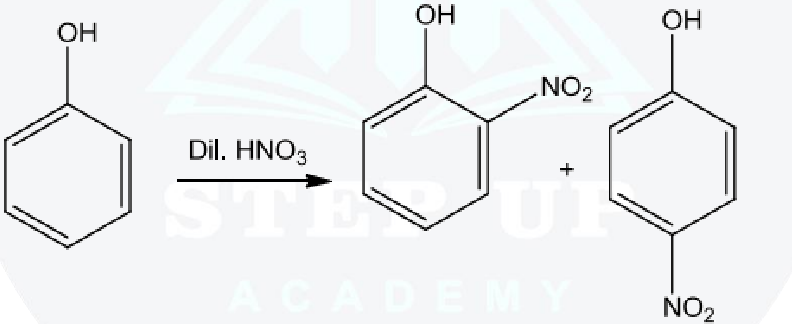
$$(CH_3)_3C-OH \xrightarrow[573K]{Cu} H_3C-C(CH_3){=}CH_2$$

Characteristics of Phenols

- Phenols show electrophilic substitution reactions.
- The –OH group activates the benzene ring towards electrophilic substitution and also directs the incoming group to ortho and para positions in the ring as these positions become electron rich due tothe resonance effect caused by –OH group.

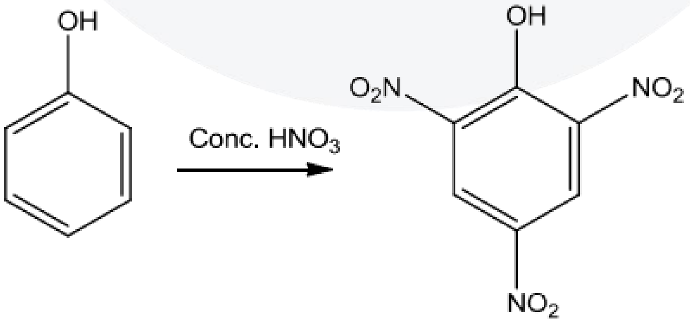
(i) Nitration

Phenol on treatment with dil.HNO_3 at low temperature yields a mixture of ortho and para nitrophenols.



o-Nitrophenol p-Nitrophenol

With conc. nitric acid, phenol is converted into 2, 4, 6-trinitrophenol.

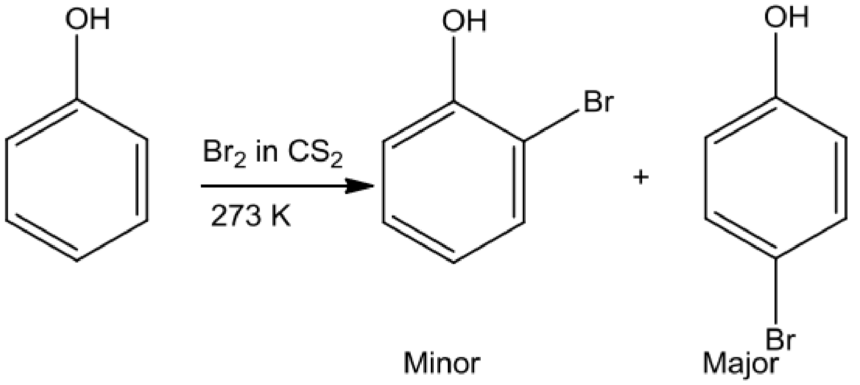


2,4,6-Trinitrophenol
(Picric acid)

(ii) Halogenation

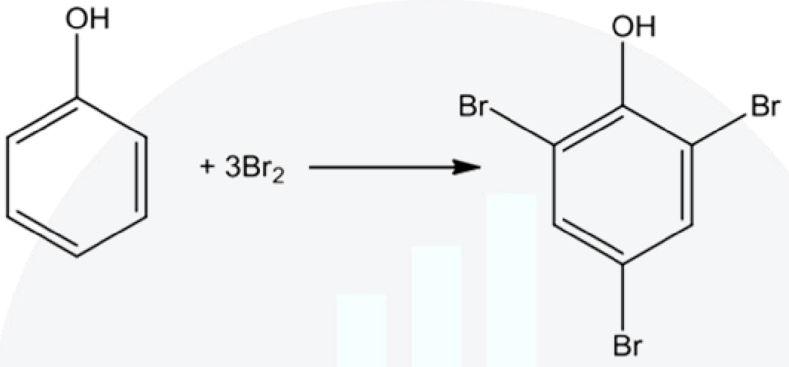
(a) Bromine in $CHCl_3$ or CS_2

Monobromophenols are formed when phenol is treated with bromine in $CHCl_3$ or CS_2 at lowtemperature.



(b) Action of Bromine water

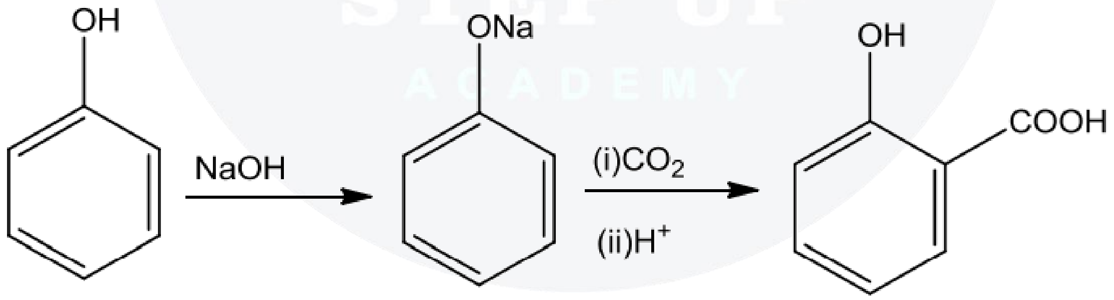
On treating phenol with bromine water, a white precipitate of 2, 4, 6-tribromophenol is formed.



2,4,6-Tribromophenol

(iii) Kolbe's Reaction

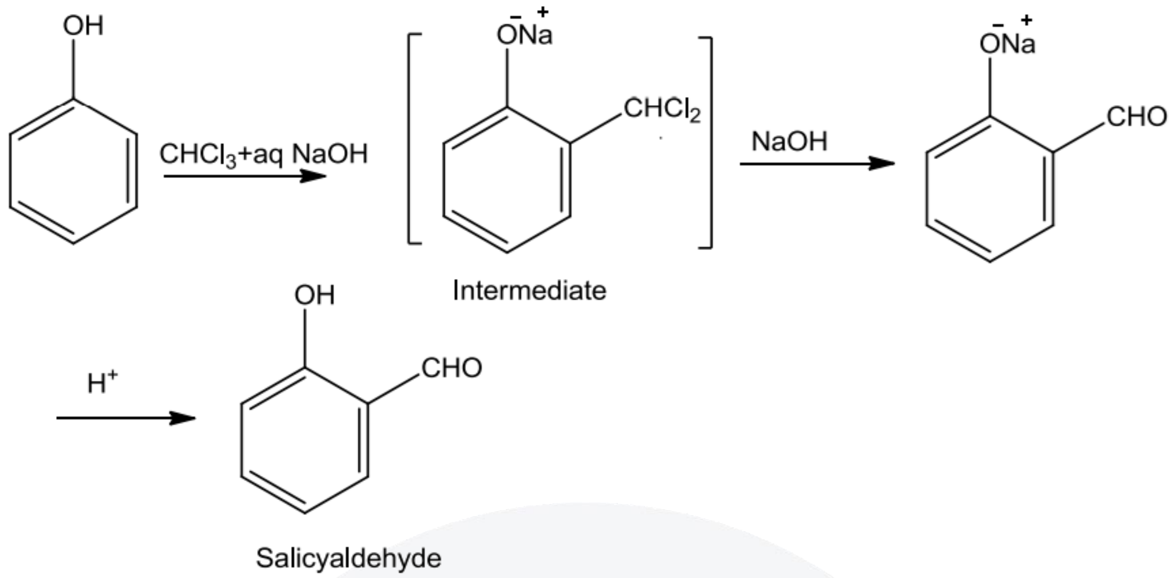
Phenols on treatment with NaOH produces phenoxide ion which is even more reactive than phenol towards electrophilic aromatic substitution and therefore it undergoes electrophilic substitution with carbon dioxide. Ortho hydroxybenzoic acid is obtained as the main product.



2-Hydroxybenzoic acid
(Salicylic acid)

(iv) Reimer-Tiemann Reaction

Phenols on treatment with chloroform in the presence of NaOH, a –CHO group is introduced atortho position of benzene ring. The substituted benzal chloride formed as intermediate on hydrolysis with alkali produce salicylaldehyde.

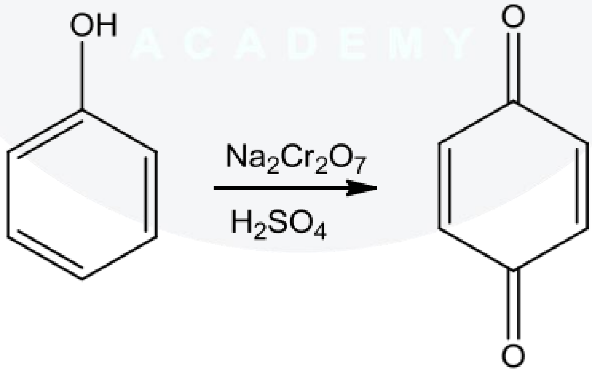


(v) Action of Zinc dust

Phenol on heating with zinc dust produces benzene.

(vi) Oxidation

Phenols on oxidation with chromic acid gives out conjugated diketone known as benzoquinone.



Some Commercially Important Alcohols

Methanol and ethanol are two commercially important alcohols.

Methanol

- Methanol also known as 'wood spirit' was produced by destructive distillation of wood.
- Now methanol is produced by catalytic hydrogenation of carbon monoxide at high pressure andtemperature in the presence of $ZnO-Cr_2O_3$ catalyst.

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

Ethanol

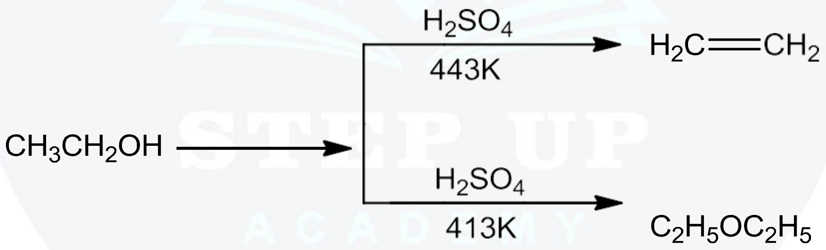
- It is commercially obtained by fermentation from sugars.
- The sugar in molasses, sugarcane or fruits like grapes is converted to glucose and fructose in thepresence of an enzyme invertase.
- Glucose and fructose undergo fermentation in the presence of another enzyme, zymase, which isfound in the yeast.

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

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

Preparation of Ethers

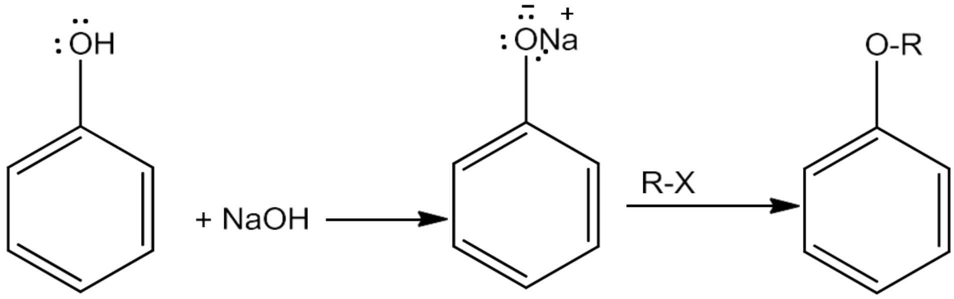
- **By Dehydration of Alcohols**
  - Alcohols on dehydration with protic acids like H_2SO_4, H_3PO_4 give alkene or ether depending on the reaction conditions.



- **Williamson Synthesis**
  - This method is used for the preparation of symmetrical and unsymmetrical ethers.
  - In this reaction, an alkyl halide is allowed to react with sodium alkoxide.

$$R\text{-}X + R'\text{-}\ddot{\underset{\cdot\cdot}{O}}^{-}\overset{+}{Na} \longrightarrow R\text{-}\ddot{\underset{\cdot\cdot}{O}}\text{-}R' + Na\,X$$

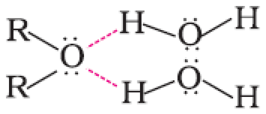
  - Phenols can also be converted into ethers using this method. In this, phenol is used as thephenoxide moiety.



Physical Properties of Ethers

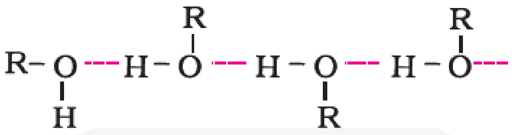
- **Miscibility**

  Miscibility of ethers with water resembles those of alcohols of the same molecular mass. This is because similar to alcohols; oxygen of ether can also form hydrogen bonds with the water molecule.



- **Boiling points**

  Ethers have much lower boiling points than alcohols. This is due to the presence of hydrogen bondingin alcohols. Hydrogen bonding is absent in ethers.



Chemical Properties of Ethers

A. Cleavage of C–O bond in ethers

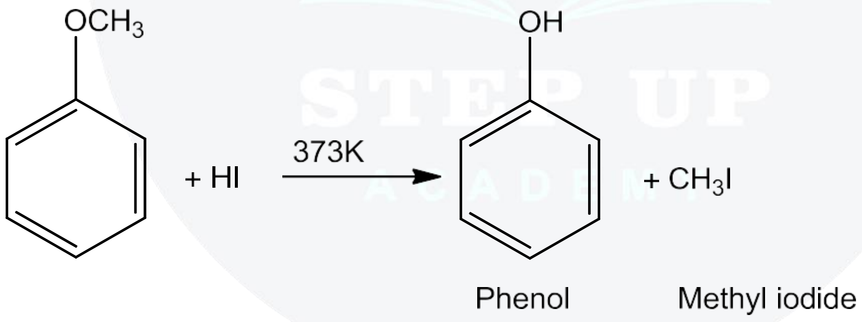
- Since ethers are least reactive of the functional groups, the cleavage of C-O bond in etherstakes place in excess of hydrogen halides.

$$R\text{-}O\text{-}R + HX \longrightarrow RX + R\text{-}OH$$

- The cleavage of ethers with two different alkyl groups also takes place in the same manner.

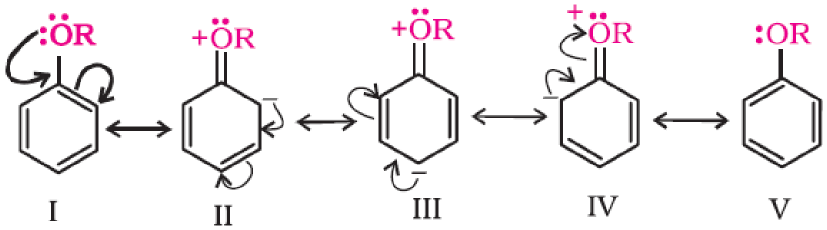
$$R\text{-}O\text{-}R' + HX \longrightarrow R\text{-}X + R'\text{-}OH$$

- In phenolic ethers, the cleavage occurs with the formation of phenol and alkyl halide.



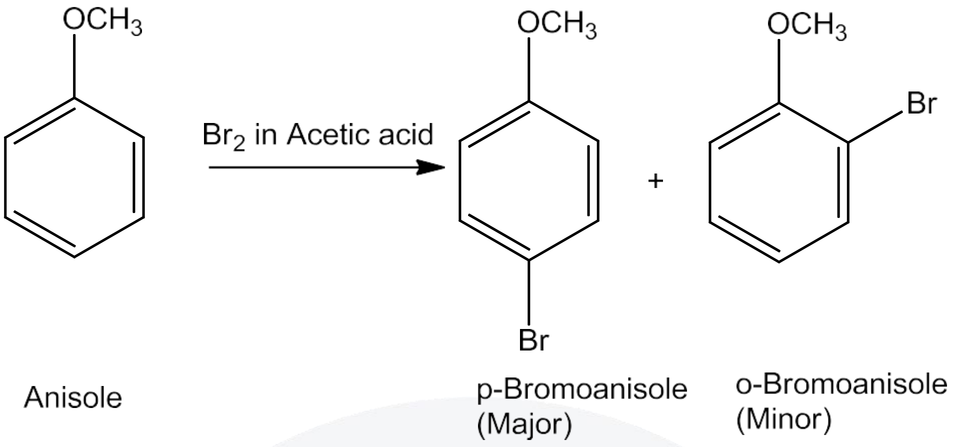
B. Electrophilic Substitution

The alkoxy group (-OR) is ortho, para directing and activates the benzene ring for aromatic substitution.



(i) Halogenation

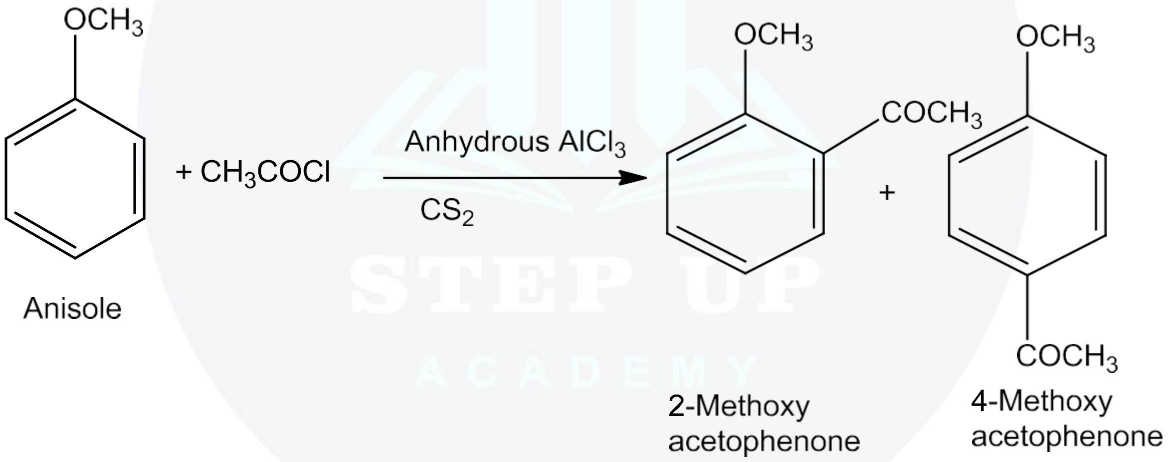
Phenyl alkyl ethers undergo halogenation reaction.



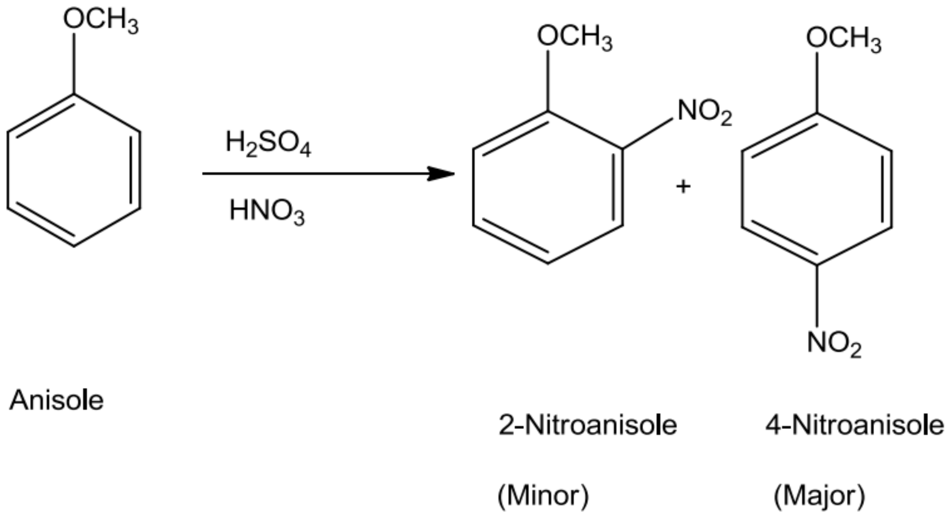
(ii) Friedel-Crafts reaction

In this reaction the alkyl groups and acyl groups are introduced at ortho and para position by treating anisole with alkyl halide and acyl halide in the presence of anhydrous chloride ascatalyst.

(iii) Nitration



Anisole on treating with a mixture of sulphuric acid and nitric gives a mixture of ortho andpara nitroanisole.



Classification of alcohols

We can classify alcohols on the basis of different factors:

Number of hydroxyl groups attached , hybridization ,number of alkyl groups attached to alpha carbon (alpha carbon is that which has functional groups attached to it)

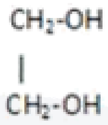
On the basis of number of -OH (hydroxyl) group attached we have :

Monohydric alcohols: They are those that have only one hydroxyl group attached.

Example: methanol (CH_3OH) ethanol (C_2H_5OH) and more

Dihydric alcohols: They have two hydroxyl groups attached.

Example: ethylene-glycol



$$\begin{array}{l} CH_2\text{-}OH \\ | \\ CH_2\text{-}OH \end{array}$$

Polyhydric alcohol: That have three or more hydroxyl groups in it.

Example: glycerol

$$\begin{array}{l} CH_2\text{-}OH \\ | \\ CH_2OH \\ | \\ CH_2\text{-}OH \end{array}$$

(propan -1,2,3- triol)

(2) Based on the type of hybridization:

It can be sp^3 like ethanol - CH_3 - CH_2 - OH

Another example :

It can be sp^2 like Benzyl alcohol-

In this second carbon is alpha carbon and that is sp^3

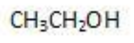
(Benzyl alcohol)

Allyl alcohol $CH_2 = CH - CH_2\ OH$ (In it also alpha carbon is sp^3 hybridised).

Another type of hybridization they possess is sp^2

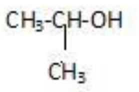
Example: Phenol C_6H_5OH, Vinyl alcohol $CH_3 - CH_2 = CH - OH$ etc

(c) Classification is on the basis of primary secondary or tertiary carbon atom (alpha carbon)



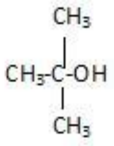
CH_3CH_2OH

ethanol



$$\begin{array}{l} CH_3\text{-}CH\text{-}OH \\ \quad\ \ | \\ \quad\ CH_3 \end{array}$$

2-propanol



$$\begin{array}{l} \quad\ CH_3 \\ \quad\ \ | \\ CH_3\text{-}C\text{-}OH \\ \quad\ \ | \\ \quad\ CH_3 \end{array}$$

2-methyl propan 2-ol

SSS

1^0 2 3^0

Class : 12th Chemistry
Chapter-11 : Alcohols, Phenols And Ethers (Part_1)

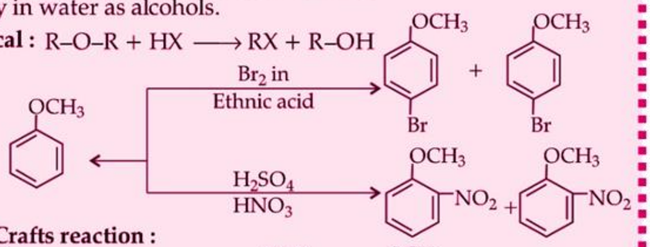
Alcohols, Phenols And Ethers

Eather

(i)Physical :

- C–O bonds are polar.
- Boiling points comparable to those of alkanes.
- Solubility in water as alcohols.

(ii)Chemical : $R–O–R + HX \longrightarrow RX + R–OH$



Friedel Crafts reaction :

Commercially important alcohols

- **Methanol (Wood spirit):** Used as solvent in paint, varnishes and making formaldehyde
- **Ethanol:** Used as solvent in paint industry and preparation of a number of carbon compounds.

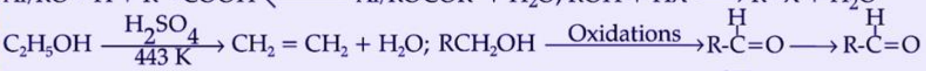
Properties

Alcohol

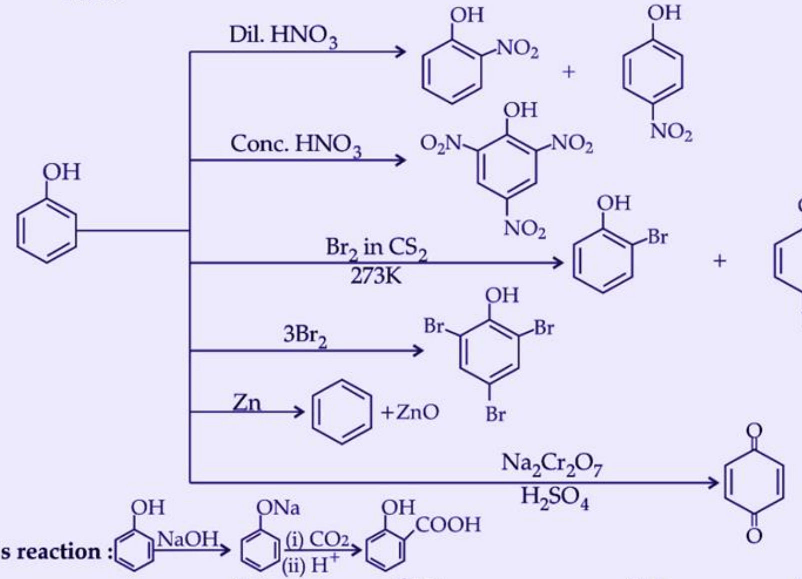
(i) Physical : •Boiling point increases with increase in the number of C atoms.
•Solubility decreases with increase in size of alky/aryl groups.

(ii) Chemical : $2–R–O–H + 2Na \longrightarrow 2R–O–Na + H_2$;Acidity – primary > secondary > tertiary

$Ar/RO – H + R' –COOH \overset{H^+}{\rightleftharpoons} Ar/ROCOR' + H_2O$; $ROH + HX \longrightarrow R –X + H_2O$



$C_2H_5OH \xrightarrow[443\ K]{H_2SO_4} CH_2 = CH_2 + H_2O$; $RCH_2OH \xrightarrow{Oxidations} R\text{-}\overset{H}{C}\text{=}O \longrightarrow R\text{-}\overset{H}{C}\text{=}O$



Kolbe's reaction :

Reimer Tiemann reaction :

Class : 12th Chemistry
Chapter-11 : Alcohols, Phenols And Ethers (Part_2)

Ethers

Common name: alkyl/aryl groups in alphabetical order followed by ether.
IUPAC name: In alkyl /aryl group 'e' replaced by oxy followed by parent hydrocarbon.

Alcohols

Common name: Alkyl group + ol;
IUPAC name: substituting 'e' of alkane with suffix 'ol'

Phenols

Common name: Terms ortho, meta and para are used.
IUPAC name: Dihydroxy derivatives as 1,2–, 1,3–and 1,4–benzenediol

Structures of functional groups

•Oxygen of –OH group is attached to C by a σ bond formed by the overlap of sp^3orbital of C with a sp^3 orbital of oxygen.
•In ethers, tetrahedral arrangement for four electron pairs.

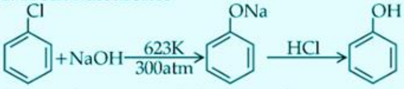
Nomenclature

Alcohols, Phenols And Ethers

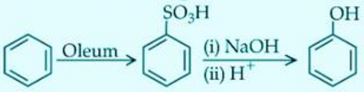
Preparation

Phenols

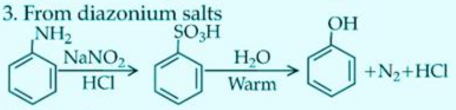
1. From haloarenes



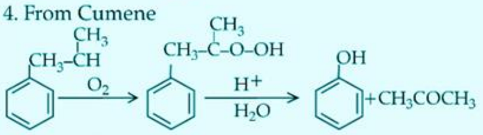
2. From benzene sulphonic acid



3. From diazonium salts

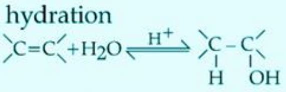


4. From Cumene



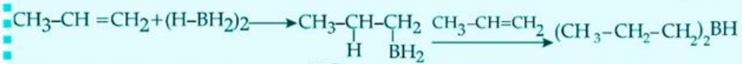
Alcohol

1. From alkenes :- (i) By acid catalysed hydration



$$\rangle C=C\langle + H_2O \overset{H^+}{\rightleftharpoons} \rangle \underset{H}{C}-\underset{OH}{C}\langle$$

(ii) By hydroboration – oxidation

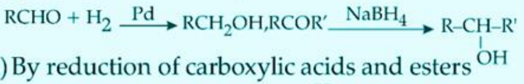


$$CH_3-CH=CH_2+(H-BH_2)_2 \longrightarrow CH_3-\underset{H}{CH}-\underset{BH_2}{CH_2} \xrightarrow{CH_3-CH=CH_2} (CH_3-CH_2-CH_2)_2BH$$

$$3CH_3-CH_2-CH_2-OH+B(OH)_3 \xrightarrow[3H_2O_2,OH]{H_2O} CH_3-CH_2-CH_2)_3B\ ,CH_3-CH_2-CH_2$$

2. From carbonyl compounds :

(i) By reduction of aldehydes and ketones

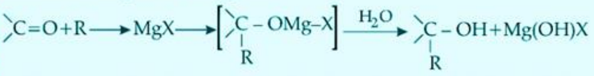


$$RCHO + H_2 \xrightarrow{Pd} RCH_2OH,RCOR' \xrightarrow{NaBH_4} R-\underset{OH}{CH}-R'$$

(ii) By reduction of carboxylic acids and esters

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

3. From Grignard reagent

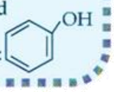


$$\rangle C=O+R\longrightarrow MgX \longrightarrow \left[\rangle \underset{R}{C}-OMg-X\right] \xrightarrow{H_2O} \rangle \underset{R}{C}-OH+Mg(OH)X$$

Classification

Mono, Di, Tri, or polyhydric

(i) Containing $C_{sp3}-OH$ bond
$\underset{(1^\circ)}{-CH_2OH} > \underset{(2^\circ)}{CHOH} \geqslant \underset{(3^\circ)}{COH}$
(ii)Containing C_{sp2}-OH bond
Vinylic alcohol :
$CH_2=CH-OH$ Phenols:



Ethers

(i) Simple/symmetrical: Alkyl or aryl attached to O_2 are same.
(ii) Mixed/Unsymmetrical: Two groups are different.

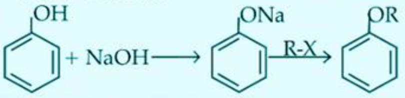
Ethers

1. By dehydration of alcohols

$$CH_3CH_2OH \xrightarrow[413\ K]{H_2SO_4} C_2H_5OC_2H_5$$

2. Williamson synthesis

$$RX + R'ONa \longrightarrow R-O-R' + NaX$$



Important Questions

Multiple Choice questions-

1. Among the following compounds, strongest acid is

   (a) H-C = C-H

   (b) C_6H_6

   (c) C_2H_6

   (d) CH_3OH

2. 1-Propanol and 2-propanol can be best distinguished by

   (a) Oxidation with $KMnO_4$ followed by reaction with Fehling solution?

   (b) Oxidation with acidic dichromate followed by reaction with Fehling solution.

   (c) Oxidation by heating with copper followed by reaction with Fehling solution.

   (d) Oxidation with cone. H_2SO_4 followed by reaction with Fehling solution.

3. The compound which gives the most stable carbonium ion on dehydration is

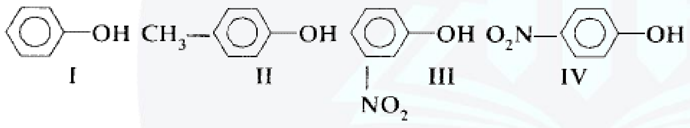
   (a) $(CH_3)_2CHCH_2OH$

   (b) $(CH_3)_3COH$

   (c) $CH_3CH_2CH_2CH_2OH$

   (d) $CH_3CH\ OH\ CH_2\ CH_3$

4. In the following compounds:



   The order of acidity is

   (a) III > IV > I > II

   (b) I > IV > III > II

   (c) II > I > III > IV

   (d) IV > III > I > II

5. In $CH_3\ CH_2\ OH$, the bond that undergoes heterolytical change most readily is

   (a) C-C

   (b) C-O

   (c) C-H

   (d) O-H

6. Phenol reacts with Br_2 in CS_2 at low temperature to give

   (a) o-Bromophenol

   (b) o-and p-promophenols

   (c) p-Bromophenol

   (d) 2, 4, 6Tribromophenol

7. In the reaction of phenol with $CHCl_3$ and aqueous NaOH at 343 K, the electrophile attacking the ring is:

   (a) $CHCl_3$

   (b) $CHCl_2$

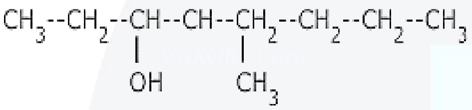
   (c) CCl_2

   (d) $COCl_2$

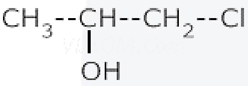
8. Which of the following is most acidic?
   - (a) Phenol
   - (b) Benzyl alcohol
   - (c) m-chlorophenol
   - (d) cyclohexanol
9. The correct order of boiling points for primary (1°), Secondary (2°) and Tertiery (3°) alcohols is
   - (a) 1° > 2° > 3°
   - (b) 3° > 2° > 1°
   - (c) 2° > 1° > 3°
   - (d) 2° > 3° > 1°
10. When Phenol is distilled with zinc dust, it gives
    - (a) Benzene
    - (b) Toluene
    - (c) Benzaldehyde
    - (d) Benzoic acid

Very Short Questions-

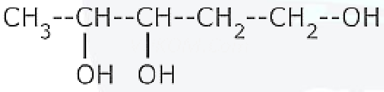
1. Write IUPAC names of :-

i. 

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

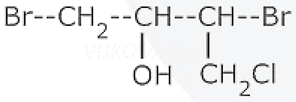
ii. 

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

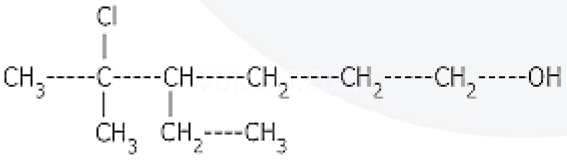
iii. 

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

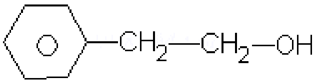
iv. $(CH_3)_3COH$

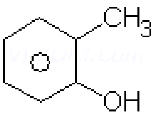
v. 

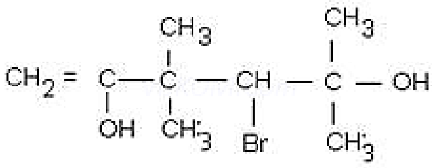
$$Br{-}{-}CH_2{-}{-}\underset{\displaystyle OH}{\underset{|}{CH}}{-}{-}\underset{\displaystyle CH_2Cl}{\underset{|}{CH}}{-}{-}Br$$

vi. 

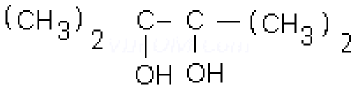
$$CH_3{-}{-}{-}{-}{-}\overset{\displaystyle Cl}{\overset{|}{\underset{\displaystyle CH_3}{\underset{|}{C}}}}{-}{-}{-}{-}{-}\underset{\displaystyle CH_2{-}{-}{-}{-}CH_3}{\underset{|}{CH}}{-}{-}{-}{-}{-}CH_2{-}{-}{-}{-}{-}CH_2{-}{-}{-}{-}{-}CH_2{-}{-}{-}{-}{-}OH$$

vii. 

viii. 

ix. 

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

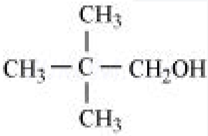
x. 
$(CH_3)_2\underset{OH}{C}-\underset{OH}{C}-(CH_3)_2$

Short Questions

1. Phenol is acidic in nature.
2. Phenol has a smaller dipole moment than methanol.
3. o-nitrophenol has lower boiling point (is more volatile) than p – nitrophenol.
4. Methanol is miscible with water while iodomethane is not.
5. Alcohols have higher boiling points than isomeric ethers.
6. Ethers are soluble in water alkanes are not.
7. The order of acidic strength in alcohols is R CH_2OH > R_2CHOH > R_3COH
8. During preparation of ester from alcohol and acid, water has to be removed as soon as it is formed.
9. Ethers can not be prepared by dehydration of secondary or tertiary alcohols.
10. Reaction of anisole with HI gives methyl iodide and phenol.

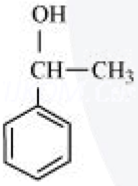
Long Questions-

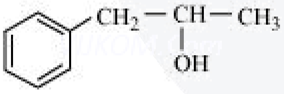
1. Classify the following as primary, secondary and tertiary alcohols:

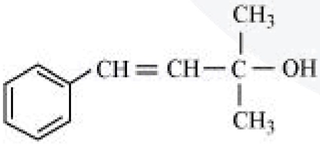
(i) 
$CH_3-\overset{CH_3}{\underset{CH_3}{C}}-CH_2OH$

(ii) $H_2C=CH-CH_2OH$

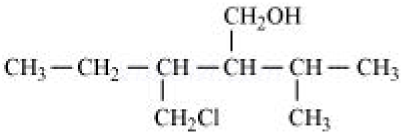
(iii) $CH_3-CH_2-CH_2-OH$

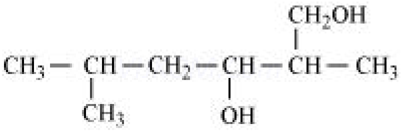
(iv) 

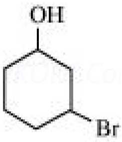
(v) 

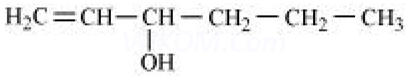
(vi) 

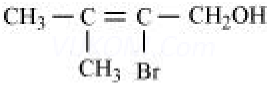
2. Name the following compounds according to IUPAC system.

(i) 
$CH_3-CH_2-\underset{CH_2Cl}{CH}-\overset{CH_2OH}{CH}-\underset{CH_3}{CH}-CH_3$

(ii) 
$CH_3-\underset{CH_3}{CH}-CH_2-\underset{OH}{CH}-\overset{CH_2OH}{CH}-CH_3$

(iii) 

(iv) 
$H_2C=CH-\underset{OH}{CH}-CH_2-CH_2-CH_3$

(v) 
$CH_3-\underset{CH_3}{C}=\underset{Br}{C}-CH_2OH$

3. Give structures of the products you would expect when each of the following alcohol reacts with

   (a) HCl – $ZnCl_2$ (b) HBr and (c) $SOCl_2$.

   (i) Butan-1-ol

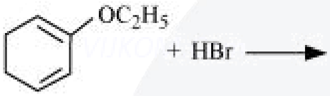
   (ii) 2-Methylbutan-2-ol

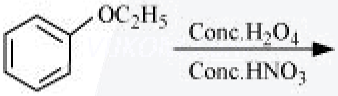
4. *Ortho* and *para* nitrophenols are more acidic than phenol. Draw the resonance structures of the corresponding phenoxide ions.

5. Write the reactions of Williamson synthesis of 2-ethoxy-3-methylpentane starting from ethanol and 3-methylpentan-2-ol.

6. Predict the products of the following reactions:

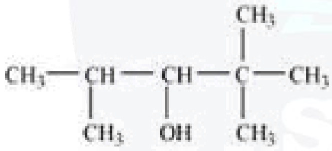
   (i) $CH_3-CH_2-CH_2-O-CH_3 + HBr \rightarrow$

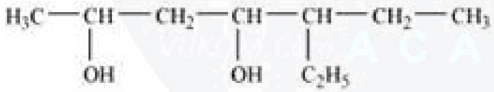
   (ii) 

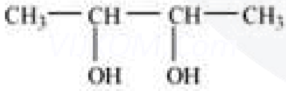
   (iii) 

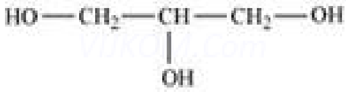
   (iv) $(CH_3)_3C-OC_2H_5 \xrightarrow{HI}$

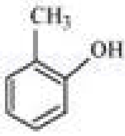
7. Write IUPAC names of the following compounds:

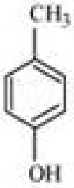
   (i) 
   $CH_3-\underset{CH_3}{CH}-\underset{OH}{CH}-\overset{CH_3}{\underset{CH_3}{C}}-CH_3$

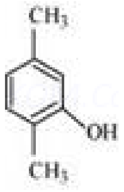
   (ii) 
   $H_3C-\underset{OH}{CH}-CH_2-\underset{OH}{CH}-\underset{C_2H_5}{CH}-CH_2-CH_3$

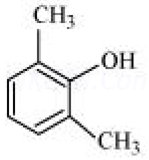
   (iii) 
   $CH_3-\underset{OH}{CH}-\underset{OH}{CH}-CH_3$

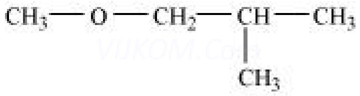
   (iv) 
   $HO-CH_2-\underset{OH}{CH}-CH_2-OH$

   (v) 

   (vi) 

(vii) 

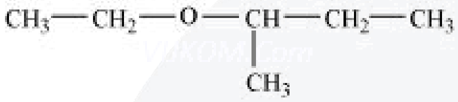
(viii) 

(ix) 

$CH_3-O-CH_2-\underset{CH_3}{\underset{|}{CH}}-CH_3$

(x) $C_6H_5-O-C_2H_5$

(xi) $C_6H_5-O-C_7H_{15}(n-)$

(xii) 

$CH_3-CH_2-O-\underset{CH_3}{\underset{|}{CH}}-CH_2-CH_3$

8. Write structures of the compounds whose IUPAC names are as follows:
   - (i) 2-Methylbutan-2-ol
   - (ii) 1-Phenylpropan-2-ol
   - (iii) 3,5-Dimethylhexane -1, 3, 5-triol
   - (iv) 2,3 – Diethylphenol
   - (v) 1 – Ethoxypropane
   - (vi) 2-Ethoxy-3-methylpentane
   - (vii) Cyclohexylmethanol
   - (viii) 3-Cyclohexylpentan-3-ol
   - (ix) Cyclopent-3-en-1-ol
   - (x) 3-Chloromethylpentan-1-ol.

Assertion and Reason Questions-

1. In these questions, a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following choices.
   - a) Assertion and reason both are correct statements and reason is correct explanation for assertion.
   - b) Assertion and reason both are correct statements but reason is not correct explanation for assertion.
   - c) Assertion is correct statement but reason is wrong statement.
   - d) Assertion is wrong statement but reason is correct statement.

   Assertion: Primary and secondary alcohols can be distinguished by Victor-Meyer's test.

   Reason: Primary alcohols form nitrolic acid which dissolves in NaOH to form blood red colouration but secondary alcohols form pseudonitrols which give blue colouration with NaOH.

2. In these questions, a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following choices.
   - a) Assertion and reason both are correct statements and reason is correct explanation for assertion.
   - b) Assertion and reason both are correct statements but reason is not correct explanation for assertion.

c) Assertion is correct statement but reason is wrong statement.

d) Assertion is wrong statement but reason is correct statement.

Assertion: Reimer-Tiemann reaction of phenol with $CHCl_3$ in Na OH at 340K gives salicylic acid as the major product.

Reason: The reaction occurs through intermediate formation of $^{+}CHCl_2$.

