UNIT - I

THE SOLID STATE

KEY CONCEPTS

1. The state of matter whose M.P is above room temp is solid state.
2. Solids have definite shape and volume, having high density and constituent particles are held strongly.
3. Crystalline solids have regular arrangement of constituent particles throughout, melting point is sharp, Anisotropic (Some Physical Properties Like Refractive Index, Electrical Conductance may vary in different directions) in nature and give clear cut cleavage.
4. Amorphous solids have no regular arrangement, no sharp M.P, isotropic (Some Physical Properties Like Refractive Index, Electrical Conductance may not vary in different directions) in nature they do not exhibit cleavage property.
5. Amorphous silica is used in photovoltaic cells.
6. Space lattice is a regular 3D arrangement of constituent particles in the crystalline solid.
7. Smallest repeating unit in a space lattice is called unit cell.
8. There are 4 types of unit cells, 7 crystal systems and 14 bravais lattices.
9. Types of unit cell

Types of unit cell	No. of atoms per unit cell
i. Simple cubic unit cell	8 X 1/8=1
ii. FCC (Face centered cubic)	8 X 1/8+6 X 1/2=4
iii. BCC (Body centered cubic)	8 X 1/8+1 X 1=2

10. Hexagonal close packing and cubic close packing have equal efficiency i.e 74% and coordination no. is 12.
11. **Coordination no.:** The no. of nearest neighbour points surrounding a particular (May point is called coordination no (point may be atom, ions & molecules).
12. Packing efficiency = $\left(\frac{Volume\ occupied\ by\ total\ spheres}{volume\ of\ unit\ cell}\right) \times 100$

13. For simple cubic unit cell the packing efficiency=$1 \times 4/3 \times \pi r^3/8 \times r^3 \times 100 = 52.4$ %
14. The packing efficiency in **bcc** =$2 \times 4/3 \times \pi r^3/64 \times 3^{3/2} r^3 \times 100 = 68\%$
15. The packing efficiency in **fcc** =$4 \times 4/3 \times \pi r^3/16 \times 2^{1/2} r^3 \times 100 = 74\%$
16. Packing efficiency in simple cubic unit cell is 52.4%, bcc arrangement in 68% and fcc is 74%.
17. Unoccupied spaces in solids are called interstitial voids or interstitial sites.
18. Two important interstitial voids are (I). Tetrahedral void and (II). Octahedral void.
19. Radius ratio is the ratio of radius of void to the radius of sphere.
    a. For tetrahedral void radius ratio =0.225

       For octahedral void radius ratio=0.414
20. No. of tetrahedral void=2 X N (N=No. of closed packed particles)
21. No. of octahedral void=N
22. Formula of a compound depends upon arrangement of constituent particles in the unit cell.
23. Density of unit cell

$$D = Z \times M/a^3 \times N_A$$

D=density, M=Molar mass, a=side of unit cell, $N_A = 6.022 \times 10^{23}$

24. The relationship between edge length and radius of atom and interatomic or interionic distance for different types of unit cell is as given below
    a. Simple cubic unit cell $a=2r$
    b. FCC $a=4r/\sqrt{2}$
    c. BCC $a=4r/\sqrt{3}$
25. Interatomic distance=2r
26. Interionic distance=Rc+Ra (Rc=Radius of cation, Ra=Radius of anion)
27. Imperfection is the irregularity in the arrangement of constituent particles.
28. Point defect or Atomic defect - It is the deviation from ideal arrangement of constituent atom. Point defects are two types (a) Vacancy defect (b) Interstitial defect

29. Vacancy defect lowers the density.
30. Interstitial defect increases the density of crystal.
31. Point defects in the ionic crystal may be classified as:
    a. Stoichiometric defect (Ratio of cation and anion is same).
    b. Non Stoichiometric defect (disturb the ratio).
    c. Impurity defects (due to presence of some other ions at the lattice sites)
32. Schottky defect arises due to missing of equal no. of cations and anions from lattice sites in the crystalline solid and it lowers the density of crystal e.g. NaCl.
33. Frenkel defect is the combination of vacancy and interstitial defects. Cations leave their actual lattice sites and occupy the interstitial space in the solid. In this defect density remains same e.g. AgCl.
34. AgBr is the compound which shows both Schottky Defect and Frenkel Defect.
35. Non stoichiometric defect
    a. Metal excess defect due to anion vacancy.
    b. Metal excess due to presence of extra cation.
    c. Metal deficiency due to absence of cation.
36. F-Center - In metal excess defect, trapping of electrons in the anion vacancies which act as color center. E.g. NaCl gives yellow color in excess of Na$^+$ ions.

SHORT ANSWER QUESTION (1)

Q1. What do you mean by paramagnetic substance?

Ans.: - Substances which are attracted by external magnetic field are called paramagnetic substances. The paramagnetic property is due to the presence of unpaired electrons in atoms or ions e.g. Cu^{2+}, Fe^{3+} etc.

Q2. Which substance exhibit schottky and Frenkel both defects.

Ans: - AgBr

Q3. Name a salt which is added to Agcl so as to produce cation vacancies.

Ans.:-$CdCl_2$

Q4. Why Frenkel defects not found in pure Alkali metal halide.

Ans: - Due to larger size of Alkali metal ions.

Q5. What is the use of amorphous silica?

Ans.:- It is used in Photovoltaic cells.

Q6. Analysis shows that a metal oxide has the empirical formula $M_{0.98}O$. Calculate the percentage of M^{2+} and M^{3+} ions in the crystal.

Ans: - Let the M^{2+} ion in the crystal be x and M^{3+} = 0.98-x

Since total charge on the compound must be zero

$2x+3(0.98-x)-2=0$

$X=0.88$

% of M^{2+} = (0.88/0.96) X 100=91.67

% of M^{3+} =100-91.67=8.33

Q7. What is the co-ordination no. of cation in Antifluorite structure?

Ans: - 4

Q8. What is the Coordination Number of cation and anion in Caesium Chloride.

Ans: 8 and 8

Q9. What is F centre?

Ans.:- F-Center - In metal excess defect, trapping of electrons in the anion vacancies which act as color center. E.g. NaCl gives yellow color in excess of Na^+ ions.

Q10. What makes Alkali metal halides sometimes coloured, which are otherwise colourless?

Ans.:- It is due to F-Center.

Very Short Answers(1 marks) :

1. How does amorphous silica differ from quartz?

-In amorphous silica, SiO_4 tetrahedral are randomly joined to each other whereas in quartz they are linked in a regular manner.

2. Which point defect lowers the density of a crystal?

-Schottky defect.

3. Why glass is called supper cooled liquids?

-It has tendency to flow like liquid.

4. Some of the very old glass objects appear slightly milky instead of being transparent. why?

-Due to conversion amorphous glass into crystalline.

5. What is anisotropy?

-Physical properties show different values when measured along different direction in crystalline solids.

6. What is the coordination number of atoms?

a) in fcc structure b) in bcc structure

a) 12 b) 8

7. How many lattice points are there in unit cell of -

a) fcc b) bcc c) simple cubic

a) 14 b) 9 c) 8

8. What are the co-ordination numbers of octahedral voids and tetrahedral voids?

-6 and 4 respectively.

9. Why common salt is sometimes yellow instead of being pure white?

-Due to the presence of electrons in some lattice sites in place of anions these sites act as F-centers. These electrons when excited impart color to the crystal.

10. A compound is formed by two elements X and Y. The element Y forms ccp and atoms of X occupy octahedral voids. What is formula of the compound?

-No. of Y atoms be N No. of octahedral voids N

No. of X atoms be =N Formula XY

HOTS Very Short Answers:

1. **Define F centers.**
2. **What type of stoichiometric defect is shown by**
    a. **ZnS**
    b. **AgBr**
3. **What are the differences between frenkel and schottky defect?**
4. **Explain the following with suitable examples**
    - **Ferromagnetism**
    - **Paramagnetism**
    - **Ferrimagnetism**
    - **12-16 and 13-15 group compounds**
5. **In terms of band theory what is the difference between**
    - **Conductor and Insulator**
    - **Conductor and Semi-conductor**

Short Answers (2 Marks):HOTS

1. **Explain how electrical neutrality is maintained in compounds showing Frenkel and Schottky defect.**

   -In compound showing Frenkel defect, ions just get displaced within the lattice. While in compounds showing Schottky defect, equal number of anions and Cations are missing from the lattice. Thus, electrical neutrality is maintained in both cases.