Case Study Questions-

1. Read the passage given below and answer the following questions:

An organic compound (A) having molecular formula C_6H_6O gives a characteristic colour with aqueous $FeCl_3$ solution. (A) on treatment with CO_2 and NaOH at 400K under pressure gives (B), which on acidification gives a compound (C). The compound (C) reacts with acetyl chloride to give (D) which is a popular pain killer.

The following questions are multiple choice questions. Choose the most appropriate answer:

(i) Compound (A) is:

a) 2-Hexanol.

b) Dimethyl ether.

c) Phenol.

d) 2-Methyl pentanol.

(ii) Compound (C) is:

a) Salicylic acid.

b) Salicyladehyde.

c) Benzoic acid.

d) Benzaldehyde.

(iii) Number of carbon atoms in compound (D) is:

a) 7

b) 6

c) 8

d) 9

(iv) The conversion of compound (A) to (C) is known as:

a) Reimer-Tiemann reaction.

b) Kolbe's reaction.

c) Schimdt reaction.

d) Swarts reaction.

(v) Compound (A) on heating with compound (C) in presence of $POCl_3$ gives a compound (D) which is used:

a) In perfumery as a flavouring agent

b) As an antipyretic

c) As an analgesic

d) As an intestinal antiseptic.

2. Read the passage given below and answer the following questions:

A compound (X) containing C, H and O is unreactive towards sodium. It also does not react with Schiff s reagent. On refluxing with an excess of hydroiodic acid, (X) yields only one organic product (Y). On hydrolysis, (Y) yields a new compound (Z) which can be converted into (Y) by reaction with red phosphorus and iodine. The compound (Z) on oxidation with potassium permanganate gives a carboxylic acid. The equivalent weight of this acid is 60.

The following questions are multiple choice questions. Choose the most appropriate answer:

(i) The compound (X) is an:

a) Acid.
b) Aldehyde.
c) Alcohol.
d) Ether.

(ii) The IUPAC name of the acid formed is:

a) Methanoic acid.
b) Ethanoic acid.
c) Propanoic acid.
d) Butanoic acid.

(iii) Compound (Y) is:

a) Ethyl iodide.
b) Methyl iodide.
c) Propyl iodide.
d) Mixture of (a) and (b).

(iv) Compound (Z) is:

a) Methanol.
b) Ethanol.
c) Propanol.
d) Butanol.

(v) Compound (X) on treatment with excess of Cl_2 in presence of tight gives:

a) ∝− Chlorodiethyl ether.
b) ∝,∝′−Dichlorodiethyl ether.
c) Perchlorodiethyl ether.
d) None of these.

Answer Key

MCQ Answers-

1. Answer: (d) CH_3OH
2. Answer: (c) Oxidation by heating with copper followed by reaction with Fehling solution.
3. Answer: (b) $(CH_3)_3COH$
4. Answer: (d) IV > III > I > II
5. Answer: (d) O-H
6. Answer: (b) o-and p-promophenols
7. Answer: (c) CCl_2
8. Answer: (c) m-chlorophenol
9. Answer: (a) 1° > 2° > 3°
10. Answer: (a) Benzene

Very Short Answers-

(i) **Ans.** 5 – Methyloctan-3-ol

(ii) **Ans.** 1-Chloro propan-2-ol

(iii) **Ans.** Pentan – 1,3,4 – triol

(iv) **Ans.** 2 – Methylpropan -2-ol

(v) **Ans.** 1,3 – Dibromo – 4- chloro – 2- butanol

(vi) **Ans.** 5 – Chloro – 4 – ethyl – 5- methyl hexanol.

(vii) **Ans.** 2 – Phenyl ethanol

(viii) **Ans.** 2- Methyl phenol.

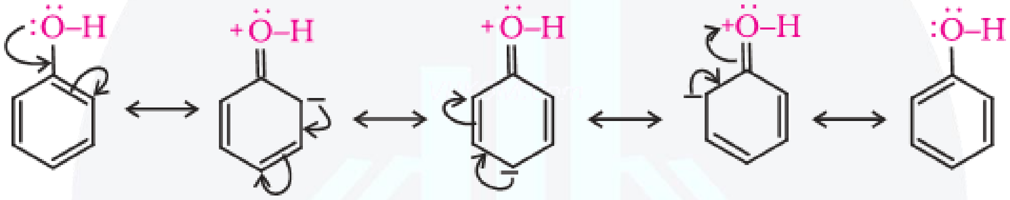
(ix) **Ans.** 4- Bromo -3, 3,5 – trimethyl – hex -1-ene- 2,5- diol

(x) **Ans.** 2,3 – Dimethylbutan – 2,3 –diol

Short Answers-

1. Phenol is acidic in nature because

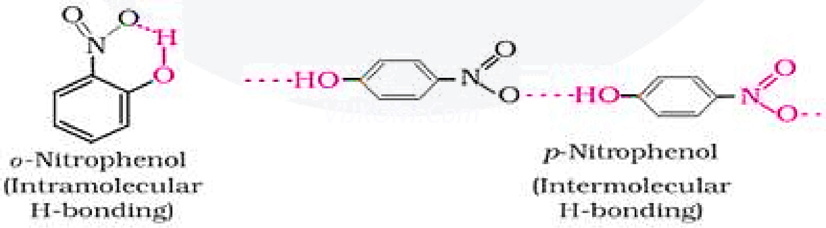
   (a) phenol, due to resonance, the positive charge rests on oxygen making the shared pair of electrons more towards oxygen and hydrogen as H^+



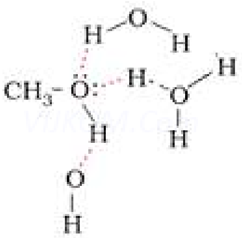
   (b) The carbon attached to OH is SP^2 hybridize and is more electronegative, this decreases the electron density on oxygen, increasing the polarity of O-H bond and ionization of phenol. The phenoxide ion formed by loss of H^+ is more resonance stabilized than phenol itself.

2. In phenol due to electron rich benzene ring the C-O bond is less polar whereas in methanol the C-O bond is highly polar. Therefore, the dipole moment of methanol is higher than phenol.

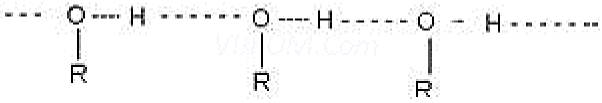
3. P- nitrophenol has intermolecular hydrogen bonding which increases the boiling point while in o- nitro phenol due to presence of intra molecular hydrogen bonding, there is a decrease in boiling point and increase in volatility.



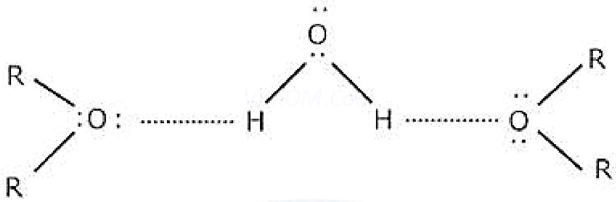
4. Methanol can form intermolecular hydrogen bonding with water but there is no hydrogen bonding in iodomethane and water. Therefore methanol in miscible in water.



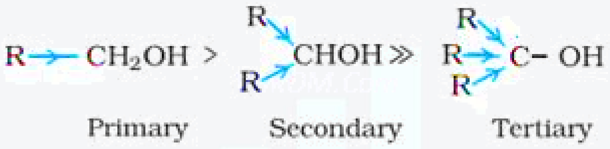
5. Alcohols can form intermolecular hydrogen bonds due to their high polarity whereas, ether cannot. Therefore alcohols have higher boiling points than isomeric ethers.



6. Ethers can form H- bonding with water molecule whereas alkenes cannot. Therefore ethers are soluble in water and alkanes are not.



7. In alcohols, the acidic strength is due to polar nature of O-H bond. An electron releasing group e.g., alkyl groups, increases electron density on oxygen tending to decrease the polarity of O-H bond. This decreases the acid strength. Therefore the order of acid strength is .



8. The reaction between alcohol and carboxylic acid is reversible and goes in backward direction if water is not removed as soon as it is formed.

$$ROH + RCOOH \overset{H^+}{\rightleftharpoons} RCOOR' + H_2O$$

9. For secondary and tertiary alcohols, elimination competes over substitution and alkenes are formed on acidic dehydration as the reaction follows Sn1 mechanism. Therefore the acidic dehydration of secondary or tertiary alcohols does not give ethers.

10. In case of anisole, methyl phenyl oxonium ion, $C_6H_5-\underset{H}{\overset{\oplus}{O}}-CH_3$ is formed by protonation of ethers during reaction with HI. The bond between O–CH_3 is weaker than the bond between O–C_6H_5 because carbon of phenyl group is SP^2 hybridised and there is a partial double bond character. Therefore, the attack by I^- ion breaks O–CH_3 bond to form CH_3I.

$$C_6H_5\ OCH_3 + HI \rightarrow C_6H_5OH + CH_3I$$

Long Answers-

1. Primary alcohol → (i), (ii), (iii)

   Secondary alcohol → (iv), (v)

   Tertiary alcohol → (vi)

2. **(i)** 3-Chloromethyl-2-isopropylpentan-1-ol

   (ii) 2, 5-Dimethylhexane-1, 3-diol

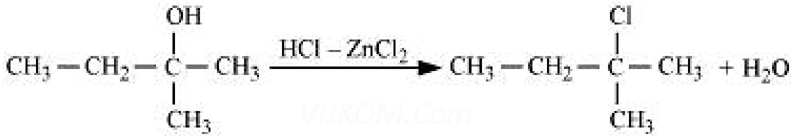
   (iii) 3-Bromocyclohexanol

   (iv) Hex-1-en-3-ol

   (v) 2-Bromo-3-methylbut-2-en-1-ol

3. **(a)** **(i)** $\underset{\text{Butan}-1-\text{ol}}{CH_3-CH_2-CH_2-CH_2-OH} \xrightarrow{HCl \cdot ZnCl_2} \text{No reaction}$

Primary alcohols do not react appreciably with Lucas' reagent (HCl-ZnCl2) at room temperature.

(ii) 

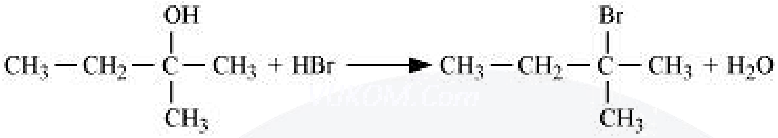
$$CH_3-CH_2-C(OH)(CH_3)-CH_3 \xrightarrow{HCl-ZnCl_2} CH_3-CH_2-C(Cl)(CH_3)-CH_3 + H_2O$$

2 – Methylbutan – 2 – ol (3°) 2 – Chloro – 2 – Methylbutane (White turbidity)

Tertiary alcohols react immediately with Lucas' reagent.

(b) **(i)** $CH_3CH_2CH_2CH_2OH + HBr \xrightarrow[-H_2O]{} CH_3CH_2CH_2CH_2Br$

Butan – 1 – ol 1-Bromobutane

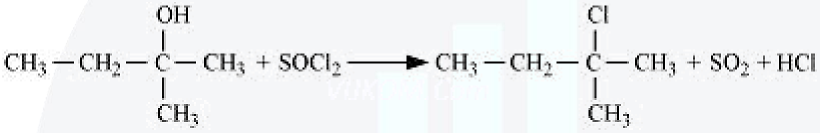
(ii) 

$$CH_3-CH_2-C(OH)(CH_3)-CH_3 + HBr \longrightarrow CH_3-CH_2-C(Br)(CH_3)-CH_3 + H_2O$$

2 – Methylbutan – 2 – ol (3°) 2 – Bromo – 2 – Methylbutane

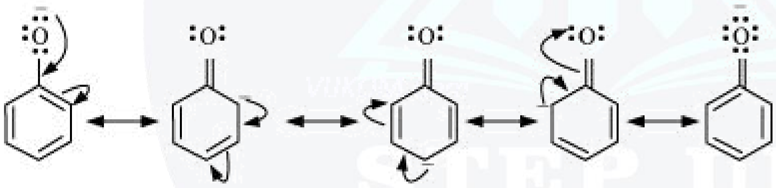
(c) **(i)** $CH_3CH_2CH_2CH_2OH + SOCl_2 \longrightarrow CH_3CH_2CH_2CH_2Cl + SO_2 + HCl$

Butan-1-ol 1-chlorobutane

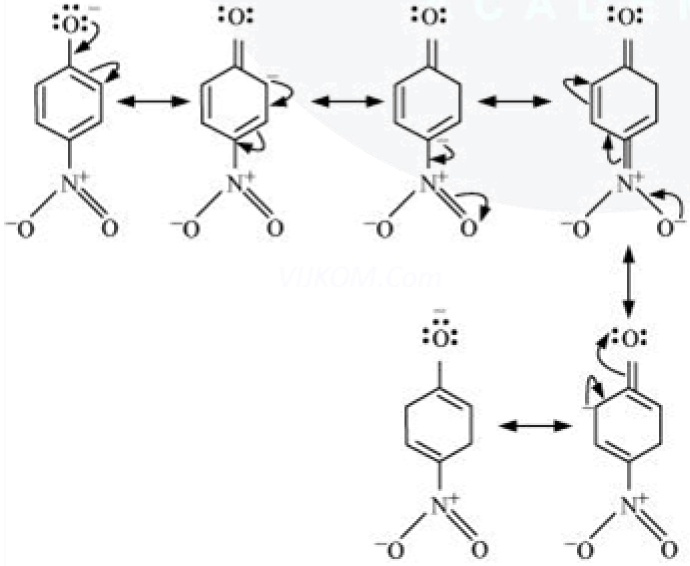
(ii) 

$$CH_3-CH_2-C(OH)(CH_3)-CH_3 + SOCl_2 \longrightarrow CH_3-CH_2-C(Cl)(CH_3)-CH_3 + SO_2 + HCl$$

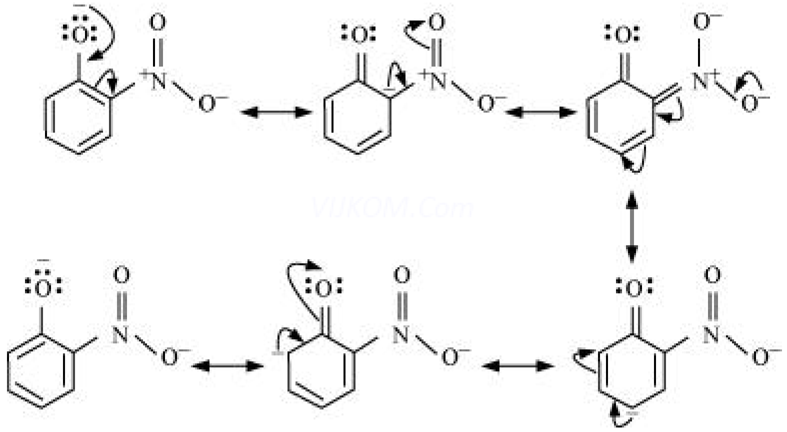
2 – Methylbutan – 2 – ol 2 – Chloro – 2 – Methylbutane

4. 

Resonance structure of the phenoxide ion



Resonance structures of *p*-nitrophenoxide ion

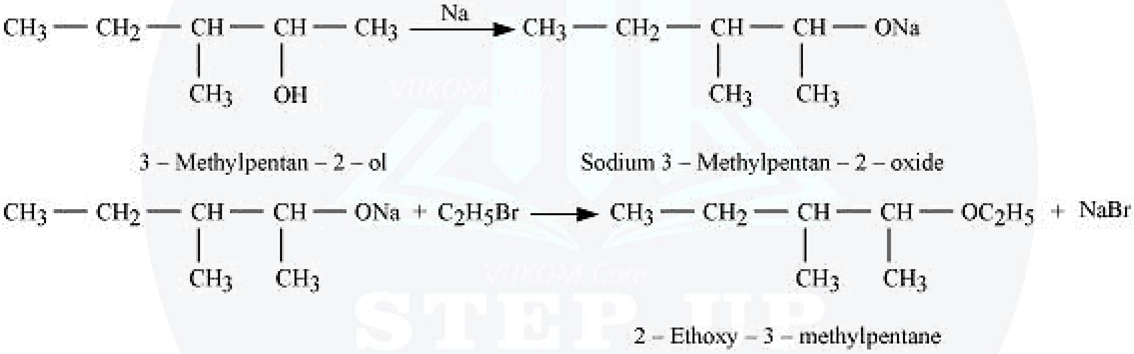


Resonance structures of *o*-nitrophenoxide ion

It can be observed that the presence of nitro groups increases the stability of phenoxide ion.

5. In Williamson synthesis, an alkyl halide reacts with an alkoxide ion. Also, it is an S^2_N reaction. In the reaction, alkyl halides should be primary having the least steric hindrance. Hence, an alkyl halide is obtained from ethanol and alkoxide ion from 3-methylpentan-2-ol.

$$\underset{\text{Ethanol}}{C_2H_5OH} \xrightarrow{HBr} \underset{\text{Bromoethane}}{C_2H_5Br}$$



$$CH_3-CH_2-\underset{CH_3}{\underset{|}{CH}}-\underset{OH}{\underset{|}{CH}}-CH_3 \xrightarrow{Na} CH_3-CH_2-\underset{CH_3}{\underset{|}{CH}}-\underset{CH_3}{\underset{|}{CH}}-ONa$$

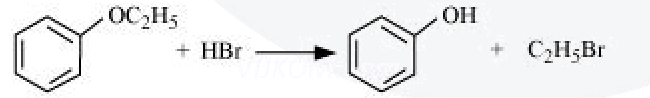
3 – Methylpentan – 2 – ol   Sodium 3 – Methylpentan – 2 – oxide

$$CH_3-CH_2-\underset{CH_3}{\underset{|}{CH}}-\underset{CH_3}{\underset{|}{CH}}-ONa + C_2H_5Br \longrightarrow CH_3-CH_2-\underset{CH_3}{\underset{|}{CH}}-\underset{CH_3}{\underset{|}{CH}}-OC_2H_5 + NaBr$$

2 – Ethoxy – 3 – methylpentane

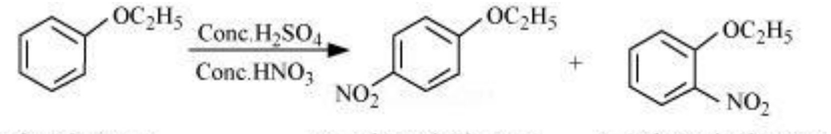
6. **(i)** $\underset{n\text{-propylmethyl ether}}{CH_3-CH_2-CH_2-O-CH_3} + HBr \longrightarrow \underset{\text{Propanol}}{CH_3-CH_2-CH_2-OH} + \underset{\text{Bromomethane}}{CH_3-Br}$

(ii)



Ethoxybenzene   Phenol   Bromoethane

(iii)



Ethoxybenzene   4 – Ethoxynitrobenzene (Major)   2 – Ethoxynitrobenzene (Minor)

(iv) $\underset{tert\text{-Butyl ethyl ether}}{(CH_3)_3C-OC_2H_5} \xrightarrow{HI} \underset{tert\text{-Butyliodide}}{(CH_3)_3C-I} + \underset{\text{Ethanol}}{C_2H_5OH}$

7. **(i)** 2, 2, 4-Trimethylpentan-3-ol

(ii) 5-Ethylheptane-2, 4-diol

(iii) Butane-2, 3-diol

(iv) Propane-1, 2, 3-triol

(v) 2-Methylphenol

(vi) 4-Methylphenol

(vii) 2, 5-Dimethylphenol

(viii) 2, 6-Dimethylphenol

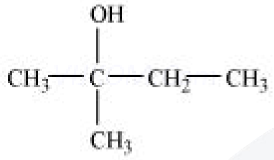
(ix) 1-Methoxy-2-methylpropane

(x) Ethoxybenzene

(xi) 1-Phenoxyheptane

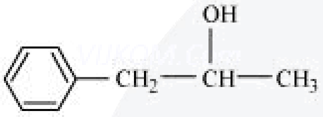
(xii) 2-Ethoxybutane

8. **(i)**



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

(ii)



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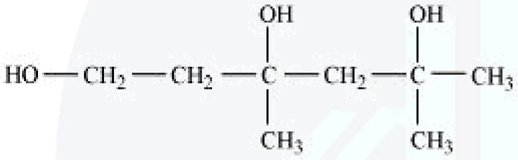
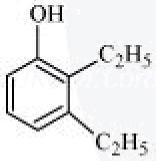


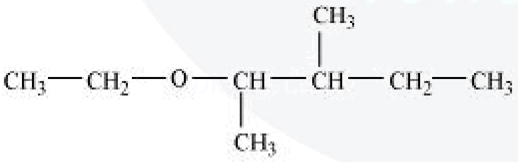
$HO-CH_2-CH_2-\overset{\overset{OH}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH_2-\overset{\overset{OH}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH_3$

(iv)



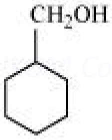
(v) $CH_3-CH_2-O-CH_2-CH_2-CH_3$

(vi)

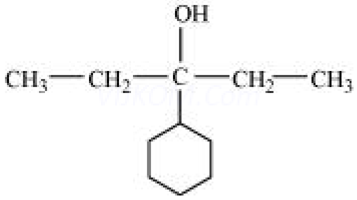


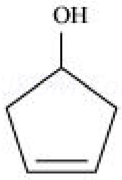
$CH_3-CH_2-O-\underset{\underset{CH_3}{|}}{CH}-\overset{\overset{CH_3}{|}}{CH}-CH_2-CH_3$

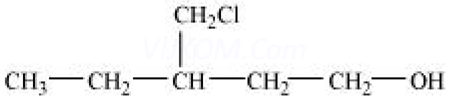
(vii)



(viii)



(ix) 

(x) 

$$CH_3-CH_2-\underset{}{\overset{\overset{\displaystyle CH_2Cl}{|}}{CH}}-CH_2-CH_2-OH$$

Assertion and Reason Answers-

1. (a) Assertion and reason both are correct statements and reason is correct explanation for assertion.
2. (c) Assertion is correct statement but reason is wrong statement.

   Explanation:

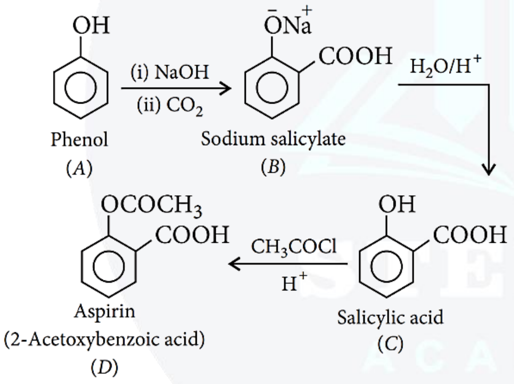
   Intermediate formed is dichlorocarbene.

Case Study Answers-

1. **Answer :**

   (i) (c) Phenol.

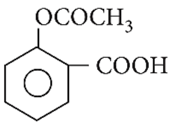
   Explanation:



   (ii) (a) Salicylic acid.

   (iii) (d) 9

   Explanation:



   It has 9 C-atoms.

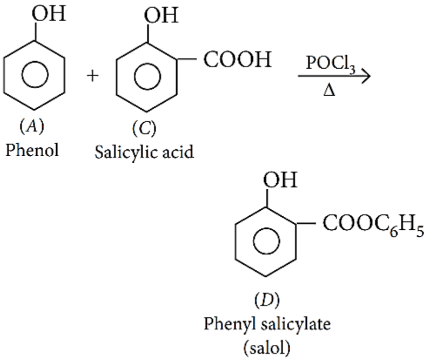
   (iv) (b) Kolbe's reaction.

   Explanation:

   Sodium phenoxide when heated with CO_2 at 400K under a pressure of 4-7 atm followed by acidification gives 2-hydroxybenzoic acid (salicylic acid) as the main product along with a small amount of 4-hydroxybenzoic acid. This reaction is called Kolbe's reaction.

(v) (d) As an intestinal antiseptic.

Explanation:



Salol is used as an intestinal antiseptic.

2. Answer:

(i) (d) Ether.

Explanation:

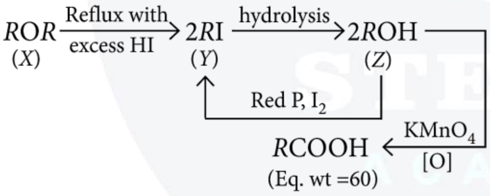
Since the compound X is unreactive towards sodium so it is neither an acid nor an alcohol. Since the compound X is unreactive towards Schiff's base so it is not an aldehyde.

The compound X forms only one product on reaction with excess HI, indicates that the compound X may be ether.

(ii) (b) Ethanoic acid.

Explanation:

The reactions can be written as:

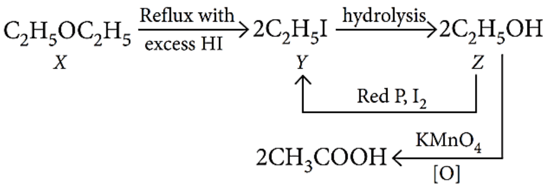


Since the equivalent weight of carboxylic acid is 60. So, it must be CH_3COOH i.e., ethanoic acid.

(iii) (a) Ethyl iodide.

Explanation:

The alcohol Z in that case should be C_2H_5OH and the compound Y should be ethyl iodide. X is therefore diethyl ether ($C_2H_5 — O — C_2H_5$)



(iv) (b) Ethanol.

(v) (c) Perchlorodiethyl ether.

Explanation:

In the presence of light and excess of chlorine, all the hydrogen atoms of diethyl ether are substituted to give perchlorodiethyl ether.

$$CH_3CH_2 - O - CH_2CH_3 + \underset{\text{(excess)}}{10Cl_2} \xrightarrow{hu}$$

$$\underset{\text{Perchlorodierhyl ether}}{CCl_3CC_2 - O - CCl_2 - CCl_3} + 10HCI$$

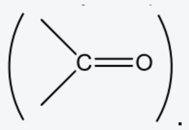
◆ ◆

Aldehydes Ketones and Carboxylic Acids

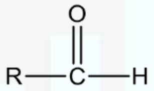
9

Introduction

- Carbonyl compounds are organic compounds containing carbon-oxygen double bond



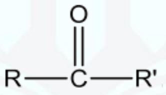
- Aldehydes have carbonyl group bonded to a carbon and hydrogen.



$R-\overset{\overset{\displaystyle O}{\|}}{C}-H$

(Where R = H or alkyl or aryl group)

- Ketones have carbonyl group bonded to two carbon atoms.O

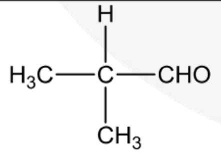
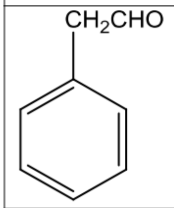


$R-\overset{\overset{\displaystyle O}{\|}}{C}-R'$

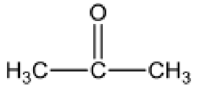
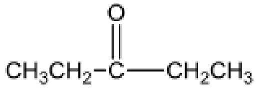
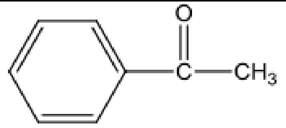
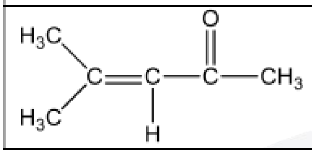
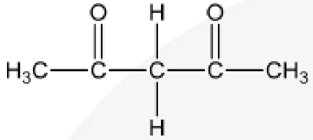
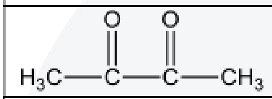
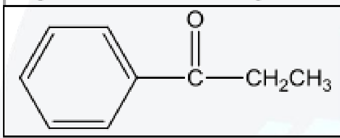
(Where R and R' may be same or different alkyl or aryl groups)

Nomenclature of Aldehydes and Ketones

ldehydes

Structure	Common name	IUPAC name
CH_3CHO	Acetaldehyde	Ethanal
 $H_3C-\overset{H}{\underset{CH_3}{C}}-CHO$	Isobutyraldehyde	2-Methylpropanal
$H_2C=CHCHO$	Acrolein	Prop-2-enal
	Phenylacetaldehyde	2-Phenylethanal
$CH_3CH=CHCHO$	Crotonaldehyde	But-2-en-al

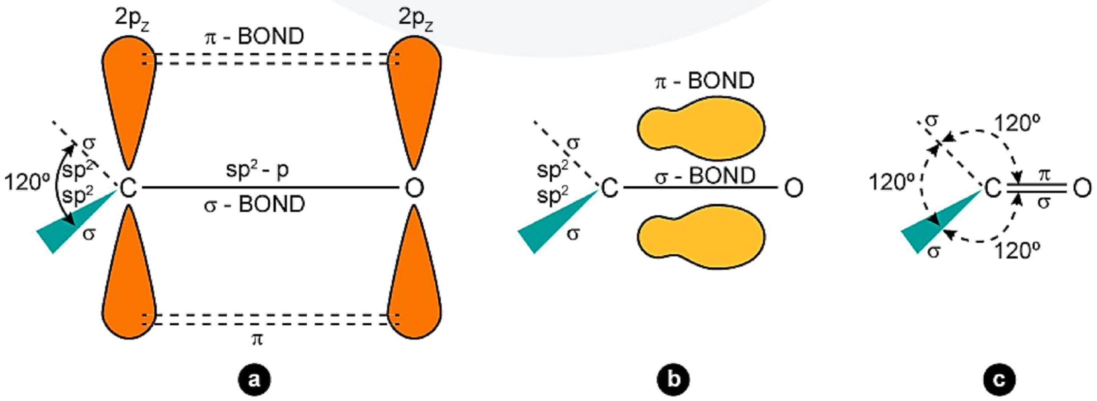
Ketones

Structure	Common name	IUPAC name
 $\mathrm{H_3C{-}\overset{O}{\overset{\|}{C}}{-}CH_3}$	Dimethyl ketone or Acetone	Propanone
 $\mathrm{CH_3CH_2{-}\overset{O}{\overset{\|}{C}}{-}CH_2CH_3}$	Diethyl ketone	Pentan-3-one
	Methyl phenyl ketone	1-Phenylethan-1-one
	Mesityl oxide	4-Methylpent-3-en-one
 $\mathrm{H_3C{-}\overset{O}{\overset{\|}{C}}{-}\underset{H}{\overset{H}{C}}{-}\overset{O}{\overset{\|}{C}}{-}CH_3}$	Acetylacetone	Pentane-2,4-dione
 $\mathrm{H_3C{-}\overset{O}{\overset{\|}{C}}{-}\overset{O}{\overset{\|}{C}}{-}CH_3}$	Biacetyl	Butane-2,3-dione
	Ethyl phenyl ketone	1-Phenylpropan-1-one

Structure and Nature of Carbonyl Group

Structure

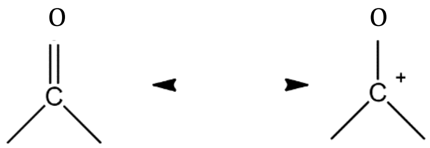
- The carbonyl carbon group is sp^2 hybridised and forms three sigma bonds.
- The fourth electron in the p-orbital forms a n-bond by overlapping with p-orbital of oxygen.
- The oxygen atom also has two non-bonding electron pairs.
- So the carbonyl carbon with the three atoms linked to it lies in the same plane and the n-cloud liesabove and below the plane.
- The bond angle is 120° with expected trigonal coplanar structure.
-



Nature

- The C-O double bond is polarised since oxygen is electronegative than carbon.
- So the carbonyl carbon is an electrophilic centre and the carbonyl oxygen is a nucleophilic centre.

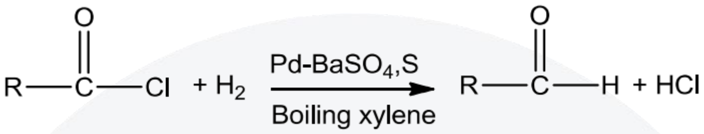
- The carbonyl compounds have substantial dipole moments and are polar than ethers.
- The high polarity of the carbonyl group can be explained on the basis of resonance involving a neutral (A) and a dipolar (B) structures given below.



Preparation of Aldehydes

Rosenmund Reduction

In this reaction, acyl chloride on hydrogenation in the presence of palladium catalyst and bariumsulphate gives aldehydes.



$$R-\overset{\overset{O}{\|}}{C}-Cl + H_2 \xrightarrow[\text{Boiling xylene}]{Pd\text{-}BaSO_4,S} R-\overset{\overset{O}{\|}}{C}-H + HCl$$

Stephen Reaction

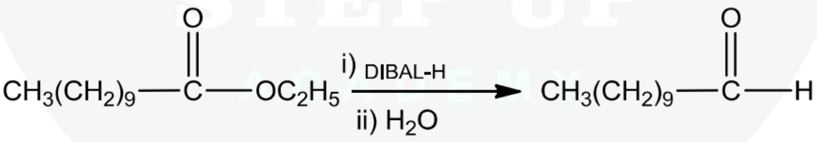
Nitriles on reduction with stannous chloride in the presence of HCl give imine which on hydrolysis gives corresponding aldehyde.

$$RCN + SnCl_2 + HCl \longrightarrow RCH{=}NH \xrightarrow{H_3O^+} RCHO$$

An alternate method to reduce nitriles selectively is by diisobutylaluminium hydride to imines which onhydrolysis yields aldehydes.

$$RCN \xrightarrow[\text{ii) } H_2O]{\text{i) } AlH(i\text{-}Bu)_2} R\text{-}CHO$$

Esters can also be reduced to aldehydes with DIBAL-H



$$CH_3(CH_2)_9-\overset{\overset{O}{\|}}{C}-OC_2H_5 \xrightarrow[\text{ii) } H_2O]{\text{i) DIBAL-H}} CH_3(CH_2)_9-\overset{\overset{O}{\|}}{C}-H$$

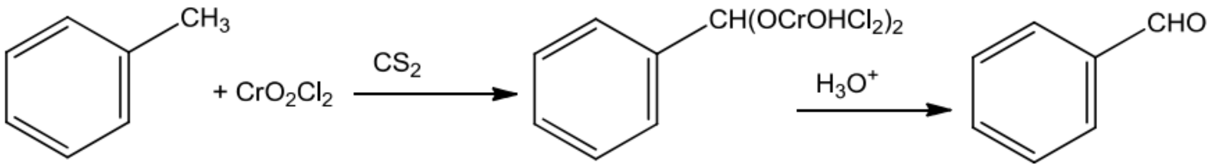
From Aromatic Hydrocarbons

Aromatic aldehydes can be prepared using the following methods.

By Oxidation of Methylbenzene

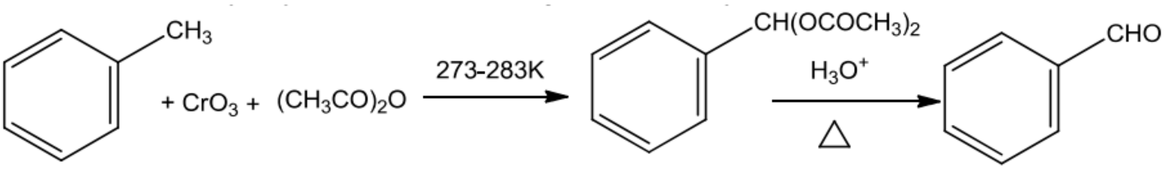
Etard Reaction (Use of Chromyl Chloride)

Chromyl chloride oxidises the methyl group to a chromium complex which on further hydrolysis gives corresponding benzaldehyde.



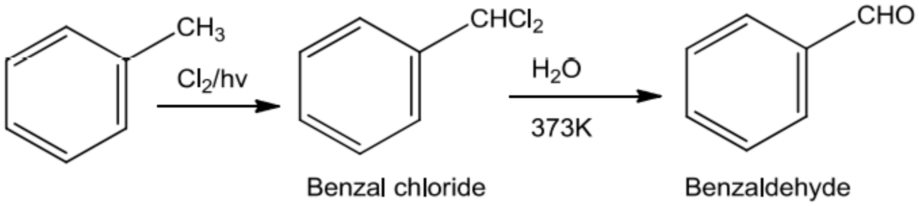
Use of Chromic oxide (CrO_3)

Toluene when treated with chromic oxide in acetic anhydride gets converted into benzylidenediacetate which on hydrolysis with aqueous acid gives benzaldehyde.



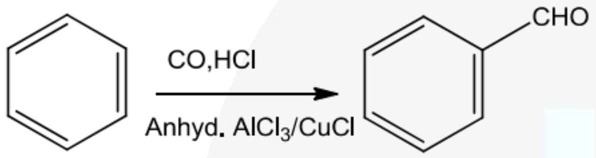
Side Chain Chlorination

Toluene on side chlorination gives benzal chloride which on hydrolysis gives benzaldehyde.



Gatterman — Koch Reaction

Benzene or toluene on treatment with CO and HCI in the presence of $AlCl_3$ or CuCI gives benzaldehyde or p-tolualdehyde.

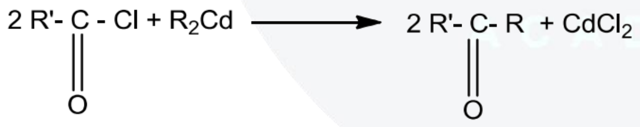


Preparation of Ketones

From Acid chlorides or Acyl chlorides

Acyl chloride on treatment with dialkylcadmium obtained by reaction of cadium chloride with Grignardreagent gives ketones.

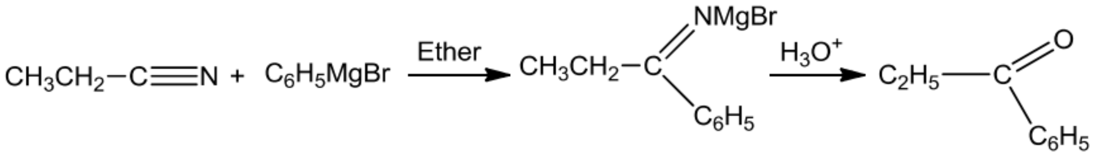
$$2\ R\text{-}Mg\text{-}X + CdCl_2 \longrightarrow R_2Cd + 2Mg(X)Cl$$



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

From Nitriles

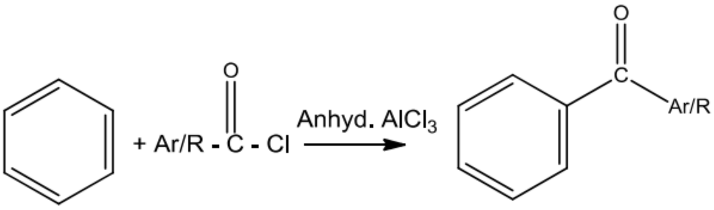
Nitriles on treatment with Grignard reagent followed by hydrolysis yields a ketone



Propiophenone
(1-Phenylpropanone)

From Benzenes or Substituted Benzenes

Benzene or substituted benzene on treatment with acid chloride in the presence of anhydrous $AlCl_3$ gives the corresponding ketone and this reaction is known as Friedel-Crafts acylation reaction.



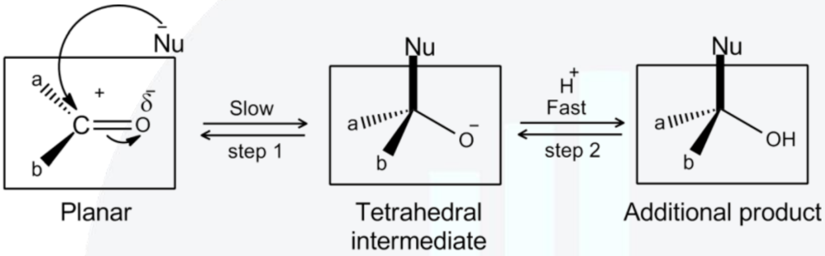
Chemical Reactions

Nucleophilic Addition Reactions

Aldehydes and Ketones undergo nucleophilic addition reactions.

(i) Mechanism for Nucleophilic Addition Reactions

- A nucleophile attacks the electrophilic carbon atom of the polar carbonyl group perpendicularly to the sp^3 hybridised orbitals of carbonyl carbon.
- The hybridisation changes from sp^2 to sp^3 and a tetrahedral alkoxide intermediate is formed.
- The intermediate grabs a proton from the reaction medium to give an electrically neutral product.
- The net result is addition of Nu- and H' across the C-O double bond.



(ii) Reactivity

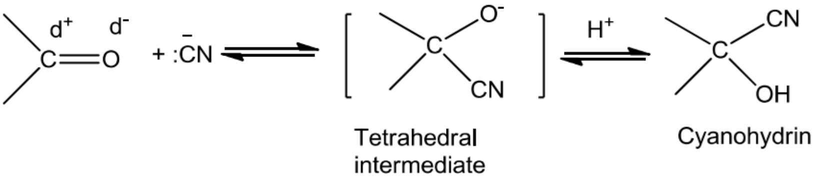
- Aldehydes are more reactive than ketones in nucleophilic reactions because of two reasons:
- Sterically, it is the presence of two relatively large groups in ketones that hinder the approach of nucleophile to carbonyl carbon than in aldehydes which have only one such substituent.
- Electronically, aldehydes are more reactive than ketones because the two alkyl groups in ketones decrease the electrophilicity of the carbonyl carbon more effectively than in aldehydes.

(iii) Important Examples of Nucleophilic Addition and Nucleophilic Addition- Elimination Reactions

(a) Addition of Hydrogen cyanide (HCN)

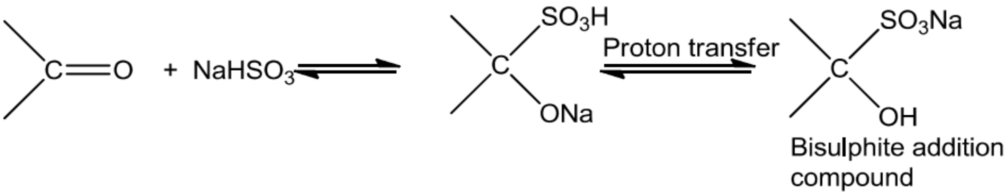
- On addition of HCN to aldehydes and ketones they yield cyanohydrins.
- Since the reaction is very slow with pure HCN, it is catalysed with the help of a base and the cyanide ion (CN-) generated as a strong nucleophile adds to carbonyl compounds to give cyanohydrins.

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



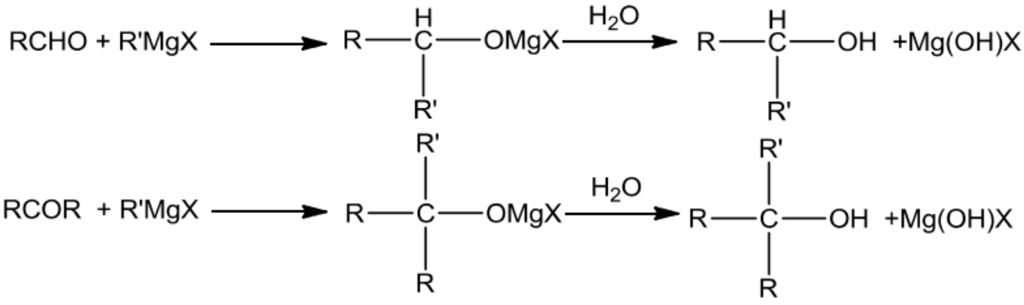
(b) Addition of Sodium Hydrogensulphite

Sodium hydrogen sulphite when added to aldehydes and ketones yield addition products.



(c) Addition of Grignard Reagents

Grignard reagents on reacting with aldehydes and ketones yield alcohols.

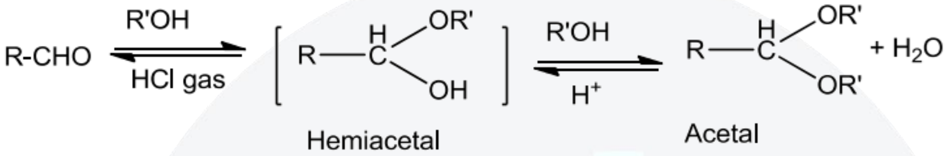


$$RCHO + R'MgX \longrightarrow R-\overset{H}{\underset{R'}{C}}-OMgX \xrightarrow{H_2O} R-\overset{H}{\underset{R'}{C}}-OH + Mg(OH)X$$

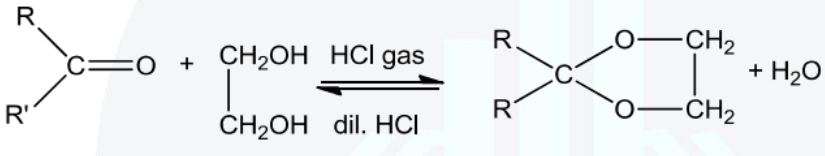
$$RCOR + R'MgX \longrightarrow R-\overset{R'}{\underset{R}{C}}-OMgX \xrightarrow{H_2O} R-\overset{R'}{\underset{R}{C}}-OH + Mg(OH)X$$

(d) Addition of Alcohols

- Aldehydes on treatment with one equivalent of monohydric alcohol in the presence of dry HCl give hemiacetal which on further treatment with one more molecule of alcohol gives acetal.



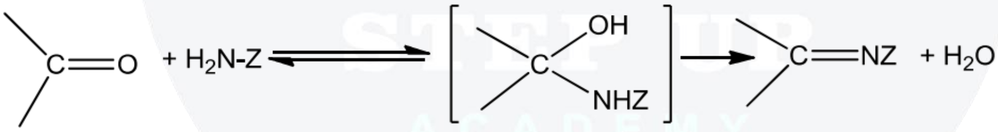
- Ketones also react with ethylene glycols under similar conditions to give ethylene glycol ketals.



Ethylene glycol ketal

(e) Addition of Ammonia and its Derivatives

Ammonia and its derivative add to the carbonyl group of an aldehydes and ketone

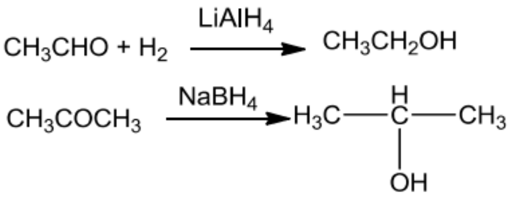


Z = Alkyl, aryl, OH, NH_2, C_6H_5NH, $NHCONH_2$, etc.

Reduction

(i) Reduction to Alcohols

Aldehydes and ketones get reduced to primary and secondary alcohols by NaBH4 or LiAIH4.



$$CH_3CHO + H_2 \xrightarrow{LiAlH_4} CH_3CH_2OH$$

$$CH_3COCH_3 \xrightarrow{NaBH_4} H_3C-\overset{H}{\underset{OH}{C}}-CH_3$$

(ii) Reduction to Hydrocarbons

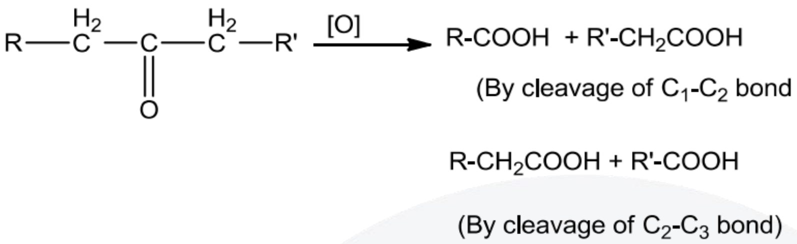
Aldehydes and ketones reduce to —CH_2 group on treatment with zinc-amalgam and conc. HCI [Clemmenson reduction] or with hydrazine which on heating with sodium or potassiumhydroxide in ethylene glycol[Wolff-Kishner reduction]

Oxidation

- Aldehydes get oxidised to carboxylic acids with common oxidising agents like nitric acid, potassium permanganate, potassium dichromate etc.

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

- Ketones undergo oxidation with strong oxidising agents and elevated temperatures. The reaction involves carbon-carbon bond cleavage to give a mixture of carboxylic acids with lessernumber of carbon atoms than the parent ketones.



$$\text{R}-\overset{H_2}{C}-\underset{\underset{O}{\|}}{C}-\overset{H_2}{C}-\text{R'} \xrightarrow{[O]} \text{R-COOH} + \text{R'-CH}_2\text{COOH}$$

(By cleavage of C_1-C_2 bond

$$\text{R-CH}_2\text{COOH} + \text{R'-COOH}$$

(By cleavage of C_2-C_3 bond)

Test to distinguish Aldehydes from Ketones

Tollens test

- Aldehydes on warming with freshly prepared ammoniacal silver nitrate solution (Tollensreagent) produce a bright silver mirror due to the formation of silver metal.
- The aldehydes are oxidised to corresponding carboxylate anion in alkaline medium.

$$\text{RCHO} + 2[Ag(NH_3)_2]^+ + 3OH^- \longrightarrow \text{RCOO}^- + 2Ag + 2H_2O + 4NH_3$$

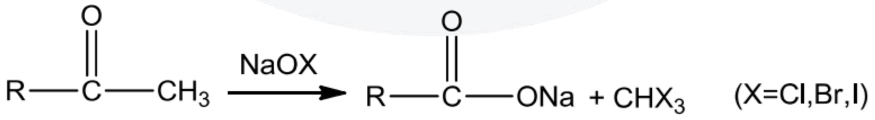
Fehling's test

- Fehling reagent comprises of Fehling solution A and Fehling B.Fehling solution A = aqueous copper sulphate Fehling solution B = Alkaline sodium potassium tartarate(Rochelle salt)
- On heating Fehling's reagent with an aldehyde, a reddish brown precipitate is obtained.
- Aldehydes are oxidised to corresponding carboxylate anion while aromatic aldehydes do notrespond to this test.

$$\text{RCHO} + 2Cu^{+2} + 5\bar{O}H \longrightarrow \text{RCOO}^- + Cu_2O + 3H_2O$$

Haloform reaction

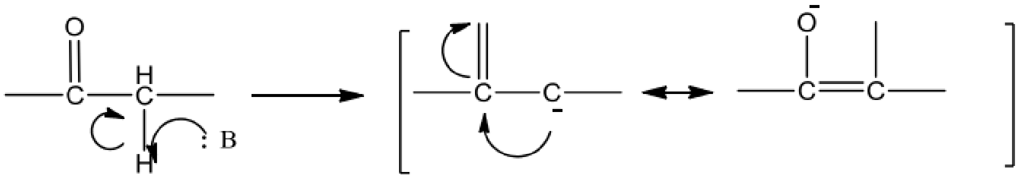
Aldehydes and ketones with at least one methyl group attached to the carbonyl carbon atom on oxidation with sodium hypohalite turn to sodium salts of corresponding acids with one carbon atomless than that of carbonyl compound. In this reaction, the methyl group is converted to haloform.



$$\text{R}-\overset{\overset{O}{\|}}{C}-CH_3 \xrightarrow{\text{NaOX}} \text{R}-\overset{\overset{O}{\|}}{C}-\text{ONa} + CHX_3 \quad (X=Cl,Br,I)$$

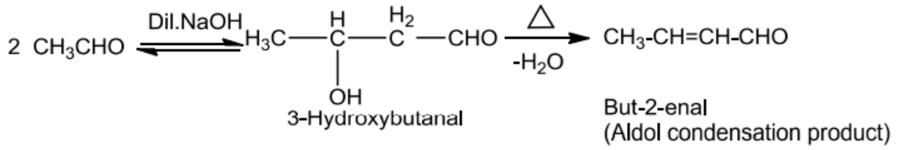
Reactions due to a-hydrogen

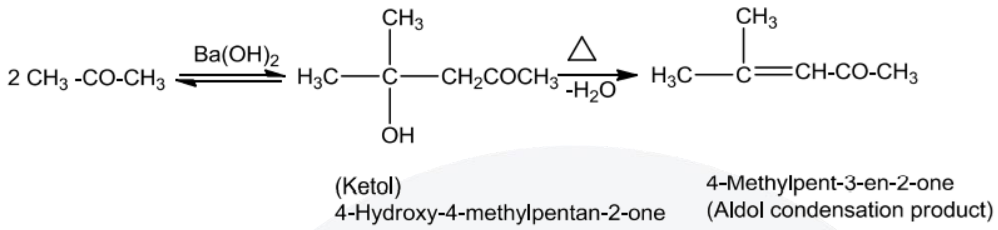
- The a-hydrogen of aldehydes and ketones is acidic in nature hence they undergo a number of reactions.
- The a-hydrogen atoms of carbonyl group is acidic due to the strong electron withdrawing effect of the carbonyl group and resonance stabilisation of the conjugate base.



(i) Aldol Condensation

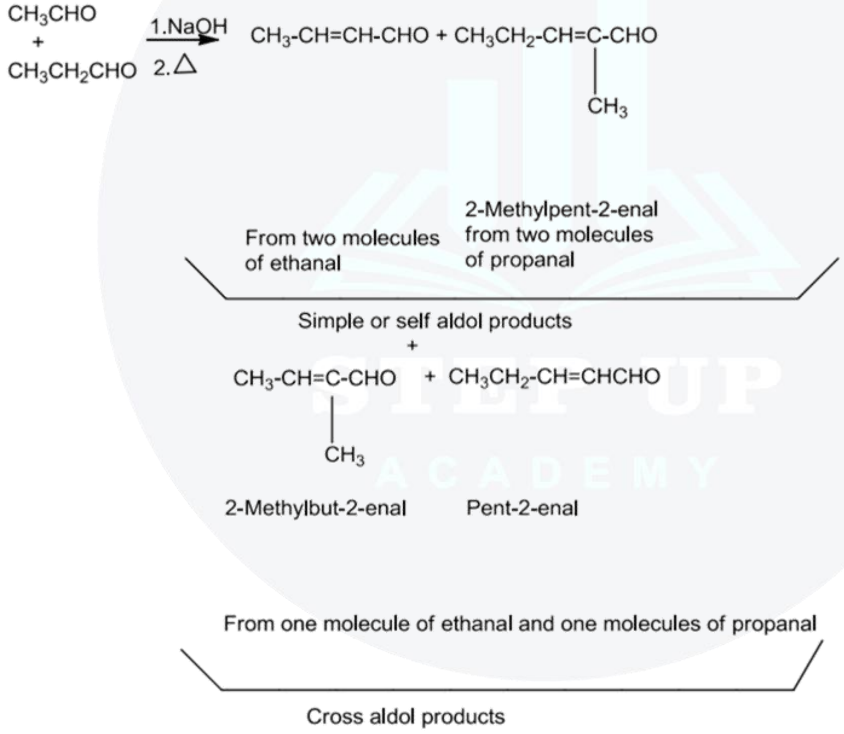
Aldehydes and ketones with at least one a-hydrogen undergo reaction in the presence of dilutealkali as catalyst to form §-hydroxy aldehydes (aldol) or §-hydroxy ketones (ketol) respectively.This is known as Aldol reaction.



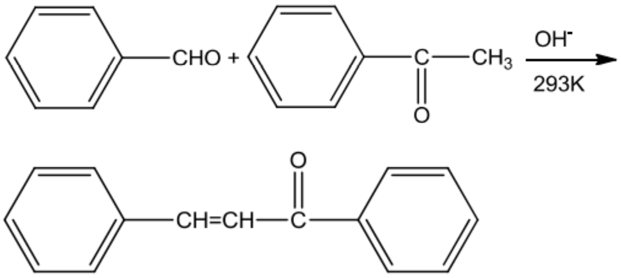


(ii) Cross Aldol Condensation

- In this reaction, two different aldehydes and/or ketones with a-hydrogen atoms reaction inthe presence of dilute alkali as catalyst give a mixture of four products.



Ketones can be taken as one the component in the cross aldol reactions.

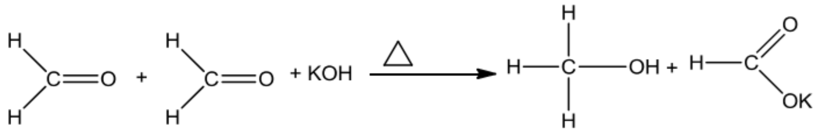


1,3-Diphenylprop-2-en-1-one
(Benzalacetophenone)
(Major product)

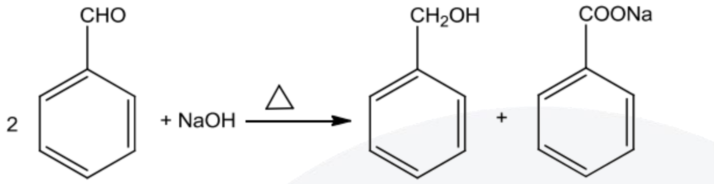
Other Reactions

(i) Cannizzaro reaction

- Aldehydes with no a-hydrogen undergo self oxidation and reduction on heating withconcentrated alkali.
- In this reaction, one molecule of the aldehyde is reduced to alcohol and another is oxidisedto carboxylic acid salt.



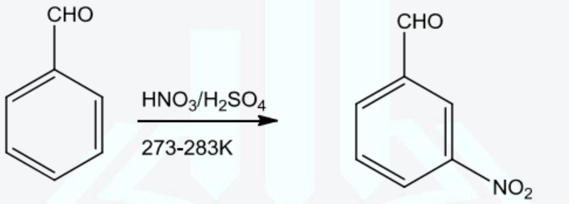
Formaldehyde Methanol Potassium formate



Benzyl alcohol Sodium benzoate

(ii) Electrophilic Substitution Reaction

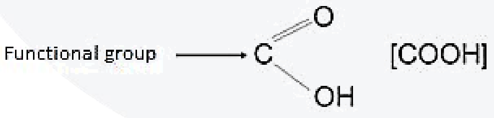
Aromatic aldehydes and ketones undergo electrophilic substitution reaction at the ring in whichthe carbonyl group acts as a deactivating and meta-directing group.



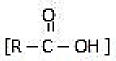
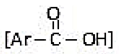
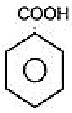
Benzaldehyde m-Nitrobenzaldehyde

Carboxylic Acids

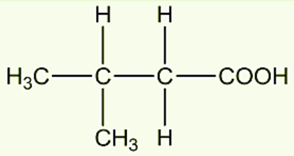
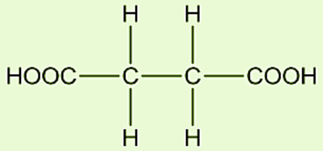
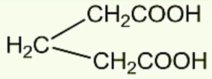
- The carbonyl compounds in which carbonyl group is bonded to oxygen are known as carboxylic acids.
- The derivative compounds of carboxylic acid where carbon is attached to nitrogen and to halogens arecalled amides and acyl halides respectively.



General structure :

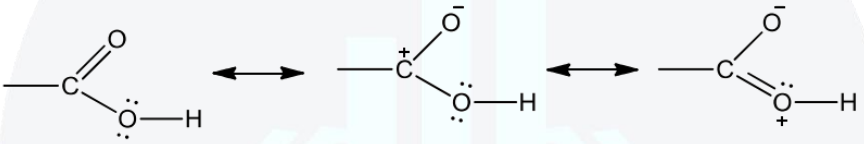
Aliphatic carboxylic acids	R COOH	 $[R-\overset{O}{\overset{\|}{C}}-OH]$
Aromatic carboxylic acid	Ar COOH	 $[Ar-\overset{O}{\overset{\|}{C}}-OH]$
Lower Members	HCOOH	(formic acid) Methanoic acid
	CH_3COOH	Ethanoic acid (acetic acid)
		Benzoic acid
	COOH | COOH	Oxalic acid

Nomenclature of Carbonyl Group

Structure	Common Name	IUPAC Name
$HCOOH$	Formic acid	Methanoic acid
 $H_3C-\underset{CH_3}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-COOH$	Isovaleric acid	3-Methylbutanoic acid
 $HOOC-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-COOH$	Succinic acid	Butane-1,4-dioic acid
$H_3C-CH=CH-COOH$	Crotonic acid	But-2-enoic acid
$COOH-COOH$	Oxalic acid	Ethane-1,2-dioic acid
	Glutaric acid	Pentan-1,5-dioic acid

Structure of Carbonyl Group

The bonds to the carboxyl carbon in carboxylic acids lie in one plane and are separated by about 120°. Due to possible resonance structure given below, the carboxylic carbon is less electrophilic than carbonyl carbon.



Preparation of Carboxylic Acids

From Primary Alcohols and Aldehydes

- Primary alcohols undergo oxidation with the help of oxidising agents like potassium permanganatein neutral, acidic or alkaline media or by potassium dichromate and chromium trioxide in acidic media to give carboxylic acid.

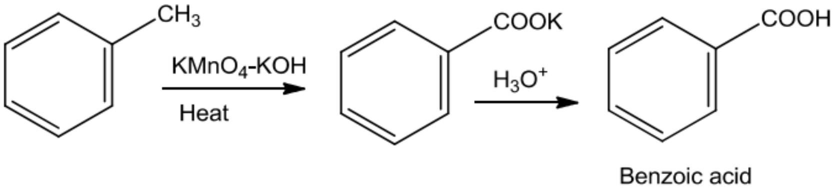
$$RCH_2OH \xrightarrow[\text{ii) } H_3O^+]{\text{i)Alkaline } KMnO_4} RCOOH$$

- Carboxylic acids can also be prepared by treating aldehydes with mild oxidising agents.

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

From Alkylbenzenes

- In this method, alkyl benzenes on vigorous oxidation with chromic acid or acidic or alkalinepotassium permanganate yield aromatic carboxylic acids.
- Primary and secondary alkyl groups are oxidised in this way while tertiary groups remainunaffected.

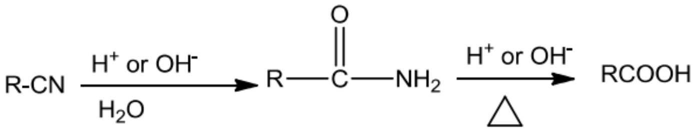


- Substituted alkenes can also be oxidised using the same oxidising agents to yield carboxylic acids.

$$RCH=CHR \xrightarrow{K_2Cr_2O_7, H_2SO_4} 2R\text{-}COOH$$

From Nitriles and Amides

- Nitriles on hydrolysis give amides and then they are converted to acids in the presence of H+ orOH- catalyst.
- Use of mild reaction conditions is done to stop the reaction at the amide stage.

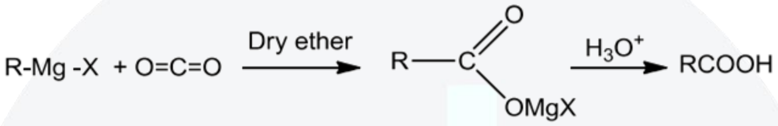


$$R\text{-}CN \xrightarrow[H_2O]{H^+ \text{ or } OH^-} R{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}NH_2 \xrightarrow[\Delta]{H^+ \text{ or } OH^-} RCOOH$$

$$CH_3CONH_2 \xrightarrow[\Delta]{H_3O^+} CH_3COOH + NH_3$$

From Grignard Reagents

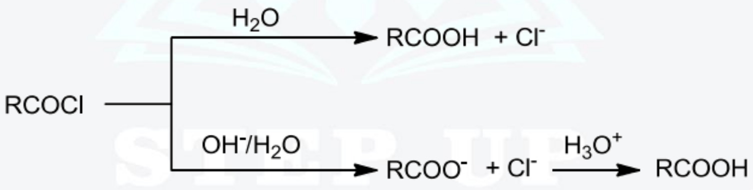
Grignard reagents on treating with carbon dioxide form salts of carboxylic acids which on acidificationwith mineral acid give corresponding carboxylic acids.



$$R\text{-}Mg\text{-}X + O{=}C{=}O \xrightarrow{\text{Dry ether}} R{-}C(=O)OMgX \xrightarrow{H_3O^+} RCOOH$$

From Acyl Halides and Anhydrides

- Acid chlorides on hydrolysis with water give carboxylic acids or readily undergo hydrolysis with aqueous base to give carboxylate ions which on acidification give corresponding carboxylic acids.
- Anhydrides on the other hand undergo hydrolysis with water to give corresponding acids.



$$RCOCl \xrightarrow{H_2O} RCOOH + Cl^-$$

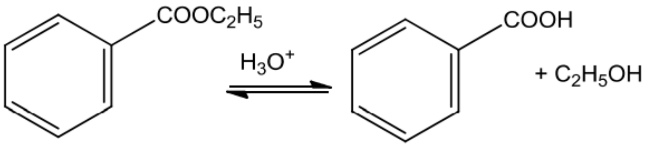
$$RCOCl \xrightarrow{OH^-/H_2O} RCOO^- + Cl^- \xrightarrow{H_3O^+} RCOOH$$

$$(C_6H_5CO)_2O \xrightarrow{H_2O} 2C_6H_5COOH$$

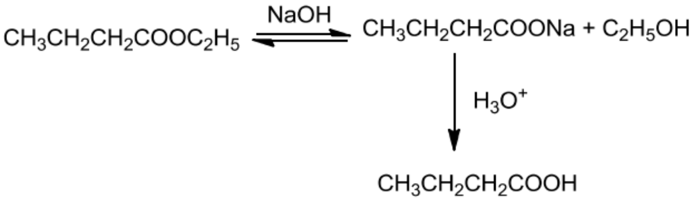
Benzoic anhydride Benzoic acid

From Esters

Esters on hydrolysis with acid give acids directly while basic hydrolysis give carboxylates which on acidification give corresponding acids.



Benzoic acid

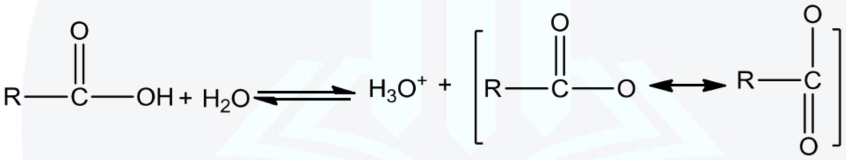


Chemical Reactions of Carboxylic Acids

Reactions involving cleavage of O-H bond

1. Acidity

- Carboxylic acids react with metals to form salts with the evolution of hydrogen gas.
- They also react with weaker bases such as carbonates and hydrogen carbonates
- This reaction is used to detect the presence of carboxyl group in an organic compound.
- Carboxylic acids dissociate in water to give resonance stabilised carboxylate anions and hydronium ion.



Acidity of carboxylic acids: Carboxylic acids are more acidic than phenols. The strength of acid depends on the extent of ionisation, which in turn depends on the stability of anion formed.

(i) Effect of electron-donating substituents on the acidity of carboxylic acids: Electron-donating substituent decreases the stability of carboxylate ion by intensifying the negative charge and hence decreases the acidity of carboxylic acids.

(ii) Effect of electron-withdrawing substituent on the acidity of carboxylic acids: The electron-withdrawing group increases the stability of carboxylate ion by delocalising negative charge and hence increases acidity of carboxylic acid.

The effect of the following groups in increasing acidity order is:

$$Ph < I < Br < CI < F < CN < NO_2 < CF_3$$

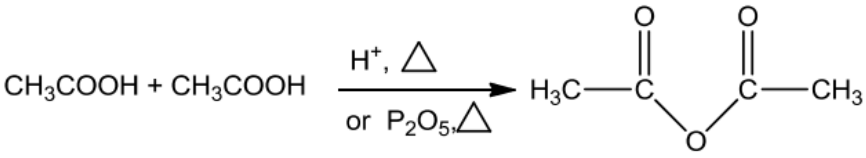
(a) Effect of the number of electron-withdrawing groups: As the number of electron-withdrawing groups increases, the —I effect increases, increasing the acid strength.

(b) Effect of position of electron-withdrawing group: As the distance between electron-withdrawing group and carboxylic group increases, electron-withdrawing influence decreases.

Reactions involving cleavage of C-OH bond

1. Formation of Anhydride

Anhydrides are obtained on treating carboxylic acids with mineral acids such as $H2SO4$ or with $P20\ 5$.



Ethanoic anhydride

2. Esterification

Esters are formed on treating alcohols or phenols with carboxylic acids in the presence of conc.H_2SO_4 or HCI gas as a catalyst.

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

3. Reactions with PCI_5, PCl_3 and $SOCl_2$

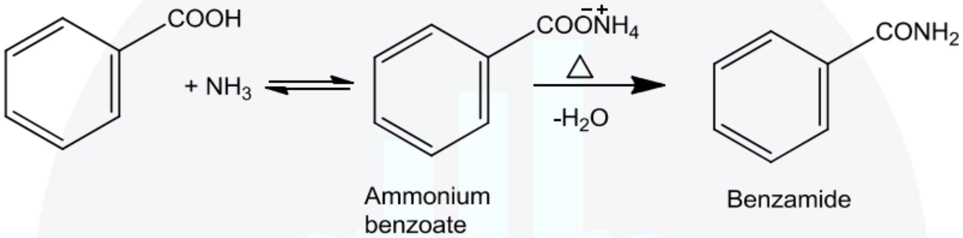
On treating with PCI_5, PCl_3 or $SOCl_2$, the hydroxyl group of alcohols is replaced by chlorine atom. $SOCI_2$ is preferred since the two products formed are volatile and escape easily making the purification of the products easier.

$RCOOH + PCl_5 \rightarrow RCOCI + POCI_3 + HCI3RCOOH + PCI_3 \rightarrow 3RCOCI + H_3PO_3$ $RCOOH + SOCl_2 \rightarrow RCOCI + SO_2 + HCI$

4. Reaction with Ammonia

When carboxylic acids are allowed to react with ammonia, ammonium salt is formed which onfurther heating at high temperature gives amides.

$$CH_3COOH + NH_3 \rightleftharpoons CH_3COO^-NH_4^+ \xrightarrow[-H_2O]{\Delta} CH_3CONH_2$$



➢ Reactions involving -COOH group

1. Reduction

On reduction with reducing agents like $LiAIH_4$ or diborane, carboxylic acids are reduced to primary alcohols.

$$RCOOH \xrightarrow[\text{(ii) } H_3O^+]{\text{(i) } LiAlH_4\text{/ether or } B_2H_6} R\text{-}CH_2OH$$

2. Decarboxylation

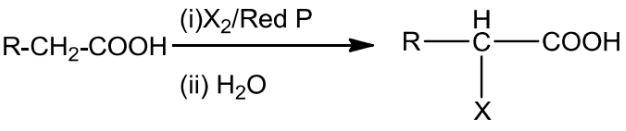
Sodium salts of carboxylic acids on heating with sodalime lose carbon dioxide to formhydrocarbons. The reaction is known as decarboxylation.

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

Substitution reactions in the Hydrocarbon

1. Halogenation

Carboxylic acids with a-hydrogen atom undergo halogenation at the a-position on treatment withsmall amount of red phosphorus to give a-halocarboxylic acids. The reaction is known as HeIl- Volhard-Zelinsky reaction.



$$R\text{-}CH_2\text{-}COOH \xrightarrow[\text{(ii) } H_2O]{\text{(i)}X_2\text{/Red P}} R-\underset{X}{\overset{H}{C}}-COOH$$

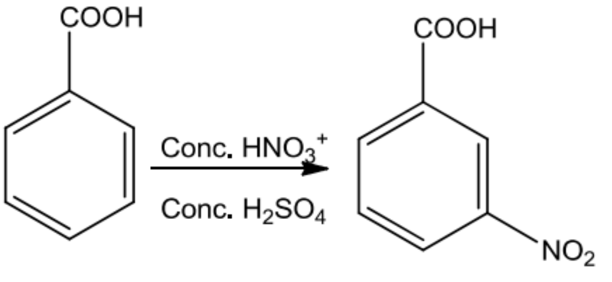
X=Cl,Br

$\alpha-$ Halocarboxylic acid

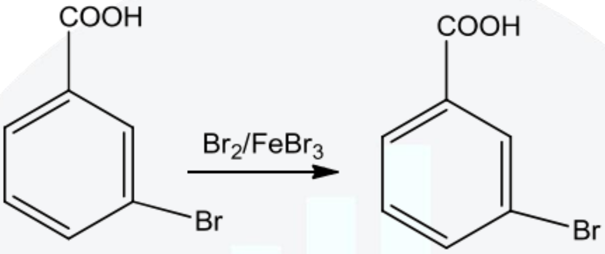
2. Ring Substitution

Aromatic carboxylic acids undergo electrophilic substitution reactions in which the carboxyl groupacts as a deactivating and meta-directing group.

They however do not undergo Friedel-Crafts reaction because the carboxyl group is deactivatingand the catalyst aluminium chloride (Lewis acid) gets bonded to the carboxyl group.



m-nitrobenzoic acid



m-Bromobenzoic acid

Comparison of acidic strength of alcohol, phenols and carboxylic acid

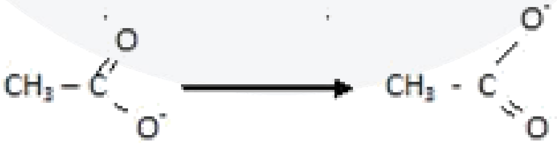
If we compare Alcohol and carboxylic acid, we see that :

In case of alcohols $ROH \longleftrightarrow RO^- + H^+$

Alkokxy gp.

In case of carboxylic acid $CH_3COOH \longleftrightarrow CH_3COO^- + H^+$

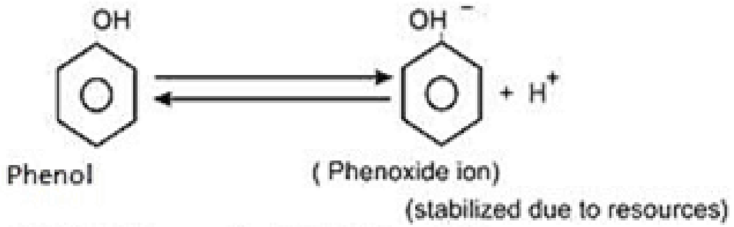
It's seen that more the ion is stablized , more the reaction will be favoured in found direction.Below you can see carboxylic acid is resonance stabilized. So, it is more stable and on the other hand the R group attached to O- in alcohol intensifies its charge. Hence, the stability is lowered in mparison to carboxylic acid.



Therefore, COOH is stronger acid than alcohol.

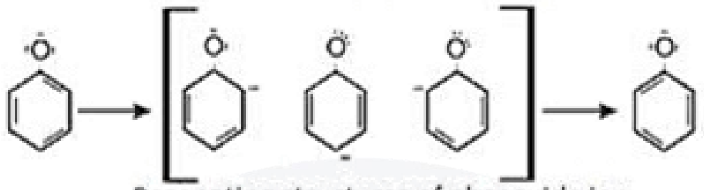
Phenols and carboxylic acid : Acidic character

Similarly, if we look for phenoxide ion and carboxylate ion that is formed by phenol and carboxylic acid after loosing hydrogen ion, we can easily make out that carboxylate ion is more stabilized. In it negative charge resides on electronegative ion (resonating structure) whereas in case of phenoxide ion the negative charge is on carbon. let's see. the structures below :

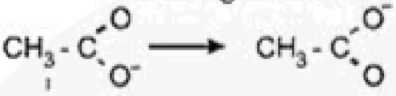


$CH_3COOH \rightleftharpoons CH_3COO^- + H^+$

Acetic acid acetate ion hydrogen ion



Resonating structures of phenoxide ion



Resonating structures of acetate ion

That is the reason ,carboxylic acid is stronger than phenols .

Reactions to prove acidic character of carboxylic acid

Reaction with metal

$CH_3COOH + Na \qquad CH_3COONa + H_2$

Acetic acid sodium Sodium acetate hydrogen

- Rxn with alkalis

$CH_3COOH + NaOH \longrightarrow CH_3COONa + H_2O$

Acetic acid sodium hydroxide sodium acetate water

- Rxn with carbonates and bicarbonates

$CH_3COOH + Na_2CO_3 \longrightarrow CH_3COONa + H_2O + CO_2$

Ethanoic acid sodium carbonate sodium acetate water

$CH_3COOH + Na_2CO_3 \longrightarrow CH_3COONa + H_2O + CO_2$

Ethanoic acid sodium carbonate sodium acetate water

Reaction involving OH group:

In this we react carboxylic acid with compounds like With PCl_5, PCl_3, $SOCl_2$.

$CH_3COOH + PCl_5 \longrightarrow CH_3COCl + POCL_3 + HCl$

ethanoic acid phosphorous pentahalide ethanoyl chloride hydrogen chloride

$CH_3COOH \xrightarrow{PCl_3} CH_3COCl + H_3PO_3$

ethanoic acid ethanovl chloride

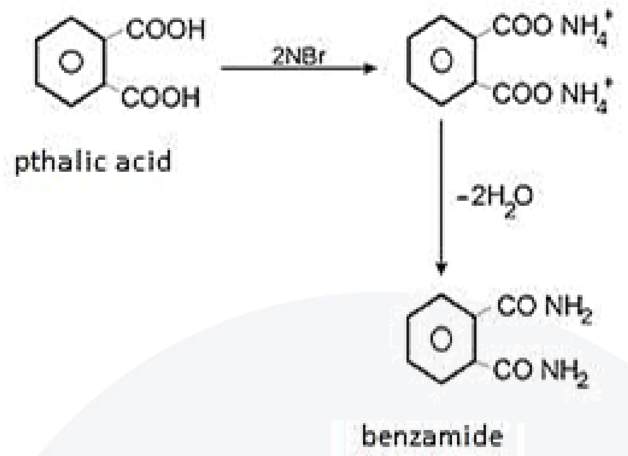
$CH_3COOH \xrightarrow{SOCl_2} CH_3COCl + SO_2 + HCl$

ethanoic acid ethanoyl chloride

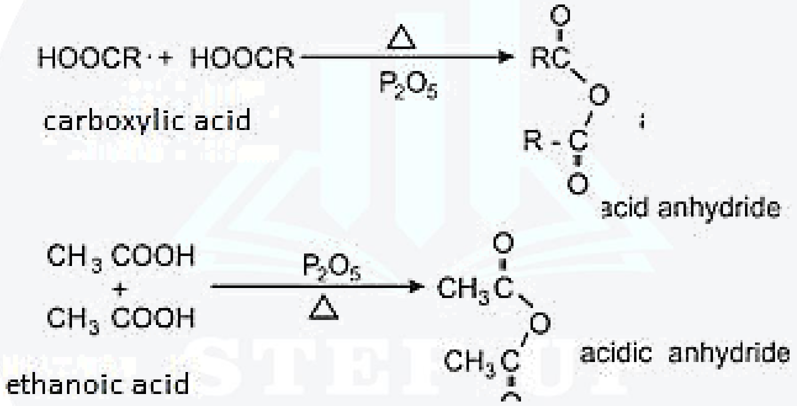
Reaction with alcohol : Esterification

$$\underset{\text{Alcohol carboxylic acid}}{ROH + RCOOH} \xrightarrow{H_2SO_4} \underset{\text{(ester)}}{RCOOR + H_2O}$$

Reaction with NH_3



Formation of acid anhydride



Reaction involving COOH group

- Decarboxylation --- Removal of CO_2 group

$$\underset{\text{Ethanoic acid}}{CH_3COOH} + \underset{\text{sodium}}{Na} \quad \underset{\text{sodium acetate}}{CH_3COONa} + H_2$$

$$\underset{\text{Sodium acetate}}{CH_3COONa} + \underset{\text{sodium hydroxide}}{NaOH} \xrightarrow{(Cao)} \underset{\text{methane}}{CH_4} + \underset{\text{sodium carbonate}}{Na_2CO_3}$$

- Electrolytic decarboxylation

$$\underset{\text{ethanoic acid}}{CH_3COOH} \xrightarrow{e.c} \underset{\text{acetate ion}}{CH_3COO^-} + \underset{\text{potassium ion}}{K^+}$$

At anode

$$2CH_3COO^- - 2e^-$$

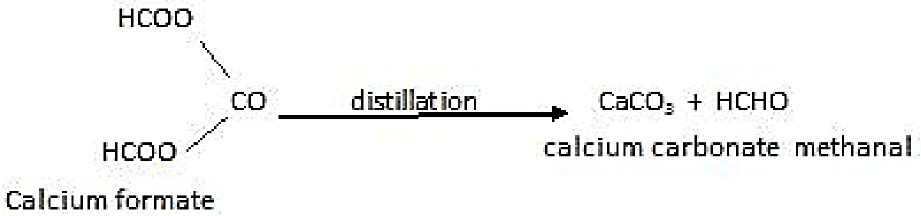
$$\underset{\text{ethane}}{CH_3\text{-}CH_3} + CO_2$$

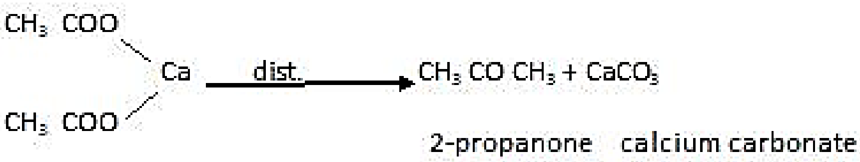
at cathode

$$K^+ + 1e^- \longrightarrow K$$

potassium ion

Reaction of carboxylic salt of Calcium





Partial Reduction

The acids on reduction in presence of reducing agents like are Li AlH4 etc forms alcohols that is :

$$RCOOH \xrightarrow[H_2]{Li\ ALH_4} RCOH$$

carboxylic acid alcohol

$$CH_3COOH \xrightarrow[H_2]{Li\,ALH_4} CH_3CH_2OH$$

ethanoic acid ethanol

Complete reduction: When complete reduction is carried out, it forms alkane in presence of red Phosphorous that is :

$$RCOOH + HI \xrightarrow{Red\ P} RCH_3 + I_2$$

Carboxylic acid hydrogen iodide alkane iodine

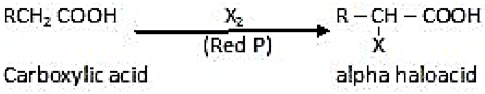
Special name reactions

- Borodine Hunsdicker Reaction

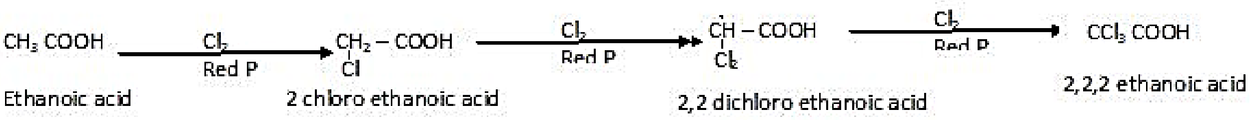
$$CH_3COOAg + Br_2 \xrightarrow{CCl_4} CH_3Br + AgBr + CO_2$$

Silveracetate bromine methyl bromide silverbromide

- Hellvolhart - Zelincky Reaction



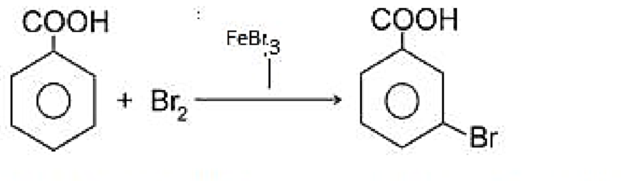
$$\underset{\text{Carboxylic acid}}{RCH_2COOH} \xrightarrow[(Red\ P)]{X_2} \underset{\text{alpha haloacid}}{R-\underset{X}{\overset{|}{C}H}-COOH}$$



$$\underset{\text{Ethanoic acid}}{CH_3COOH} \xrightarrow[Red\ P]{Cl_2} \underset{\text{2 chloro ethanoic acid}}{\underset{Cl}{CH_2}-COOH} \xrightarrow[Red\ P]{Cl_2} \underset{\text{2,2 dichloro ethanoic acid}}{\underset{Cl_2}{CH}-COOH} \xrightarrow[Red\ P]{Cl_2} \underset{\text{2,2,2 ethanoic acid}}{CCl_3COOH}$$

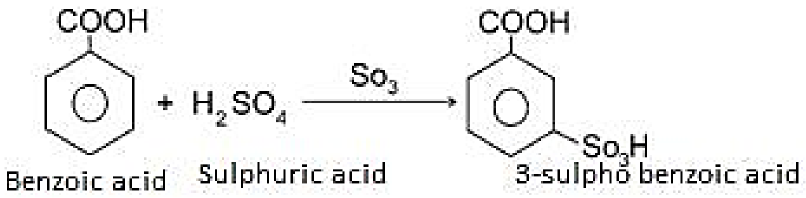
Ring substitution reactions :

Bromination

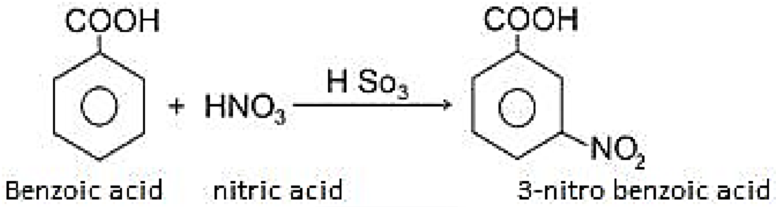


Benzoic acid bromine 3-bromo benzoic acid

Sulphonation



Nitration



Uses of carboxylic acid

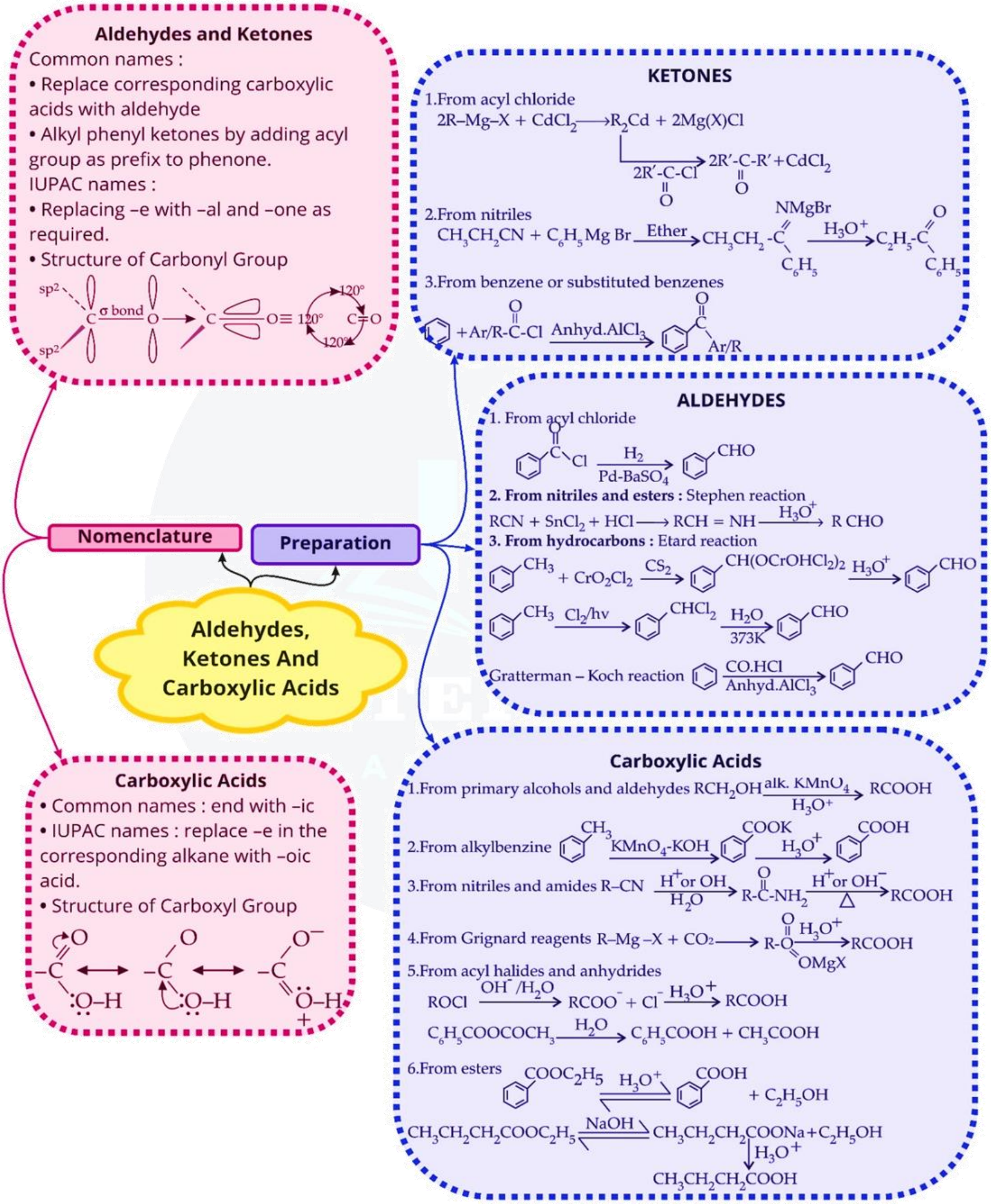
Methanoic acid is used as coagulating agent in rubber industry.