2. **Calculate the number of atoms in a cubic unit cell having one atom on each corner and two atoms on each body diagonal.**
   8 corner X (1/8) atom per unit cell = 1 atom

   -There are four body diagonals in a cubic unit cell and each has two body centre atoms.

   So **4 X 2=8 atoms** therefore total number of atoms per unit cell =1+8=9

3. **Gold crystallizes in an FCC unit cell. What is the length of a side of the cell (r=0.144 nm)**
   r=0.144 nm

   a=2 X √2r

   =2 X 1.414 X 0.144 nm

   =0.407 nm

4. **Classify each of the following as either p-type or n-type semi-conductor.**
   a) Ge doped with In

   b) B doped with Si

(a) Ge is group 14 elements and In is group 13 element. Therefore, an electron deficit hole is created. Thus semi-conductor is p-type.

(b) Since B is group 13 element and Si group 14 element, there will be a free electron, thus it is n-type semi-conductor.

5. **In terms of band theory what is the difference between a conductor, an insulator and a semi-conductor?**

-The energy gap between the valence band and conduction band in an insulator is very large while in a conductor, the energy gap is very small or there is overlapping between valence band and conduction band. In semi-conductor there is small energy gap between the valence band and conduction band.

6. **$CaCl_2$ will introduce Schottky defect if added to AgCl crystal. Explain**

Two Ag+ ions will be replaced by one Ca^{2+} ions to maintain electrical neutrality. Thus a hole is created at the lattice site for every Ca^{2+} ion introduced.

7. **The electrical conductivity of a metal decreases with rise in temperature while that of a semi-conductor increases. Explain.**

In metals with increase of temperature, the kernels start vibrating and thus offer resistance to the flow of electrons. Hence conductivity decreases. In case of semi-conductors, with increase of temperature, more electrons can shift from valence band to conduction band. Hence conductivity increases.

8. **What type of substances would make better permanent magnets, ferromagnetic or ferrimagnetic, why?**

Ferromagnetic substances make better permanent magnets. This is because the metal ions of a ferromagnetic substance are grouped into small regions called domains. Each domain acts as tiny magnet and get oriented in the direction of magnetic field in which it is placed. This persists even in the absence of magnetic field.

9. **In a crystalline solid, the atoms A and B are arranged as follows:-**
    a. **Atoms A are arranged in ccp array.**
    b. **Atoms B occupy all the octahedral voids and half of the tetrahedral voids. What is the formula of the compound?**

Let no. of atoms of A be N

No. of octahedral voids = N

No. of tetrahedral voids= 2N

i) There will be one atom of B in the octahedral void
ii) There will be one atom of B in the tetrahedral void ((1/2) X 2N)

Therefore, total 2 atoms of B for each atom of A

Therefore formula of the compound =AB_2

10. In compound atoms of element Y forms ccp lattice and those of element X occupy 2/3rd of tetrahedral voids. What is the formula of the compound?

No. of Y atoms per unit cell in ccp lattice=4

No. of tetrahedral voids= 2 X 4=8

No. of tetrahedral voids occupied by X= (2/3) X 8=16/3

Therefore formula of the compound =$X_{16/3}\,Y_4$

$=X_{16}\,Y_{12}$

$=X_4\,Y_3$

HOTS Short Answer:

1. **How many lattice points are there in one unit cell of the following lattices?**
   - ○ **F.C.C.**
   - ○ **B.C.C.**
   - ○ **S.C.C. (Simple Cubic Cell)**
2. **A cubic solid is made of two elements X and Y. Atom Y are at the corners of the cube and X at the body centers. What is the formula of the compound?**
3. **Silver forms ccp lattice and X –ray studies of its crystal show that the edge length of its unit cell is 408.6 pm. Calculate the density of silver (Atomic mass= 107.9 u).**
4. **A cubic solid is made up of two elements P and Q. Atoms of the Q are present at the corners of the cube and atoms of P at the body centre. What is the formula of the compound? What are the co-ordination number of P and Q.**
5. **What happens when:-**
   - ○ **CsCl crystal is heated**
   - ○ **Pressure is applied on NaCl crystal.**

Short Answers (3 marks):

1. **The density of chromium is 7.2g cm^{-3}. If the unit cell is a cubic with length of 289pm, determine the type of unit cell (Atomic mass of Cr=52 u and N_A = 6.022 X 10^{23} atoms mol^{-1}).**

$$d = \frac{Z\times M}{a^3\times N_A}$$

Z=? , a= 289 pm =28910^{-10} cm, M=52g mol^{-1}, d=7.2g cm^{-3}

$$Z = \frac{d \times a^3 N_A}{M} = \frac{7.2 \times [289 \times 10^{-10}]^3 \times 6.022 \times 10^{23}}{52}$$

2. **An element crystallizes in FCC structure; 200 g of this element has 4.12 X 10^{24} atoms. If the density of A is 7.2 g cm^{-3}, calculate the edge length of unit cell.**
3. **Niobium crystallizes in bcc structure. If its density is 8.55 g cm^{-3}, calculate atomic radius of Niobium. [At. Mass of Niobium = 92.9u, N_A = 6.022 X 10^{23} atoms mol^{-1}].**
4. **If radius of octahedral void is r and radius of atom in close packing is R, derive the relationship between r and R.**
5. **Non stoichiometric cuprous oxide can be prepared in the laboratory. In this oxide, copper to oxygen ratio is slightly less than 2:1 can you account for the fact that the substance is a p-type semiconductor?**
6. **The unit cell of an element of atomic mass 50 u has edge length 290pm. Calculate its density the element has bcc structure (N_A = 6.022 X 10^{23} atoms $\text{mol}^{-1).}$**
7. **Calculate the density of silver which crystallizes in face centered cubic form. The distance between nearest metal atoms is 287pm (Ag= 107.87g mol^{-1}, N_A= 6.022 X 10^{23}).**

8. **What is the distance between Na^+ and Cl^- ions in NaCl crystal if its density 2.165 g $\text{cm}^{-3.}$ NaCl crystallizes in FCC lattice.**

9. **Analysis shows that Nickel oxide has $Ni_{0.98}O_{1.00}$ what fractions of nickel exist as Ni^{2+} ions and Ni^{3+} ions?**

10. **Find the type of lattice for cube having edge length of 400pm, atomic mass = 60 and density =6.25 g/cc.**

<u>HOTS Short Answer:</u>

1. **Aluminium crystallizes in cubic closed pack structure. Its metallic radius is 125 pm**
    - **What is the length of the side of the unit cell?**
    - **How many unit cell are there in 100 cm^3 of Aluminium.**

2. **Classify the following as either p-type or n-type semiconductors.**

    Ge doped with In

    B doped with Si

3. **Zinc oxide is white but it turns yellow on heating. Explain.**

<u>Long Answer(3 Marks):</u>

1. **In a face centered cubic lattice Edge length of lattice cell is $2A^0$. The density of metal is 2.4 g $\text{cm}^{-3.}$ How many units cell are present in 200g of metal.**

2. **A metal crystallizes as face centered cubic lattice with edge length of 450pm. Molar mass of metal is 50g mol^{-1}. Calculate the density of metal.**

3. **A compound forms hexagonal close packed structure. What is the total number of voids in 0.5 mol of it? How many of these are tetrahedral voids?**

4. **Copper Crystallizes into FCC lattice with edge length 3.61 X 10^{-8} cm. Show that calculated density is in agreement with measured value of 8.92 g/cc.**

5. **Niobium crystallizes in bcc structure with density 8.55 g/cc, Calculate atomic radius using atomic mass i.e. 93 u.**

HOTS Long Answer:

1. The compound CuCl has Fcc structure like ZnS, its density is 3.4 g cm^{-3}. What is the length of the edge of unit cell?