Benzoic acid is used as antiseptic and also in perfumery.

Ethanoic acid is used as solvent and also in cooking as vinegar and much more.

Reaction involving COOH group

Class : 12th Chemistry
Chapter-12 : Aldehydes, Ketones And Carboxylic Acids (Part_1)



Aldehydes, Ketones And Carboxylic Acids

Nomenclature

Preparation

Aldehydes and Ketones

Common names :
- Replace corresponding carboxylic acids with aldehyde
- Alkyl phenyl ketones by adding acyl group as prefix to phenone.

IUPAC names :
- Replacing –e with –al and –one as required.
- Structure of Carbonyl Group

KETONES

1.From acyl chloride

$2R\text{–}Mg\text{–}X + CdCl_2 \longrightarrow R_2Cd + 2Mg(X)Cl$

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

2.From nitriles

$CH_3CH_2CN + C_6H_5MgBr \xrightarrow{Ether} CH_3CH_2\text{-}\overset{NMgBr}{\overset{\|}{C}}\text{-}C_6H_5 \xrightarrow{H_3O^+} C_2H_5\text{-}\overset{O}{\overset{\|}{C}}\text{-}C_6H_5$

3.From benzene or substituted benzenes

$C_6H_6 + Ar/R\text{-}\overset{O}{\overset{\|}{C}}\text{-}Cl \xrightarrow{Anhyd.AlCl_3} C_6H_5\text{-}\overset{O}{\overset{\|}{C}}\text{-}Ar/R$

ALDEHYDES

1. From acyl chloride

$C_6H_5\text{-}\overset{O}{\overset{\|}{C}}\text{-}Cl \xrightarrow[Pd\text{-}BaSO_4]{H_2} C_6H_5CHO$

2. **From nitriles and esters :** Stephen reaction

$RCN + SnCl_2 + HCl \longrightarrow RCH = NH \xrightarrow{H_3O^+} R\,CHO$

3. **From hydrocarbons :** Etard reaction

$C_6H_5CH_3 + CrO_2Cl_2 \xrightarrow{CS_2} C_6H_5CH(OCrOHCl_2)_2 \xrightarrow{H_3O^+} C_6H_5CHO$

$C_6H_5CH_3 \xrightarrow{Cl_2/hv} C_6H_5CHCl_2 \xrightarrow[373K]{H_2O} C_6H_5CHO$

Gratterman – Koch reaction $C_6H_6 \xrightarrow[Anhyd.AlCl_3]{CO.HCl} C_6H_5CHO$

Carboxylic Acids

- Common names : end with –ic
- IUPAC names : replace –e in the corresponding alkane with –oic acid.
- Structure of Carboxyl Group

Carboxylic Acids

1.From primary alcohols and aldehydes $RCH_2OH \xrightarrow[H_3O^+]{alk.\ KMnO_4} RCOOH$

2.From alkylbenzene $C_6H_5CH_3 \xrightarrow{KMnO_4\text{-}KOH} C_6H_5COOK \xrightarrow{H_3O^+} C_6H_5COOH$

3.From nitriles and amides $R\text{–}CN \xrightarrow[H_2O]{H^+ or\ OH^-} R\text{-}\overset{O}{\overset{\|}{C}}\text{-}NH_2 \xrightarrow[\Delta]{H^+ or\ OH^-} RCOOH$

4.From Grignard reagents $R\text{–}Mg\text{–}X + CO_2 \longrightarrow R\text{-}\overset{O}{\overset{\|}{C}}\text{-}OMgX \xrightarrow{H_3O^+} RCOOH$

5.From acyl halides and anhydrides

$ROCl \xrightarrow{OH^-/H_2O} RCOO^- + Cl^- \xrightarrow{H_3O^+} RCOOH$

$C_6H_5COOCOCH_3 \xrightarrow{H_2O} C_6H_5COOH + CH_3COOH$

6.From esters

$C_6H_5COOC_2H_5 \xrightleftharpoons{H_3O^+} C_6H_5COOH + C_2H_5OH$

$CH_3CH_2CH_2COOC_2H_5 \xrightleftharpoons{NaOH} CH_3CH_2CH_2COONa + C_2H_5OH \xrightarrow{H_3O^+} CH_3CH_2CH_2COOH$

Class : 12th Chemistry
Chapter-12 : Aldehydes, Ketones And Carboxylic Acids (Part_2)

Aldehydes, Ketones And Carboxylic Acids

Properties

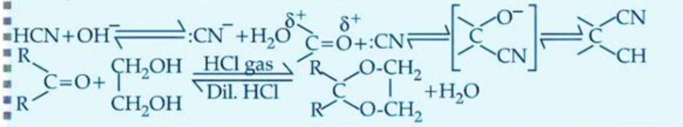
ALDEHYDES AND KETONES:

(i) Physical:

Boiling points are higher than hydrocarbons and ethers of comparable molecular masses.

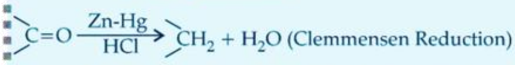
(ii)Chemical :Nucleophilic addition reactions :

Aldehydes are more reactive than ketones due to steric and electronic reasons.



Reduction : (a) To alcohols – aldehydes and ketones reduce to primary and. secondary alcohols respectively by $NaBH_4$ or $LiAlH_4$.

(b) To hydrocarbons –



(Clemmensen Reduction)

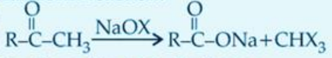
(Wolf-Kishner)

Oxidation: $RCHO \xrightarrow{[O]} R\text{–}COOH$

Tollen's test : $RCHO + 2[Ag(NH_3)]_2^+ + 3OH^- \longrightarrow RCOO^- + 2Ag + 2H_2O + 4NH_3$

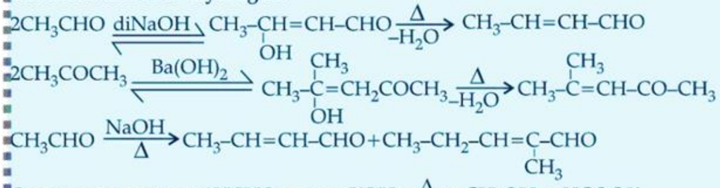
Fehling's test : $RCHO + 2Cu^{2+} + 5OH^- \longrightarrow RCOO^- + \underset{\text{Red brown ppt}}{Cu_2O} + 3H_2O$

Haloform reaction:



$$R\text{–}\overset{\overset{\displaystyle O}{\|}}{C}\text{–}CH_3 \xrightarrow{NaOX} R\text{–}\overset{\overset{\displaystyle O}{\|}}{C}\text{–}ONa + CHX_3$$

Reactions due to α - hydrogen:



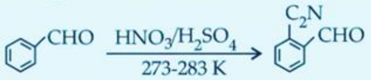
$$2CH_3CHO \underset{}{\overset{diNaOH}{\rightleftharpoons}} CH_3\text{–}\underset{\underset{\displaystyle OH}{|}}{CH}\text{=CH–CHO} \xrightarrow[-H_2O]{\Delta} CH_3\text{–CH=CH–CHO}$$

$$2CH_3COCH_3 \overset{Ba(OH)_2}{\rightleftharpoons} CH_3\text{–}\underset{\underset{\displaystyle OH}{|}}{\overset{\overset{\displaystyle CH_3}{|}}{C}}\text{=}CH_2COCH_3 \xrightarrow[-H_2O]{\Delta} CH_3\text{–}\overset{\overset{\displaystyle CH_3}{|}}{C}\text{=CH–CO–}CH_3$$

$$CH_3CHO \xrightarrow[\Delta]{NaOH} CH_3\text{–CH=CH–CHO} + CH_3\text{–}CH_2\text{–CH=}\underset{\underset{\displaystyle CH_3}{|}}{C}\text{–CHO}$$

Cannizzaro reaction : $2HCHO + \text{conc } KOH \xrightarrow{\Delta} CH_3OH + HCOOK$

Electrophilic substitution reaction:



Carboxylic acids:

(i) Physical:

Higher boiling points than aldehydes, ketones or alcohols.
Solubility decreases with increasing number of C atoms

(ii)Chemical :

$2RCOOH + 2Na \longrightarrow 2RCOONa + H_2$

Forms corresponding anhydride on heating with mineral acid

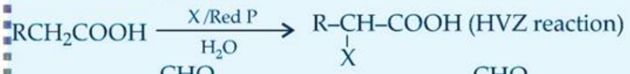
$RCOOH + R'OH \underset{}{\overset{H^+}{\rightleftharpoons}} RCOOR' + H_2O$

$RCOOH + PCl_5 \longrightarrow RCOCl + POCl_3 + HCl$

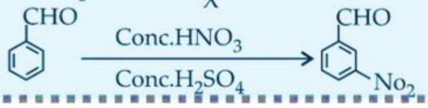
$CH_3COOH + NH_3 \rightleftharpoons CH_3COONH_4 \xrightarrow[-H_2O]{\Delta} CH_3CONH_2$

$RCOOH \xrightarrow[H_3O^+]{B_2H_6} RCH_2OH$

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



$$RCH_2COOH \xrightarrow[H_2O]{X/Red\ P} R\text{–}\underset{\underset{\displaystyle X}{|}}{CH}\text{–}COOH \text{ (HVZ reaction)}$$



Uses

(a) Carboxylic acids
- Methanoic acid in rubber, textile, dyeing, leather industries.
- Ethanoic acid as solvent
- Higher tatty acids in manufacture of soaps and detergents.

(b) Aldehydes of ketones
- As solvents.
- Starting materials and reagents for synthesis ofproducts.

Important Questions

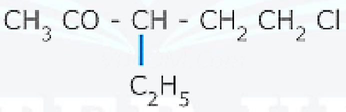
Multiple Choice questions-

1. Which of the following cannot reduce Fehling's solution?
   (a) Formic acid
   (b) Acetic acid
   (c) Formaldehyde
   (d) Acetaldehyde
2. Which of the following acids does not form anhydride?
   (a) Formic add
   (b) Acetic acid
   (c) Propionic add
   (d) n-butyric acid
3. The acid which does not contain-COOH group is.
   (a) Ethanoic acid
   (b) Lactic acid
   (c) Picric add
   (d) Palmitic acid
4. Trans-esterification is a reaction between
   (a) two ester molecules
   (b) alcohol and carboxylic acid
   (c) alcohol and ether
   (d) alcohol and ester.
5. Acetone on heating with ammonia produces
   (a) Acetaldehyde
   (b) Diacetone alcohol
   (c) Diacetoneamine
   (d) Hydrobenzamide
6. Methyl ketones are usually characterised through
   (a) Tollen's reagent
   (b) Iodoform test
   (c) Schiff'stest
   (d) Benedict solution test.
7. Which of the following reagents can be used to prepare ketone from acid chloride?
   (a) Grignard's reagent
   (b) $LiAlH_4$
   (c) Dimethyl cadmium
   (d) Cadmium chloride
8. HVZ reaction is used to prepare
   (a) ß-haloacid
   (b) α-haloacid
   (c) α, ß-unsaturated add
   (d) None of these

9. An alkene C_7H_{14} on reductive ozonolysis gives an aldehyde with formula C_3H_6O and and a ketone. The ketone is
   (a) 2-butanone
   (b) 2-pentanone
   (c) 3-pentanone
   (d) propanone
10. Acetaldol is a condensation product of
   (a) two molecules of ethanal
   (b) two molecules of propanone
   (c) ethanal and methanal
   (d) ethanal and propanone.

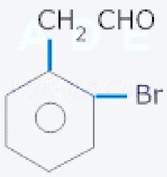
Very Short Questions-

1. Give one use of Formalin.
2. What is the chemical name of Tollen's reagent and Fehling's solution.
3. Write the structure of alkenes that on ozonolysis will give ketone only.
4. What is the function of $BaSO_4$ in rosenmund reaction?
5. Name the isomers with molecular formula C_3H_6O. Which one will have high boiling point?
6. Write a chemical test to distinguish between aldehyde and ketone.
7. What happens when acetaldehyde is kept with a trace of sulphuric acid? Write the structure of product.
8. What is the Hofmann bromamide reaction? Illustrate with one example.
9. Give IUPAC name of following



$CH_3CO-\underset{\underset{C_2H_5}{|}}{CH}-CH_2CH_2Cl$

10. Give IUPAC name of following



Short Questions-

1. Ethanoic acid has molar mass of 120 in vapour state.
2. Carboxylic acids do not give characteristic reactions of Carboxylic acid is stronger acid than phenol.
3. Ethanol is more soluble in water than ethyl chloride
4. Aldehydes are more reactive than Ketones towards nucleophilic additions.
5. Carboxylic acids has higher boiling points than alcohols of same no. of carbon atoms.
6. Carbonyl group.
7. Formaldehyde does not undergo aldol condensation.
8. Floro acetic acid is a stronger acid than acetic acid.
9. Toluene to benzaldehyde
10. Acetaldehyde to Acetamide

Long Questions-

1. A compound 'A' with formula $C_5H_{10}O$ gives a positive 2, 4 –DNP test but a negative Tollen's test It can be oxidizing to carboxylic acid 'B' of molecular formula $C_3H_6O_2$, when treated with alk. $KMnO_4$ under vigorous conditions. The salt of 'B' gives a hydrocarbon 'C' on Kolbes' electrolytic decarboxylation. Identify A, B.C & write chemical equations.
2. Acompound A with molecular formula $C_5H_{12}O$ on oxidation forms compound B with molecular formula $C_5H_{10}O$. The compound B gives iodoform test but does not reduce ammoniacal silver nitrate. The compound B on reduction with Zn – Hg/ HCl gives compound C with molecular formula C_5H_{12}. Identify A, B, C & give the chemical reactions involved.
3. An organic compound A, which has a characteristic odour, on treatment with NaOH forms two compound B and C. Compound B has molecular formula C_7H_8O which on oxidation gives back A. Compound C is the sodium salt of an acid. C, when heated with soda lime yields an aromatic hydrocarbon D. deduce the structures of A to D.
4. $CH_3COOH \xrightarrow{Cl_2/redP} \underline{(A)} \xrightarrow{alc.NH_3} \underline{(B)}$
5. $C_6H_5CONH_2 \xrightarrow{Br_2/KOH} \textcircled{A} \xrightarrow{NaNO_2/HCl} \textcircled{B} \xrightarrow[K_2Cr_2O_7/H_2SO_4]{} \textcircled{C}$
6. $CH_3Cl \xrightarrow{KCN} \textcircled{A} \xrightarrow{H_2O/H^+} \textcircled{B} \xrightarrow{PCl_5} \textcircled{C}$
7. $CH_3COOH \xrightarrow{Ca(OH)_2} (A) \xrightarrow{dry\ distribution} (B) \xrightarrow{I_2/NaOH} (C)$
8. $CH_3COCH_3 \xrightarrow{LiAlH_4} X \xrightarrow{SOCl_2} Y \xrightarrow{alc.-KOH} Z$

Assertion and Reason Questions-

1. In these questions, a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following choices.

a) Assertion and reason both are correct statements and reason is correct explanation for assertion.
b) Assertion and reason both are correct statements but reason is not correct explanation for assertion.
c) Assertion is correct statement but reason is wrong statement.
d) Assertion is wrong statement but reason is correct statement.

Assertion: Aromatic aldehydes and formaldehyde undergo Cannizzaro reaction.

Reason: Aromatic aldehydes are almost as reactive as formaldehyde.

2. In these questions, a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following choices.

a) Assertion and reason both are correct statements and reason is correct explanation for assertion.
b) Assertion and reason both are correct statements but reason is not correct explanation for assertion.
c) Assertion is correct statement but reason is wrong statement.
d) Assertion is wrong statement but reason is correct statement.

Assertion: O-Substituted benzoic acids are generally stronger acids than benzoic acids.

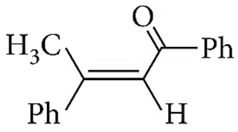
Reason: Increased strength is due to ortho-effect.

Case Study Questions-

1. Read the passage given below and answer the following questions:

A tertiary alcohol H upon acid catalysed dehydration gives a product I. Ozonolysis of I leads to compounds J and K. Compound J upon reaction with KOH gives benzyl alcohol and a compound I, whereas K on reaction with KOH gives only M.

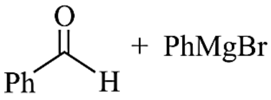
$M =$



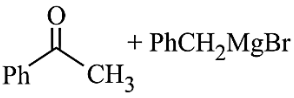
The following questions are multiple choice questions. Choose the most appropriate answer:

(i) Compound H is formed by the reaction of:

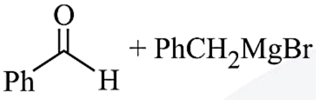
(a)



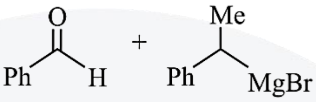
(b)



(c)

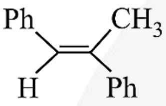


(d)

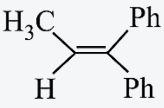


(ii) The structure of compound I is:

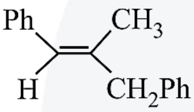
(a)



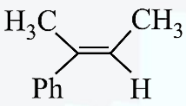
(b)



(c)



(d)



(iii) The structures of compound J, K and I, respectively, are:

a) $PhCOCH_3$, $PhCH_2COCH_3$ and $PhCH_2COO^-K^+$

b) $PhCHO$, $PhCH_2CHO$ and $PhCOO^-K^+$

c) $PhCOCH_3$, $PhCH_2CHO$ and $CH_3COO^-K^+$

d) $PhCHO$, $PhCOCH_3$ and $PhCOO^-K^+$

(iv) When (J) is treated with acetic anhydride, in the presence of corresponding salt of an acid, the product obtained is:

a) Cinnamic acid.

b) Crotonic acid.

c) Maleic acid.

d) Benzylic acid.

(v) Which of the following statements is correct for compound (K)?

a) It reacts with alkaline KMn04 followed by acidic hydrolysis and forms benzoic acid.

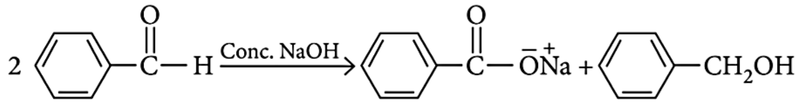
b) It reacts with iodine and NaOH to form triiodomethane.

c) It is prepared by the reaction of benzene with benzoyl chloride in presence of anhydrous aluminium chloride.

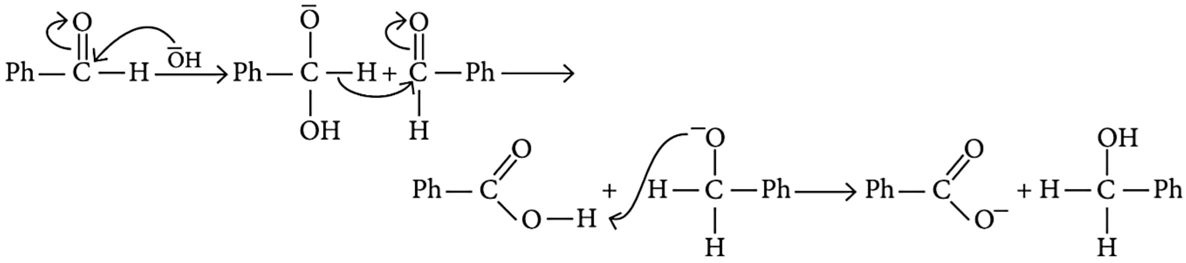
d) It reacts with freshly prepared ammoniacal silver nitrate solution.

2. Read the passage given below and answer the following questions:

When an aldehyde with no et-hydrogen reacts with concentrated aqueous NaOH, half the aldehyde is converted to carboxylic acid salt and other half is converted to an alcohol. In other words, half of the reactant is oxidized and other half is reduced. This reaction is known as Cannizzaro reaction.



Mechanism :



The following questions are multiple choice questions. Choose the most appropriate answer:

(i) A mixture of benzaldehyde and formaldehyde on heating with aqueous NaOH solution gives:

- a) Benzyl alcohol and sodium formate.
- b) Sodium benzoate and methyl alcohol.
- c) Sodium benzoate and sodium formate.
- d) Benzyl alcohol and methyl alcohol.

(ii) Which of the following compounds will undergo Cannizzaro reaction?

- a) CH_3CHO
- b) CH_3COCH_3
- c) C_6H_5CHO
- d) $C_6H_5CH_2CHO$

(iii) Trichloroacetaldehyde is subjected to Cannizzaro's reaction by using NaOH. The mixture of the products contains sodium trichloroacetate ion and another compound. The other compounds is:

- a) 2, 2, 2-trichloroethanol.
- b) Trichloromethanol.
- c) 2, 2, 2-trichloropropanol.
- d) Chloroform.

(iv) In Cannizzaro reaction given below:

$$2PhCHO \xrightarrow{\bar{O}H} PhCH_2 + OH + PhCO_2^-$$

the slowest step is:

- a) The attack $^-$OH at the carboxyl group.
- b) The transfer of hydride to the carbonyl group.
- c) The abstraction of proton from the carboxylic group.
- d) The deprotonation of $PhCH_2OH$.

(v) Which of the following reaction will not result in the formation of carbon-carbon bonds?

- a) Cannizzaro reaction.
- b) Wurtz reaction.
- c) Reimer-Tiemann reaction.
- d) Friedel-Crafts' acylation.

Answer Key

MCQ Answers-

1. Answer: (b) Acetic acid
2. Answer: (a) Formic add
3. Answer: (c) Picric add
4. Answer: (d) alcohol and ester.
5. Answer: (c) Diacetoneamine
6. Answer: (b) Iodoform test
7. Answer: (c) Dimethyl cadmium
8. Answer: (b) α-haloacid
9. Answer: (a) 2-butanone
10. Answer: (a) two molecules of ethanal

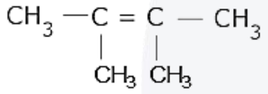
Very Short Answers-

1. Formalin is used as a disinfectant, preservative for biological specimens and in leather industry.

2. Tollen’s reagent = Ammoniacal Silver Nitrate

Fehlings solution = Sodium Potassium Tartarate.

3.



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

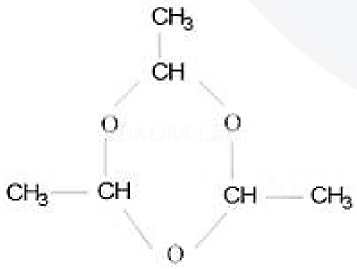
2, 3 - dimethyl but - 2 - ene

4. $BaSO_4$ acts as a catalytic poison which prevents further reduction of aldehyde to alcohol.

5. The two isomers are CH_3COCH_3 and CH_3CH_2CHO. Acetone boils at higher temperature due to presence of two electron donating alkyl groups.

6. Aldehydes and ketones can be distinguished by Tollen’s test. Aldehydes give a silver mirror on reacting with Tollen’s reagent whereas ketones will not react.

7. A trimer of acetaldehyde, called paraldchyde is formed.



8. Hoffman bromamide reaction is a reaction in which amides are converted to amines of one carbon less than the starting amide. It is a very important step – down reaction.

$$RCONH_2+Br_2+KOH\rightarrow RNH_2+KBr+K_2CO_3+H_2O$$

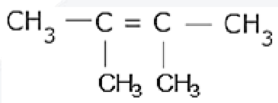
9. 5-Chloro -3- ethylpentan -2-one.

10. 2 –(2-bromophenyl) ethanal

Short Answers-

1. Carboxylic acid on dissociation form carboxylate ion which is stabilized by two equivalent resonance structure in which negative charge is at the more electronegative oxygen atom, whereas the conjugate base of phenol, phenoxide ion, has non – equivalent resonance structures in which negative charge is at the less electronegative carbon atom. Therefore resonance is not as important as it is in carboxylate ion. Moreover the negative charge is delocalized over two more electronegative oxygen atoms in carboxylate ion whereas it is less effectively delocalized over one oxygen atom and one carbon atom in phenoxide ion. Therefore the carboxylate ion is more stabilized than phenoxide ion and carboxylic acids are stronger acids than phenol.

2. Ethanol can form intermolecular Hydrogen bonding with water molecules, ethyl chloride can not. Therefore ethanol is soluble in water and ethyl chloride is not.
3. Aldehydes are more reactive than Ketones due to steric and electronic reasons. In Ketones due to presence of two relatively large alkyl groups, the approach of nucleophile is more hindered than in aldehydes having only one such substitute. More over the +I effect of alkyl groups reduces the electophilicity of carbonyl group more in Ketone than in aldehydes.
4. Carboxylic acids have more extensive association of molecules through intermolecular hydrogen bonding than alcohols. Moreover their boiling points are higher than alcohols of same carbon atoms.
5. Ethanoic acid exists as dimer in vapour state in which two molecules remain together by hydrogen bonding. This increases the effective molecular mass to 120.



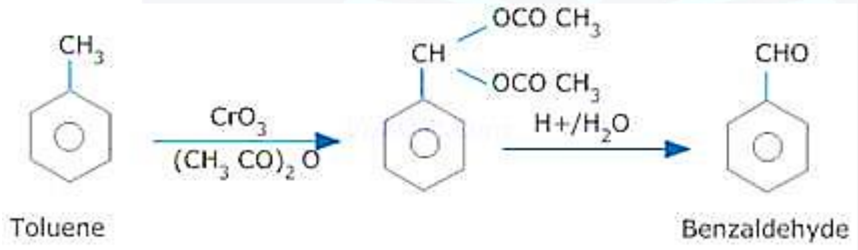
$$CH_3-\underset{CH_3}{\underset{|}{C}}=\underset{CH_3}{\underset{|}{C}}-CH_3$$

2, 3 - dimethyl but - 2 - ene

6. In carboxylic acids due to presence of resonance, the C=O group is not a pure carbonyl group & therefore they do not show characteristic reactions of carbonyl group.
7. Formaldehyde does not have any $BaSO_{4-}$ hydrogen and therefore it can not show aldol condensation.
8. In fluoroacetic acid, Fluorine being electron withdrawing group stabilizes the conjugate base through delocalization of the negative charge C_3H_6O.

   Therefore fluoroacetic acid is a stronger acid than acetic acid.

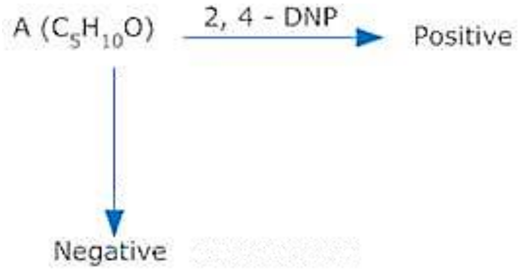
9\.



10\.

$$\underset{\text{Acetaldehyde}}{CH_3CHO}\xrightarrow[KMnO4]{(O)}CH_3COOH\xrightarrow{NH_3}CH_3COONH_4\xrightarrow{\Delta}\underset{\text{Acetamide}}{CH_3CONH_2}$$

Long Answers-

1. 

$$A \xrightarrow{\text{alk. KMnO4}} B\ (C_3H_6O_2)$$

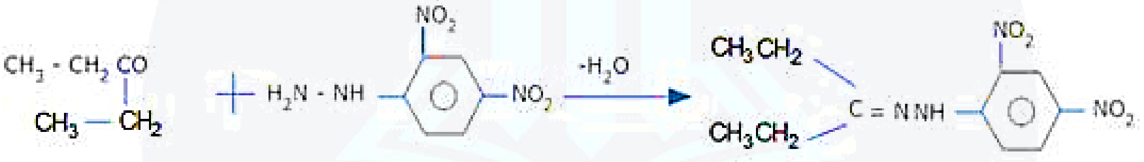
$$C_3H_6O_2\text{ - Na} \xrightarrow[\text{decarboxylation}]{\text{Kolbe's}} C$$

As the compound A gives a positive 2, 4-DNP test but negative Tollen's test, it is a ketone. Since on oxidation, it gives an acid B, of molecular formula $C_3H_6O_2$, it is $CH_3CH_2COCH_2CH_3$ and B is CH_3CH_2COOH. As C is obtained by Kolbes decarboxylation of B, C is $CH_3CH_2CH_2CH_3$.

Therefore A = Pentan -3 one, $CH_3CH_2COCH_2CH_3$

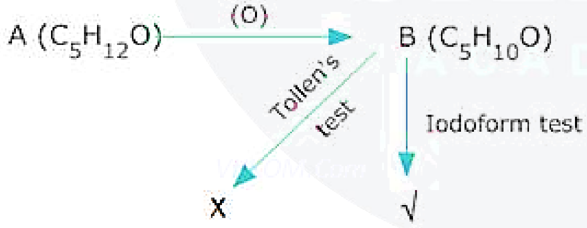
B = Propanoic acid CH_3CH_2COOH and C = Butane $CH_3CH_2CH_2CH_3$

The sequence of reactions is



$$CH_3\ CH_2\ CO\ CH_2\ CH_3 \xrightarrow{\text{alk. kmNo}_4} CH_3CH_2COOH + CH_3\ COOH$$

$$CH_3\ CH_2\ COOK \xrightarrow[\text{decarbaxylation}]{\text{kolbe's}} CH_3\ CH_2\ CH_2\ CH_3 + CO_2 + KOH + H_2$$

2. 

$$B \xrightarrow[\text{HCl}]{\text{Zn - Hg}} C\ (C_5H_{12})$$

Since B gives a negative Tollen's test but positive Iodoform test, it is methyl ketone, i.e, $CH_3CO\ CH_2CH_2CH_3$.

Also it is formed by oxidation of A.

Therefore A is secondary alcohol i.e, $CH_3\ \underset{\text{OH}}{CH}\ CH_2\ CH_2\ CH_2CH_3$ on reduction B gives pentane with Zn –Hg/ HCl.

Therefore C is $CH_3CH_2CH_2CH_2CH_3$

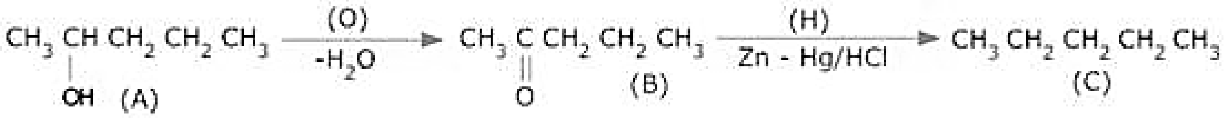
Therefore

A = $CH_3CHOH\ CH_2CH_2CH_3$

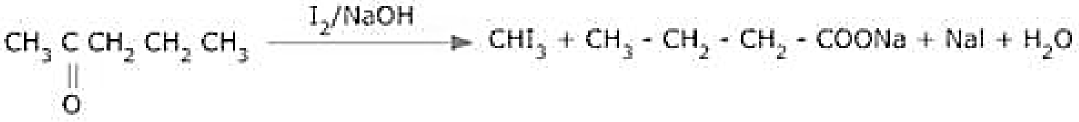
B = $CH_3CO\ CH_2CH_2CH_3$

C = $CH_3CH_2CH_2CH_2CH_3$

Reactions:

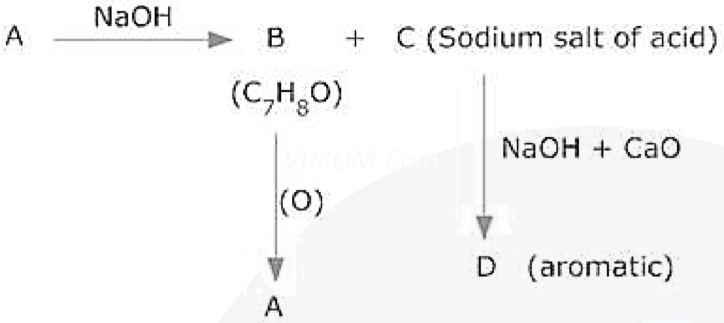


$$CH_3\underset{\underset{OH}{|}}{CH}CH_2CH_2CH_3\ (A) \xrightarrow[-H_2O]{(O)} CH_3\underset{\underset{O}{\|}}{C}CH_2CH_2CH_3\ (B) \xrightarrow[Zn-Hg/HCl]{(H)} CH_3CH_2CH_2CH_2CH_3\ (C)$$



$$CH_3\underset{\underset{O}{\|}}{C}CH_2CH_2CH_3 \xrightarrow{I_2/NaOH} CHI_3 + CH_3-CH_2-CH_2-COONa + NaI + H_2O$$

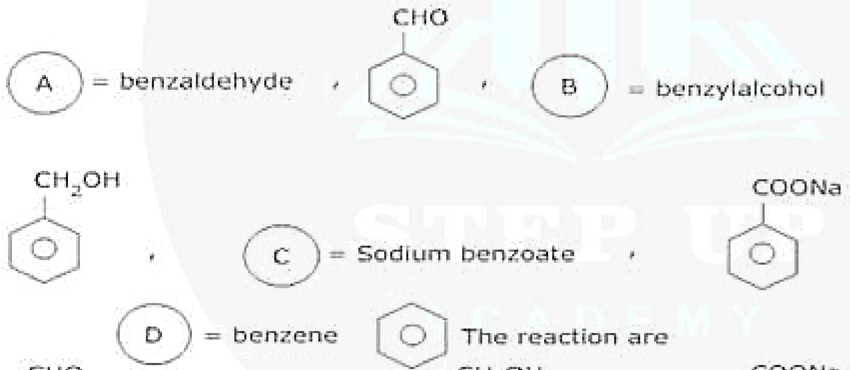
3.

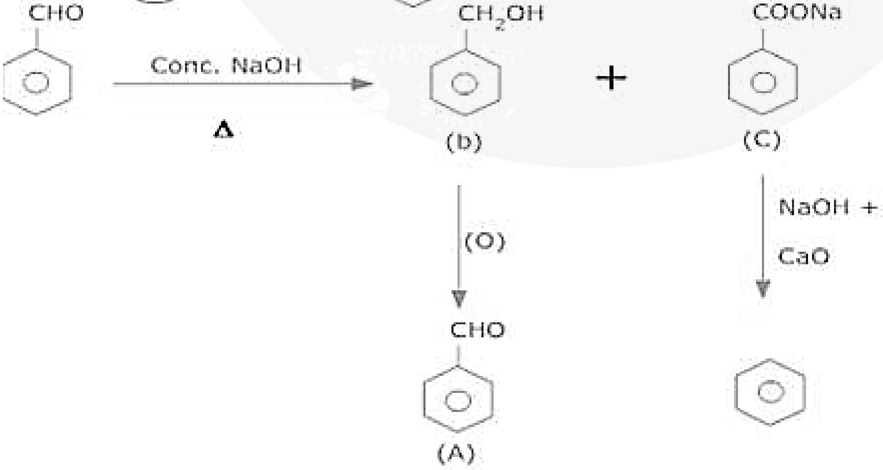


$$\begin{tikzcd}A \arrow[r, "NaOH"] & \underset{(C_7H_8O)}{B} \arrow[d, "(O)"] & + & C\text{ (Sodium salt of acid)} \arrow[d, "NaOH + CaO"] \\ & A & & D\ \text{(aromatic)}\end{tikzcd}$$

The molecular formula of (B) and characteristic odour of (A) suggests that (A) is an aromatic aldehyde, C_6H_5CHO and (B) is alcohol, $C_6H_5CH_2OH$. As (C) is a sodium salt of an acid & gives hydrocarbon (D) on heating with soda lime, (C) is sodium benzoate and (D) is benzene.

Therefore:





4.

$$A = \underset{\underset{Cl}{|}}{CH_2}COOH, \quad B = \underset{\underset{NH_2}{|}}{CH_2}COOH$$

5. (A) = $C_6H_5CH_2NH_2$

(B) = 

(C) = 

6. (A) = CH_3CN

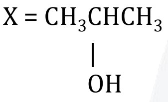
(B) = CH_3COOH

(C) = CH_3COCl

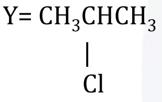
7. (A) = $(CH_3COO)_2\ Ca$

(B) = CH_3COCH_3

(C) = CHI_3

8. 

$X = CH_3\underset{\underset{OH}{|}}{C}HCH_3$



$Y = CH_3\underset{\underset{Cl}{|}}{C}HCH_3$

$Z = CH_3 - CH = CH_2$

Assertion and Reason Answers-

1. (c) Assertion is correct statement but reason is wrong statement.

Explanation:

Aromatic aldehydes and formaldehyde do not contain α-hydrogen and thus undergo Cannizzaro reaction. Formaldehyde is more reactive than aromatic aldehydes.

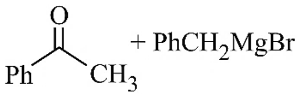
2. (a) Assertion and reason both are correct statements and reason is correct explanation for assertion.

Explanation:

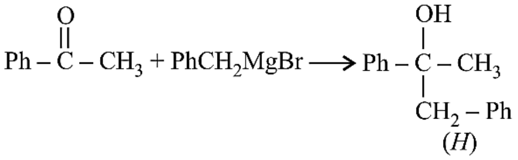
O-Substituted benzoic acids are generally stronger acids than benzoic acid. This is regardless of the nature (+I or -I) of the substituent. This is called ortho-effect and is probably due to a combination of steric and electronic factors.

Case Study Answers-

1. **Answer :**

(i) (b) 

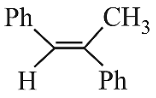
Explanation:



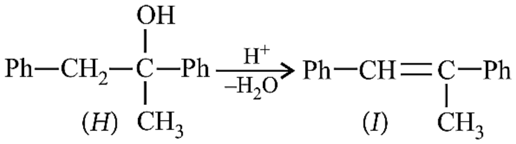
$$Ph-\overset{\overset{O}{||}}{C}-CH_3 + PhCH_2MgBr \longrightarrow Ph-\underset{\underset{CH_2-Ph}{|}}{\overset{\overset{OH}{|}}{C}}-CH_3$$

(H)

(ii) (a)



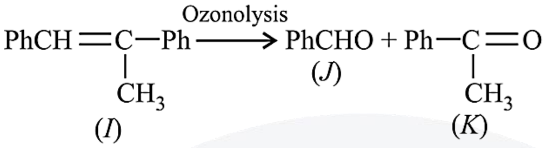
Explanation:



$$\underset{(H)}{Ph-CH_2-\overset{OH}{\underset{CH_3}{C}}-Ph} \xrightarrow[-H_2O]{H^+} \underset{(I)}{Ph-CH=\underset{CH_3}{C}-Ph}$$

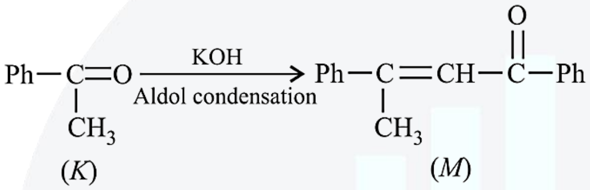
(iii) (d) PhCHO, $PhCOCH_3$ and $PhCOO^-K^+$

Explanation:



$$\underset{(I)}{PhCH=\underset{CH_3}{C}-Ph} \xrightarrow{\text{Ozonolysis}} \underset{(J)}{PhCHO} + \underset{(K)}{Ph-\underset{CH_3}{C}=O}$$

$$\underset{(J)}{Ph-CHO} \xrightarrow[\text{Cannizzaro reaction}]{KOH} Ph-CH_2-OH + \underset{(L)}{Ph-COO^- K^+}$$



$$\underset{(K)}{Ph-\underset{CH_3}{C}=O} \xrightarrow[\text{Aldol condensation}]{KOH} \underset{(M)}{Ph-\underset{CH_3}{C}=CH-\overset{O}{\overset{\|}{C}}-Ph}$$

(iv) (a) Cinnamic acid.

Explanation:

$$\underset{\text{Benzaldehyde}}{C_6H_5CHO} + \underset{\text{Acetic anhydride}}{(CH_2CO)_2O} \xrightarrow[\text{-}CH_3COOH]{CH_3COONa}$$

$$\underset{\text{Cinnarnlc add}}{C_6H_5 - CH = CH - COOH}$$

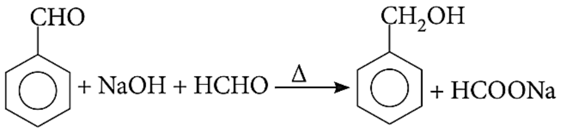
(v) (b) It reacts with iodine and NaOH to form triiodomethane.

2. Answer :

(i) (a) Benzyl alcohol and sodium formate.

Explanation:

It is an example of cross Cannizzaro reaction where aromatic aldehyde gets reduced to alcohol and aliphatic aldehyde gets oxidised to its sodium salt (both aldehydes must not contain any ∝–∝–hydrogen).

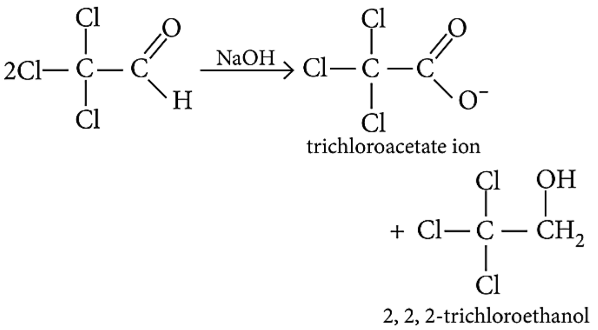


(ii) (c) C_6H_5CHO

(iii) (a) 2, 2, 2-trichloroethanol.

Explanation:

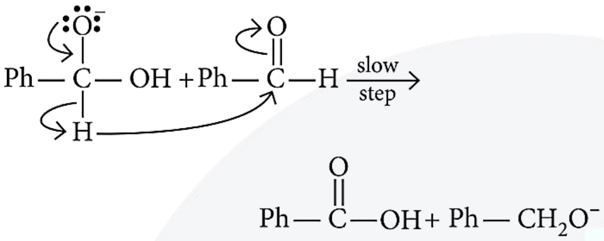
The Cannizzaro product of given reaction yields 2, 2, 2-trichloroethanol.



(iv) (b) The transfer of hydride to the carbonyl group.

Explanation:

Hydride transfer is the slowest step.



(v) (a) Cannizzaro reaction.

Explanation:

C-C bond is not formed in Cannizzaro reaction while other reactions result in the formation of C-C bond.