Hint: d=((Z X M) /(a^3 X N$_A$)

a^3=(4 X 99) / (3.4 X 6.022 X 10^{23})

a^3=193.4 X 10-24 cm^3

a=5.78 X 10^{-8}cm

2. If NaCl is doped with 10^{-3} mol% SrCl$_2$. What is the concentration of cation valancies?

3. If the radius of the octahedral void is r and the radius of the atom in the close packing is R. derive relationship between r and R.

4. The edge length of the unit cell of metal having molecular mass 75 g/mol is 1 A^0 which crystallizes into cubic lattice. If the density is 2g/cm^3 then find the radius of metal atom (N$_A$ = 6.022 X 10^{23})

UNIT-II

Solution

KEY CONCEPTS

Solution is the homogeneous mixture of two or more substances. The substances which make the solution are called components. Most of the solutions are binary i.e., consists of two components out of which one is solute and other is solvent.

Solute - The component of solution which is present in smaller quantity.

Solvent – The component of solution present in larger quantity or whose physical state is same as the physical state of resulting solution.

Solubility - The amount of solute which can be dissolved in 100 gm. of solvent at particular temperature to make saturated solution.

Solid solutions are of 2 types -

1. Substitutional solid solution e.g. Brass (Components have almost similar size)

2. Interstitial solid solution e.g. steel (smaller component occupies the interstitial voids)

Expression of concentration of solution

1. **Mass percentage**= amount of solute in gm. present in 100 gm. solution.

   Percentage = $\frac{mass\ of\ solute W_B}{mass\ of\ solution(W_A+W_B)} \times 100$

For liquid solutions percentage by volume is expressed as = $\frac{Volume\ of\ solute(\ V_B)}{volume\ of\ solution(V_A+V_B)} \times 100$

2. **Mole fraction** it is the ratio of no. of one component to the total no. of moles of all components. It is expressed as 'x'. For two component system made of A and B, $X_A = (n_A)/(n_A + n_B)$, $X_B = (n_B)/(n_A + n_B)$, Sum of all the components is 1 ; $X_A + X_B = 1$

3. **Molarity (M)** = $\frac{no.of\ moles\ of\ solute}{volume\ of\ solution(L)}$

It decreases with increase in temperature

4. **Molality (m)** = $\frac{No.of\ moles\ of\ solute}{Mass\ of\ solvent(in\ kg)}$

No effect of change of temperature on molality.

5. **Normality (N)** = $\frac{no.of\ gram\ equivalent\ of\ solute}{volume\ of\ solution(L)}$

It changes with changes temperature.

6. **Parts per million (ppm)** concentration of very dilute solution is expressed in ppm.

Ppm = $\frac{W_B}{W_B + W_A} \times 10^6$

Vapor pressure – It is defined as the pressure exerted by the vapour of liquid over the liquid in equilibrium with liquid at particular temperature. Vapour pressure of liquid depends upon nature of liquid and temperature.

Raoult's Law –

1. For the solution containing non-volatile solute the vapor pressure of the solution is directly proportional to the mole fraction of solvent at particular temperature

   $P_A \propto X_A$

   $P_A = P^0_A.X_A$

2. For the solution consisting of two miscible and volatile liquids the partial vapor pressure of each component is directly proportional to its own mole fraction in the solution at particular temperature.

   $P_A=P^0_{A.}X_{A,}$ $\quad$ $P_B=P^0_B.X_B$

   And total vapor pressure is equal to sum of partial pressure. $P_{total} = P_A + P_B$

Ideal solution – The solution which obeys Raoult's law under all conditions of temperature and concentration and during the preparation of which there is no change in enthalpy and volume on mixing the component.

Conditions –

$P_A = P^0_A X_{A,}$ $\quad$ $P_B = P^0_B.X_B$

$\Delta H_{Mix} = 0,$ $\quad$ $\Delta V_{mix} = 0$

This is only possible if A-B interaction is same as A-A and B-B interaction.

Nearly ideal solutions are –

1. Benzene and Toluene
2. Chlorobenzene and Bromobenzene

Non-ideal solution –

(a) $P_A \neq P^0_A.X_A$ $\quad$ (b) $P_B \neq P^0_B.X_B$

(b) $\Delta H_{mix} \neq 0$ $\quad$ (d) $\Delta V_{mix} \neq 0$

For non-ideal solution the A-B interaction is different from A-A and B-B interactions

i. For solution showing positive deviation

   $P_A > P^0_A X_A$ & $P_B > P^0_B X_B$

   ΔH_{Mix} = positive, ΔV_{mix}=positive (A-B interaction is weaker than A-A and B-B interaction)

   e.g. alcohol and water

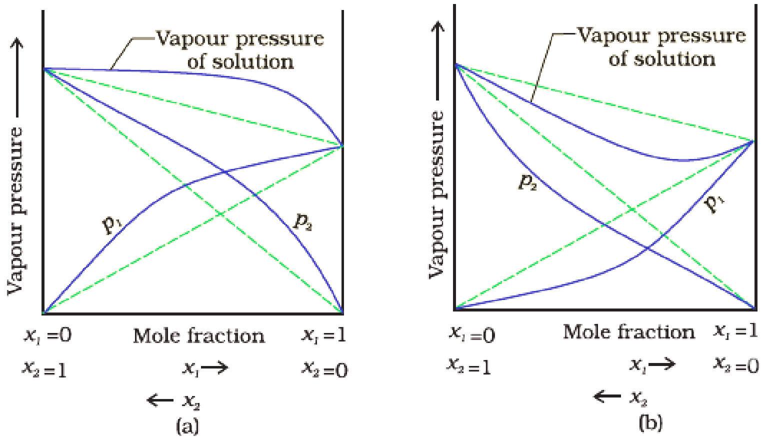
ii. For the solution showing negative deviation

$P_A < P^0_{A}.X_A$, $P_B < P^0_B.X_B$

ΔH_{Mix}= negative, ΔV_{mix} = negative

A-B interaction is stronger than A-A and B-B interactions

e.g. Chloroform and acetone, HCl and water



The vapour pressures of two component systems as a function of composition (a) a solution that shows positive deviation from Raoult's law and (b) a solution that shows negative deviation from Raoult's law.

What is Azeotrope? – The mixture of liquids at particular composition which has constant boiling point which behaves like a pure liquid and cannot be separated by simple distillation. Azeotropes are of two types:

(a) minimum boiling Azeotrope (mixture which shows +ve deviations) ex. alcohol and water

(b) maximum boiling Azeotrope (which shows –ve deviations) ex. acetone and chloroform

Colligative Properties - Properties of ideal solution which depends upon no. of particles of solute but independent of the nature of particle are called colligative property

Relative lowering in vapour pressure:

$$(P^o_A - P_A)/ P^o_A = X_B$$

Determination of molar mass of solute

$$M_B = (W_A \times M_A \times P^o_A)/W_A \times (P^o_A - P_A)$$

Elevation in Boiling Point

$$\Delta T_b = K_b . m$$

Where $\Delta T_b = T'_b - T^o_b$

Kb = molal elevation constant (Ebullioscopic constant)

m = molality

$M_B = (K_b \times 1000 \times W_B)/\Delta T_b \times W_A$

Depression in Freezing Point:

$\Delta T_f = k_f \cdot m$

Where $\Delta T_f = T°_f - T_f$, m = molality

K_f = molal depression constant (Cryoscopic Constant)

unit = $k.kg\ mol^{-1}$

Osmotic Pressure

The hydrostatic pressure which is developed on solution side due movement of solvent particles from lower concentration to higher concentration through semipermeable membrane denoted as **π** and it is expressed as

$$\Pi = \frac{n}{V}RT$$

$$\Pi = CRT$$

n = No. of moles of solute; v = volume of solution (L)

R = 0.0821 L atm $K^{-1}mol^{-1}$; T = temperature in kelvin.

Isotonic solutions have same osmotic pressure and same concentration.

Hypertonic solutions have higher osmotic pressure and hypotonic solutions have lower osmotic pressure.

0.91% solutions of sodium chloride is hypertonic to blood and RBC swells up or burst.

Q1- What do you mean by Henry's Law? The Henry's Law constant for oxygen dissolved in water is 4.34×10^4 atm at 25^o C. If the partial pressure of oxygen in air is 0.2 atm, under atmospheric pressure conditions. Calculate the concentration in moles per Litre of dissolved oxygen in water in equilibrium with water air at 25^o C.