◆ ◆

Amines 10

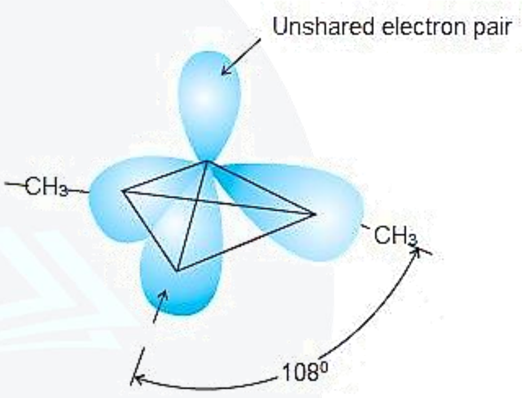
Introduction

Amines are the derivatives of ammonia prepared by the replacement of one, two or all the three hydrogenatoms by alkyl and/or aryl groups.

Examples:

(i) $CH_3—NH_2$

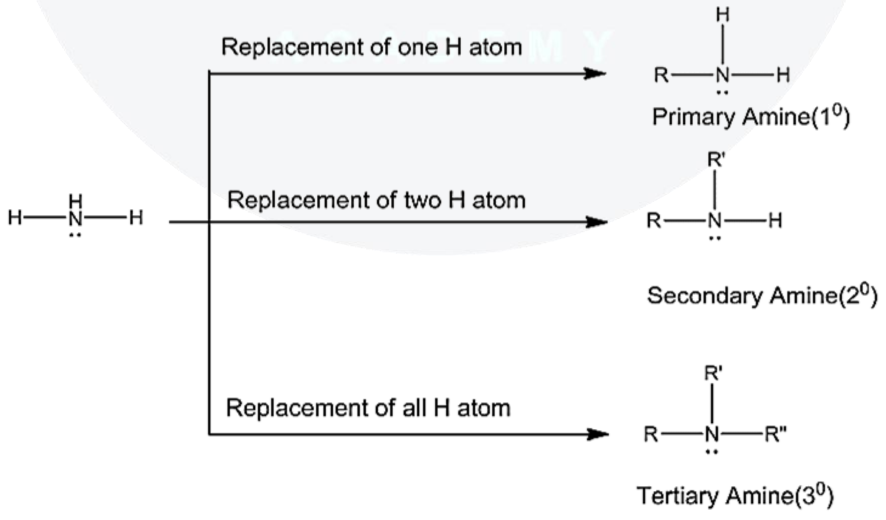
Structure of Amines



- In amines, the nitrogen atom is trivalent and has an unshared pair of electrons. Hence the nitrogenorbitals are sp^3 hybridised with pyramidal geometry.
- The three sp^3 hybrid orbitals of nitrogen overlap with orbitals of hydrogen or carbon depending on thenature of the amines.
- The fourth orbital of nitrogen in all amines contains an unshared pair of electrons. It is due to the presence of unshared pair of electrons, the angle C-N-E is less than 109.5°.

  For example: The bond angle for trimethyl amine is 108°.

Classification of Amines



R, R' and R" can be alkyl or aryl

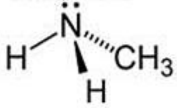
Nomenclature of Amines by IUPAC System

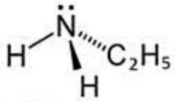
Common Names of Amines

An aliphatic amine is named by prefixing alkyl group to amine, i.e. alkylamine as 1 word.

We are considering primary amines.

MethylAmine

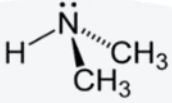


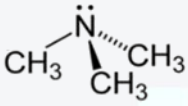


EthylAmine as ethyl amine is attached to this amine

In secondary and tertiary amines, when two or more groups are the same, the prefix di or tri is added to the before the name of alkyl group.

Dimethylamine

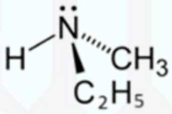




Trimethylamine

In case of mixed amine, alkyl group are written in alphabetical order.

Ethyl Methyl Amine



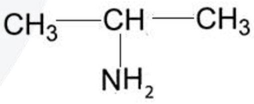
IUPAC System

In IUPAC system, amines are named as alkanamines, derived by replacement by ‘e’ of alkane by the word amine.

For Example: Methanamine (CH_3NH_2), Ethan amine (C_2H5NH_2).

For naming higher member hydrocarbon, longest chain containing amino group is selected. C atom to which amino group is attached is given to lower number.

Propan 2 Amine



$$\underset{\displaystyle NH_2}{CH_3-\underset{|}{CH}-CH_3}$$

In case, more than one amino group is present at different positions in the parent chain, their positions are specified by giving numbers to carbon atoms bearing –NH2 groups and suitable prefix such as di, tri etc. is attached to the amine. The letter ’e’ of the suffix of the hydrocarbon part is retained.

For Example: (Ethane 1,2 diamine) $H_2N\text{-}CH_2\text{ - }CH_2\text{ - }NH_2$

Each alkyl group bonded to the N atom is named as N-alkyl group.

Aryl Amines

In aryl amines, -NH2 group is directly attached to the benzene ring.

$C_6H_5NH_2$ is the simplest example of aryl amine. It is also known as aniline.

Naming aryl amines according to IUPAC system, suffix ‘e’ of arene is replaced by ‘amine’.

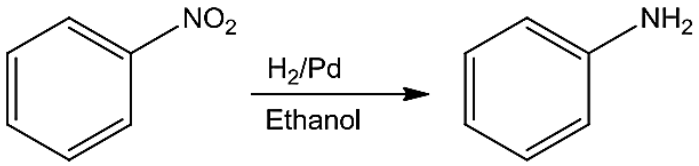
For Example: - $C_6H_5\text{ - }NH_2$ is named as benzenamine.

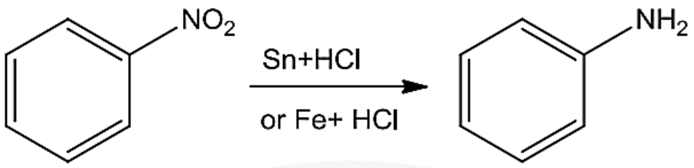
Preparation of Amines

Reduction of Nitro Compounds

Nitro compounds on reduction with hydrogen gas in the presence of finely divided nickel, palladium orplatinum and also on reduction with metals in acidic medium give amines.

$$CH_3NO_2 \xrightarrow[\text{Ethanol}]{H_2/Pd} CH_3NH_2$$





Ammonolysis

Alkyl halides or benzyl halide on reaction with an ethanolic solution of ammonia undergoes nucleophilic substitution reaction in which halogen atom is replaced by an amino (-NH_2) group.The process of cleavage of the C-X bond by ammonia molecule is known as ammonolysis.

$$\underset{\text{Nucleophile}}{\ddot{N}H_3} + R - X \longrightarrow \underset{\text{Substituted ammonium salt}}{R\overset{+}{N}H_3\overset{-}{X}}$$

The primary amine prepared behaves as a nucleophile and reacts with further alkyl halide to formsecondary, tertiary amines, and finally quaternary ammonium salt.

$$\underset{(1^0)}{R - NH_2} \xrightarrow{RX} \underset{(2^0)}{R_2NH} \xrightarrow{RX} \underset{(3^0)}{R_3N} \xrightarrow{RX} \underset{\text{Quaternary ammonium salt}}{R_4\overset{+}{N}\overset{-}{X}}$$

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

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

In this method, a mixture of primary, secondary and tertiary and also a quaternary ammonium salt. However a primary amine is prepared by taking large excess of ammonia.

The order of reactivity of halides with amines is RI > RBr > RCl

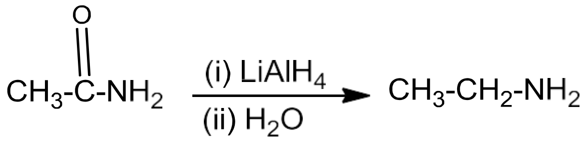
Reduction of Nitriles

Nitriles on reducing with $LiAlH_4$ or catalytic hydrogenation produce primary amines.

$$CH_3C \equiv N \xrightarrow[Na(Hg)/C_2H_5OH]{H_2/Ni} CH_3 - CH_2 - NH_2$$

Reduction of Amides

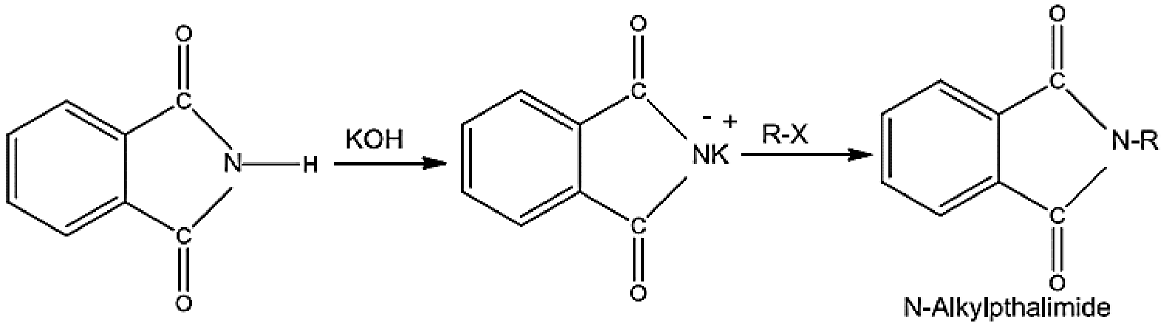
Amides on reducing with $LiAlH_4$ yield amines.

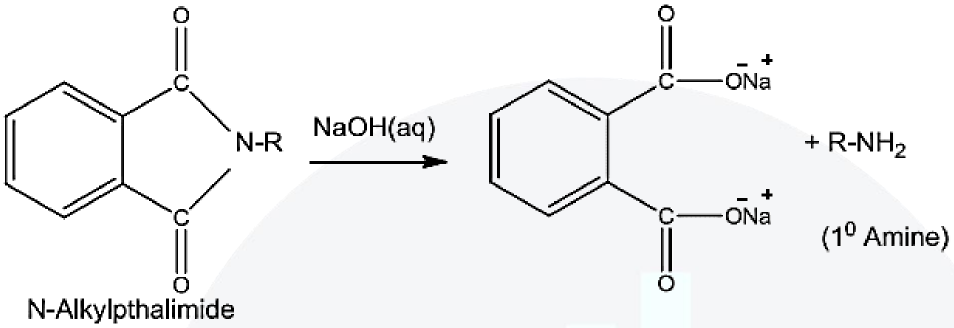


$$CH_3\overset{\overset{O}{\|}}{C}\text{-}NH_2 \xrightarrow[\text{(ii) } H_2O]{\text{(i) } LiAlH_4} CH_3\text{-}CH_2\text{-}NH_2$$

Gabriel pthalimide synthesis

Pthalimide on reacting with ethanolic solution of KOH forms potassium salt of pthalimide which onheating with alkyl halide followed by alkaline hydrolysis yields the corresponding primary amine.





Hoffmann bromamide degradation reaction

In this method, primary amines are prepared by treating an amide with bromine in an aqueous orethanolic solution of NaOH.

The amine formed has one carbon atom less than the starting amide.

$$H_3C-\overset{\overset{O}{\|}}{C}-NH_2 + Br_2 + 4NaOH \longrightarrow CH_3\text{-}NH_2 + Na_2CO_3 + 2NaBr + 2H_2O$$

Physical Properties of Amines

- **Solubility**

  Lower aliphatic amines are soluble in water because they can form a hydrogen bond with water.Solubility decreases with increase in molar mass of amines due to an increase in the size of thehydrophobic group.

- **Boiling points**

  Among the isomeric amines, primary and secondary amines have a high boiling point because theycan form hydrogen bonds.

  Tertiary amines cannot form hydrogen bonds due to the absence of a hydrogen atom for hydrogenbond formation.

  Hence, the order of boiling points of isomeric amines isPrimary > Secondary > Tertiary

Chemical Properties of Amines

a) Basic character of amines

- Amines have an unshared pair of electrons on the nitrogen atom due to which they act as a Lewisbase.
- The basic character of amines can be better understood in terms of their K_b and pK_b values.

$$R-NH_2 + H_2O \rightleftharpoons R-\overset{+}{N}H_3 + OH^-$$

$$K = \frac{[R-\overset{+}{N}H_3][OH^-]}{[R-NH_2][H_2O]}$$

$$K[H_2O] = \frac{[R-\overset{+}{N}H_3][OH^-]}{[R-NH_2]}$$

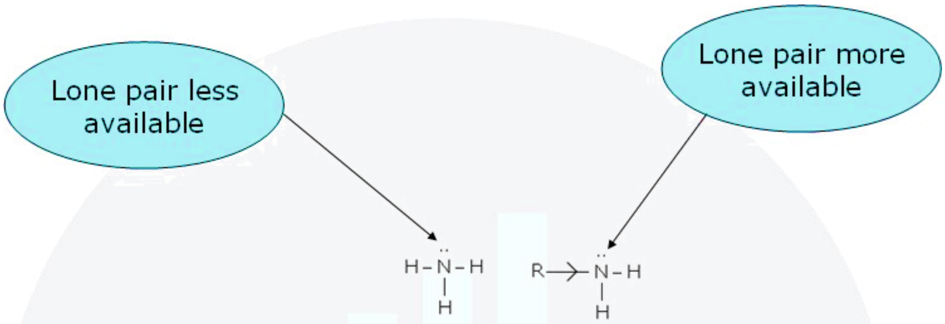
$$K_b = \frac{[R-\overset{+}{N}H_3][OH^-]}{[R-NH_2]}$$

$$pK_b = -\log K_b$$

- Greater K_b value or smaller pK_b indicates that a base is strong.

b) *Comparison of basic strength of aliphatic amines and ammonia*

Aliphatic amines are stronger bases than ammonia due to the +I effect of alkyl groups, leading to highelectron density on the nitrogen atom.



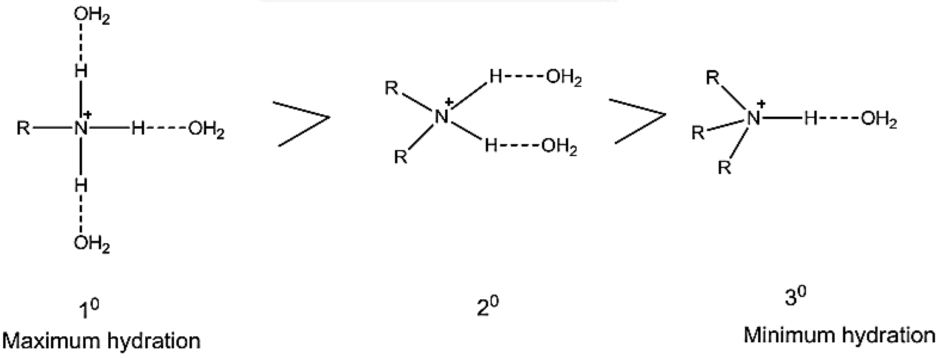
c) *Comparison of basic strength of primary, secondary and tertiary amines*

- The order of basicity of amines in the gaseous phase follows the expected order on the basis ofthe +I effect:
- In aqueous solution, tertiary amines are less basic than either primary or secondary amines. Thiscan be explained on the basis of the following factors:

  Tertiary amine > Secondary amine > Primary amine > NH_3

Solvation effect

- ✓ Greater the stability of the substituted ammonium cation formed, stronger is the correspondingamine as a base.
- ✓ The tertiary ammonium ion is less hydrated than the secondary ammonium ion, which is less hydrated than the primary amine. Thus, tertiary amines have less tendency to form ammonium ion and consequently are least basic.
- ✓ On the basis of the solvation effect, the order of basicity of aliphatic amines should be:Primary amine > Secondary amine > Tertiary amine NH_3



Steric factor

- ✓ As the crowding of the alkyl group increases from primary to tertiary, amine hindrance to hydrogen bonding increases which eventually decreases the basic strength. Thus, there is asubtle interplay of the inductive effect, solvation effect and steric hindrance of the alkyl groupwhich decides the basic strength of alkyl amines in the aqueous state.

✓ When the alkyl group is small like CH_3, there is no steric hindrance to hydrogen bonding. In this case, the order of basicity in aqueous medium is:

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

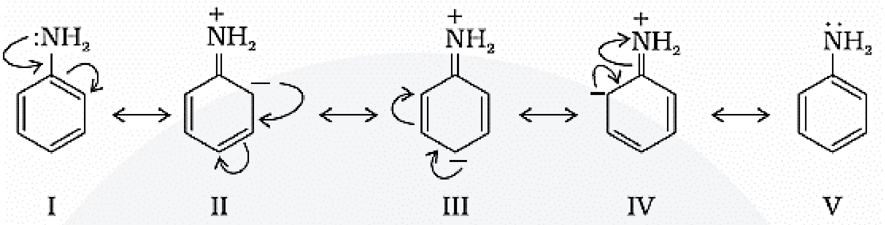
✓ When the alkyl group is the ethyl group, the group order of basicity in the aqueous medium is $(C_2H_5)_2NH > (C_2H_5)_3N > C_2H_5NH_2 > NH_3$

➢ **Comparison of basic strength of aryl amines and alkanamines**

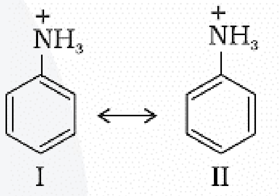
✓ Generally, aryl amines are considerably less basic than alkyl amines.

Example: Ethyl amine is more basic than aniline.

✓ In aniline, the $-NH_2$ group is directly attached to the benzene ring. Hence, the unshared pair ofelectrons on nitrogen is less available for protonation because of resonance.



✓ In the above resonating structures, there is a positive charge on the nitrogen atom making the lone pair less available for protonation. Hence, aniline is less basic than ethyl amine which hasno resonating structures.



✓ Less basicity of aniline can also be explained by comparing the relative stability of aniline andanilinium ion obtained by accepting a proton.

✓ Greater the number of resonating structures, greater is the stability of that species.

✓ Aniline is a resonance hybrid of five resonating structures, whereas anilinium ion has only two resonating structures.

✓ Thus, aniline has less tendency to accept a proton to form the anilinium ion.

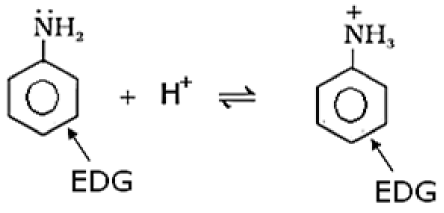
➢ **Effect of substituent on the basic character of amines**

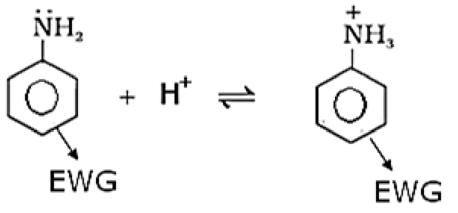
✓ An electron-donating or electron-releasing group (EDG) increases basic strength.

✓ An electron-withdrawing group (EWG) decreases basic strength.

EDG: releases electrons, stabilizes the cation and increases basic strength

EWG: withdraws electrons, destabilizes the cation and decreases basic strength





EDG = $-CH_3, -OCH_3, -NH_2$

EWG = $-NO_2, -CN, -X$ (Halogen)

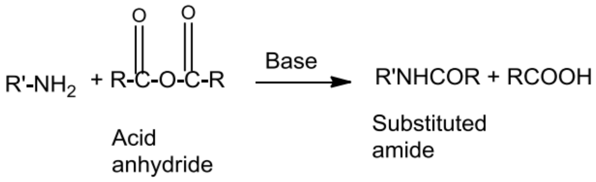
Reaction of Amines

Acylation reaction

➢ Aliphatic and aromatic primary and secondary amines (which contain replaceable hydrogenatoms) react with acid chlorides, anhydrides and esters to form substituted amide.

- The process of introducing an acyl group (R–CO–) into the molecule is called acylation.
- The reaction is carried out in the presence of a stronger base than the amine, such as pyridine,which removes HCl formed and shifts the equilibrium to the product side.

$$\text{R-NH}_2 + \underset{\text{Acid chloride}}{\text{RCOCl}} \xrightarrow{\text{Base}} \underset{\text{Substitutd amide}}{\text{RNHCOR}} + \text{HCl}$$



$$\text{R'-NH}_2 + \underset{\text{Acid anhydride}}{\text{R-}\overset{\text{O}}{\overset{\|}{\text{C}}}\text{-O-}\overset{\text{O}}{\overset{\|}{\text{C}}}\text{-R}} \xrightarrow{\text{Base}} \underset{\text{Substituted amide}}{\text{R'NHCOR}} + \text{RCOOH}$$

$$\text{R}_2\text{NH} + \text{RCOCl} \xrightarrow{\text{Base}} \text{R}_2\text{NCOR} + \text{HCl}$$

Important Note: Because tertiary amines do not contain a replaceable hydrogen atom, they do notundergo acylation.

Carbylamine reaction

- On heating aliphatic and aromatic primary amines with chloroform and ethanolic KOH they formisocyanides or carbylamines which have foul odour.
- Secondary and tertiary amines do not show this reaction.
- This reaction is used as a test for primary amines.

$$CH_3-NH_2+CHCl_3+3KOH \xrightarrow{\text{Heat}} CH_3-NC+3KCl+3H_2O$$

Reaction with Nitrous acid

- Primary aliphatic amines react with nitrous acid to form aliphatic diazonium salts. Being unstable diazonium salts liberate nitrogen gas quantitatively which is used in the estimation of amino acidsand proteins.

$$CH_3-NH_2+HNO_3 \xrightarrow{NaNO_2+HCl} [CH_3-\overset{+}{N_2}Cl^-] \xrightarrow{H_2O} CH_3OH+N_2+HCl$$

- Aromatic amines on treating with nitrous acid at low temperatures to form diazonium salts whichare used in the synthesis of a variety of aromatic compounds.

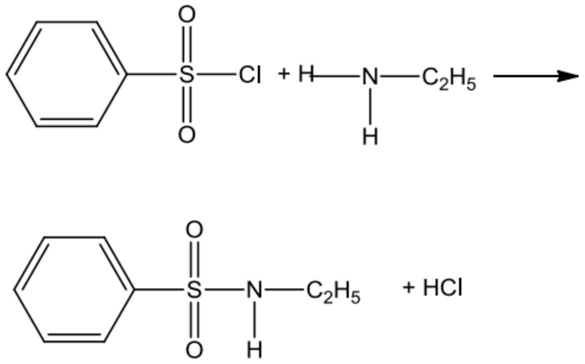
$$C_6H_5-NH_2 \xrightarrow[273-278K]{NaNO_2+HCl} C_6H_5-\overset{+}{N_2}Cl^- + NaCl + 2H_2O$$

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

Reaction with arylsulphonyl chloride

Hinsberg's reagent or benzenesulphonyl chloride ($C_6H_5SO_2Cl$) reacts with primary amines andsecondary amines to form sulphonamides.

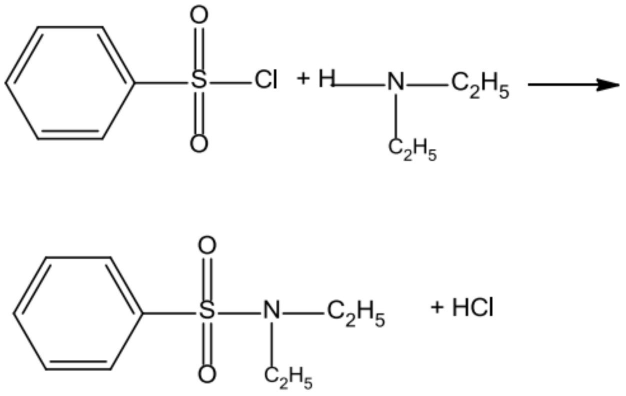
- Primary amine reacts with benzenesulphonyl chloride to form N-ethylbenzenesulphonyl amide.



N-ethylbenzenesulphonamide

The hydrogen bonded to nitrogen is strongly acidic due to the presence of strong electronwithdrawing sulphonyl group and is hence soluble in alkali.

- With secondary amine,N,N-diethyl-benzenesulphonamide is formed.



N,N-diethylbenzenesulphonamide

N, N-diethylbenzene sulphonamide does not contain any H atom attached to nitrogen atom so it is not acidic and is therefore insoluble in alkali.

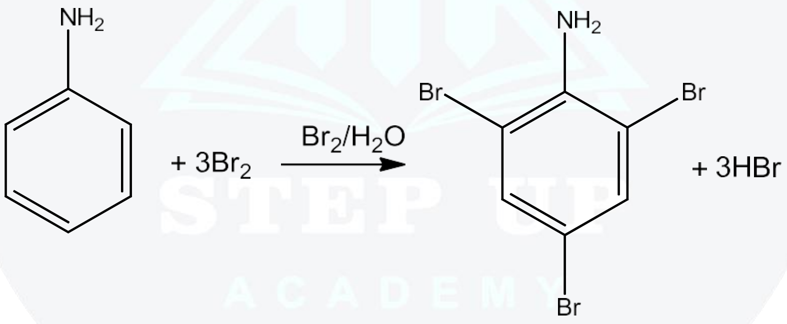
- Tertiary amines do not react with benzenesulphonyl chloride.

Electrophilic substitution

Ortho- and para-positions to the -NH_2 group become centres of high electron density.So -NH_2 group is ortho and para directing and a powerful activating group.

(a) Bromination

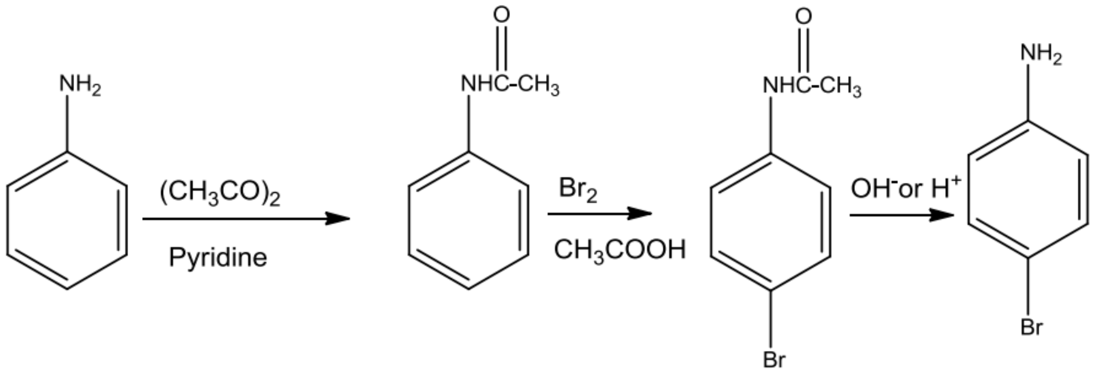
Aniline reacts with bromine water at room temperature to give a white precipitate of 2, 4,6-tribromoaniline



2,4,6-tribromoaniline

Due to the high reactivity of aromatic amines, electrophilic substitution takes place at ortho- and para-positions.

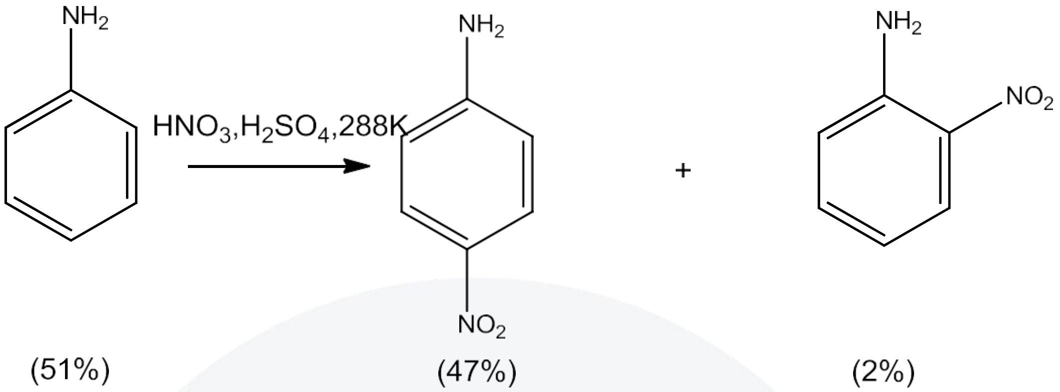
For preparing monosubstituted aniline derivative, the -NH_2 group is protected by acetylation with aceticanhydride then carrying out the desired substitution followed by the hydrolysis of the substituted amide to the substituted amine.



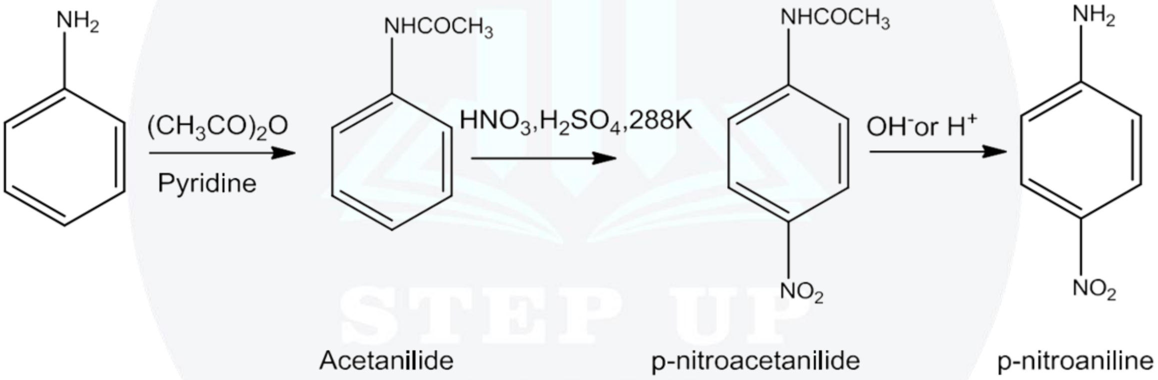
4-Bromoaniline

(b) Nitration

- Nitric acid is a nitrating agent plus a good oxidising agent. So direct oxidation of aromatic amines isnot useful since it gives tarry oxidation products along with some nitro derivatives.
- In strong acidic medium, aniline is protonated to form the anilinium ion which is meta directing. Hence besides the ortho and para derivatives, significant amount of meta derivative is also formed.

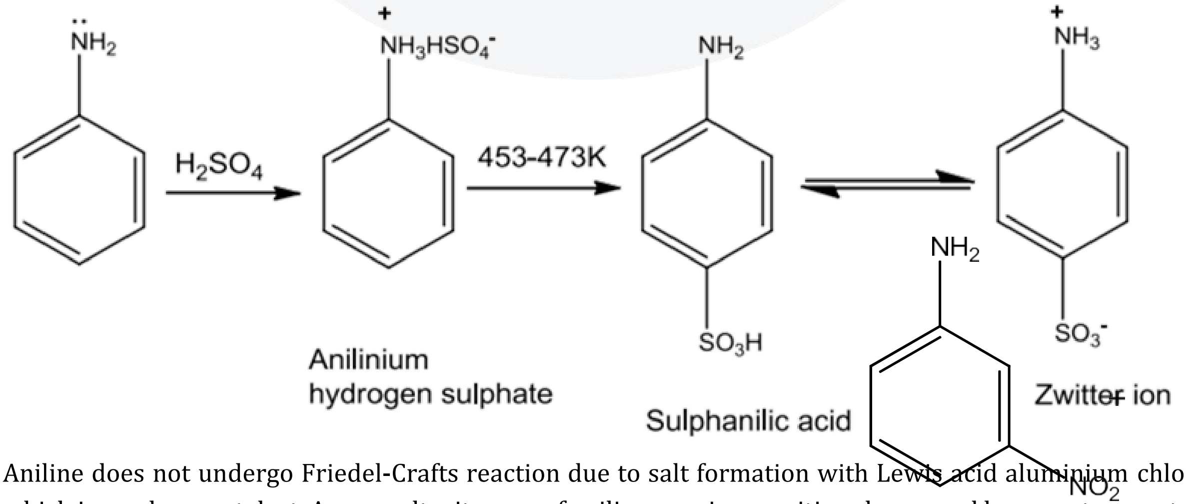


- However, if we protect the –NH2 group by acetylation reaction with acetic anhydride, the nitrationreaction can be controlled and the p-nitro derivative derivative can be prepared as the major product.



(c) Sulphonation

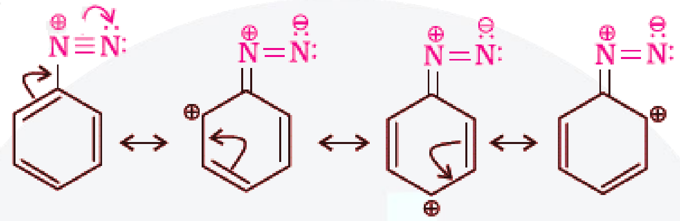
Aniline on reacting with sulphuric acid forms anilinium hydrogen sulphate which on heating withsulphuric acid at 453-473K gives p-aminobenzene sulphonic acid as the major product.



Aniline does not undergo Friedel-Crafts reaction due to salt formation with Lewis acid aluminium chloride which is used as a catalyst. As a result, nitrogen of aniline acquires positive charge and hence acts as a strong deactivating group for further reaction.

Diazonium Salts

- Diazonium salts have the general formula $R\overset{+}{N}_2\overline{X}$.
  - ✓ Where R = Aryl group
  - ✓ X^- ion = Cl^- Br^-, HSO_4^-, BF_4^- etc.
- A suffix diazonium is added to the parent hydrocarbon from which they are formed followed by thename of the anion.
  - ✓ Anion = chloride, hydrogensulphate, etc.
  - ✓ Diazonium group = $N^+{}_2$
- Primary aliphatic amines form highly unstable alkyldiazonium salts whereas primary aromatic aminesform arenediazonium salts which are stable for a short time in a solution at low temperatures.
- The stability of arenediazonium ion is explained on the basis of resonance.



Preparation of Diazonium Salts

- Benzenediazonium chloride is prepared by the action of aniline with nitrous acid at 273-278K.
- The conversion of primary aromatic amines into diazonium salts is known as diazotisation.

$$C_6H_5NH_2 + NaNO_2 + 2HCl \xrightarrow{273-278K} C_6H_5\overset{+}{N_2}Cl^- + NaCl + 2H_2O$$

Physical Properties

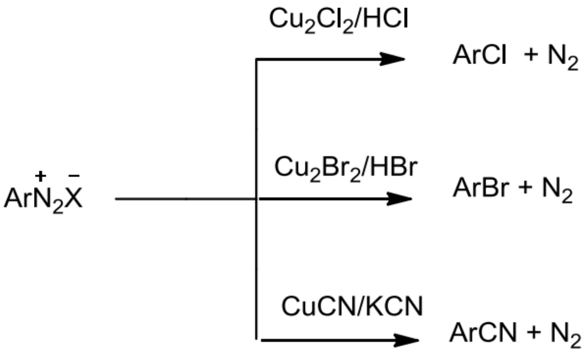
- Benzenediazonium chloride is a colourless crystalline solid.
- It is readily soluble in water and is stable in cold but reacts with warm water.
- It decomposes easily in the dry state.
- Benzenediazonium fluoborate is water insoluble and stable at room temperature.

Chemical Reactions

Reactions involving displacement of Nitrogen

➢ Replacement by halide or cyanide ion:

This reaction is called Sandmeyer reaction in which nucleophiles like Cl^-,$Br^-$and CN^- can be easilyintroduced in the benzene ring in the presence of Cu(I) ion.



Alternatively, chlorine or bromine can also be introduced in the benzene ring by treating the diazonium salt solution with corresponding halogen acid in the presence of Cu powder. This isreferred as Gatterman reaction.

$$Ar\overset{+}{N}_2\overset{-}{X} \xrightarrow{Cu/HCl} ArCl + N_2 + CuX$$

$$Ar\overset{+}{N}_2\overset{-}{X} \xrightarrow{Cu/HBr} ArCN + N_2 + CuX$$

➢ **Replacement by iodide ion:**

Iodobenzene is formed on treating diazonium salt solution with potassium iodide.

$$Ar\overset{+}{N}_2\overset{-}{X} + KI \longrightarrow ArI + KCl + N_2$$

➢ **Replacement by fluoride ion:**

Arenediazonium chloride on treating with fluoboric acid gives a precipitate of arene diazoniumfluoroborate which on heating decomposes to give aryl fluoride.

$$Ar\overset{+}{N}_2\overset{-}{Cl} + HBF_4 \longrightarrow Ar\text{-}\overset{+}{N}_2\overset{-}{BF}_4 \xrightarrow{\triangle} Ar\text{-} F + BF_3 + N_2$$

➢ **Replacement by H:**

Hypophosphorus acid or ethanol are mild reducing agents and reduce diazonium salts to arenes and themselves get oxidised to phosphorus acid and ethanal respectively.

$$Ar\overset{+}{N}_2\overset{-}{Cl} + H_3PO_3 + H_2O \longrightarrow Ar\,H + N_2 + H_3PO_3 + HCl$$

$$Ar\overset{+}{N}_2\overset{-}{Cl} + CH_3\,CH_2OH \longrightarrow Ar\,H + N_2 + CH_3CHO + HCl$$

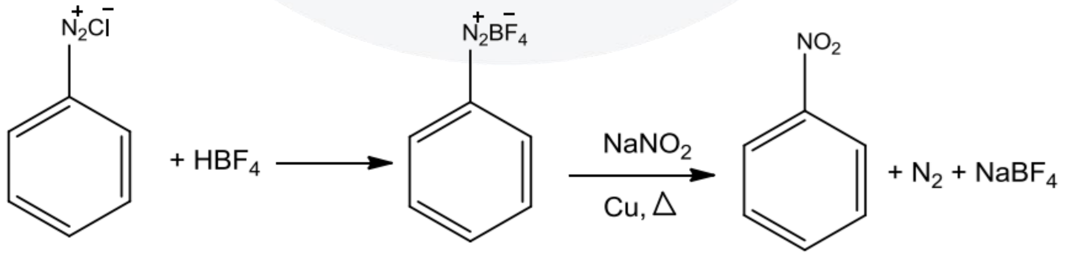
➢ **Replacement by hydroxyl group:**

Diazonium salt solution gets hydrolysed to phenol when the temperature is allowed to rise up to283K.

$$Ar\overset{+}{N}_2\overset{-}{Cl} + H_2O \longrightarrow ArOH + N_2 + HCl$$

➢ **Replacement by –NO₂ group:**

On heating diazonium fluoroborate with aqueous sodium nitrite solution in the presence of copper,the diazonium group is replaced by –NO₂ group.

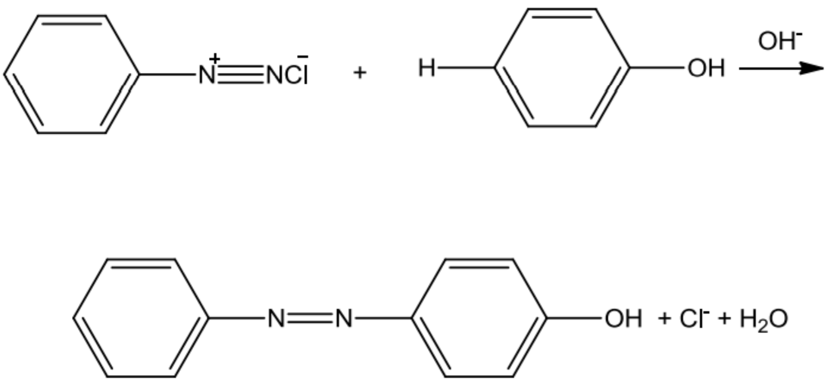


Reactions involving retention of diazo group coupling reactions

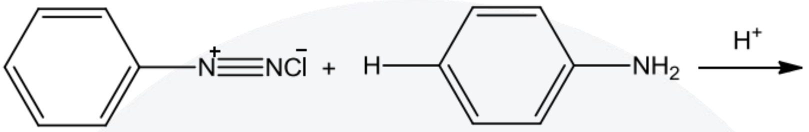
✓ Benzene diazonium chloride reacts with phenol in which the phenol at its para position is coupledwith the diazonium salt to form orange colour dye called p-hydroxyazobenzene.

✓ The reaction of diazonium salt with aniline gives yellow dye p-aminoazobenzene.

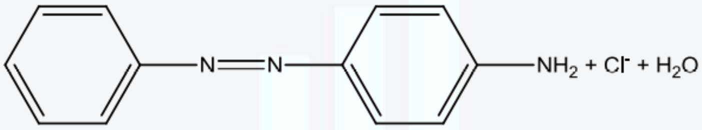
✓ The reaction is known as coupling reaction and it is an example of electrophilic substitutionreaction.



p-hydroxyazobenzene (orange dye)



p-aminoazobenzene (yellow dye)



p-hydroxyazobenzene (orange dye)

Importance of Diazonium Salts in Synthesis of Organic Compounds

- Diazonium salts are very good intermediates for introducing –F, –Cl, –Br, –I, –CN, –OH,–NO_2 groupsinto the aromatic ring.
- Direct halogenation method cannot be used for preparing aryl fluorides and iodides.
- Cyanobenzene can be easily prepared from diazonium salt.
- Thus the replacement of diazo group by other groups is useful in preparing substituted aromaticcompounds which cannot be prepared by direct substitution in benzene or substituted benzene.

Class : 12th Chemistry
Chapter-13 : Amines (Part_1)

Amines

Diazonium Salts RN_2X

Diazonium Salts

Preparation :

$$C_6H_5NH_2 + NaNO_2 + 2HCl \xrightarrow{273\text{-}278K} C_6H_5N_2Cl + NaCl + 2H_2O$$

Physical properties : Colourless crystalline solid, soluble in water, stable in cold but reacts with water on warming.

Chemical properties :

(i) Sandmeyer reaction: $ArN_2X \xrightarrow{Cu_2Cl_2/HCl} ArCl + N_2$; $ArN_2X \xrightarrow{Cu_2Br_2/HBr} ArBr + N_2$; $ArN_2X \xrightarrow{CuCN/KCN}$

Gattermann reaction :

$$ArN_2X \xrightarrow{Cu/HCl} ArCl + N_2 + CuX$$
$$ArN_2X \xrightarrow{Cu/HBr} ArBr + N_2 + CuX$$

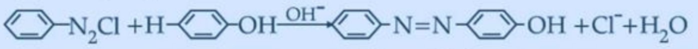
(ii) $ArN_2Cl + KI \longrightarrow ArI + KCl + N_2$

(iii) $ArN_2Cl + HBF_4 \longrightarrow ArN_2BF_4 \xrightarrow{\Delta} ArF + BF_3 + N_2$

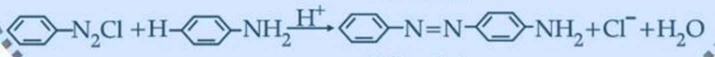
(iv) $ArN_2Cl + H_3PO_2 + H_2O \longrightarrow ArH + N_2 + H_3PO_3 + HCl$

(v) $ArN_2Cl + H_2O \longrightarrow ArOH + N_2 + HCl$

(iv) **Coupling reaction :**



(Orange dye)



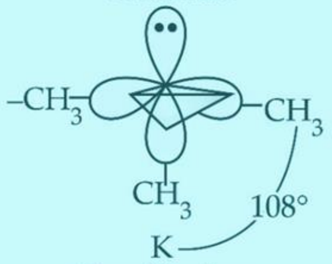
(Yellow dye)

Physicals Properties

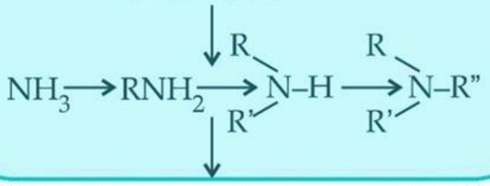
- Lower aliphatic amines are gases. Primary amines with three or more C atoms are liquid and higher ones are solid.
- Arylamines are colourless but get coloured on storage.
- Lower aliphatic amines are soluble in water, while higher are insoluble.
- Primary and secondary amines form intermolecular association
- Boiling point : primary > secondary > tertiary

Derivatives of ammonia, obtained by replacement of one, two or all the three Hatoms by alkyl and/or groups

Structure



Classification

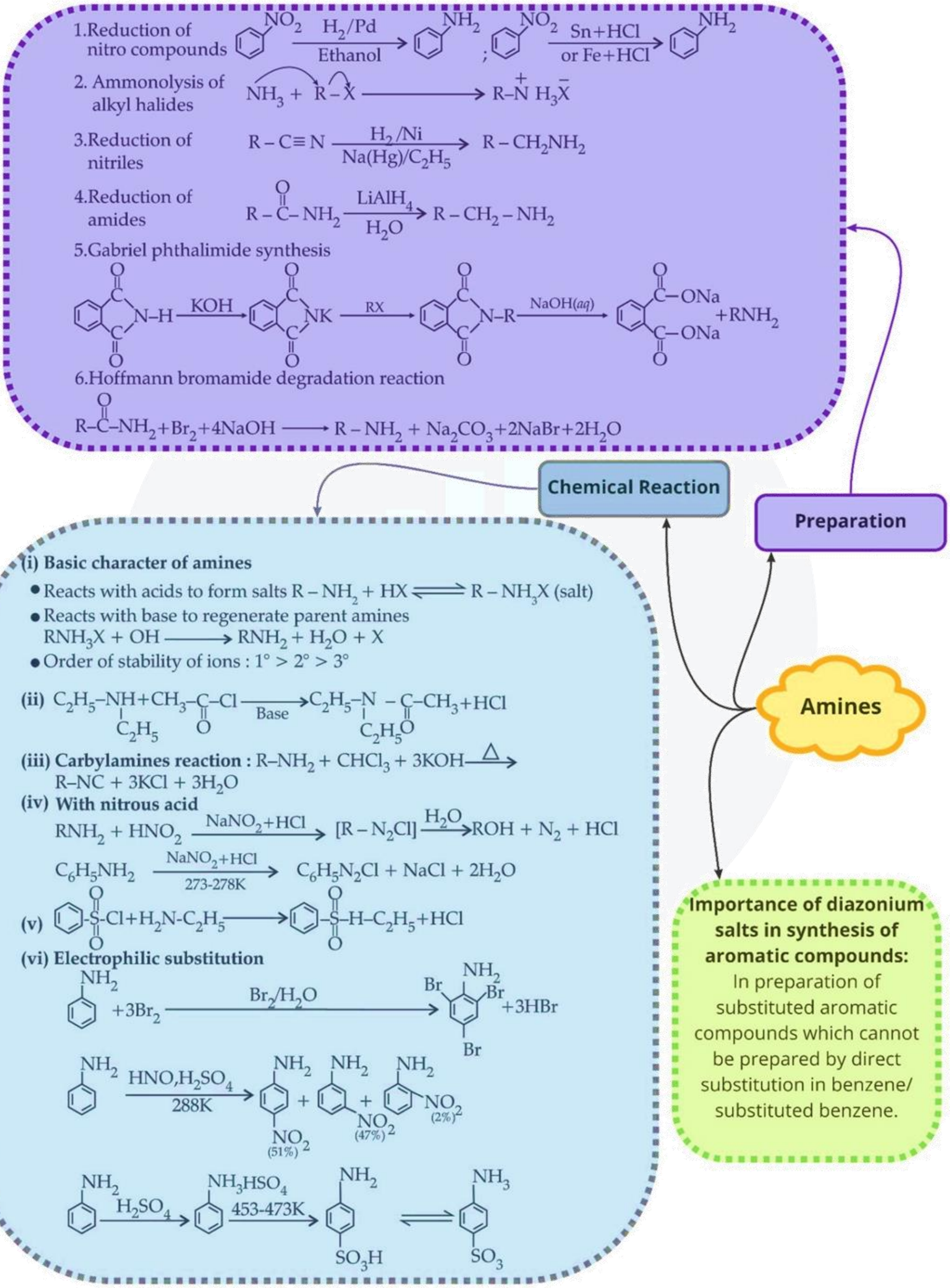


$$NH_3 \rightarrow RNH_2 \rightarrow \overset{R}{\underset{R'}{>}}N\text{–}H \rightarrow \overset{R}{\underset{R'}{>}}N\text{–}R''$$

Nomenclature:

Common name: Aliphatic amine is named by prefixing alkyl group to amine. In secondary and tertiary amines prefix di or tri is put before name of alkyl group. IUPAC name : replacement of 'e' of alkane by the word amine. Suffix 'e' of arene is replaced by amine.

Class : 12th Chemistry
Chapter-13 : Amines (Part_2)



Amines

Preparation

1.Reduction of nitro compounds

2. Ammonolysis of alkyl halides

$$NH_3 + R-X \longrightarrow R-\overset{+}{N}H_3\overset{-}{X}$$

3.Reduction of nitriles

$$R-C\equiv N \xrightarrow[Na(Hg)/C_2H_5]{H_2/Ni} R-CH_2NH_2$$

4.Reduction of amides

$$R-\overset{O}{\overset{\|}{C}}-NH_2 \xrightarrow[H_2O]{LiAlH_4} R-CH_2-NH_2$$

5.Gabriel phthalimide synthesis

6.Hoffmann bromamide degradation reaction

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

Chemical Reaction

(i) Basic character of amines

- Reacts with acids to form salts $R-NH_2 + HX \rightleftharpoons R-NH_3X$ (salt)
- Reacts with base to regenerate parent amines
  $RNH_3X + OH \longrightarrow RNH_2 + H_2O + X$
- Order of stability of ions : 1° > 2° > 3°

(ii) $$C_2H_5-\underset{C_2H_5}{\underset{|}{N}}H+CH_3-\underset{O}{\underset{\|}{C}}-Cl \xrightarrow[Base]{} C_2H_5-\underset{C_2H_5}{\underset{|}{N}}-\underset{O}{\underset{\|}{C}}-CH_3+HCl$$

(iii) Carbylamines reaction : $R-NH_2 + CHCl_3 + 3KOH \xrightarrow{\Delta}$
$R-NC + 3KCl + 3H_2O$

(iv) With nitrous acid

$$RNH_2 + HNO_2 \xrightarrow{NaNO_2+HCl} [R-N_2Cl] \xrightarrow{H_2O} ROH + N_2 + HCl$$

$$C_6H_5NH_2 \xrightarrow[273\text{-}278K]{NaNO_2+HCl} C_6H_5N_2Cl + NaCl + 2H_2O$$

(v)

(vi) Electrophilic substitution

Importance of diazonium salts in synthesis of aromatic compounds:
In preparation of substituted aromatic compounds which cannot be prepared by direct substitution in benzene/ substituted benzene.

Important Questions

Multiple Choice questions-

1. Which of the following does not react with Hinsberg reagent?

   (a) Ethylamine

   (b) $(CH_3)_2NH$

   (c) $(CH_3)_3N$

   (d) Propan-2-amine

2. $C_2H_5NH_2 \xrightarrow{NaNO_2/HCl} X \xrightarrow{P/Br_2} Y \xrightarrow[\text{(excess)}]{NH_3} Z$

   in above sequence, Z is

   (a) Cyanoethane

   (b) Ethanamide

   (c) Methanamine

   (d) Ethanamine

3. Oxidation of aniline with $K_2Cr_2O_7/H_2SO_4$ gives

   (a) phenylhydroxylamine

   (b) p-benzoquinone

   (c) nitrosobenzene

   (d) nitrobenzene

4. Which of the following amines can exhibit enantiomerism?

   (a) Benzeamine

   (b) 2-Butanamine

   (c) 2-Propanamine

   (d) 2-Methyl-propanamine.

5. Which of the following: when heated with a mixture of ethanmine and alcoholic potash gives ethyl isocyanide?

   (a) 2-chloropropane

   (b) 2,2-dichloropropane

   (c) trichloromethane

   (d) tetrachloromethane

6. Which of the following pair of species will yield carbylamine?

   (a) CH_3CH_2Br and KCN

   (b) CH_3CH_2Br and NH_3 (excess)

   (c) CH_3CH_2Br and AgCN

   (d) $CH_3CH_2NH_2$ and HCHO

7. Which one of the following methods is neither meant for the synthesis nor for separation of amines?

   (a) Hinsberg method

   (b) Hoffmann method

   (c) Wurtz reaction

   (d) Curticus reaction

8. $C_6H_5CONHCH_3$ can be converted into $C_6H_5CH_2NHCH_3$ by
   (a) $NaBH_4$
   (b) H_2-Pd/C
   (c) $LiAlH_4$
   (d) Zn-Hg/HCl
9. $C_6H_5N^+_2\ Cl^- + CuCN \rightarrow C_6H_5CN + N_2 + CuCl$. The above chemical reaction is associated with which of the following name:
   (a) Balz Schiemen
   (b) Gattermann
   (c) Shimonini
   (d) Sandmeyer.
10. The reaction of aniline with benzoyl chloride gives
   (a) Benzoin
   (b) Benzanilide
   (c) Benzalaniline
   (d) Benzamide

Very Short Questions-

1. For an amine RNH_2, write an expression to indicate its basic strength.
2. Give one use of quaternary ammonium salts.
3. Give one example of Hoffmann – Bromamide reaction
4. Distinguish between ethylamine and aniline.
5. The IUPAC name of secondary amine having lowest molecular mass is ________.
6. Give an example of diazotization
7. Write one use of diazonium salt
8. How can the reactivity of aromatic amines be controlled?
9. Give one use of tertiary amines.
10. Name a reagent which can distinguish between primary, secondary and tertiary amine

Short Questions-

1. It is difficult to prepare pure amines by ammonolysis of alkylhalides.
2. Amines have higher boiling points than hydrocarbons of similar molecular mass.
3. Aniline is weaker base than cyclohexylamine.
4. Methylamine is a stronger base than aniline.
5. Before nitration, aniline is converted to acetanilide.
6. It is easier to brominate aniline as compared to benzene.
7. Reduction of nitro compound to aniline using iron scrap and HCl is preferred.
8. Aromatic amines cannot be prepared by Gabriel Phthalimide synthesis.
9. During acylation of amines, pyridine is added.
10. Aniline does not undergo Friedel – Craft's reaction.

Long Questions-

1. (i) Write structures of different isomeric amines corresponding to the molecular formula, $C_4H_{11}N$
   (ii) Write IUPAC names of all the isomers.
   (iii) What type of isomerism is exhibited by different pairs of amines?

2. Arrange the following in increasing order of their basic strength:
   - (i) $C_2H_5NH_2$, $C_6H_5NH_2$, NH_3, $C_6H_5CH_2NH_2$ and $(C_2H_5)_2$ NH and
   - (ii) $C_2H_5NH_2$, $(C_2H_5)_2$ NH_2 $(C_2H_5)_3$ N, $C_6H_5NH_2$
   - (iii) CH_3NH_2, $(CH_3)_2$ NH, $(CH_3)_3$ N, $C_6H_5NH_2$, $C_6H_5CH_2NH_2$
3. Write structures of different isomers corresponding to the molecular formula C_3H_9N. Write IUPAC names of the isomers which will liberate nitrogen gas on treatment with nitrous acid.
4. Write IUPAC names of the following compounds and classify them into primary, secondary and tertiary amines.
   - (i) $(CH_3)_2$ $CHNH_2$
   - (ii) $CH_3(CH_2)_2$ NH_2
   - (iii) $CH_3NHCH(CH_3)_2$
   - (iv) $(CH_3)_3$ CNH_2
   - (v) $C_6H_5NHCH_3$
   - (vi) $(CH_3CH_2)_2$ NCH_3
   - (vii) m–$BrC_6H_4NH_2$
5. Give one chemical test to distinguish between the following pairs of compounds.
   - (i) Methylamine and dimethylamine
   - (ii) Secondary and tertiary amines
   - (iii) Ethylamine and aniline
   - (iv) Aniline and benzylamine
   - (v) Aniline and N-methylaniline.
6. Account for the following:
   - (i) p*Kb* of aniline is more than that of methylamine.
   - (ii) Ethylamine is soluble in water whereas aniline is not.
   - (iii) Methylamine in water reacts with ferric chloride to precipitate hydrated ferric oxide.
   - (iv) Although amino group is *o*, *p*- directing in aromatic electrophilic substitution reactions, aniline on nitration gives a substantial amount of *m*-nitroaniline.
   - (v) Aniline does not undergo Friedel-Crafts reaction.
   - (vi) Diazonium salts of aromatic amines are more stable than those of aliphatic amines.
   - (vii) Gabriel phthalimide synthesis is preferred for synthesising primary amines.
7. Arrange the following:
   - (i) In decreasing order of the p*Kb* values:
     $C_2H_5NH_2$, $C_6H_5NHCH_3$, $(C_2H_5)_2$ NH and $C_6H_5NH_2$
   - (ii) In increasing order of basic strength:
     $C_6H_5NH_2$, $C_6H_5N(CH_3)_2$, $(C_2H_5)_2$ NH and CH_3NH_2
   - (iii) In increasing order of basic strength:
     - (a) Aniline, *p*-nitroaniline and *p*-toluidine
     - (b) $C_6H_5NH_2$, $C_6H_5NHCH_3$, $C_6H_5CH_2NH_2$
   - (iv) In decreasing order of basic strength in gas phase:
     $C_2H_5NH_2$, $(C_2H_5)_2NH$, $(C_2H_5)Nz$ and NH_3
   - (v) In increasing order of boiling point:
     C_2H_5OH, $(CH_3)_2NH$, $C_2H_5NH_2$
   - (vi) In increasing order of solubility in water:
     $C_6H_5NH_2$, $(C_2H_5)_2NH$, $C_6H_5NH_2$

8. How will you convert:
   - (i) Ethanoic acid into methanamine
   - (ii) Hexanenitrile into 1-aminopentane
   - (iii) Methanol to ethanoic acid
   - (iv) Ethanamine into methanamine
   - (v) Ethanoic acid into propanoic acid
   - (vi) Methanamine into ethanamine
   - (vii) Nitromethane into dimethylamine
   - (viii) Propanoic acid into ethanoic acid

Assertion and Reason Questions-

1. In these questions, a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following choices.

a) Assertion and reason both are correct statements and reason is correct explanation for assertion.
b) Assertion and reason both are correct statements but reason is not correct explanation for assertion.
c) Assertion is correct statement but reason is wrong statement.
d) Assertion is wrong statement but reason is correct statement.

Assertion: Ortho substituted anilines are usually weaker bases than anilines.

Reason: This is due to ortho effect.

2. In these questions, a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following choices.

a) Assertion and reason both are correct statements and reason is correct explanation for assertion.
b) Assertion and reason both are correct statements but reason is not correct explanation for assertion.
c) Assertion is correct statement but reason is wrong statement.
d) Assertion is wrong statement but reason is correct statement.

Assertion: In strongly acidic solutions, aniline becomes more reactive towards electrophilic reagents.

Reason: The amino group being completely protonated in strongly acidic solution, the lone pair of electrons on the nitrogen is no longer available for resonance.

Case Study Questions-

1. Read the passage given below and answer the following questions:

Amines are alkyl or aryl derivatives of ammonia formed by replacement of one or more hydrogen atoms. Alkyl derivatives are called aliphatic amines and aryl derivatives are known as aromatic amines. The presence of aromatic amines can be identified by performing dye test. Aniline is the simplest example of aromatic amine. It undergoeselectrophilic substitution reactions in which -NH_2 group strongly activates the aromatic ring through delocalisation of lone pair of electrons of N-atom. Aniline undergoes electrophilic substitution reactions. Ortho and para positions to the -NH_2 group become centres of high electrons density. Thus, -NH_2 group is ortho and para-directing and powerful activating group.

The following questions are multiple choice questions. Choose the most appropriate answer:

(i) Cyclohexylamine and aniline can be distinguished by:

a) Hinsberg test.
b) carbylamine test.
c) Lassaigne test.
d) azo dye test.

(ii) Which of the following compounds gives dye test?

a) Aniline.

b) Methyl amine.

c) Diphenyl amine.

d) Ethyl amine.

(iii) Aniline when acetylated, the major product on nitration followed by alkaline hydrolysis gives:

a) Acetanilide.

b) o-nitroacetanitide.

c) p-nitroaniline.

d) m-nitroanitine.

(iv) Oxidation of aniline with manganese dioxide and sulphuric acid produces:

a) Phenylhydroxylamine.

b) Nitrobenzene.

c) p-benzoquinone.

d) Phenol.

(v) Aniline when treated with cone. HNO_3 and H_2S0_4 gives:

a) p-phenylenediamine.

b) m-nitroaniline.

c) p-benzoquinone.

d) Nitrobenzene.

2. Read the passage given below and answer the following questions:

The amines are basic in nature due to the presence of a lone pair of electron on N-atom of the $-NH_2$ group, which it can donate to electron deficient compounds. Aliphatic amines are stronger bases than NH_3 because of the +I effect of the alkyl groups. Greater the number of alkyl groups attached to N-atom, higher is the electron density on it and more will be the basicity. Thus, the order of basic nature of amines is expected to be 3° > 2° > 1°, however the observed order is 2° > 1° > 3°. This is explained on the basis of crowding on N-atom of the amine by alkyl groups which hinders the approach and bonding by a proton, consequently, the electron pair which is present on N is unavailable for donation and hence 3° amines are the weakest bases.

Aromatic amines are weaker bases than ammonia and aliphatic amines. Electron-donating groups such as $-CH_3$, $-OCH_3$, etc. increase the basicity while electron-withdrawing substitutes such as $-NO_2$, -CN, halogens, etc. decrease the basicity of amines. The effect of these substituents is more at p than at m-positions.

The following questions are multiple choice questions. Choose the most appropriate answer:

(i) Which one of the following is the strongest base in aqueous solution?

a) Methyl amine.

b) Tri methyl amine.

c) Aniline.

d) Dimethyl amine.

(ii) Which order ofbasicity is correct?

a) Aniline > m-toluidine > o-toluidine

b) Aniline> o-toluidine > m-toluidine

c) o-toluidine > aniline> m-toluidine

d) o-toluidine < aniline < m-toluidine

(iii) What is the decreasing order of basicity of primary, secondary and tertiary ethylamines and NH_3?

a) $NH_3 > C_2H_5NH_2 > (C_2H_5)_2NH > (C_2H_5)_3N$
b) $(C_2H_5)_3N > (C_2H_5)_2NH > C_2H_5NH_2 > NH_3$
c) $(C_2H_5)_2NH > C_2H_5NH_2 > (C_2H_5)_3N > NH_3$
d) $(C_2H_5)_2NH > (C_2H_5)_3N > C_2H_5NH_2 > NH_3$

(iv) The order of basic strength among the following amines in benzene solution is:
a) $CH_3NH_2 > (CH_3)_3N > (CH_3)_2NH$
b) $(CH_3)_3N > (CH_3)_2NH > CH_3NH_2$
c) $CH_3NH_2 > (CH_3)_2NH > (CH_3)_3N$
d) $(CH_3)_3N > CH_3NH_2 > (CH_3)_2NH$

(v) Choose the correct statement.
a) Methylamine is slightly acidic.
b) Methylamine is less basic than ammonia.
c) Methylamine is a stronger base than ammonia.
d) Methylamine forms salts with alkalies.

Answer Key

MCQ Answers-

1. **Answer:** (c) $(CH_3)_3N$
2. **Answer:** (d) Ethanamine
3. **Answer:** (b) p-benzoquinone
4. **Answer:** (b) 2-Butanamine
5. **Answer:** (c) trichloromethane
6. **Answer:** (c) CH_3CH_2Br and AgCN
7. **Answer:** (c) Wurtz reaction
8. **Answer:** (c) $LiAlH_4$
9. **Answer:** (d) Sandmeyer.
10. **Answer:** (b) Benzanilide

Very Short Answers-

1. $RNH_2 + H_2O \rightleftharpoons RNH_3^+ + OH^-$

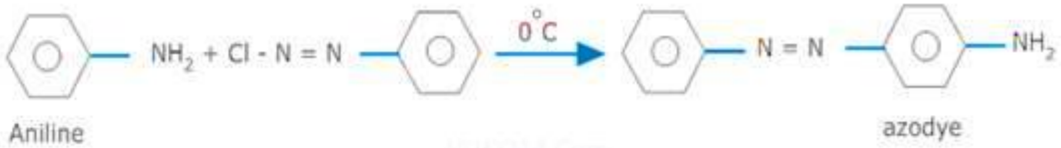
$$K_b = \frac{[RNH_3^+][OH^-]}{[RNH_2]}$$

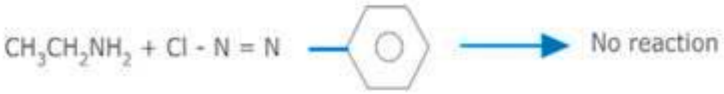
2. Quaternary ammonium salts are widely used for manufacture of synthetic detergents.

3. In Hoffmann – Bromamide reaction an acid amide is reacted with Bromine in presence of a base to give a primary amine having one carbon less than the starting amide.

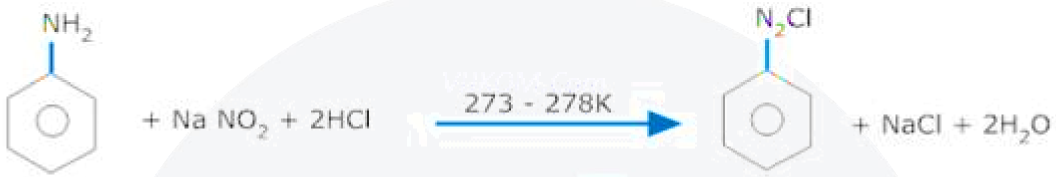
$RCONH_2 + Br_2 + 4\ NaOH \rightarrow RNH_2 + Na_2\ CO_3 + 2\ NaBr + 2H_2O$

4. Ethylamine and aniline can be distinguished by azodye test. On treating aniline with benzene diazonium salt, orange or red coloured azodye is formed which is not formed with ethyl amine.





5. N- Methylmethanamine.
6. During diazotization benzene diazonium chloride is prepared by the reaction of aniline with nitrous acid at 273 – 278 K



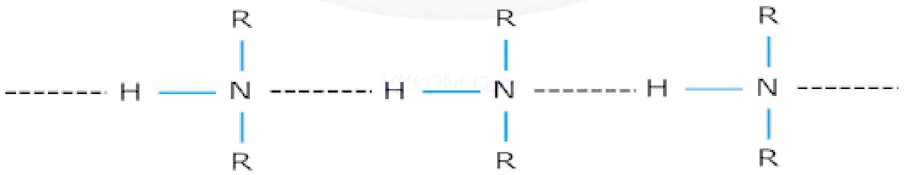
7. Diazonium salts are used in preparation of substituted aromatic compounds.
8. The reactivity of aromatic amines can be controlled by acylation.
9. Tertiary amines like trimethylamine are used as insect attractants.
10. P-Toluenesulphonyl chloride Hinsberg reagent can be used as a distinguishing reagent for primary, secondary and tertiary amines.

Short Answers-

1. The process of ammonolysis yields a mixture of primary, secondary, tertiary amines and quaternary salts. The separation of this amines is a very complicated process and difficult. Therefore, it is difficult to prepare pure amines by ammonolysis of alkyl halides.

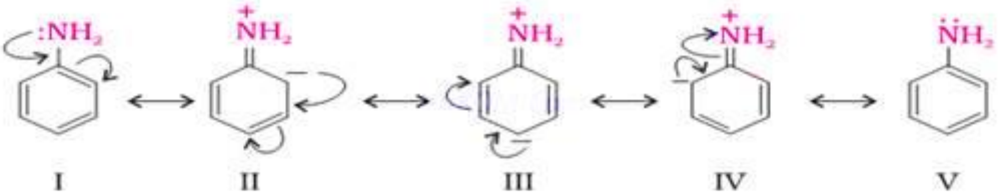
$$Rx \xrightarrow[-Hx]{NH_3} RNH_2 \xrightarrow[-Hx]{Rx} R_2NH \xrightarrow[-Hx]{Rx} R_3N \xrightarrow{Rx} [R_3N]^+ X^-$$

2. Amines have higher boiling points than hydrocarbons of comparable molecular mass due to the presence of intermolecular hydrogen bond in amines which is absent in hydrocarbons. Therefore, amines exist as associated molecules and have higher boiling points.

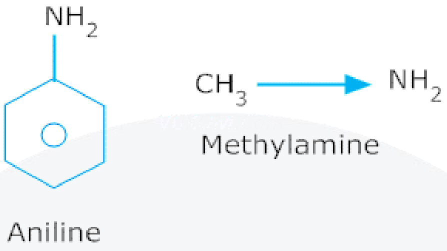


In alcohols and carboxylic acids, the electro- negativity of oxygen is more than nitrogen of amines. Therefore, the hydrogen bonds of alcohols and acids are stronger than in amines and alcohols & carboxylic acids have higher boiling points.

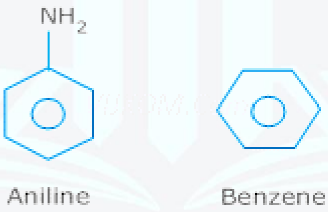
3. As a result of resonance in aniline; the lone pair on nitrogen delocalized over the benzene ring and is less available for protonation than in cyclohexyl amine which does not undergo resonance. Resonating structure of aniline –



4. Due to electron donating nature of CH_3, group, electron pair. Availability at N- atom in methyl amine is much higher than that in aniline; in aniline the benzene ring decreases the electron density at N- atom in aniline. Thus CH_3NH_2 is a stronger base than aniline.



5. Aniline is very much susceptible to nitration and nitric acid is a strong oxidizing agent. Therefore to avoid oxidation of aniline, $-NH_2$ group is protected by its acetylation to acetanilide which undergo nitration smoothly without any oxidation.



6. In aniline, due to +R effect of $-NH_2$ group the benzene ring gets activated to a large extent and it becomes easier to brominates aniline as compared to benzene.

7. For reduction of nitro compounds to aniline, iron scrap and HCl is preferred because $FeCl_2$ formed gets hydrolysed to release HCl during the reaction & therefore only a small amount of HCl is required to initiate the reaction.

8. Aromatic amines cannot be prepared by Gabriel pythalimide synthesis as aryl halides do not undergo nucleophilic substitution with the anion formed by pythalimide.

9. Acylation of amines is carried out in presence of pyridine or another base stronger than amines as it removes HCl so formed and shifts the equilibrium in forward direction.

$$C_2H_5NH_2 + CH_3COCl \overset{\text{Base}}{\rightleftharpoons} C_2H_5NHCOCH_3 + HCl$$

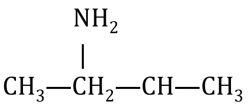
10. During Fridel Craft's reaction, aniline forms salt with aluminum chloride, the catalyst of reaction due to which nitrogen acquires a positive charge and acts as a strong deactivating group for further reaction.

Long Answers-

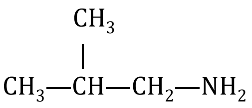
1. **(i), (ii)** The structures and their IUPAC names of different isomeric amines corresponding to the molecular formula, $C_4H_{11}N$ are given below:

   (a) $CH_3—CH_2—CH_2—CH_2—NH_2$

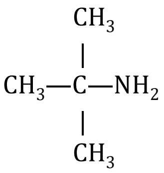
   Butanamine (1°)

(b) 
$CH_3—CH_2—\overset{\overset{NH_2}{|}}{C}H—CH_3$

Butan-2-amine (1°)

(c) 
$CH_3—\overset{\overset{CH_3}{|}}{C}H—CH_2—NH_2$

2-Methylpropanamine (1°)

(d) 
$CH_3—\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}—NH_2$

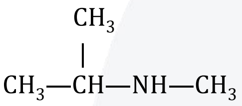
2-Methylpropan-2-amine (1°)

(e) $CH_3—CH_2—CH_2—NH—CH_3$

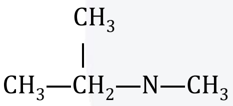
N-Methylpropanamine (2°)

(f) $CH_3—CH_2—NH—CH_2—CH_3$

N-Ethylethanamine (2°)

(g) 
$CH_3—\overset{\overset{CH_3}{|}}{C}H—NH—CH_3$

N-Methylpropan-2-amine (2°)

(h) 
$CH_3—CH_2—\overset{\overset{CH_3}{|}}{N}—CH_3$

N, N-Dimethylethanamine (3°)

(iii) The pairs (a) and (b) and (e) and (g) exhibit position isomerism.

The pairs (a) and (c); (a) and (d); (b) and (c); (b) and (d) exhibit chain isomerism.

The pairs (e) and (f) and (f) and (g) exhibit metamerism.

All primary amines exhibit functional isomerism with secondary and tertiary amines and vice-versa.

2. **(i)** Considering the inductive effect of alkyl groups, NH_3, $C_2H_5NH_2$ and $(C_2H_5)_2$ NH can be arranged in the increasing order of their basic strengths as:

$$NH_3 < C_2H_5NH_2 < (C_2H_5)_5\ NH$$

Again, $C_6H_5NH_2$ has proton acceptability less than NH_3. Thus, we have:

$$C_6H_5NH_2 < NH_3 < C_2H_5NH_2 < (C_2H_5)_2\ NH$$

Due to the – I effect of C_6H_5 group, the electron density on the N-atom in $C_6H_5CH_2NH_2$ is lower than that on the N-atom in $C_2H_5NH_2$, but more than that in NH_3. Therefore, the given compounds can be arranged in the order of their basic strengths as:

$$C_6H_5NH_2 < NH_3 < C_6H_5CH_2NH_2 < C_2H_5NH_2 < (C_2H_5)_2\ NH$$

(ii) Considering the inductive effect and the steric hindrance of the alkyl groups, $C_2H_5NH_2$, $(C_2H_5)_2$ NH_2 and their basic strengths as follows:

$$C_2H_5NH_2 < (C_2H_5)_2\ N < (C_2H_5)_2\ NH$$

Again, due to the – R effect of C_6H_5 group, the electron density on the N atom in $C_6H_5NH_2$ is lower than that on the N atom in $C_2H_5NH_2$. Therefore, the basicity of $C_6H_5NH_2$ is lower than that of $C_2H_5NH_2$. Hence, the given compounds can be arranged in the increasing order of their basic strengths as follows:

$$C_6H_5NH_2 < C_2H_5NH_2 < (C_2H_5)_3\,N < (C_2H_5)_2\,NH$$

(iii) Considering the inductive effect and the steric hindrance of alkyl groups, CH_3NH_2, $(CH_3)_2$ NH and $(CH_3)_3$ N can be arranged in the increasing order of their basic strengths as:

$$(CH_3)_3\,N < CH_3NH_2 < (CH_3)_2\,NH$$

In $C_6H_5NH_2$, N is directly attached to the benzene ring. Thus, the lone pair of electrons on the N – atom is delocalized over the benzene ring. In $C_6H_5CH_2NH_2$, N is not directly attached to the benzene ring. Thus, its lone pair is not delocalized over the benzene ring. Therefore, the electrons on the N atom are more easily available for protonation in $C_6H_5CH_2NH_2$ than in $C_6H_5NH_2$ *i.e.*, $C_6H_5CH_2NH_2$ is more basic than C_6H_5 NH_2. Again, due to the – I effect of C_6H_5 group, the electron density on the N – atom in C_6H_5 CH_2NH_2 is lower than that on the N – atom in $(CH_3)_3$ N. Therefore, $(CH_3)_3$ N is more basic than C_6H_5 CH_2NH_2. Thus, the given compounds can be arranged in the increasing order of their basic strengths as follows:

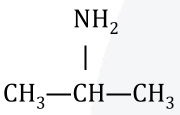
$$C_6H_5 < C_6H_5CH_2NH_2 < (CH_3)_3\,N < CH_3NH_2 < (CH_3)_2\,NH$$

3. The structures of different isomers corresponding to the molecular formula, C_3H_9N are given below:

(a) $CH_3—CH_2—CH_2—NH_2$

Propan-1-amine (1°)

(b)



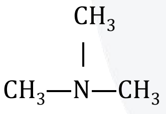
$$\underset{}{CH_3—\overset{\overset{\displaystyle NH_2}{|}}{C}H—CH_3}$$

Propan-2-amine (1°)

(c) $CH_3—NH—C_2H_5$

N—Methylethanamine (2°)

(d)



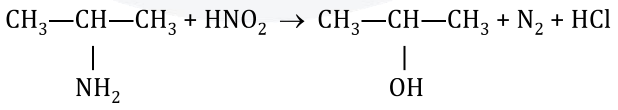
$$CH_3—\overset{\overset{\displaystyle CH_3}{|}}{N}—CH_3$$

N, N-Dimethylmethanamine (3°)

1° amines, (a) propan-1-amine, and (b) Propan-2-amine will liberate nitrogen gas on treatment with nitrous acid.

$$CH_3CH_2CH_2NH_2 + HNO_2 \rightarrow CH_3CH_2CH_2OH + N_2 + HCl$$

Propan–1–amine Propan–1–ol



$$CH_3—\underset{\underset{\displaystyle NH_2}{|}}{C}H—CH_3 + HNO_2 \rightarrow CH_3—\underset{\underset{\displaystyle OH}{|}}{C}H—CH_3 + N_2 + HCl$$

Propan–2–amine Propan–2–ol

4. **(i)** 1-Methylethanamine (1° amine)

(ii) Propan-1-amine (1° amine)

(iii) N-Methyl-2-methylethanamine (2° amine)

(iv) 2-Methylpropan-2-amine (1° amine)

(v) N-Methylbenzamine or N-methylaniline (2° amine)

(vi) N-Ethyl-N-methylethanamine (3° amine)

(vii) 3-Bromobenzenamine or 3-bromoaniline (1° amine)

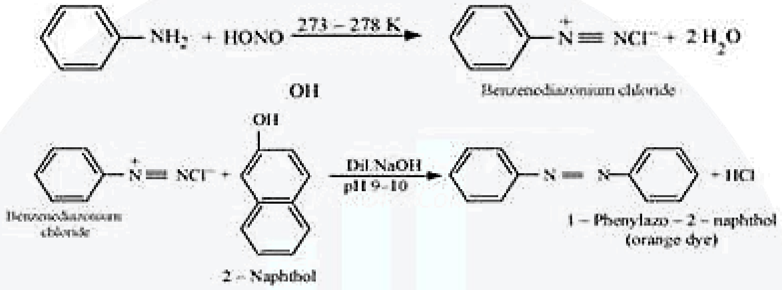
5. **(i)** Methylamine and dimethylamine can be distinguished by the carbylamine test.

Carbylamine test: Aliphatic and aromatic primary amines on heating with chloroform and ethanolic potassium hydroxide form foul-smelling isocyanides or carbylamines. Methylamine (being an aliphatic primary amine) gives a positive carbylamine test, but dimethylamine does not.

(ii) Secondary and tertiary amines can be distinguished by allowing them to react with Hinsberg's reagent (benzenesulphonyl chloride, $C_6H_5SO_2Cl$).

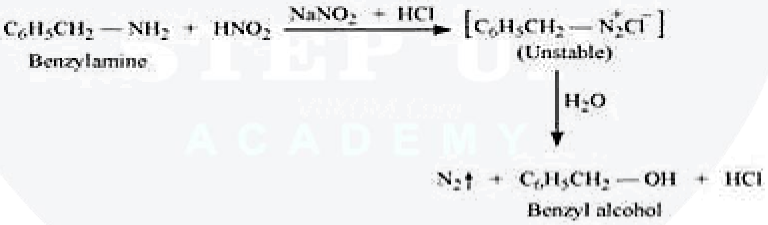
Secondary amines react with Hinsberg's reagent to form a product that is insoluble in an alkali. For example, N, N – diethylamine reacts with Hinsberg's reagent to form N, N – diethylbenzenesulphonamide, which is insoluble in an alkali. Tertiary amines, however, do not react with Hinsberg's reagent.

(iii) Ethylamine and aniline can be distinguished using the azo-dye test. A dye is obtained when aromatic amines react with HNO_2 ($NaNO_2$ + dil.HCl) at 0–5°C, followed by a reaction with the alkaline solution of 2-naphthol. The dye is usually yellow, red, or orange in colour. Aliphatic amines give a brisk effervescence due (to the evolution of N_2 gas) under similar conditions.



$$CH_3CH_2-NH_2+HONO\xrightarrow{0\text{–}5^\circ}C_2H_5OH+N_2\uparrow+H_2O$$

(iv) Aniline and benzylamine can be distinguished by their reactions with the help of nitrous acid, which is prepared in situ from a mineral acid and sodium nitrite. Benzylamine reacts with nitrous acid to form unstable diazonium salt, which in turn gives alcohol with the evolution of nitrogen gas.

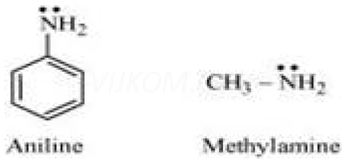


On the other hand, aniline reacts with HNO_2 at a low temperature to form stable diazonium salt. Thus, nitrogen gas is not evolved.

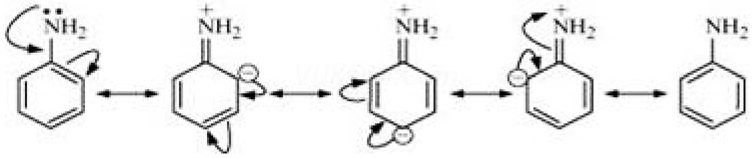
$$C_6H_5NH_2\xrightarrow[273-278\,K]{NaNO_2+HCl}C_6H_5-\overset{+}{N_2}\overset{-}{Cl}+NaCl+2H_2O$$

(v) Aniline and N-methylaniline can be distinguished using the Carbylamine test. Primary amines, on heating with chloroform and ethanolic potassium hydroxide, form foul-smelling isocyanides or carbylamines. Aniline, being an aromatic primary amine, gives positive carbylamine test. However, N-methylaniline, being a secondary amine does not.

6. **(i) p*Kb*of aniline is more than that of methylamine:**



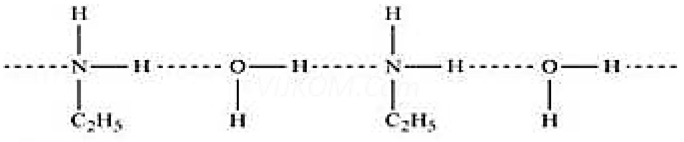
Aniline undergoes resonance and as a result, the electrons on the N-atom are delocalized over the benzene ring. Therefore, the electrons on the N-atom are less available to donate.



On the other hand, in case of methylamine (due to the +I effect of methyl group), the electron density on the N-atom is increased. As a result, aniline is less basic than methylamine. Thus, *pKb* of aniline is more than that of methylamine.

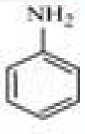
(ii) Ethylamine is soluble in water whereas aniline is not:

Ethylamine when added to water forms intermolecular H – bonds with water. Hence, it is soluble in water.



Ethylamine

But aniline does not undergo H – bonding with water to a very large extent due to the presence of a large hydrophobic – C6H5 group. Hence, aniline is insoluble in water.



Aniline

(iii) Methylamine in water reacts with ferric chloride to precipitate hydrated ferric oxide:

$$CH_3 \rightarrow NH_2 \qquad H-OH$$

Methylamine Water

Due to the +I effect of $-CH_3$ group, methylamine is more basic than water. Therefore, in water, methylamine produces OH – ions by accepting H+ ions from water.

$$CH_3-NH_2+H-OH \longrightarrow CH_3-\overset{+}{N}H_3+OH^-$$

Ferric chloride ($FeCl_3$) dissociates in water to form Fe^{3+} and Cl^- ions.

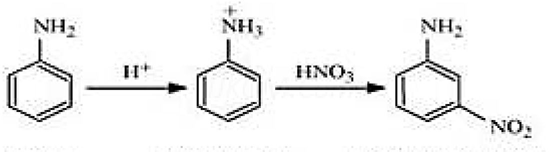
$$FeCl_3 \longrightarrow Fe^{3+} + 3Cl^-$$

Then, OH – ion reacts with Fe3+ ion to form a precipitate of hydrated ferric oxide.

$$2Fe^{3+} + 6OH^- \longrightarrow \underset{\text{Hydrated ferric oxide}}{Fe_2O_3 \cdot 3H_2O}$$

(iv) Although amino group is *o*, *p* – directing in aromatic electrophilic substitution reactions, aniline on nitration gives a substantial amount of *m*-nitroaniline:

Nitration is carried out in an acidic medium. In an acidic medium, aniline is protonated to give anilinium ion (which is meta-directing).

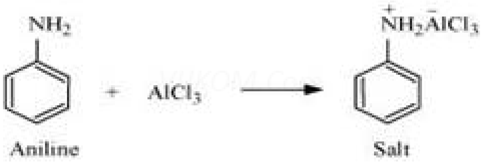


Aniline Anilinium ion *m*-Nitroaniline (47%)

For this reason, aniline on nitration gives a substantial amount of m-nitroaniline.

(v) Aniline does not undergo Friedel-Crafts reaction:

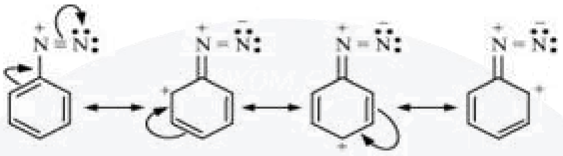
A Friedel-Crafts reaction is carried out in the presence of $AlCl_3$. But $AlCl_3$ is acidic in nature, while aniline is a strong base. Thus, aniline reacts with $AlCl_3$ to form a salt (as shown in the following equation).



Due to the positive charge on the N-atom, electrophilic substitution in the benzene ring is deactivated. Hence, aniline does not undergo the Friedel-Crafts reaction.

(vi) Diazonium salts of aromatic amines are more stable than those of aliphatic amines:

The diazonium ion undergoes resonance as shown below:



This resonance accounts for the stability of the diazonium ion. Hence, diazonium salts of aromatic amines are more stable than those of aliphatic amines.

(vii) Gabriel phthalimide synthesis is preferred for synthesising primary amines:

Gabriel phthalimide synthesis results in the formation of amine only. 2° or 3° amines are not formed in this synthesis. Thus, a pure 1° amine can be obtained. Therefore, Gabriel phthalimide synthesis is preferred for synthesizing primary amines.

7. **(i)** In $C_2H_5NH_2$, only one $–C_2H_5$ group is present while in $(C_2H_5)_2$ NH, two $–C_2H_5$ groups are present. Thus, the +I effect is more in $(C_2H_5)_2$ NH than in $C_2H_5NH_2$. Therefore, the electron density over the N-atom is more in $(C_2H_5)_2$ NH than in $C_2H_5NH_2$. Hence, $(C_2H_5)_2$ NH is more basic than $C_2H_5NH_2$.

Also, both $C_6H_5NHCH_3$ and $C_2H_5NH_2$ are less basic than $(C_2H_5)_2$ NH and $C_2H_5NH_2$ due to the delocalization of the lone pair in the former two. Further, among $C_2H_5NHCH_3$ and $C_2H_5NH_2$, the former will be more basic due to the +T effect of $–CH_3$ group. Hence, the order of increasing basicity of the given compounds is as follows:

$$C_6H_5NH_2 < C_6H_5NHCH_3 < C_2H_5NH_2 < (C_2H_5)_2NH$$

We know that the higher the basic strength, the lower is the p*Kb* values.