Ans: Partial pressure of the gas is directly proportional to its mole fraction in solution at particular temperature.

$$P_A \alpha X_A \text{ ; } K_{H =} \text{ Henry's constant}$$

$$P_A = K_H \times A$$

$$K_H = 4.34\times10^4 \text{ atm}$$

$$PO_2 = 0.2 \text{ atm}$$

$$Xo_2 = PO_2 / K_H \quad =0.2 / 4.34\times10^4 = 4.6\times10^{-6}$$

If we assume 1L solution = 1L water

n water = 1000/18 = 55.5

$$XO_2 = \quad nO_2 \ /(nO_2 + n\, H_2O) \approx \quad nO_2 / nH_2O$$

$nO_2 = 4.6 \text{ X } 10^{-6} \text{ X } 55.5 = 2.55 \text{ X } 10^{-4}$ mol

$M = 2.55 \text{ X } 10^{-4}$ M

Q.2. What is Vant Hoff factor?

Ans. It is the ratio of normal molecular mass to observed molecular mass . It is denoted as 'i'

i = normal m.m / observed m.m

= no. of particles after association or dissociation / no. of particles before

Q.3. What is the Vant Hoff factor in $K_4[Fe(CN)_6]$ and $BaCl_2$?

Ans 5 and 3 respectively

Q.4. Why the molecular mass becomes abnormal?

Ans. Due to association or dissociation of solute in given solvent .

Q.5. Define molarity, how it is related with normality ?

Ans. N = M x Basicity or acidity.

Q.6. How molarity is related with percentage and density of solution ?
Ans. M = P x d x10/M.M

Q.7. What role does the molecular interaction play in the solution of alcohol and water?

Ans. Positive deviation from ideal behavior .

Q.8. What is Vant Hoff factor , how is it related with

a. degree of dissociation b. degree of association

Ans. a. $\alpha=(i-1)/(n-1)$ b. $\alpha=(i-1)/(1/n-1)$

Q.9. Why NaCl is used to clear snow from roads ?

Ans. It lowers f.p of snow

Q10. Why the boiling point of solution is higher than pure liquid

Ans. Due to lowering in v.p.

HOTS

Q1. Out of 1M and 1m aqueous solution which is more concentrated

Ans. 1M as density of water is 1gm/Ml

Q2. Henry law constant for two gases are 21.5 and 49.5 atm, which gas is more soluble .

Ans. K_H is inversely proportional to solubility.

Q.3. Define azeotrope , give an example of maximum boiling azeotrope.

Q.4. Calculate the volume of 75% of H_2SO_4 by weight (d=1.8 gm/ml) required to prepare 1L of 0.2M solution

Hint: M_1 = P x d x 10 /98

$M_1 V_1 = M_2 V_2$

14.5ml

Q.5. Why water cannot be completely separated from aqueous solution of ethyl alcohol?

Ans. Due to formation of Azeotrope at (95.4%)

SHORT ANSWERS (2 MARKS)

Q.1. How many grams of KCl should be added to 1kg of water to lower its freezing point to -8.0^{0}C (kf = 1.86 K kg /mol)

Ans. Since KCl dissociate in water completely i=2

$\Delta Tf = i\,kf \times m$; m =$\Delta Tf/ikf$

m= 8 / 2X1.86 = 2.15mol/kg.

Grams of KCl= 2.15 X 74.5 = 160.2 gm.

Q.2. With the help of diagram: show the elevation in boiling point colligative properties?

Q.3. what do you mean by colligative properties, which colligative property is used to determine molecular mass of polymer and why?

Q.4. Define reverse osmosis, write its one use.

Ans. When the pressure more than osmotic pressure is applied on the solution side, and the process of osmosis is reversed this is called reverse osmosis. e.g. Desalination of water.

Q.5. Why does an azeotropic mixture distills without any change in composition.

Hint: It has same composition of components in liquid and vapour phase.

Q.6. Under what condition Vant Hoff's factor is

a. equal to 1 b. less than 1 c. more than 1

Q.7. If the density of some lake water is 1.25 gm /ml and contains 92gm of Na^+ ions per kg of water. Calculate the molality of Na^+ ion in the lake .

Ans. n = 92/23 = 4

m= 4/1 = 4m

Q.8. An aqueous solution of 2% non-volatile exerts a pressure of 1.004 Bar at the normal boiling point of the solvent . What is the molar mass of the solute .

Hint: $P^0_A – P_A/P^0_A = w_B X m_A / m_B X w_A$

1.013 – 1.004 / 1.013 = 2X 18 /m_B X 98

$m_{B =}$ 41.35gm/mol

Q.9. Why is it advised to add ethylene glycol to water in a car radiator in hill station?

Because it make the anti-freezing solution and lower the freezing point of water.

Q.10. what do you mean by hypertonic solution, what happens when RBC is kept in 0.91% solution of sodium chloride?

UNIT-3

ELECTROCHEMISTRY CONCEPTS

Electrochemistry may be defined as the branch of chemistry which deals with the relationships between electrical energy taking place in redox reactions.
A cell is of two types:-

I. Galvanic Cell
II. Electrolytic cell.

In Galvanic cell the chemical energy of a spontaneous redox reaction is converted into electrical work.
In Electrolytic cell electrical energy is used to carry out a non-spontaneous redox reaction.

The Standard Electrode Potential for any electrode dipped in an appropriate solution is defined with respect to standard electrode potential of hydrogen electrode taken as zero. The standard potential of the cell can be obtained by taking the difference of the standard potentials of cathode and anode.

$E^0_{cell} = E^0 cathode - E^0 anode$
The standard potential of the cells are related of standard Gibbs energy.
$\Delta_r G° = -nFE^0_{cell}$
The standard potential of the cells is related to equilibrium constant.
$\Delta_r G° = -RT \ln k$
Concentration dependence of the potentials of the electrodes and the cells are given by Nernst equation.

$aA + bB \rightarrow cC + dD$

Nernst equation can be written as

$$E_{cell} = E^0_{cell} - \frac{RT}{nF} \ln \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

The conductivity, K of an electrolytic solution depends on the concentration of the electrolyte, nature of solvent and temperature.
Molar Conductivity, Δ_m, is defined by K/C where C is the concentration.
Conductivity decrease but molar conductivity increases with decrease in concentration. It increases slowly with decrease in concentration for strong electrolyte while the increase is very sharp in dilute solutions.

Kohlrausch law of independent migration of ions. The law states that limiting molar conductivity of an electrolyte can be represented as the sum of the individual contribution of the anions and cations of the electrolyte.

Faraday's laws of Electrolysis

I. The amount of chemical substance deposited at any electrode during electrolysis is proportional to the quantity of electricity passed through the electrolyte.
II. The amount of different substances liberated by the same quantity of electricity passed in same time through the electrolytic solution is proportional to their chemical equivalent weights.

Batteries and fuel cells are very useful forms of galvanic cells
There are mainly two types of batteries.
(a) Primary (b) Secondary (Rechargeable)

Corrosion of metals is an electrochemical phenomenon
In corrosion metal is oxidized by loss of electrons to oxygen and formation of oxides.
Anode (Oxidation): $2Fe(s) \rightarrow 2Fe^{2+} + 4e^-$
Cathode (Reduction): $O_2(g) + 4H^+(aq) + 4e^- \rightarrow 2H_2O$

Atmospheric Oxidation:
$2Fe^{2+}(aq) + 2H_2O(l) + 1/2O_2(g) \rightarrow Fe_2O_3(s) + 4H^+(aq)$

QUESTION CARRING 1 MARK

1. What is the effect of temperature on molar conductivity?
   Molar conductivity of an electrolyte increases with increase in temperature.
2. Why is it not possible to measure single electrode potential?
   (It is not possible to measure single electrode potential because the half cell containing single electrode cannot exist independently, as charge cannot flow on its own in a single electrode.)
3. Name the factor on which emf of a cell depends:-
   emf of a cell depends on following factor-
   a. Nature of reactants.
   b. Concentration of solution in two half cells.
   c. Temperature
   d. Pressure of gas.
4. What are the units of molar conductivity?
   ($cm^2\ ohm^{-1}\ mol^{-1}$ or Scm^2mol^{-1})

5. Write Nernst equation –
   For the general cell reaction

aA+bB→cC+dD

$$E_{cell} = E^0_{cell} - \frac{RT}{nF}\ln\frac{[C]^c[D]^d}{[A]^a[B]^b}$$

6. What is the emf of the cell when the cell reaction attains equilibrium?
   Zero

7. What is the electrolyte used in a dry cell?
   A paste of NH_4Cl, MnO_2 and C

8. How is cell constant calculated from conductance values?
   Cell constant= specific conductance/ observed conductance.