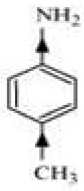
$$C_6H_5NH_2 < C_6H_5NHCH_3 < C_2H_5NH_2 < (C_2H_5)_2NH$$

(ii) $C_6H_5N(CH_3)_2$ is more basic than $C_2H_5NH_2$ due to the presence of the +I effect of two $–CH_3$ groups in $C_6H_5N(CH_3)_2$. Further, CH_3NH_2 contains one $–CH_3$ group while $(C_2H_5)_2$ NH contains two $–C_2H_5$ groups. Thus, $(C_2H_5)_2$ NH is more basic than $C_2H_5NH_2$.

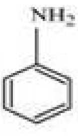
Now, $C_2H_5N(CH_3)_2$ is less basic than CH_3NH_2 because of the-R effect of $–C_6H_5$ group. Hence, the increasing order of the basic strengths of the given compounds is as follows:

$$C_6H_5NH_2 < C_6H_5N(CH_3)_2 < CH_3NH_2 < (C_2H_5)_2NH$$

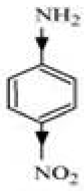
(iii) (a)



p-Toluidine



Aniline



p-Nitroaniline

In *p*-toluidine, the presence of electron-donating $–CH_3$ group increases the electron density on the N-atom.

Thus, *p*-toluidine is more basic than aniline.

On the other hand, the presence of electron-withdrawing $–NO_2$ group decreases the electron density over the N-atom in *p*-nitroaniline. Thus, *p*-nitroaniline is less basic than aniline. Hence, the increasing order of the basic strengths of the given compounds is as follows: *p*-Nitroaniline< Aniline <*p*-Toluidine

(b) $C_6H_5NHCH_3$ is more basic than $C_6H_5NH_2$ due to the presence of electron-donating $–CH_3$ group in $C_6H_5NHCH_3$.

Again, in $C_6H_5NHCH_3$, $– C_6H_5$ group is directly attached to the N-atom. However, it is not so in $C_6H_5NH_2NH_2$. Thus, in $C_6H_5NHCH_3$, the -R effect of $– C_6H_5$ group decreases the electron density over the N-atom. Therefore, $C_6H_5NHCH_3$ is more basic than $C_6H_5NHCH_3$.

Hence, the increasing order of the basic strengths of the given compounds is as follows:

$$C_6H_5NH_2 < C_6H_5NHCH_3 < C_6H_5NH_2NH_2$$

(iv) In the gas phase, there is no solvation effect. As a result, the basic strength mainly depends upon the +I effect. The higher the +I effect, the stronger is the base. Also, the greater the number of alkyl groups, the higher is the +I effect. Therefore, the given compounds can be arranged in the decreasing order of their basic strengths in the gas phase as follows:

$$(C_2H_5)_3\ N > (C_2H_5)_3\ NH > C_2H_5NH_2 > NH_3$$

(v) The boiling points of compounds depend on the extent of H-bonding present in that compound. The more extensive the H-bonding in the compound, the higher is the boiling point. $(CH_3)_2$ NH contains only one H-atom whereas $C_2H_5NH_2$ contains two H-atoms. Then, $C_2H_5NH_2$ undergoes more extensive H-bonding than $(CH_3)_2$ NH. Hence, the boiling point of $C_2H_5NH_2$ is higher than that of $(CH_3)_2$ NH.

Further, O is more electronegative than N. Thus, C_2H_5OH forms stronger H-bonds than $C_2H_5NH_2$. As a result, the boiling point of C_2H_5OH is higher than that of $C_2H_5NH_2$ and $(CH_3)_2$ NH.

Now, the given compounds can be arranged in the increasing order of their boiling points as follows:

$$(CH_3)_2\ NH < C_2H_5NH_2 < C_2H_5OH$$

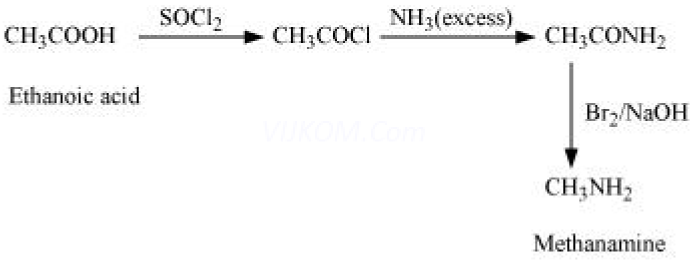
(vi) The more extensive the H-bonding, the higher is the solubility. $C_2H_5NH_2$ contains two H-atoms whereas $(C_2H_5)\ _2NH$ contains only one H-atom. Thus, $C_2H_5NH_2$ undergoes more extensive H-bonding than $(C_2H_5)_2NH$. Hence, the solubility in water of $C_2H_5NH_2$ is more than that of $(C_2H_5)_2$ NH.

Further, the solubility of amines decreases with increase in the molecular mass. This is because the molecular mass of amines increases with an increase in the size of the hydrophobic part. The molecular mass of $C_2H_5NH_2$ is greater than that of $C_2H_5NH_2$ and $(C_2H_5)_2NH$.

Hence, the increasing order of their solubility in water is as follows:

$$C_6H_5NH_2 < (C_2H_5)_2\ NH < C_2H_5NH_2$$

8. **(i)**



(ii)

$$\begin{tikzcd}
\begin{array}{c}C_5H_{11}CN\\ \text{Hexanenitrile}\end{array} \arrow[r, "H^+/H_2O"] & C_5H_{11}-COOH \arrow[r, "SOCl_2"] & C_5H_{11}-COCl \arrow[d, "NH_3(\text{excess})"] \\
 & \begin{array}{c}C_5H_{11}-NH_2\\ \text{1-Aminopentane}\end{array} & C_5H_{11}-CONH_2 \arrow[l, "Br_2/KOH"']
\end{tikzcd}$$

(iii)

$$\begin{tikzcd}
\begin{array}{c}CH_3OH\\ \text{Methanol}\end{array} \arrow[r, "PCl_5"] & CH_3Cl \arrow[r, "\text{Ethanolic NaCN}"] & CH_3CN \arrow[d, "H^+/H_2O"] \\
 & & \begin{array}{c}CH_3COOH\\ \text{Ethanoic acid}\end{array}
\end{tikzcd}$$

(iv)

$$\begin{tikzcd}
\begin{array}{c}CH_3-CH_2-NH_2\\ \text{Ethanamine}\end{array} \arrow[r, "NaNO_2/HCl"] & {[CH_3-CH_2-\overset{+}{N_2}\overset{-}{Cl}]} \arrow[r, "H_2O"] & CH_3-CH_2-OH \arrow[d, "KMnO_4/H^+"] \\
\begin{array}{c}CH_3-NH_2\\ \text{Methanamine}\end{array} & CH_3CONH_2 \arrow[l, "Br_2/NaOH"'] & CH_3COOH \arrow[l, "NH_3\ (\text{excess})"', "\Delta"]
\end{tikzcd}$$

(v)

$$\begin{tikzcd}
\begin{array}{c}CH_3COOH\\ \text{Ethanoic acid}\end{array} \arrow[r, "\text{(i) } LiAlH_4/\text{ether}", "\text{(ii) } H_3O^+"'] & CH_3CH_2OH \arrow[r, "PCl_5"] & CH_3CH_2Cl \arrow[d, "\begin{array}{l}\text{Ethanolic}\\ \text{NaCN}\end{array}"] \\
 & \begin{array}{c}CH_3CH_2COOH\\ \text{Propanoic acid}\end{array} & CH_3CH_2CN \arrow[l, "H^+/H_2O"']
\end{tikzcd}$$

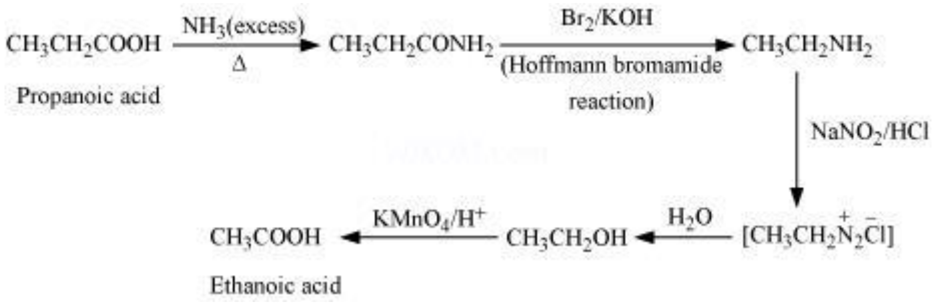
(vi)

$$\begin{tikzcd}
\begin{array}{c}CH_3-NH_2\\ \text{Methanamine}\end{array} \arrow[r, "NaNO_2/HCl"] & {[CH_3-\overset{+}{N_2}\overset{-}{Cl}]} \arrow[r, "H_2O"] & CH_3OH \arrow[d, "PCl_5"] \\
\begin{array}{c}CH_3CH_2NH_2\\ \text{Ethanamine}\end{array} & CH_3CN \arrow[l, "H_2/Ni"', "Na(Hg)/C_2H_5OH"] & CH_3Cl \arrow[l, "\text{Ethanolic NaCN}"']
\end{tikzcd}$$

(vii)

$$\begin{tikzcd}
\begin{array}{c}CH_3-NO_2\\ \text{Nitromethane}\end{array} \arrow[r, "Sn/HCl"] & CH_3-NH_2 \arrow[r, "CHCl_3/KOH/\Delta", "\begin{array}{l}\text{(Carbylamine}\\ \text{reaction)}\end{array}"'] & CH_3-NC \arrow[d, "Na/C_2H_5OH"] \\
 & & \begin{array}{c}CH_3-NH-CH_3\\ \text{Dimethylamine}\end{array}
\end{tikzcd}$$

(viii)



Assertion and Reason Answers-

1. (a) Assertion and reason both are correct statements and reason is correct explanation for assertion.

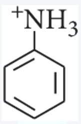
Explanation:

Ortho effect is a consequence of steric and electronic factors.

2. (d) Assertion is wrong statement but reason is correct statement.

Explanation:

In strongly acidic medium, aniline gets protonated and so the lone pair of electrons is not available to produce +E or + M effects. On the other hand, the −N+H3−N+H3 group exerts strong -I effect and thus it causes the deactivation of the ring.



Case Study Answers-

1. **Answer :**

(i) (d) Azo dye test.

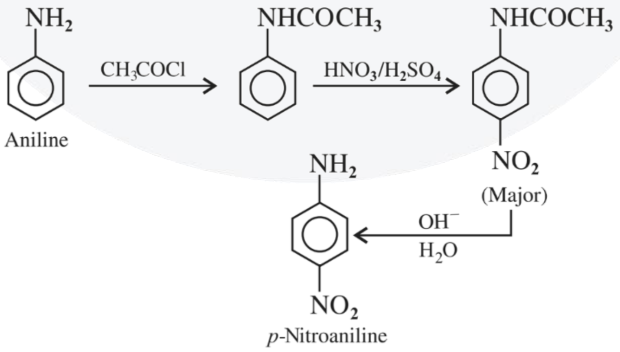
(ii) (a) Aniline.

Explanation:

Aromatic primary amines give dye test.

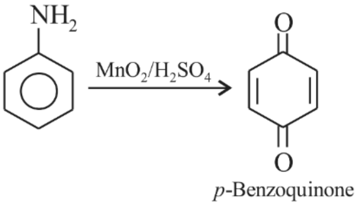
(iii) (c) p-nitroaniline.

Explanation:



(iv) (c) p-benzoquinone.

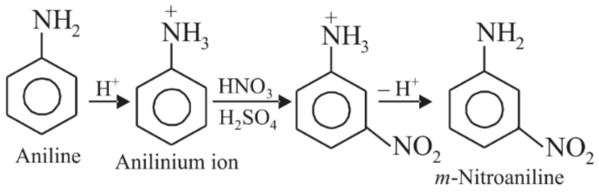
Explanation:



(v) (b) m-nitroaniline.

Explanation:

In acidic medium aniline gets protonated to anilinium ion which is meta-directing.



2. Answer :

(i) (d) Dimethyl amine.

Explanation:

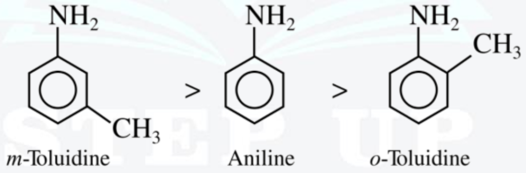
The increasing order of basicity of the given compounds is $(CH_3)_2NH > CH_3NH_2 > (CH_3)_3N > C_6H_5NH_2$. Due to the +I effect of alkyl groups, the electron density on nitrogen increases and thus, the availability of the lone pair of electrons to proton increases and hence, the basicity of amines also increases. So, aliphatic amines are more basic than aniline. In case of tertiary amine $(CH_3)_3N$, the covering of alkyl groups over nitrogen atom from all sides makes the approach and bonding by a proton relatively difficult, hence the basicity decreases. Electron withdrawing groups decrease electron density on nitrogen atom and thereby decreasing basicity.

(ii) (d) o-toluidine < aniline < m-toluidine

Explanation:

In general, electron donating (+R) group which when present on benzene ring ($-NH_2$, -OR, -R, etc.) at the para position increases the basicity of aniline.

Ortho substituted anilines are weaker bases than aniline due to ortho effect.



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

Explanation:

In case of ethylamines, the combined effect of (c) inductive effect, steric effect and salvation effect gives the order of basic strength as

$$\underset{(2^\circ)}{(C_2H_5)_2NH} > \underset{(3^\circ)}{(C_2H_5)_3N} > \underset{(1^\circ)}{C_2H_5NH_2} > NH_3$$

(iv) (b) $(CH_3)_3N > (CH_3)_2NH > CH_3NH_2$

Explanation:

In non-aqueous solvents the basic strength of alkyl amines follows the order:

tertiary amines> secondary amines> primary amines.

(v) (c) Methylamine is a stronger base than ammonia.

Explanation:

Methyl amine is stronger base than ammonia due to electron releasing inductive effect of methyl group.

◆◆

Biomolecules 11

Introduction

In this Unit, Structures and functions of some of biomolecules will be discuss. The structure and functions of biomolecules inside the living being is studied in biochemistry. Living systems are made up of various complex biomolecules such as carbohydrates, proteins, enzymes, lipids, vitamins, hormones, nucleic acids and compounds for storage and exchange of energy such as ATP, etc.

Carbohydrates:

Classification of Carbohydrates

On the basis of their behaviour upon hydrolysis, carbohydrates can be divided into three main groups :

i. **Monosaccharides:** A carbohydrate which cannot be hydrolyzed into simpler unit of polyhydroxy aldehyde or ketone is called monosaccharide. About 20 monosaccharides are known to occur in nature. e.g., glucose, fructose, ribose etc.

ii. **Oligosaccharides:** A carbohydrate which upon hydrolysis yields 2–10 unit of monosaccharide is called oligosaccharide. They are further classified as disaccharides, trisaccharides, etc., depending upon the number of monosaccharides, they provide on hydrolysis. For example, sucrose is a disaccharide which on hydrolysis yields two unit of monosaccharides i.e., glucose and fructose whereas raffinose is a trisaccharide which on hydrolysis yields three unit of monosaccharides i.e., glucose, fructose and galactose.

iii. **Polysaccharides:** A high molecular mass carbohydrate which upon hydrolysis yields a large number of monosaccharide units is called polysaccharide e.g., starch, cellulose, glycogen, gums, etc.

$$(C_6H_{10}O_5)n + nH_2O \longrightarrow nC_6H_{12}O_6$$

Sugar and non-sugars : In general monosaccharides and oligosaccharides, are crystalline solids, soluble in water and sweet to taste, are collectively known as **sugars**. The polysaccharides, on the other hand, are amorphous insoluble in water and tasteless, are known as **non-sugars.**

Reducing and non-reducing carbohydrates : The carbohydrates containing free aldehydic or ketonic group can reduce Fehling's solution and Tollen's reagent are known as **reducing** carbohydrates. All monosaccharides whether aldose or ketose are reducing in nature. The carbohydrates in which the reducing parts are not free cannot reduce Fehling's solution and Tollen's reagent are known as **non-reducing** carbohydrates. All polysaccharides like starch, cellulose, glycogen etc. are non-reducing carbohydrates.

i. Monosaccharides

If a monosaccharide contains an aldehyde group, it is known as an aldose and if it contains a keto group, it is known as a ketose.

Carbon atoms	General Term	Aldehyde	Ketone
3	Triose	Aldotriose	Ketotriose
4	Tetrose	Aldotetrose	Ketotetrose
5	Pentose	Aldopentose	Ketopentose
6	Hexose	Aldohexose	Ketohexose
7	Heptose	Aldoheptose	Ketoheptose

Glucose

Glucose occurs in nature in free as well as in the combined forms. It is present in sweet fruits and honey. Ripe grapes contain ~20% of glucose.

Preparation of Glucose

1. **From Sucrose (Cane Sugar)**: When sucrose is boiled with dilute HCl or H_2SO_4 in alcoholic solution, glucose and fructose are obtained in equimolar proportion.

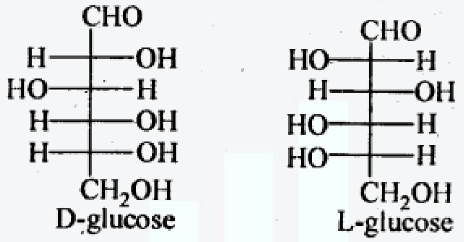
$$C_{12}H_{22}O_{11} + H_2O \longrightarrow C_6H_{12}O_6 + C_6H_{12}O_6$$

2. **From Starch :** When starch is boiled with dilute H_2SO_4 at 393 K under pressure, glucose is obtained. This is the commercial method for the preparation of glucose.

$$(C_6H_{10}O_5)n + nH_2O \longrightarrow nC_6H_{12}O_6$$

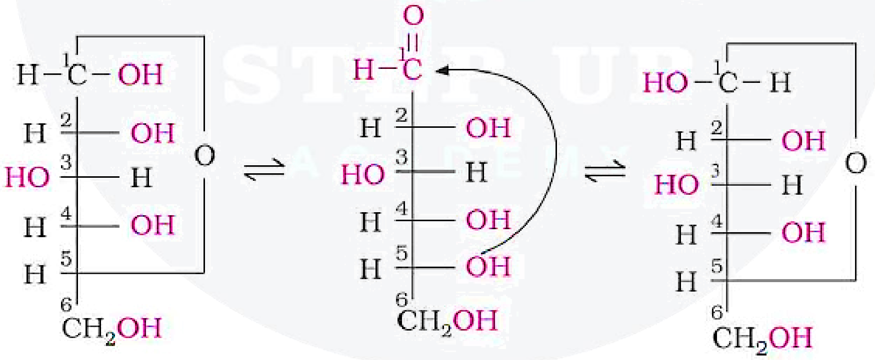
Structure of Glucose

Glucose is an aldohexose and is the monomer of many larger carbohydrates like starch, cellulose etc. It is the most abundant organic compound on the Earth.



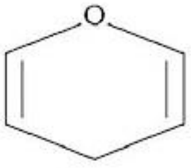
Cyclic Structure of Glucose

It was proposed that glucose can form a six-membered ring in which –OH at C-5 can add to the –CHO group and can form a cyclic hemiacetal structure. This explains the absence of –CHO group and also the existence of glucose in α and β-anomeric forms as

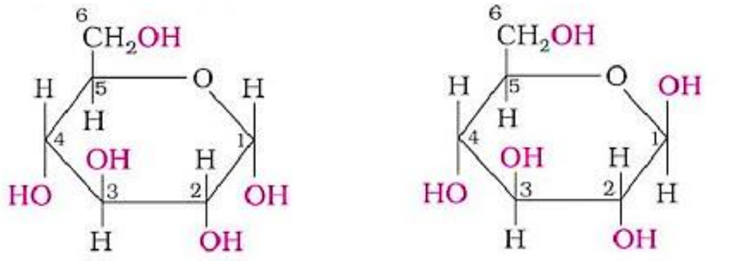


α – D – (+) – Glucose β – D– (+) – Glucose

The two cyclic hemiacetal forms of glucose differ only in the configuration of the hydroxyl group at C-1, called anomeric carbon and the corresponding α and β-forms are called anomers. It should be noted that α and β-forms of glucose are not mirror images of each other, hence are not enantiomers.



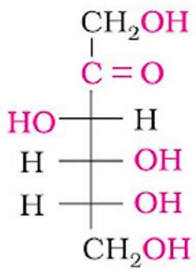
Pyran



α – D – (+) – Glucopyranose β – D – (+) – Glucopyranose

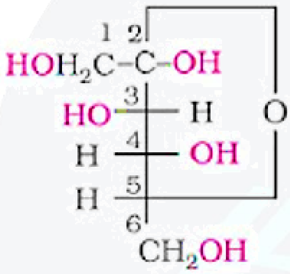
Fructose

Fructose is an important ketohexose. It is obtained by the hydrolysis of sucrose. On the basis of molecular weight determination, elemental analysis and various reaction its molecular formula is found to be $C_6H_{12}O_6$ and open chain structure of it can be written as

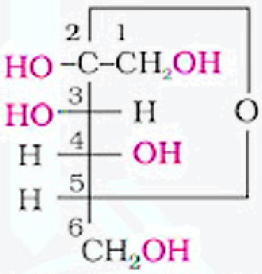


D-(—)-Fructose

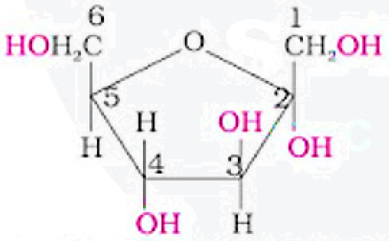
Fructose also exists in two cyclic forms like glucose i.e., α-D-(–) - fructose and β-D- (–) - fructose. The five membered cyclic structure of fructose is formed by the involvement of –OH at C-5 and carbonyl group. The five-membered ring of fructose is named as furanose with analogy to the compound furan.



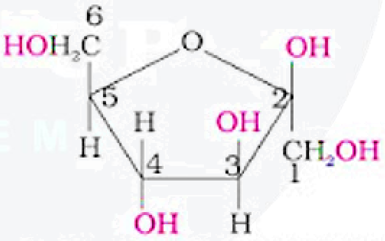
α – D – (–) – Fructofuranose



β – D – (–) – Fructofuranose



α – D – (–) – Fructofuranose



β – D – (–) – Fructofuranose

ii. **Disaccharides**

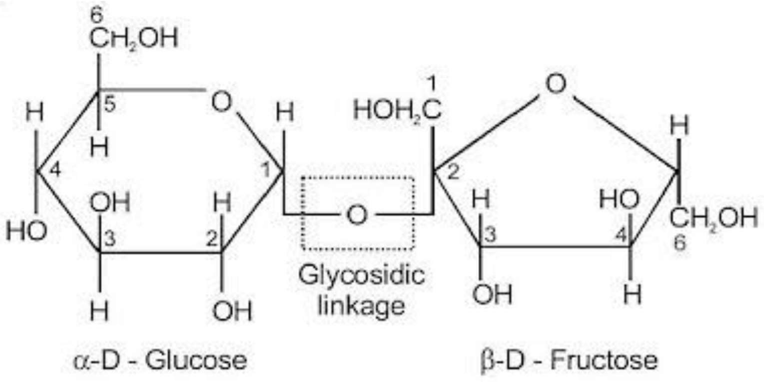
The disaccharides are composed of two units of monosaccharides. On hydrolysis with dilute acids or specific enzymes they give the corresponding monomers.

$$C_{12}H_{22}O_{11} + H_2O \longrightarrow C_6H_{12}O_6 + C_6H_{12}O_6$$

In disaccharides the two monosaccharides units are joined together by an oxide linkage formed by the loss of a water molecule and the linkage is known as glycosidic linkage.

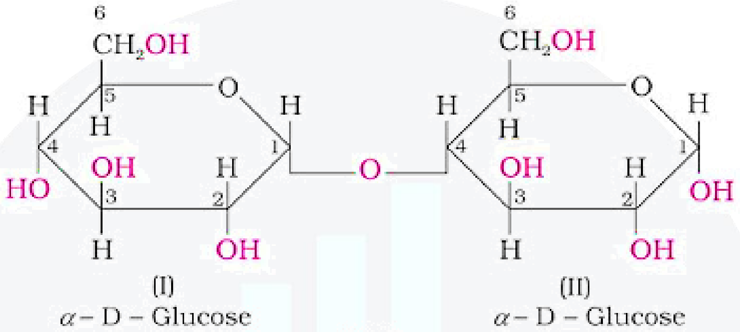
a) Sucrose

Sucrose is formed by the glycosidic linkage between C-1 of α-D-(+)-glucose and C-2 of β-D-(–) fructose:



b) Maltose

Maltose is formed by the glycosidic linkage between C-1 of one glucose unit to the C-4 of another glucose unit.



Maltose

c) Lactose

Lactose is found in milk so it is also known as milk sugar. It is formed by the glycosidic linkage between C-1 of α-D-galactose unit and C-4 of β-D-glucose unit. Lactose is a reducing sugar.

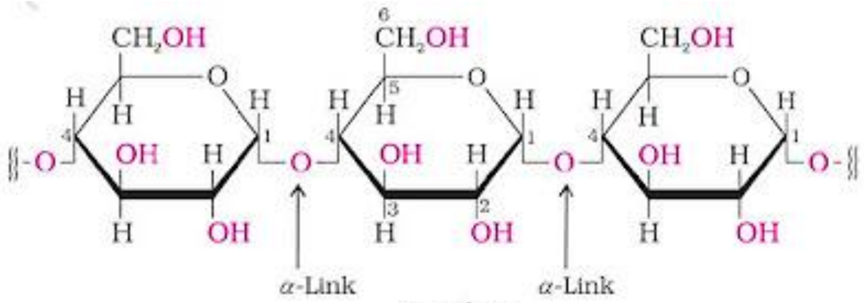
iii. <u>**Polysaccharides**</u>

Polysaccharides are long chain polymer of monosaccharides joined together by glycosidic linkages. For example, starch, cellulose, glycogen etc. They mainly act as the food storage or structural materials.

Starch $(C_6H_{10}O_5)n$

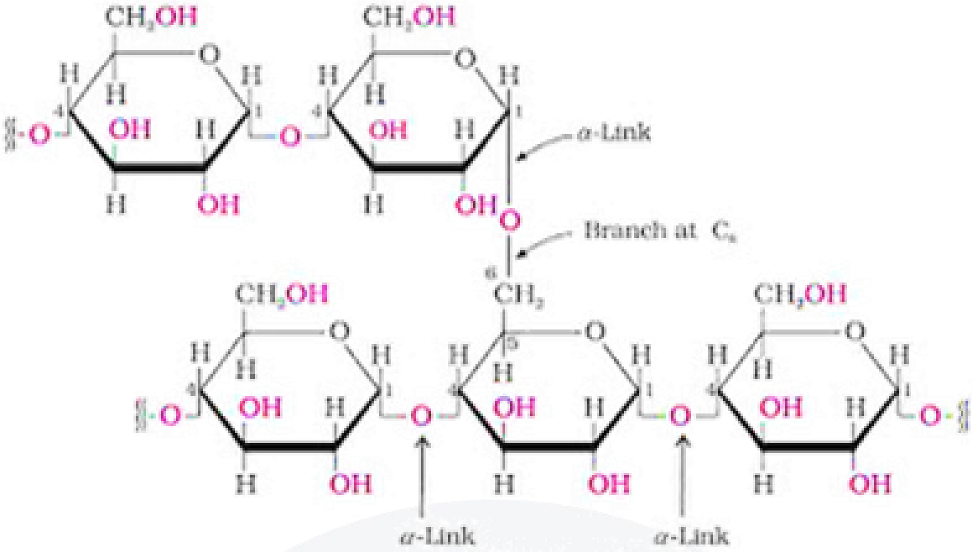
Starch is the main storage polysaccharide of plants. High content of starch is found in cereals, roots, tubers and some vegetables. Starch is a polymer of α-D-(+) Glucose coming of two components namely Amylose and Amylopectin.

Amylose is water soluble component, which constitutes about 15 - 20% of starch. It is a straight chain polysaccharide containing α-D-(+)-glucose units joined together by β-glycosidic linkage involving C-1 of one glucose unit and C-4 of the next.



Amylose

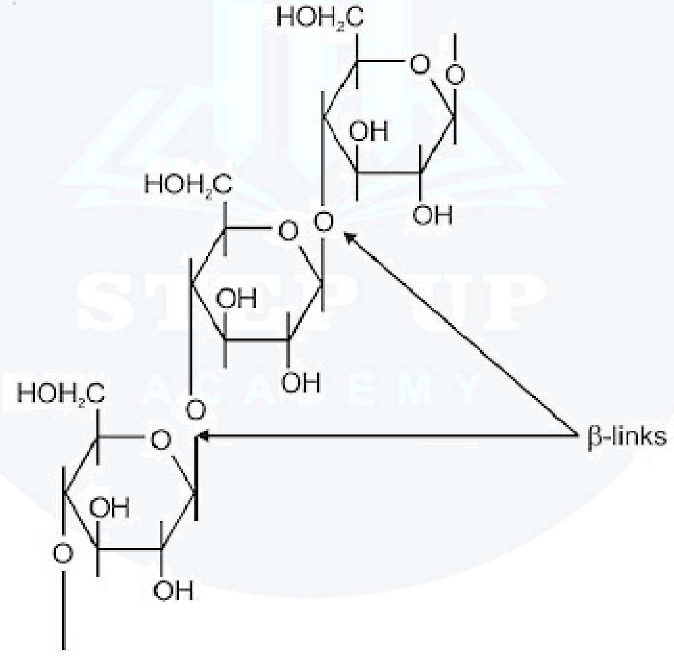
Amylopectin is a branched chain polysaccharide insoluble in water. It constitutes about 80 – 85% starch. It is a branched chain polymer of α-D-glucose units in which chain is formed by C-1 - C-4 glycosidic linkage whereas branching occurs by C-1 – C-6 glycosidic linkage.



Amylopectin

Cellulose

Cellulose is a straight chain polysaccharide composed of only β-D-glucose units. In cellulose there is β-glycosidic linkages between C-1 of one glucose unit and C-4 of the next glucose unit. Cellulose occurs mainly in plants and it is the most abundant organic substance in plant kingdom.



Glycogen

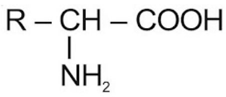
Its structure is similar to amylopectin with more branching than in amylopectin. It is also known as animal starch. In body, carbohydrates are stored as glycogen and when the body needs glucose, enzymes break the glycogen down to glucose. **Glycogen** is present in liver, muscle and brain.

Note: Carbohydrates are essential for life in both plants and animals. Carbohydrates are stored in plant as starch and in animals as glycogen.

Proteins:

Proteins are high molecular mass complex biopolymer of α-amino acids present in all living cells. They occur in every part of the body and form the fundamental basis of structure and functions of life. The term **protein** is derived from the Greek word "proteios" which means of prime importance. Proteins are the most abundant biomolecules of the living system. Chief sources of proteins are milk, cheese, pulses, peanuts, fish etc.

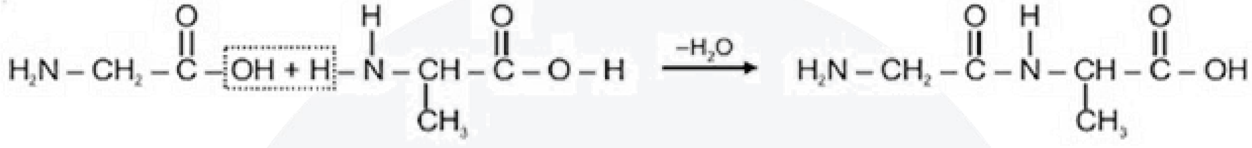
Amino Acids: The compound containing –NH_2 and –COOH functional groups are known as amino acid, depending upon the relative position of –NH_2 group with respect to –COOH group, amino acids are classified into α, β, γ, δ and so on amino acid. Hydrolysis of proteins gives only α-amino acids represented as



$$R-\underset{\displaystyle NH_2}{\underset{|}{CH}}-COOH$$

Essential and non-essential amino acids: The amino acids which cannot be synthesized in the body are known as essential amino acids which must be taken through diet. The amino acids, which can be synthesized in the body are known as non-essential amino acids.

Peptides: When amino acids are joined together by amide bonds, they form larger molecules called **peptides** and **proteins**.



Glycylalanine (Gly-Ala)

Polypeptide: A dipeptide contains two amino acids linked by one peptide linkage, a tripeptide contains three amino acids linked by two peptide linkages and so on. When number of such amino acids is more than ten, then the products are called **polypeptides**.

Classification of Protein

On the basis of molecular shape, proteins are classified into two types:

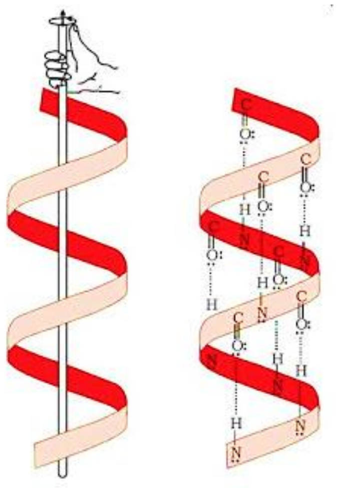
1) **Fibrous Proteins:** When the polypeptide chains run parallel and are held together by hydrogen and disulphide bonds, then fibre-like structure is formed, known as fibrous proteins. Such proteins are insoluble in water.

   For example: Keratin, Myosin etc.

2) **Globular Proteins:** When the polypeptide chains coil around to give a spherical shape, the formation of globular protein takes place. Such proteins are usually soluble in water.

   For example: Insulin, Albumins etc.

Primary, Secondary, Tertiary & Quaternary Structures of Proteins:



1) **Primary Structure:** Proteins may have one or more polypeptide chains. Each polypeptide in a protein has amino acids linked with each in a specific sequence and it is this sequence of amino acids that is said to be the primary structure of that protein.

2) **Secondary Structure:** The secondary structure of protein refers to the shape in which a long polypeptide chain can exist. They are found to exist in two different types of structure namely α-helix and β-pleated sheet structure.

3) **Tertiary Structure :** The tertiary structure of proteins represents overall folding of the polypeptide chains i.e., further folding of secondary structure. It gives rise to two major molecular shapes namely fibrous and globular.

4) **Quaternary Structure :** Some of the proteins are composed of two or more polypeptide chains referred to as sub units. The spatial arrangement of these subunits with respect to each other is known as quaternary structure.

Denaturation of Proteins : The loss in biological activity of a protein due to unfolding of globules and uncoiling of helix is called denaturation of protein. During denaturation secondary and tertiary structures are destroyed but primary structure remains intact. The coagulation of egg white on boiling is a common example of denaturation.

Enzymes:

Colloidal solution of protein which works as biological catalyst is known as enzyme. All enzymes are globular proteins. Zymase, Invertase, Maltase, Lactase, Emulsin, Urease, Pepsin, Trypsin, α-Amylase etc are the example of **enzyme**.

Note : The enzymes work best at an optimum temperature range of 298 K to 313 K. Their activity decreases with decrease or increase in temperature and stops at 273 K.

Properties of enzymes

- Enzymes are required only in small amounts.
- They are highly specific.
- Enzymes are efficient catalyst: they speed up reaction.
- They work at optimum pH, at optimum temperature.
- Their mechanism is controlled by various mechanisms and stopped by various organic and inorganic compounds.
- The action of enzymes follows lock and key mechanism .however enzyme action is inhibited by certain organic molecules called inhibitors.

It is of two types:

- **Cofactor:** The prosthetic group which is covalently attached with the enzyme molecule is known as cofactor.
- **Coenzyme:** The prosthetic group which get attached to the enzyme at the time of a reaction is known as coenzyme.

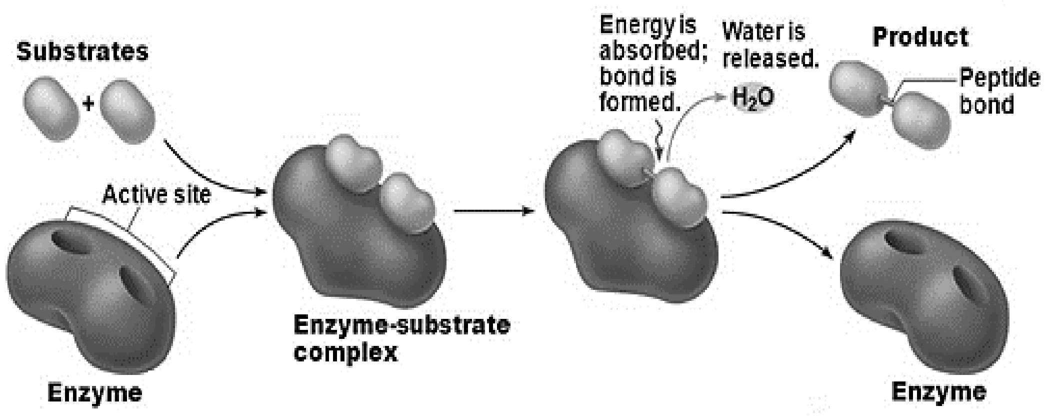
Nomenclature of Enzymes

Enzymes are usually named by adding the suffix 'ase' to the root name of the substrate, e.g., urease, maltase, invertase, etc.

Mechanism of Enzyme Action

- There is a lock and key arrangement between the an enzyme and a substrate.
- Substrates bind at active site, temporarily forming an enzyme-substrate (E-S) complex.
- The E-S complex undergoes internal rearrangements that form the product.
- The enzyme gets regenerated for the next molecule of the substrate.

Mechanism of enzyme action



Vitamins:

Vitamins are organic compounds which are essential for normal growth of life for animals, some bacteria and micro organism. Vitamins are not synthesized by animals (except vitamin D). Vitamins are supplied to the organism through food. They are essential dietary factor.

- Vitamins are a group of organic compounds which are essential for normal growth and nutrition and are required in very small amounts for maintaining optimum growth and a good health.
- Their absence causes specific deficiency diseases.
- Most of the vitamins cannot be synthesised in our body but plants can synthesise almost all of them.
- Vitamin D is an exception because it can be made in the skin from exposure to sunlight.

Classification of Vitamins

On the basis of solubility in water, vitamins are classified into the following two types:

- Fat soluble vitamins: Vitamins A, D, E and K are oil soluble.
- Water soluble vitamins: The group includes Vitamins B and C. These are stored in much lesser amounts in the cells.

Note: Vitamin H (Biotin) is an exception, since it is neither soluble in water nor in fat.

Some important Vitamins, their Sources and their Deficiency Diseases are dictated in the table given below

Name of Vitamin	Important Sources	Deficiency Diseases
Vitamin A	Fish liver oil, Milk, butter, egg yolk, green and yellow vegetables.	Night blindness, Xerophthalmia (hardening of cornea of eye).
Vitamin B_1	Yeast, milk, green vegetables, cereals, fruits, egg yolk.	Beriberi (loss of appetite, retarded growth)
Vitamin B_2	Egg yolk, liver, milk, green leafy vegetables.	Cracked lips, sore tongue, digestive disorders and burning sensation of the skin.
Vitamin B_6	Milk, egg yolk, cereals, yeast, legumes.	Nervous disturbances and convulsions.
Vitamin B_{12}	Meat, fish, kidney, eggs.	Pernicious anaemia (RBC deficient in haemoglobin)
Vitamin C	Citrus fruits, amla and green leafy vegetables.	Scurvy (bleeding gums)
Vitamin D	Exposure to sunlight, fish and egg yolk	Rickets (bone deformities in children) and osteomalacia (soft bones and joint pain in adults)
Vitamin E	Milk, ghee, vegetable oils like wheat germ oil, sunflower oil, cotton seed oil.	Increased fragility of RBCs and muscular weakness
Vitamin H	Milk, yeast, liver, kidney.	Loss of hair, dermatitis.
Vitamin K	Green leafy vegetables, fish, meat, cereals.	Increased blood clotting time

Nucleic Acid:

The particles in nucleus of the cell, responsible for heredity are called chromosomes which are made up of proteins and another type of biomolecules called **nucleic acid.** These are natural biopolymers made of nucleotide units i.e., polynucleotides. **Nucleic acid** contain the elements carbon, oxygen, nitrogen and phosphorous.

Nucleic acids

- Nucleic acids are the polymers in which nucleotides are monomers. These are biomolecules present in nuclei of all living cells in the form of nucleoproteins .They are also called as polynucleotides .

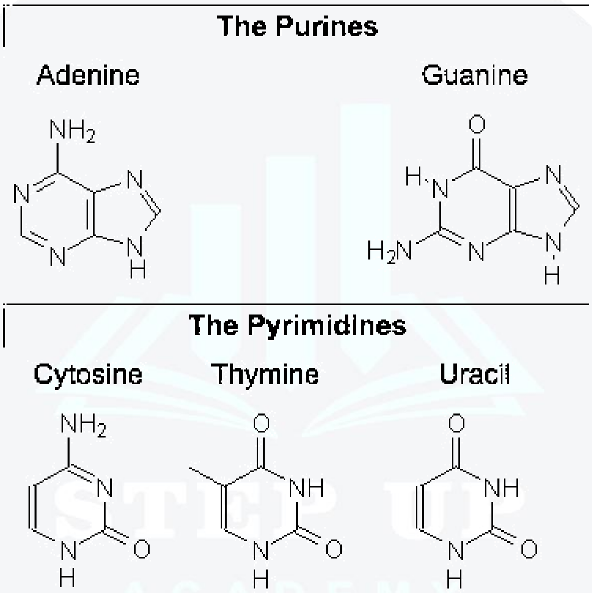
They help in the role of transmission of hereditary characters and synthesis of proteins.

Each nucleotide consists of 3 parts:

- A pentose sugar
- A nitrogenous base
- A phosphate group
- The nitrogenous base and a pentose sugar are called as nucleoside.

Nitrogenous bases are of two types: Purines and Pyrimidines

- Purines: adenine and guanine
- Pyrimidines: cytosine , thiamine and uracil



Please note that Purines and Pyrimidines are linked together by hydrogen bonds

- Adenine always bond with thiamine by double bond or vice versa.
- Cytosine always pairs with guanine by triple bond or vice versa.

Types of nucleic acids

- Deoxyribonucleic acid (DNA)
- Ribonucleic acid (RNA)

DNA

- It occurs in nucleus of cell. It has double stranded helical structure

DNA contains:

- Deoxyribose sugar
- Nitrogenous bases :
- Purines (adenine and guanine), Pyrimidines (thiamine and cytosine)
- A phosphate group

- It can undergo replication
- It helps in transfer of genetic information from parents to offspring

RNA

- It occurs in cytoplasm of cell

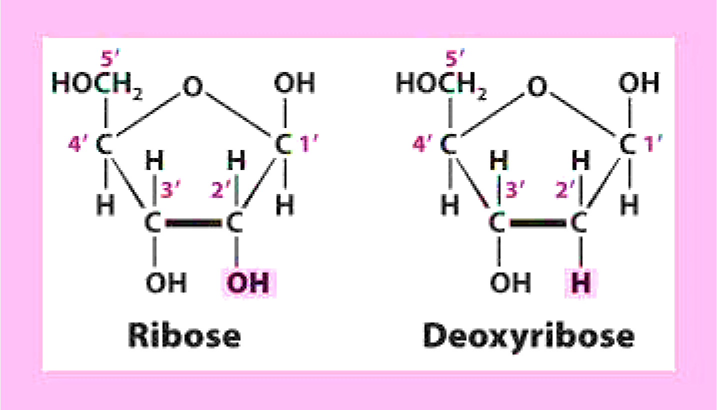
It consist of:

- Ribose sugar
- Nitrogenous base
- Purines: adenine and guanine
- Pyrimidines: cytosine and uracil
- A phosphate group
- It has a single strand helical structure
- It doesn't undergo replication
- It controls synthesis of proteins

The structure of deoxyribose and ribose sugar is given:

Structure of nucleic acids

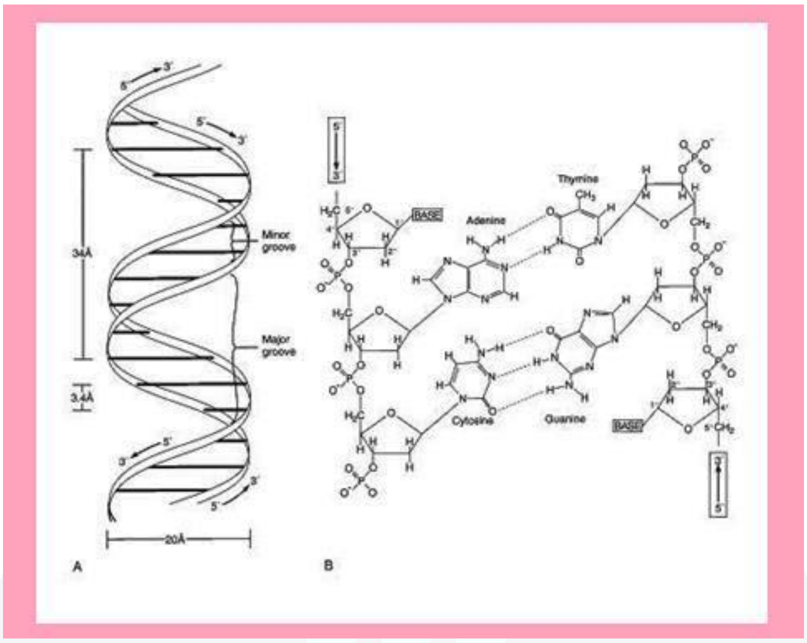
1. **Primary structure**
    - The nucleic acids are formed by the condensation of thousands of molecules of nucleotides.
    - On hydrolysis the nucleotides produces phosphoric acid and nucleoside .it means nucleosides on hydrolyses form Purine and Pyrimidines base and sugar moiety.
    - A nucleic acid-- ^{NH_3}ànucleotides –$^{aq\ NH3}$à nucleosides + phosphoric acid –$^{dilute\ HCL}$--àPurines + Pyrimidines + sugar.
    - Nucleotides are building blocks of nucleic acids.
    - These nucleotides are linked together with one another in a particular sequence, phosphate groups forming bridges between C-5 of the sugar residue of the one nucleoside and C-3 of the sugar residue of the other nucleoside.
    - The manner in which the sugar, phosphate and bases are linked with one another in nucleic acids is known as primary structure of nucleic acids.



2. **Secondary structure:**
    - Watson and Crick explained the double helix structure of DNA. The nucleotides in each strand are connected by phosphate ester bond and bases of one strand by hydrogen bonds.
    - Adenine pairs with thiamine through two double hydrogen bonds whereas cytosine pairs with guanine by triple hydrogen bonds.

- The two strands of DNA are complementary to each other that is if one side there is Purine then on other side at same position Pyrimidine is present. For example if base sequence on strand is ACTCGCCA, then on the other strand the sequence will be complementary that is: TGAGCGGT

The primary and secondary structure is shown below:



Watson and Crick model of DNA

Functions of nucleic acids

- **Replication**: The genetic information of cell is contained in the sequence of bases A, T, C and G in DNA molecule .In the division of cell, DNA molecules replicate and makes exact copies of themselves so that each daughter cell will have DNA identical to that of the parent cell.
- **Protein synthesis: The** specific information coded on DNA has to be translated and expressed in the form of synthesis of specific proteins which performs various functions in the cell. This synthesis is done in two steps:
- Transcription and translation.
- **Gene and genetic code**: Each segment of DNA molecule that codes for specific protein or a polypeptide is known as The relationship between nucleotides triplets and the amino acids are called the genetic code .This is gene and genetic code.
- **Mutation**: It is a chemical change in DNA molecule, which leads to the synthesis of proteins with a changed amino acid sequence.
- These changes are caused by radiation, viruses or chemical agents.
- The majority of changes in DNA are replicated by special enzymes in the cell, but if there is failure to repair by the enzymes then it can cause mutation.

Hormones:

Hormones are molecules that act as intercellular messengers. These are produced by endocrine glands in the body and are poured directly in the blood stream which transports them to the site of action. Hormones have several functions in the body. They help to maintain the balance of biological activities in the body. **Testosterone** is the major sex hormone produced in males.

Class : 12th Chemistry
Chapter-14 : Biomolecules (Part_1)

Biomolecules

Nucleic Acid

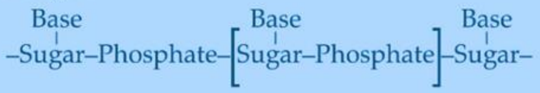
Chromosomes : Particles in nucleus responsible for heredity. Chromosomes are made up of proteins and nucleic acid.

Two types : Deoxyribonucleic acid (DNA), ribonucleic acid (RNA)

Composition : In DNA, sugar is β–D–2–deoxyribose whereas in RNA is β–D–ribose. DNA contains A,G,C,T whereas RNA has A,G,C,U.

Structure : –

Nucleoside : Formed by attachment of a base to 1′ of sugar′ Nucleotide : Formed by link to phosphoric acid at 5′ of sugar.



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

Types of RNA : m–RNA, r–RNA, t–RNA

Biological Functions :

- Chemical basis of heredity.
- Responsible for identity of different species of organisms.
- Nucleic acids are responsible for protein synthesis in cell.

DNA Fingerprint: Unique sequence bases on DNA

Proteins

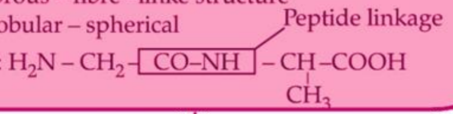
(Polymers of α–amino acids)

Amino acids contain $-NH_2$ and $-COOH$ group.

Classification:

- On the basis of relative number of $-NH_2$ and $-COOH$ group
  - (I) Neutral–equal number of $-NH_2$ and $-COOH$ group.
  - (ii) Basic – more number of $-NH_2$ than $-COOH$ group.
  - (iii) Acidic – more number of $-COOH$ than $-NH_2$ group.
- On the basis of place of synthesis
  - (i) Essential – cannot be synthesized in the body.
  - (ii) Non-essential – synthesized in the body.
- On the basis of shape
  - (I) Fibrous – fibre –linke structure
  - (ii) Globular – spherical

Structure :



$$H_2N-CH_2-\overset{\text{Peptide linkage}}{\boxed{CO-NH}}-\underset{CH_3}{CH}-COOH$$

Enzymes

Globular proteins specific for particular reaction and for particular substrate. Mechanism : Reduces the magnitude of activation energy

Denaturation of proteins:

When a protein in its native form is subjected to physical change, globules unfold, helix get uncoiled and protein loses its biological activity.

Class : 12th Chemistry
Chapter-14 : Biomolecules (Part_2)

Vitamins

Organic compounds required in diet in small amounts to perform specific biological functions for maintenance and growth.

Classification:

(i) Fat soluble : Soluble in fats and oils but insoluble in water. (vitamins A,D,E and K)

(ii) Water soluble : B group and vitamin C are soluble in water.

Biomolecules

Carbohydrates

- **Classification:**

(I) Monosaccharides : (Aldehyde group – aldose, keto group –ketose)

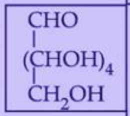
Glucose : Preparation :

(a) From sucrose : $\underset{\text{Sucrose}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow{H^+} \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Fructose}}{C_6H_{12}O_6}$

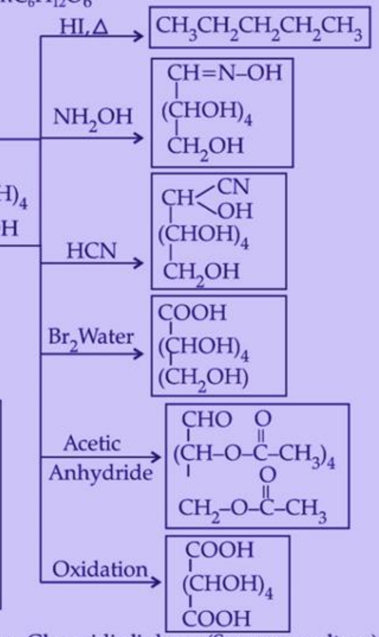
(b) From starch : $(C_6H_{10}O_5)n + nH_2O \xrightarrow[393K;\ 2\text{-}3\ atm]{H^+} nC_6H_{12}O_6$

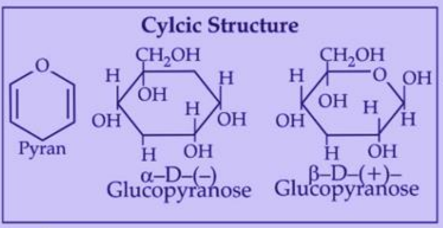
- **Structure:**

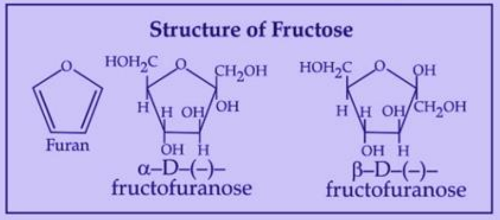
$CHO-(CHOH)_4-CH_2OH$



$CHO-(CHOH)_4-CH_2OH$







(ii) Disaccharides : Linkage between 2 monosaccharides– Glycosidic linkage (Sucrose, maltose)

(iii) Polysaccharides : Large number of monosaccharides units joined by glycosidic linkages.

(a) Starch : Polymer of α–glucose with two components amylase and amylopectin

(b) Cellulose

(c) Glycogen

Importance:

- Form a major portion of food.
- As storage molecules.
  Cellulose forms cell wall of bacteria
- Raw materials for industries like tex

Important Questions

Multiple choice questions-

1. The linkage which holds various amino acid units in primary structure of proteins is
   - (a) glycosidic linkage
   - (b) hydrogen bond
   - (c) peptide linkage
   - (d) ionic bond
2. Vitamin A is called
   - (a) Ascorbic acid
   - (b) Retinol
   - (c) Calciferol
   - (d) Tocoferol
3. The deficiency of vitamin B1 causes which disease?
   - (a) Beriberi
   - (b) Rickets
   - (c) Anaemia
   - (d) Xerosis
4. Deficiency of vitamin C causes
   - (a) Scurvy
   - (b) Rickets
   - (c) Anaemia
   - (d) None of these
5. An example of non-reducing sugar is
   - (a) Sucrose
   - (b) Lactose
   - (c) Maltose
   - (d) None
6. Which of the following is not an essential amino acid?
   - (a) Glycine
   - (b) Lysine
   - (c) Phenyl alanine
   - (d) Valine
7. Which of the following is a water-soluble vitamin?
   - (a) Vitamin E
   - (b) Vitamin K
   - (c) Vitamin B
   - (d) Vitamin A
8. Vitamin B1 is
   - (a) Riboflavin
   - (b) Cobalamin

- (c) Thiamine
- (d) Pyridoxine

9. Which is sweetest of the following:
   - (a) Sucrose
   - (b) Glucose
   - (c) Fructose
   - (d) Maltose
10. Rickets may be caused by the deficiency of which vitamin?
    - (a) Vitamin D
    - (b) Vitamin C
    - (c) Vitamin A
    - (d) Vitamin B

Very Short Question:

1. Give some examples of bimolecules
2. What are carbohydrates?
3. Give one example of each- Monosaccharide, disaccharide and polysaccharide
4. Which disaccharides are non – reducing sugars?
5. Classify the following as monosaccharides disaccharides and polysaccharides Glucose, Sucrose, maltose, ribose, glycogen, lactose, fructose.
6. What is the meaning of statement- Glucose is an aldohexose.
7. Why are polysaccharides considered non- sugars?
8. Give two examples of reducing sugars.
9. Which sugar is present in milk?
10. Name the reagents used to check the reducing nature of carbohydrates.

Short Questions:

1. What are the expected products of hydrolysis of lactose?
2. The melting points and solubility in water of amino acids are generally higher than that of the corresponding halo acids. Explain.
3. When RNA is hydrolysed, there is no relationship among the quantities of different bases obtained. What does this fact suggest about the structure of RNA?
4. What are monosaccharides?
5. What do you understand by the term glycosidic linkage?
6. What are the hydrolysis products of (i)sucrose and (ii)lactose?
7. What happens when D-glucose is treated with the following reagents?
8. Enumerate the reactions of D-glucose which cannot be explained by its open chain structure.
9. Differentiate between globular and fibrous proteins.
10. How do you explain the amphoteric behavior of amino acids?

Long Questions:

1. How do you explain the absence of aldehyde group in the pentaacetate of D-glucose?
2. What is the basic structural difference between starch and cellulose?
3. Define the following as related to proteins

4. What are the common types of secondary structure of proteins?
5. Write the important structural and functional differences between DNA and RNA.

Assertion and Reason Questions:

1. In these questions, a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following choices.

a) Assertion and reason both are correct statements and reason is correct explanation for assertion.
b) Assertion and reason both are correct statements but reason is not correct explanation for assertion.
c) Assertion is correct statement but reason is wrong statement.
d) Assertion is wrong statement but reason is correct statement.

Assertion: Uracil occurs in DNA.

Reason: DNA undergoes replication.

2. In these questions, a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following choices.

a) Assertion and reason both are correct statements and reason is correct explanation for assertion.
b) Assertion and reason both are correct statements but reason is not correct explanation for assertion.
c) Assertion is correct statement but reason is wrong statement.
d) Assertion is wrong statement but reason is correct statement.

Assertion: Cysteine can cross link peptide chains.

Reason: Amino acids are classified as essential and non-essential amino acids.

Case Study Questions:

1. Read the passage given below and answer the following questions:

When a protein in its native form, is subjected to physical changes like change in temperature or chemical changes like change in pH, the hydrogen bonds are disturbed. Due to this, globules unfold and helix get uncoiled and protein loses its biological activity. This is called denaturation of protein.

The denaturation causes change in secondary and tertiary structures but primary structures remains intact. Examples of denaturation of protein are coagulation of egg white on boiling, curdling of milk, formation of cheese when an acid is added to milk.

The following questions are multiple choice questions. Choose the most appropriate answer:

(i) Mark the wrong statement about denaturation of proteins.
  a) The primary structure of the protein does not change.
  b) Globular proteins are converted into fibrous proteins.
  c) Fibrous proteins are converted into globular proteins.
  d) The biological activity of the protein is destroyed.

(ii) Which structure(s) of proteins remains(s) intact during denaturation process?
  a) Both secondary and tertiary structures.
  b) Primary structure only.
  c) Secondary structure only.
  d) Tertiary structure only.

(iii) α-helix and β-pleated structures of proteins are classified as:
  a) Primary structure.
  b) Secondary structure.
  c) Tertiary structure.
  d) Quaternary structure.

(iv) Cheese is a:

a) Globular protein.

b) Conjugated protein.

c) Denatured protein.

d) Derived protein.

(v) Secondary structure of protein refers to:

a) Mainly denatured proteins and structure of prosthetic groups.

b) Three-dimensional structure, especially the bond between amino acid residues that are distant from each other in the polypeptide chain.

c) Linear sequence of amino acid residues in the polypeptide chain.

d) Regular folding patterns of continuous portions of the polypeptide chain.

2. Read the passage given below and answer the following questions:

Carbohydrates are polyhydroxy aldehydes and ketones and those compounds which on hydrolysis give such compounds are also carbohydrates. The carbohydrates which are not hydrolysed are called monosaccharides. Monosaccharides with aldehydic group are called aldose and those which free ketonic groups are called ketose. Carbohydrates are optically active. Number of optical isomers = 2^n

Where n = number of asymmetric carbons. Carbohydrates are mainly synthesised by plants during photosynthesis. The monosaccharides give the characteristic reactions of alcohols and carbonyl group (aldehydes and ketones). It has been found that these monosaccharides exist in the form of cyclic structures. In cyctization, the -OH groups (generally C_5 or C_4 in aldohexoses and C_5 or C_6 in ketohexoses) combine with the aldehyde or keto group. As a result, cyclic structures of five or six membered rings containing one oxygen atom are formed, e.g., glucose forms a ring structure. Glucose contains one aldehyde group, one IO alcoholic group and four 2° alcoholic groups in its open chain structure.

The following questions are multiple choice questions. Choose the most appropriate answer:

(i) First member of ketos sugar is:

a) Ketotriose.

b) Ketotetrose.

c) Ketopentose.

d) Ketohexose.

(ii) In $CH_2OHCHOHCHOHCHOHCHOHCHO$, the number of optical isomers will be:

a) 16

b) 8

c) 32

d) 4

(iii) Some statements are given below:

1. Glucose is aldohexose.
2. Naturally occurring glucose is dextrorotatory.
3. Glucose contains three chiral centres.
4. Glucose contains one 1° alcoholic group and four 2° alcoholic groups.

Among the above, correct statements are:

a) 1 and 2 only

b) 3 and 4 only

c) 1, 2 and 4 only

d) 1, 2, 3 and 4

(iv) Two hexoses fonn the same osazone, find the correct statement about these hexoses.

  a) Both of them must be aldoses.
  b) They are epimers at C-3.
  c) The carbon atoms I and 2 in both have the same configuration.
  d) The carbon atoms 3, 4 and 5 in both have the same configuration.

(v) Which of the following reactions of glucose can be explained only by its cyclic structure?

  a) Glucose forms cyanohydrin with HCN.
  b) Glucose reacts with hydroxylamine to form an oxime.
  c) Pentaacetate of glucose does not react with hydroxylamine.
  d) Glucose is oxidised by nitric acid to gluconic acid.

Answers key

MCQ answers:

1. Answer: (c) peptide linkage
2. Answer: (b) Retinol
3. Answer: (a) Beriberi
4. Answer: (a) Scurvy
5. Answer: (a) Sucrose
6. Answer: (a) Glycine
7. Answer: (c) Vitamin B
8. Answer: (c) Thiamine
9. Answer: (c) Fructose
10. Answer: (a) Vitamin D

Very Short Answers:

1. Examples of biomolecules –
   carbohydrates, proteins, Nucleic acids, Lipids, enzymes etc.
2. Carbohydrates are optically active polyhydroxy aldehydes or ketones or the compounds which produce such units on hydrolysis.
3. **Answer:**
   - Monosaccharide – Glucose, Fructose etc.
   - Disaccharide – Sucrose, maltose etc.
   - Polysaccharide – Cellulose, starch etc.
4. **Answer:** In disaccharides, if the reducing groups of monosaccharides, i.e. aldehydic or ketonic groups are bonded eg. In sucrose, these are non- reducing.
5. **Answer:**

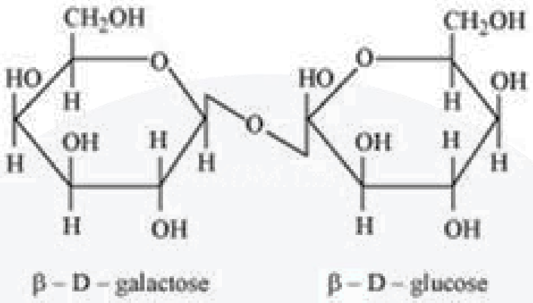
Monosaccharide	Disaccharides	Polysaccharides
Glucose	Sucrose	Glycogen
Fructose	Maltose	
Ribose	Lactose	

6. Glucose is an aldohexose means that it contains six carbon atoms and aldehyde group.
7. **Answer:** Polysaccharides are not sweet in taste & hence are called non – sugars.
8. **Answer:** Examples of reducing sugars: Maltose and Lactose.
9. In milk, lactose is present.
10. Tollen’s reagent and Fehlings solution can be used to check reducing nature of sugars.

Short Answers:

1. **Answer**

   Lactose is composed of β-D-galactose and β-D-glucose. Thus, on hydrolysis, it gives β-D-galactose and β-D-glucose.



Lactose

$$\underset{\text{Lactose}}{C_{12}H_{22}O_{11}} + H_2O \rightarrow \underset{\text{D-(+)-Glucose}}{C_6H_{12}O_6} + \underset{\text{D-(+)-Galactose}}{C_6H_{12}O_6}$$

2. **Answer:**

   Both acidic (carboxyl) as well as basic (amino) groups are present in the same molecule of amino acids. In aqueous solutions, the carboxyl group can lose a proton and the amino group can accept a proton, thus giving rise to a dipolar ion known as a zwitter ion.

   Due to this dipolar behaviour, they have strong electrostatic interactions within them and with water. But halo-acids do not exhibit such dipolar behaviour.

   For this reason, the melting points and the solubility of amino acids in water is higher than those of the corresponding halo-acids.

3. **Answer:**

   A DNA molecule is double-stranded in which the pairing of bases occurs. Adenine always pairs with thymine, while cytosine always pairs with guanine. Therefore, on hydrolysis of DNA, the quantity of adenine produced is equal to that of thymine and similarly, the quantity of cytosine is equal to that of guanine.

   But when RNA is hydrolyzed, there is no relationship among the quantities of the different bases obtained. Hence, RNA is single-stranded.

4. **Answer :**

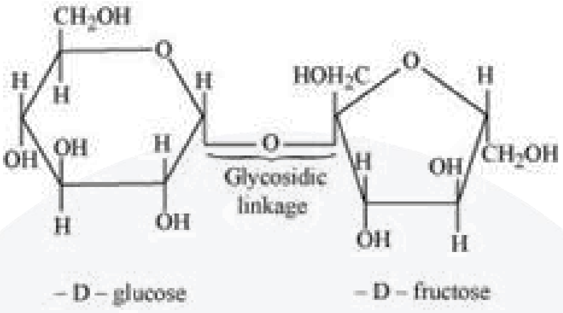
   Monosaccharides are carbohydrates that cannot be hydrolysed further to give simpler units of polyhydroxy aldehyde or ketone.

   Monosaccharides are classified on the bases of number of carbon atoms and the functional group present in them. Monosaccharides containing an aldehyde group are known as aldoses and those containing a keto group are known as ketoses. Monosaccharides are further classified as trioses, tetroses, pentoses, hexoses, and heptoses according to the number of carbon atomsthey contain. For example, a ketose containing 3 carbon atoms is called ketotriose and an aldose containing 3 carbon atoms is called aldotriose.

5. Answer

Glycosidic linkage refers to the linkage formed between two monosaccharide units through an oxygen atom by the loss of a water molecule.

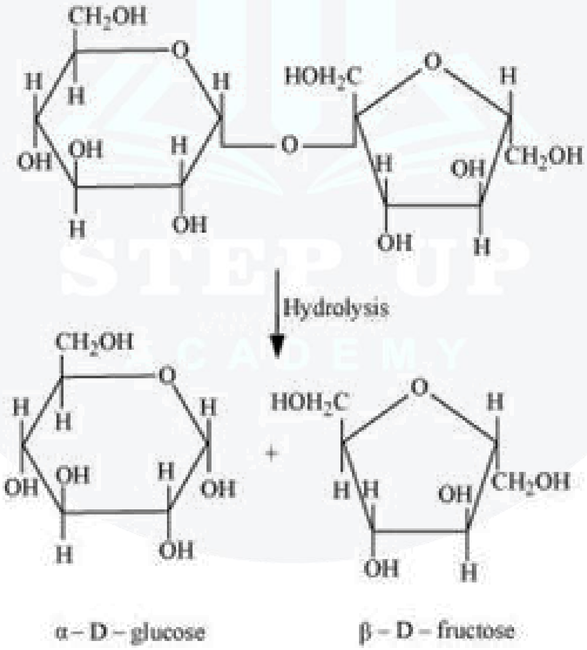
For example, in a sucrose molecule, two monosaccharide units, α-glucose and β-fructose, are joined together by a glycosidic linkage.



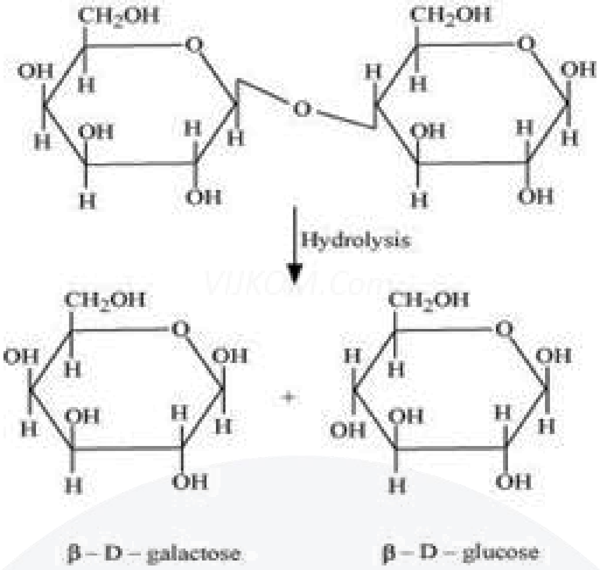
Surcose

6. Answer:

(i) On hydrolysis, sucrose gives one molecule of α-D glucose and one molecule of β-fructose.



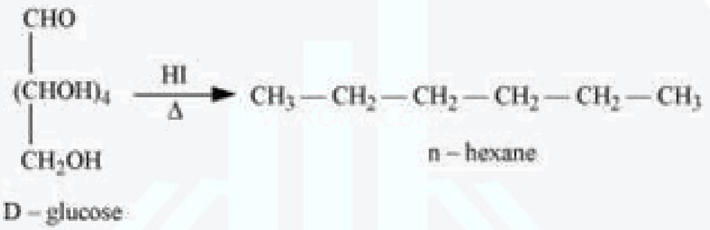
(ii) The hydrolysis of lactose gives β-galactose and β-glucose.



β – D – galactose β – D – glucose

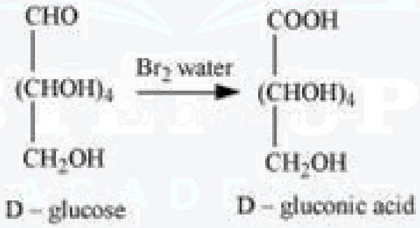
7. Answer:

(i) When D-glucose is heated with HI for a long time, n-hexane is formed.



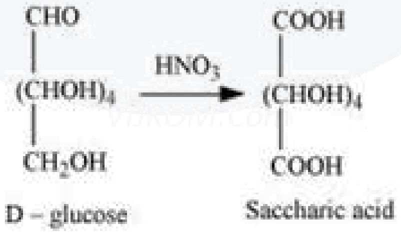
$$\underset{\text{D - glucose}}{\begin{array}{c}CHO\\|\\(CHOH)_4\\|\\CH_2OH\end{array}} \xrightarrow[\Delta]{HI} \underset{\text{n - hexane}}{CH_3-CH_2-CH_2-CH_2-CH_2-CH_3}$$

(ii) When D-glucose is treated with Br_2 water, D-gluconic acid is produced.



$$\underset{\text{D - glucose}}{\begin{array}{c}CHO\\|\\(CHOH)_4\\|\\CH_2OH\end{array}} \xrightarrow{Br_2\text{ water}} \underset{\text{D - gluconic acid}}{\begin{array}{c}COOH\\|\\(CHOH)_4\\|\\CH_2OH\end{array}}$$

(iii) On being treated with HNO_3, D-glucose get oxidised to give saccharic acid.



$$\underset{\text{D - glucose}}{\begin{array}{c}CHO\\|\\(CHOH)_4\\|\\CH_2OH\end{array}} \xrightarrow{HNO_3} \underset{\text{Saccharic acid}}{\begin{array}{c}COOH\\|\\(CHOH)_4\\|\\COOH\end{array}}$$

8. Answer :

(1) Aldehydes give 2, 4-DNP test, Schiff's test, and react with $NsHSO_4$ to form the hydrogen sulphite addition product. However, glucose does not undergo these reactions.

(2) The pentaacetate of glucose does not react with hydroxylamine. This indicates that a free -CHO group is absent from glucose.

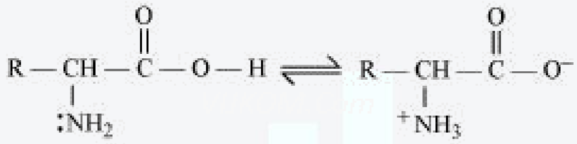
(3) Glucose exists in two crystalline forms – α and β. The ∝ form (m.p. = 419K) crystallises from a concentrated solution of glucose at 303 K and the β form (m.p = 423 K) crystallises from a hot and saturated aqueous solution at 371 K. This behavior cannot be explained by the open chain structure of glucose.

9. Answer :

Fibrous protein	Globular protein
1. It is a fibre-like structure formed by the polypeptide chain. These proteins are held together by strong hydrogen and disulphide bonds.	1. The polypeptide chain in this protein is folded around itself, giving rise to a spherical structure.
2. It is usually insoluble in water.	2. It is usually soluble in water.
3. Fibrous proteins are usually used for structural purposes. For example, keratin is present in nails and hair; collagen in tendons; and myosin in muscles.	3. All enzymes are globular proteins. Some hormones such as insulin are also globular proteins.

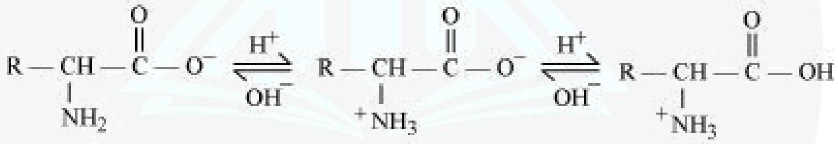
10. Answer:

In aqueous solution, the carboxyl group of an amino acid can lose a proton and the amino group can accept a proton to give a dipolar ion known as zwitter ion.



Zwitter ion

Therefore, in zwitter ionic form, the amino acid can act both as an acid and as a base.

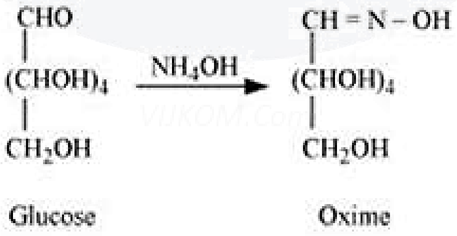


Thus, amino acids show amphoteric behaviour.

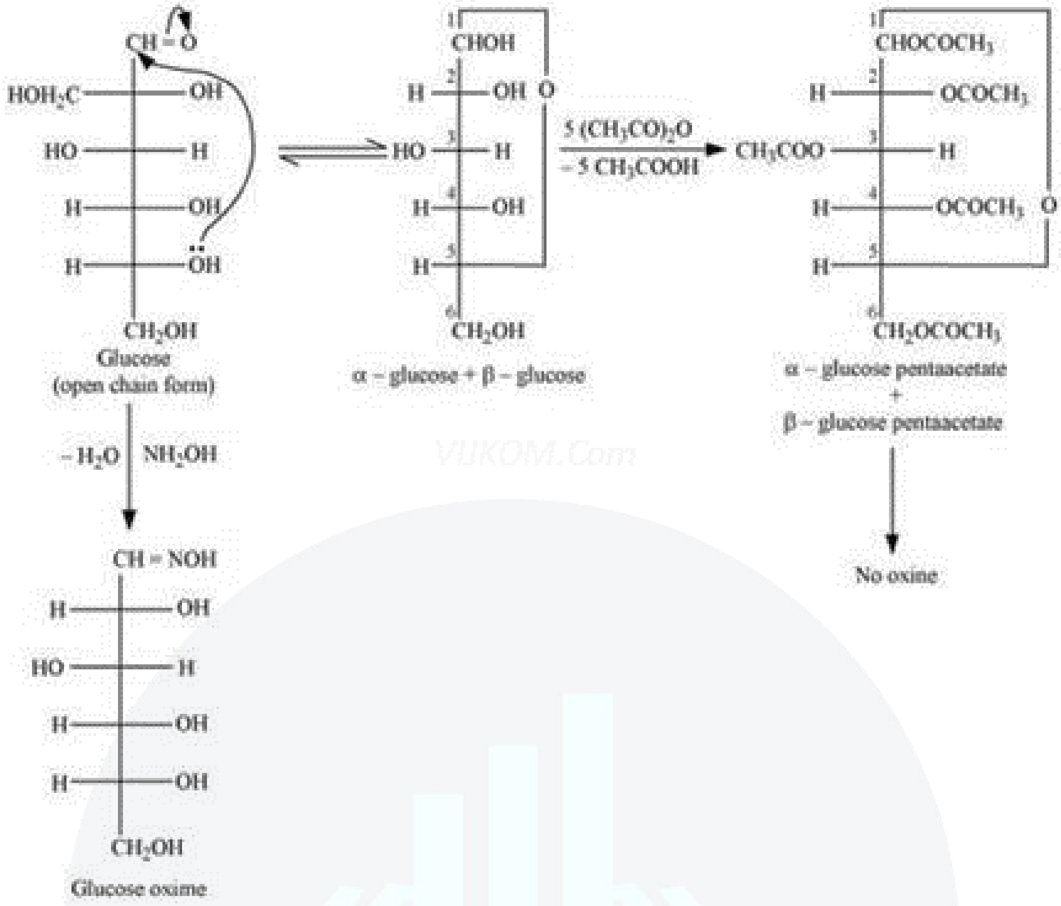
Long Answers:

1. Answer:

D-glucose reacts with hydroxylamine(NH_2OH) to form an oxime because of the presence of aldehydic (-CHO) group or carbonyl carbon. This happens as the cyclic structure of glucose forms an open chain structure in an aqueous medium, which then reacts with NH_2OH to give an oxime.

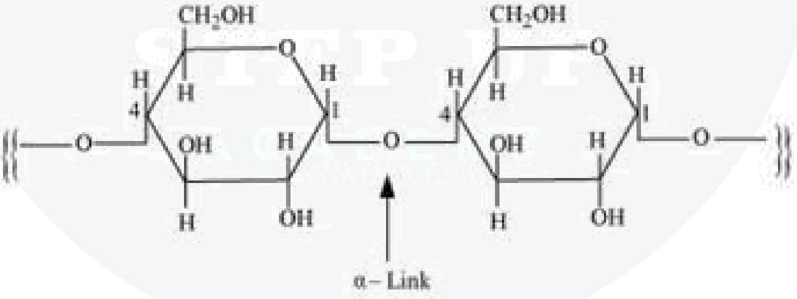


But pentaacetate of D-glucose does not react with NH_2OH. This is because pentaacetate does not form an open chain structure.



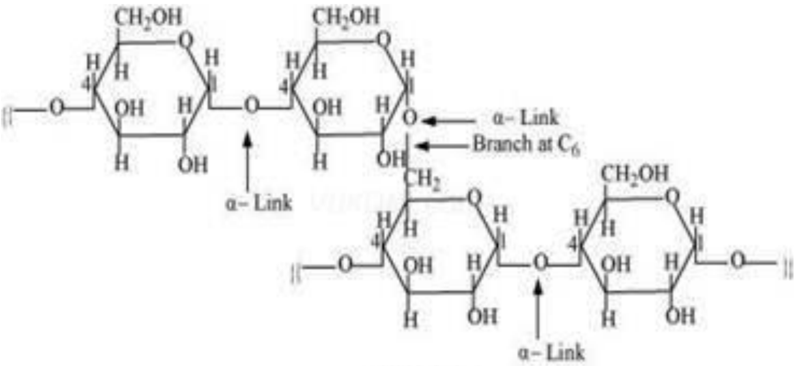
2. **Answer:**

Starch consists of two components – amylose and amylopectin. Amylose is a long linear chain of∝-D-(+)-glucose units joined by C_1-C_4 glycosidic linkage (∝--link).



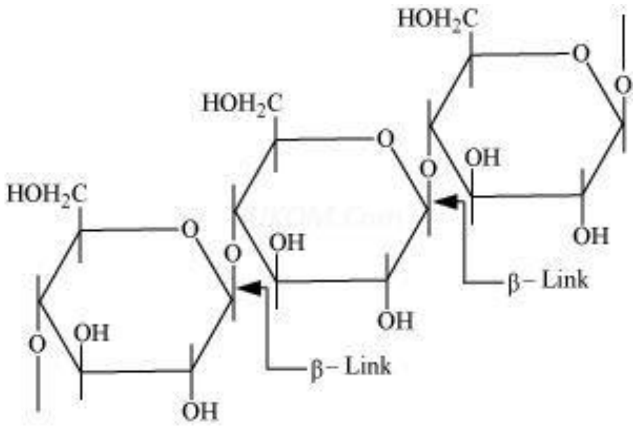
Amylose

3. Amylopectin is a branched-chain polymer of ∝-D-glucose units, in which the chain is formed by C_1-C_4 glycosidic linkage and the branching occurs by C_1-C_6 glycosidic linkage.



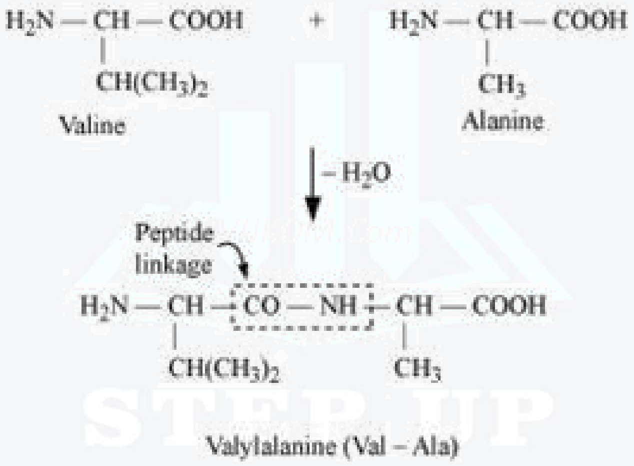
Amylopectin

4. On the other hand, cellulose is a straight-chain polysaccharide of β -D-glucose units joined by C_1-C_4 glycosidic linkage (β -link).



5. **Answer:**

(i) Peptide linkage: The amide formed between -COOH group of one molecule of an amino acid and -NH_2 group of another molecule of the amino acid by the elimination of a water molecule is called a peptide linkage.



$$H_2N-\underset{\substack{|\\CH(CH_3)_2}}{CH}-COOH + H_2N-\underset{\substack{|\\CH_3}}{CH}-COOH \xrightarrow{-H_2O} H_2N-\underset{\substack{|\\CH(CH_3)_2}}{CH}-\boxed{CO-NH}-\underset{\substack{|\\CH_3}}{CH}-COOH$$

(ii) Primary structure: The primary structure of protein refers to the specific sequence in which various amino acids are present in it, i.e., the sequence of linkages between amino acids in a polypeptide chain. The sequence in which amino acids are arranged is different in each protein. A change in the sequence creates a different protein.

(iii) Denaturation: In a biological system, a protein is found to have a unique 3-dimensional structure and a unique biological activity. In such a situation, the protein is called native protein. However, when the native protein is subjected to physical changes such as change in temperature or chemical changes such as change in pH, its H-bonds are disturbed. This disturbance unfolds the globules and uncoils the helix. As a result, the protein loses its biological activity. This loss of biological activity by the protein is called denaturation. During denaturation, the secondary and the tertiary structures of the protein get destroyed, but the primary structure remains unaltered.

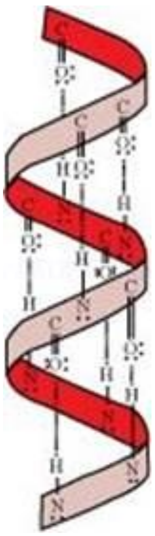
One of the examples of denaturation of proteins is the coagulation of egg white when an egg is boiled.

4. **Answer:**

There are two common types of secondary structure of proteins:

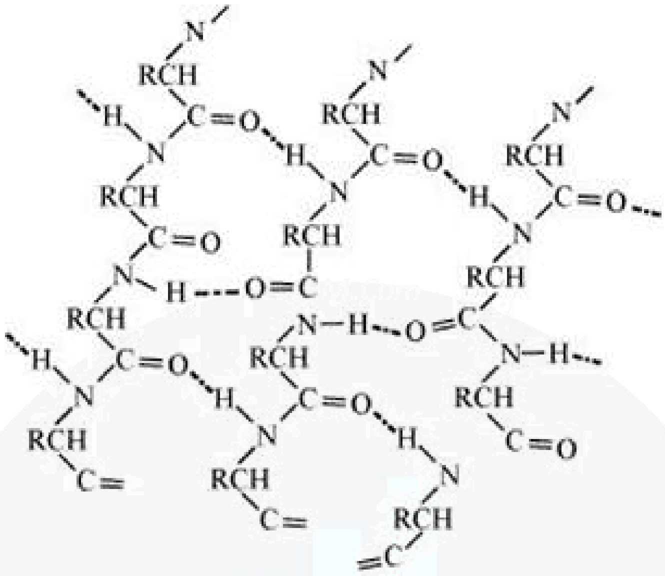
(i) α-helix structure

(ii) β pleated sheet structure α – Helix structure:



In this structure, the -NH group of an amino acid residue forms H-bond with the $>C=O$ group of the adjacent turn of the right-handed screw (α-helix).

β pleated sheet structure: This structure is called so because it looks like the pleated folds of drapery. In this structure, all the peptide chains are stretched out to nearly the maximum extension and then laid side by side. These peptide chains are held together by intermolecular hydrogen bonds.



5. **Answer:**

The structural differences between DNA and RNA are as follows:

DNA		RNA	
1.	The sugar moiety in DNA molecules is β -D-2 deoxyribose.	1.	The sugar moiety in RNA molecules is β -D-ribose.
2.	DNA contains thymine (T). It does not contain uracil (U).	2.	RNA contains uracil (U). It does not contain thymine (T).
3.	The helical structure of DNA is double – stranded.	3.	The helical structure of RNA is single-stranded.

The functional differences between DNA and RNA are as follows:

DNA		RNA	
1	DNA is the chemical basis of heredity.	1	RNA is not responsible for heredity.
2	DNA molecules do not synthesise proteins, but transfer coded message for the synthesis of proteins in the cells.	2	Proteins are synthesised by RNA molecules in the cells.

Assertion and Reason Answers:

1. (d) Assertion is wrong statement but reason is correct statement.

Explanation:

Uracil occurs in RNA

2. (b) Assertion and reason both are correct statements but reason is not correct explanation for assertion.

Explanation:

Cysteine can cross link peptide chains through disulphide bridge. Cross linking by disulphide bridge can occur either between the distant, properly oriented parts of the same polypeptide chain (as in oxytocin or vasopressin) or between different polypeptide chains.

Case Study Answers:

1. Answer :

(i) (c) Fibrous proteins are converted into globular proteins.

(ii) (b) Primary structure only.

(iii) (b) Secondary structure.

(iv) (c) Denatured protein.

Explanation:

Cheese is a denatured protein.

(v) (d) Regular folding patterns of continuous portions of the polypeptide chain.

2. Answer :

(i) (a) Ketotriose.

(ii) (a) 16

(iii) (c) 1, 2 and 4 only

Explanation:

Glucose contains four chiral centres.

(iv) (d) The carbon atoms 3, 4 and 5 in both have the same configuration.

Explanation:

In the formation of osazone, C-1 and C-2 react with phenylhydrazine to form phenylhydrazone. If C-3, C-4, C-5 have same configuration they will form same osazone even if they differ in configuration at C-1 or C-2.

(v) (c) Pentaacetate of glucose does not react with hydroxylamine.

Explanation:

Pentacetate of glucose does not react with hydroxylamine showing absence of free -CHO group. This cannot be explained by open structure of glucose.

❖❖