9. What flows in the internal circuit of a galvanic cell.
   Ions

10. Define electrochemical series.
    The arrangement of various electrodes in the decreasing or increasing order of their standard reduction potentials is called electrochemical series.

QUESTIONS CARRYING TWO MARKS

1. How can you increase the reduction potential of an electrode.?
   For the reaction

   $M^{n+}(aq) + ne^{-}$- → M (s)

   Nernst equation is:

   $$E_{M^{n+}/M} = E^0_{M^{n+}/M} - \frac{2.303RT}{nF}\log\frac{1}{[M^{n+}]}$$

$E_{M^{n+}/M}$ can be increased by

a. increase in concentration of M^{n+} ions in solution
b. by increasing the temperature.

2. Calculate emf of the following cell at 298K
   Zn/Zn^{2+} $(10^{-4}$ M) || Cu^{2+} $(10^{-2}$M)/Cu
   Given E^0 Zn^{2+}/Zn=-0.76V
   E^0Cu^{2+}/Cu=+0.34V
   Cell reaction is as follows.
   $Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$
   n=2

T=298K

$$E_{cell}=(E^0Cu^{2+}/Cu-E^0Zn^{2+}/Zn)-0.0591V \log \frac{[Zn^{2+}(aq)]}{[Cu^{+}(aq)]}$$

$$= 0.34V-(-0.76)-0.02955V \log \frac{10^{-4}}{10^{-2}}$$

$= 1.10V-0.02955V \log 10^{-2}$

$= 1.10V + 2 X 0.02955 V$

$= 1.10V + 0.0591 V$

$= 1.1591V$

3. Electrolysis of KBr(aq) gives Br_2 at anode but KF(aq) does not give F_2. Give reason

Oxidation takes place at anode. Now higher the oxidation Potential, easier to oxidize. Oxidation potential of Br^-, H_2O, F^- are in the following order.

$Br^- > H_2O > F^-$

Therefore in aq. Solution of KBr. Br^- ions are oxidized to Br_2 in preference to H_2O. On the other hand, in aq. Solution of KF, H_2O is oxidized in preference to F^-. Thus in this case oxidation of H_2O at anode gives O_2 and no F_2 is produced.

4. What happens when a piece of copper is added to (a) an aq solution of $FeSO_4$(b) an Aq solution of $FeCl_3$?

a. Nothing will happen when the piece of copper is added to $FeSO_4$ because reduction potential E^0 Cu_2/Cu(0.34) is more than the reduction potential $E^0(Fe^{2+}/Fe)$ (0.44V).

b. Copper will dissolve in an aq solution of $FeCl_3$ because reduction potential E^0Fe^{3+}/Fe^{2+}(0.77V) is more than the reduction potential of E^0Cu^{2+}/Cu(0.34)

$Cu(s)+ 2FeCl_3 (aq) \rightarrow Cu^{2+}(aq) + 2 FeCl_2(aq)$

5. Define corrosion. Write chemical formula of rust.

Corrosion is a process of destruction of metal as a result of its reaction with air and water, surrounding it. It is due to formulation of sulphides, oxides, carbonates, hydroxides, etc.

Formula of rust- $Fe_2O_3.XH_2O$

6. Write short notes on reduction and oxidation potentials.
7. How are standard electrode potentials measured?
8. What is cell constant? How it is determined?
9. Why it is necessary to platinize the electrodes of a conductivity cell before it is used for conductance measurement?

QUESTION CARRYING THREE MARKS

1. Write any three differences between potential difference and e.m.f.

E.M.F	POTENTIAL DIFFERENCE
1.It is difference between electrode potential of two electrodes when no current is flowing through circuit.	1.it is difference of potential between electrode in a closed circuit.
2. it is the maximum voltage obtained From a cell.	2.it is less than maximum voltage Obtained from a cell.
3. it is responsible for steady flow of Current.	3.it is not responsible for steady Flow of current.

2. Why an electrochemical cell stops working after sometime?
   The reduction potential of an electrode depends upon the concentration of solution with which it is in contact.

   As the cell works, the concentration of reactants decrease. Then according to Le chatelier's principle it will shift the equilibrium in backward direction. On the other hand if the concentration is more on the reactant side then it will shift the equilibrium in forward direction. When cell works concentration in anodic compartment in cathodic compartment decrease and hence E^0 cathode will decrease. Now EMF of cell is
   $E^0_{cell} = E^0_{cathode} - E^0_{anode}$

   A decrease in $E^0_{cathode}$ **and a corresponding increase in** E^0 anode it means that EMF of the cell will decrease and will ultimately become zero i.e., cell stops working after some time.

3. for the standard cell
   $Cu(s)/Cu^{2+}(aq)||\ Ag^+(aq)/Ag(s)$

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

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

i. Identify the cathode and the anode as the current is drawn from the cell.
ii. Write the reaction taking place at the electrodes.
iii. Calculate the standard cell potential.

1. From the cell representation
Ag/Ag^+ electrode is cathode and Cu/Cu^{2+} electrode is anode .
2. At anode :

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

$E^0_{cell} = E^0_{cathode} - E^0_{anode}$

= $E^0_{Ag+/Ag} – E^0_{Cu2+ /Cu}$
= +.80 V – (+0.34V)
= +0.80V-0.34V
= 0.46V

3. Can we store copper sulphate in (i)Zinc vessel (ii) Silver vessel? Give reasons**.**
Given E^0 Cu^{2+}/Cu = +0.34V, $E^0 Zn^{2+}/Zn$= -0.76V) , E0Ag^+/Ag = +0.80V

A metal having lower reduction potential can displace a metal having higher reduction potential from solution of its salt.

I. Since standard reduction potential of Zn^{2+}($E^0 Zn^{2+}/Zn$ = -0.76V) is less than the standard reduction potentialof Cu^{2+} ($E^0 Cu^{2+}/Cu$=+0.34V), Zn can displace copper from copper sulphate solution. Thus, $CuSO_4$ solution can be stored in silver vessel.

4. How many grams of chlorine can be produced by the electrolysis of molten NaCl with a current of 1.02 A for 15 min?
$2NaCl(l) \rightarrow 2Na^+(l)+2Cl^-(l)$
$2\ Cl^- \rightarrow Cl_2(g) + 2e^-$
2 mole 1mol
Q= nf
Q= 2 x 96500 C/mol= 1.93 x 10^5C

Quantity of electricity used = it
= 1.02 A X (15 X 60)sec
= 900C
Molar mass of Cl_2 = 2 X 35.5 = 71 $gmol^{-1}$ X 10^5 C of charge produce chlorine = 71g
1.93 X 10^5 C of charge produce chlorine = 71gm
900 C of charge produce chlorine $\frac{71 \times 900}{1.93 \times 10^5}$
= 0.331 gm

5. What is understood by a normal hydrogen electrode? Give its significance.
6. Define electrode potential. Why absolute value of reduction potential of electrode cannot be determined?
7. Write the equation showing the effect of concentration on the electrode potential.
8. Derive the relationship between Gibb's free energy change and the cell potential.
9. How Nernst equation can be applied in the calculation of equilibrium constant of any cell reaction.
10. The cell reaction as written is spontaneous if the overall EMF of the cell is positive. Comment on this statement.

QUESTIONS CARRYING 5 MARKS

1. Explain the term electrolysis. Discuss briefly the electrolysis of (i) molten NaCl (ii) aqueous sodium chloride solution (iii) molten lead bromide (iv) water.
2. state and explain Faraday's laws of electrolysis. What is Electrochemical equivalent?
3. What do you understand by 'electrolytic conduction'? what are the factors on which electrolyte conduction depends.? What is the effect of temperature on electrolytic conduction?
4. How is electrolytic conductance measured experimentally?

HOT QUESTIONS

<u>1 Mark questions</u>:-

1. Why in a concentrated solution, a strong electrolyte shows deviations from Debye-Huckle- Onsagar equation?
Ans:- Because interionic forces of attractions are large.

2. What is the use of Platinum foil in the hydrogen electrode?
A: It is used for inflow and outflow of electrons.
3. Corrosion of motor cars is a greater problem in winter when salts are spread on roads to melt ice and snow. Why?

4. Is it safe to stir $AgNO_3$ solution with copper spoon? ($E^0_{Ag+/Ag} = 0.80$ Volt; $E^0_{Cu+/Cu} = 0.34$ Volt)
Ans: No it is not safe because reacts with $AgNO_3$ Solution (emf will be positive.)
5. Why is it necessary to use salt bridge in a galvanic cell?
Ans: To complete inner circuit and to maintain electrical neutrality of the solution.

<u>2 mark questions</u>:-

1. Why Li is best reducing agent where as Fluorine is best oxidizing agent ?
2. Equilibrium constant is related to E^o cell but not to Ecell. Explain.
3. Why sodium metal is not obtained at cathode when aq NaCl is electrolysed with Pt electrodes but obtained when molten NaCl is electrolysed ?
4. Zn rod weighing 25 g was kept in 100 mL of 1M copper sulphate solution. After certain time interval, the molarity of Cu^{2+} was found to be 0.8 M. What is the molarity of SO_4^{-2} in the resulting solution and what should be the mass of Zn rod after cleaning and drying ?

5. Which will have greater molar conductivity and why?
   Sol A. 1mol KCl dissolved in 200 cc of the solution or Sol B. 1 mol KCl dissolved in 500cc of the solution.

<u>3/ 5 mark questions</u>:-

1. What do you mean by (i) negative standard electrode potential and
(ii) positive standard electrode potential ?

2. Which cell is generally used in hearing aids? Name the material of the anode, cathode and the electrolyte. Write the reactions involved.

3. Iron does not rust even if Zinc coating is broken in a galvanized iron pipe but rusting occurs much faster if tin coating over iron is broken .Explain.

4. ‘ Corrosion is an electrochemical phenomenon’, explain.

5. Calculate the pH of following cell: Pt, H_2/ H_2SO_4, if its electrode potential is 0.03V.

6 . A cell contains two hydrogen electrodes. The negative electrode is in contact with a solution of 10^{-5} M H+ ions. The emf of the cell is 0.118 V at 298 K. Calculate the concentration of the H+ ions at the positive electrode.

7. Crude copper containing Fe and Ag as contaminations was subjected to electro refining by using a current of 175 A for 6.434 min. The mass of anode was found to decrease by 22.260 g, while that of cathode was increased by 22.011 g. Estimate the % of copper, iron and silver in crude copper.

8 Zinc electrode is constituted at 298 K by placing Zn rod in 0.1 M aq solution of zinc sulphate which is 95 % dissociated at this concentration. What will be the electrode potential of the electrode given that $E^o Zn^{2+}/Zn = -0.76$ V.

9. At what pH will hydrogen electrode at 298 K show an electrode potential of -0.118 V, when Hydrogen gas is bubbled at 1 atm pressure ?

10 Electrolysis of the solution of $MnSO_4$ in aq sulphuric acid is a method for the preparation of MnO_2 as per the chemical reaction
$Mn^{2+} + 2H_2O \rightarrow MnO_2 + 2H^+ + H_2$
Passing a current of 27 A for 24 Hrs gives 1 kg of MnO_2. What is the current efficiency ? What are the reactions occurring at anode and cathode ?

UNIT-4

CHEMICAL KINETICS

CONCEPT

Chemical kinetics- The branch of physical chemistry which deals with the study of rate of reaction and their mechanism is called chemical kinetics.

Rate of chemical reaction- The change in concentration of any reactant or product per unit time is called rate of reaction.

TYPES OF RATE OF REACTION-

1. **Average rate of reaction-** The rate of reaction measured over the long time interval is called average rate of reaction.

Avg rate $\Delta x/\Delta t = -\Delta[R]/\Delta t = +\Delta[p]/\Delta t$

2. **Instantaneous rate of reaction-** The rate of reaction measured at a particular instant of time is called instantaneous rate of reaction.

Instantaneous rate $dx/dt = -d[R]/dt = +d[P]/dt$

FACTORS AFFECTING RATE OF REACTION-

1. **Concentration of reactant**
2. **Surface area**
3. **Temperature**
4. **Nature of reactant**
5. **Presence of catalyst**
6. **Radiation**

RATE CONSTANT (k)- It is equal to the rate of reaction when molecular concentration of reactant is at unity.

RATE LAW- The rate of reaction is directly proportional to the product of concentration of reactant and each concentration is raised to some power.

For a reaction

$aA + bB \rightarrow cC + dD$

Rate law = $k[A]^p[B]^q$

MOLECULARITY – The total no. of reactants taking part in a chemical reaction is called molecularity.

ORDER OF REACTION- The sum of powers to which the concentrations of the terms are raised in a rate law expression is called order of reactions.

HALF-LIFE PERIOD- The time during which the concentration of the reactant is reduced to half of its initial concentration is called half-life period.

ACTIVATION ENERGY- The minimum extra amount of energy absorbed by reactant molecules so that their energy becomes equal to the threshold energy is called activation energy.

Activation energy = Threshold energy – kinetic energy

TEMPERATURE COEFFICIENT- The ratio of rate constant at two temperatures having difference of 10^0C is called temperature coefficient.

Temperature coefficient = (Rate constant at $T+10^0C$) / Rate constant at T^0C

Arrhenius Equation-

$$K = Ae^{-Ea/RT}$$

K-rate constant
A-Arrhenius energy
E_a-Activation energy
R- Rate constant
T-Temperature

1 MARKS QUESTION

1. The gas phase decomposition of acetaldehyde

$$CH_3CHO \rightarrow CH_4+CO$$

It is found that the rate of reaction is proportional to$[CH_3CHO]^{1.5}$

What is the order of reaction

Ans. Order is 1.5

2. State the order with respect to each reactant and overall reaction.

$$H_2O + 3I^- + 2H^+ \rightarrow 2H_2O + I_3^-$$

Rate = $k[H_2O_2]^1[I^-]^1$

Ans. Order of reaction= 1+1= 2

3. Give one example of pseudo first order reaction**.**

Ans. Hydrolysis of an ester
$CH_3COOC_2H_5 + H_2O \rightarrow CH_3COOH + C_2H_5OH$

4. The conversion of molecules X to Y follows the second order of kinetics. If concentration of X is increased 3 times, how will it affect the rate of formation of Y.

Ans. Rate = $k\,[A]^2$
$= k\,[3A]^2$
$= k\,[9a]^2$

The rate of formation will become nine times.

5. The rate law for a reaction is
Rate = $K\,[A]\,[B]^{3/2}$
Can the reaction be an elementary process? Explain.

Ans. No, an elementary process would have a rate law with orders equal to its molecularities and therefore must be in integral form.

6. What do you understand by 'rate of reaction'?
7. Name the factors on which the rate of a particular reaction depends.
8. Why rate of reaction does not remain constant throughout?
9. Define specific reaction rate or rate constant.
10. What is half-life period of a reaction?

2 MARKS QUESTION

1. The rate of a particular reaction quadruples when the temperature changes from 293K to 313K. Calculate activation energy.

Ans. $K_2/K_1 = 4$,

T_1= 293K $T_2 = 313K$

$\text{Log}\,[K_2/K_1] = E_a[T_2-T_1]$

Thus on calculating and substituting values we get…..

$E_a = 52.86\ \text{KJ mol}^{-1}$

2. If the decomposition of nitrogen oxide as

$2N_2O_5 \longrightarrow 4NO_2 + O_2$
follows a first order kinetics.

(i) Calculate the rate constant for a 0.05 M solution if the instantaneous rate is 1.5×10^{-6} mol/l/s?

Ans. Rate = K $[N_2O_5]$

$$K = \frac{Rate}{[N_2O_5]}$$

$$K = \frac{1.5 \times 10^{-6}}{0.05}$$

$K = 3.0 \times 10^{-5}$

ii) What concentration of N_2O_6 would give a rate of 2.45×10^{-5} mol $L^{-1}s^{-1}$

Rate = 2.45×10^{-5} mol $L^{-1}s^{-1}$

$$[N_2O_5] = \frac{Rate}{K} = \frac{2.45 \times 10^{-5}}{3.0 \times 10^{-5}}$$

$= 0.82$ M

3) Write the difference between order and molecularity of reaction.

Ans.

ORDER	MOLECULARITY
It is the sum of the powers of concentration terms in the rate law expression.	It is the number of reacting species undergoing simultaneously Collision in a reaction.
It is determined experimentally	it is a theoretical concept
Order of reaction need not be a whole number	
Order of reaction can be zero.	

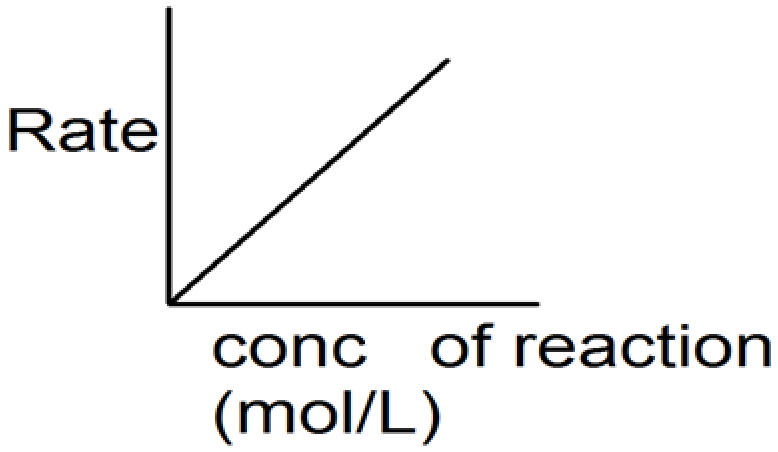
4) Define Threshold energy and activation energy. How they are related?

Ans. Threshold Energy: It is the minimum amount of energy which the reactant molecules must possess for the effective collision in forming the products.

Activation Energy: It is the excess energy required by the reactants to undergo chemical reaction.

Activation energy = Threshold energy – Average kinetic energy of molecules.

5(a). Draw a schematic graph showing how the rate of a first order reaction changes in concentration of reactants.



Variation of rate of first of first order reaction with concentration.

(b). rate of reaction is given by the equation

Rate = k $[A]^2[B]$

What are the units of rate constant for this reaction?

Ans. Rate = k $[A]^2[B]$

$$K = \frac{\text{mol L}^{-1}\text{s}^{-1}}{(\text{mol L}^{-1})^2(\text{mol}^{-1})}$$

$K = \text{mol}^{-2}\text{L}^2\text{s}^{-1}$

6. List the factors affecting the rate of reaction.

7. Explain with suitable example, how the molecularity of a reaction is different from the order of a reaction.

8. Define the term 'rate constant' of 'specific reaction rate'.

9. What are Pseudo unimolecular reactions? Explain with the help of a suitable example.

10. What is half life period? Derive and expression for half-life period in case of a first order reaction.

3 marks question

Q1. The rate constant for first order reaction is 60/s. How much time will it take to reduce the concentration of the reaction to 1/10 of its initial value.

Ans:-

$$t = \frac{2.303}{K}\log\frac{[R_0]}{[R]}$$

$$t = \frac{2.303}{K}\log\frac{[R_0]}{\left[\frac{R_0}{10}\right]}$$

$$t = \frac{2.303}{60} \log 10$$

$$t = \frac{2.303}{60} = 3.38X\ 10^{-2}s^{-1}$$

2. The rate of most of reaction double when their temperature is raised from 298k to 308k. Calculate the activation energy of such a reaction.

Ans:-

$$\text{Log}\ \frac{K_2}{K_1} = \frac{E_a}{2.303\ R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

$$Ea = \frac{2.303\ X\ 8.314\ X\ 298\ X\ 308\ X\ 0.3010}{1000}$$

Ea = 52.89KJ/mol

3. A first order reaction takes 69.3 min for 50% completion. Determine the time needed for 80% completion.

Ans. $K=\frac{0.693}{T^{1/2}}$

= 0.693/69.3min

= $10^{-2}min^{-1}$

$$T= \frac{2.303}{K} \log \frac{[R_0]}{[R]}$$

$T= 2.303/10^{-2}\log5$

T= 160.9min

4. Following reaction takes place in one step

$2NO + O_2 \rightarrow 2NO_2$

How will the rate of the reaction of the above reaction change if the volume of reaction vessel is diminished to 1/3 of its original volume? Will there be any change in the order of reaction with reduced volume?

Ans. $2NO+ O_2 \rightarrow 2NO_2$

$dx/dt = k[NO]^2[O_2]^1$

[Since it is one step]

If the volume of reaction vessel is diminished to 1/3, conc. Of both NO and O_2 will become 3 time, the rate of reaction increased 27 times.
In the order of reaction with the reduced volume.

5. The decomposition of NH_3 on platinum surface is a zero order reaction. What are the rate of production of N_2 and H_2.
If $k= 2.5 \times 10^{-4}$

Ans. $2NH_3 \rightarrow N_2 + 3H_2$

$$\frac{-1}{2}\ \frac{d\,[NH_3]}{dt} = \frac{d[NH_2]}{dt} + \frac{1}{3}\ \frac{d[H_2]}{dt}$$

$$\frac{-d[NH_3]}{dt} = \text{rate} = k \text{ x } [NH_3]^0$$

$$= 2.5 \text{ X } 10^{-4} \text{ molL}^{-1}\text{sec}^{-1}$$

$$\frac{d\,[N_2]}{dt} = -\frac{1}{2}\ \frac{d\,[NH_3]}{dt}$$

$$= 1/2 \text{ X}2.5\text{X}10^{-4} \text{ molL}^{-1}\text{sec}^{-1}$$

$$d[H_2] = -\frac{3}{2}\ \frac{d[NH_3]}{dt} = 3/2 \text{ X}2.5\text{X}10^{-4}$$

$$= 3.75\text{X}10^{-44}\text{molL}^{-1}\text{sec}^{-1}$$

$$\text{Rate} = -\frac{d[NH3]}{dt} = k \text{ X}[NH3]^0$$

$$= 2.5 \text{ X } 10^{-4} \text{ molL}^{-1}\text{sec}^{-1}$$

Rate of production of $N_2 = 2.5\text{X}10^{-4} \text{ molL}^{-1}\text{sec}^{-1}$

6. How is the rapid change in concentration of reactants/products monitored for fast reactions.

7. What are photochemical reactions? Give two examples,

8. What is the effect of temperature on the rate of reaction? Explain giving reasons.

9. Comment on free energy change of 'photochemical reactions'.

10. State the role of activated complex in a reaction and state its relation with activation energy.

QUESTIONS CARRYING 5 MARKS

1. What do you understand by the rate of a reaction? How it is expressed? How it is the rate of reaction determined?
2. What do you understand by order of a reaction? How does rate law differ from law of mass action? Give two example of each of the reactions of (i) zero order (ii) first order (iii) second order
3. Derive the equation for the rate constant for a first order reaction. What would be the units of the first order rate constant if the concentration is expressed in mole per litre and time in seconds.
4. Explain why the rate of reaction increases with increase in temperature.
5. Briefly explain the effect of temperature on the rate constant of a reaction.

HOTS

1. The half-life period of two samples are 0.1 and 0.4 seconds. Their initial Concentrations are 200 and 50 mol L_{-1} respectively. What is the order of reaction?

2. What is the ratio of $t_{3/4}$: $t_{1/2}$ for a first order reaction ?
3. Higher molecularity reactions (viz. molecularity, 4 and above) are very rare. Why?
4. Consider the reaction 2A + B → Products

When concentration of B alone was doubled, half life time does not change. When conc. of A alone is doubled, the rate increases by two times. What is the unit of K and what is the order of the reaction?

5. For the reaction, the energy of activation is 75KJ / mol. When the energy of activation of a catalyst is lowered to 20KJ / mol. What is the effect of catalyst on the rate of reaction at 20^0C.

6. The gas phase decomposition of CH_3OCH_3 follows first order of kinetics
$CH_3OCH_3 \rightarrow CH_4 (g) + H_2 (g) + CO (g)$
The reaction is carried out at a constant volume of the container at 500^0 C and has $t_{1/2}$ =14.5min.
Initially only dimethyl ether is present at a pressure of 0.40 atm. What is the total pressure of the system after 12 min? Assume ideal behavior.

Chapter-5 SURFACE CHEMISTRY

POINTS TO BE REMEMBERED: ---

1. **Adsorption**: - *The accumulation of molecules species at the surface rather in the bulk of a solid or liquid is termed adsorption.*

2. **Desorption**:-Removal of *adsorbate from the surface of adsorbent is known as Desorption.*

3. **Sorption**:-*When adsorption and absorption both takes place simultaneously.*

4. **Type of adsorption**: - On *the basis of interaction between adsorption and absorption, adsorbate are of two types*:

(i)**Physical adsorption/physisorption**: - *When weak vander waal interaction involve between adsorbate and adsorbent.*

(ii) **Chemical adsorption/chemisortion**:-*When chemical bonds form between adsorbate and adsorbent.*

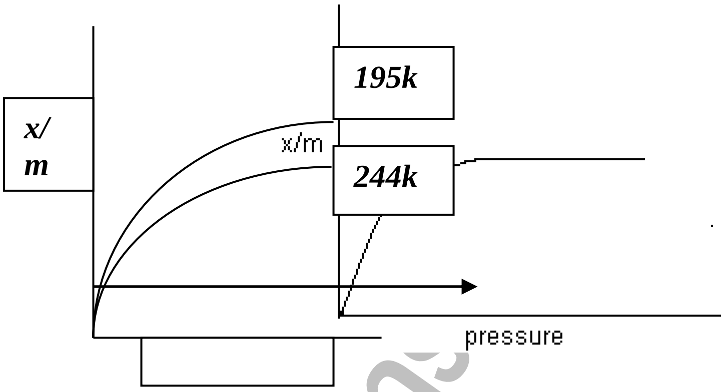
5. **Adsorption isotherm**:-*The variation in the amount of gas adsorbed by the adsorbent with pressure at constant temperature can be expressed by means of a curve termed as adsorption isotherm.*

6. **Application of adsorption**:-

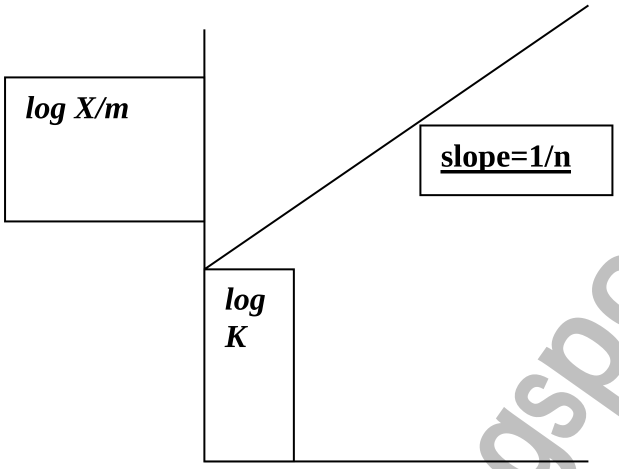
(a) *Removal of colouring matter from solution using animal charcoal.*

(b)Chromatographic analysis is based on adsorption.

7. **Freundlich adsorption isotherm**:-*It is a graph which shows relationship between the quality of gas adsorbed by unit mass of solid adsorbent and pressure at a particular temperature.*



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



8 .<u>**Factors affecting adsorption**</u>:-

(i)<u>**Surface area**</u>: - *Adsorption increases with increases of surface area of adsorbent.*

(ii)<u>**Nature of adsorbate**</u>:- *Easily liquefiable gases are readily adsorbed.*

(iii)<u>**Temperature**</u>:-*Low temperature is favorable for physical adsorption and High temperature for chemisortion.*

(iv)<u>**Pressure**</u>**: -** *Pressure increases, adsorption increases.*

9. <u>**CATALYSIS**</u>**:-** *Substances which alter the rate of chemical reaction and themselves remain chemically and quantitatively unchanged after the reaction are known as catalyst and the phenomenon is known as catalysis.*

10. <u>**PROMOTERS AND POISONS**</u>

Promoters are substance that enhance the activity of catalyst while poisons decrease the activity of catalyst.

$$N_2 + 3H_2 \xrightarrow[Mo]{Fe} 2NH_{3\,(g)}$$

$_{Fe}$ =*catalyst* *Mo= promoter*

11. <u>**Homogenous catalyst**</u> – *when reactants and catalyst are in same phase.*

e.g. $2\,SO_{2\,(g)} + O_{2\,(g)} \xrightarrow{NO(g)} 2SO_{3(G)}$

12. <u>**Heterogeneous catalyst**</u> – *the catalytic process in which the reactants and catalyst are in different phase.*

e.g. $SO_2 + O_2 \xrightarrow{Pt} 2SO_3\,(g)$

13. <u>**Adsorption theory of Heterogeneous catalysis**</u> – *It explains the mechanism of heterogeneous catalyst.*

<u>**The mechanism involves 5 steps:-**</u>

a. Diffusion of reactants to the surface of catalyst.
b. Adsorption of reactant molecules on the surface of catalyst.
c. Chemical reaction on the catalyst surface through formation of an intermediate.
d. Desorption of reaction product from the catalyst surface.
e. Diffusion of reaction product away from the catalyst surface.

14. <u>**IMPORTANT FEATURES OF SOLID CATALYST**</u>

<u>**Activity**</u> - *The activity of a catalyst depend on the strength of chemisorption. Catalytic activity increases from group 5 to group 11 elements of the periodic table.*

$$2H_2 + O_2 \xrightarrow{Pt} 2H_2O$$

Selectivity – *The selectivity of a catalyst is its ability to direct a reaction to yield a particular product.*

1. $CO + 3H_2 \xrightarrow{Ni} CH_4 + H_2O$
2. $CO + H_2 \xrightarrow{Cu} HCHO$

15. SHAPE SELECTIVE CATALYSIS

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

e.g. Zeolites are good shape selective catalysis

16. ENZYME CATALYSIS

Enzymes are protein molecules of high molecular mass which catalyse the biochemical reaction.

e.g. Inversion of cane sugar by invertase enzyme.

17. Characteristic of enzyme catalysis –

a. **Enzymes are specific to substrate.**
b. **Enzymes are highly active under optimum temperature.**
c. **Enzymes are specific to pH. e.g. Pepsin act in acidic medium**
d. **Enzymes are inhabited by the presence of certain substance.**

Mechanism of enzyme catalysis –

1. *Binding of enzyme to substrate to form an activated complex.*

$$E + S \rightarrow ES^*$$

2. *Decomposition of activated complex to form product.*

$$ES^* \rightarrow E + P$$

18. *Colloid*-a colloid is a heterogeneous system in which one substance is dispersed(dispersed phase)in another substance called dispersion medium.

19. TYPES OF COLLOIDS

(1) On the basis of nature of interaction between dispersed phase and dispersion medium.

(a) Lyophobic colloid-Solvent hating colloid, these colloids can not be prepared by simply mixing of dispersed phase into dispersion medium.

e.g. metallic sols.

(b) Lyophobic colloid-solvent loving these colloids can be prepared by simply mixing of dispersion phase into dispersion medium.

e.g. Starch sol.

(2) On the basis of types of particles of the dispersed phase

(a) Multimolecular colloid-on dissolution, a large number of atoms or smaller molecules of a substance aggregate together to form species having size in colloidal range. The species thus formed are called Multimolecular colloids.

e.g. Sulphur sol.

(b) Macromolecular colloids - macromolecules in suitable solvent form solution in which size of the particles are in range of colloidal range.

e.g. starch sol.

(c) Associated colloids (micelles)-some substances in low concentration behaves as normal strong electrolyte but at higher concentration exhibit colloidal behavior due to formation of aggregates. The aggregated particles are called micelles and also known as associated colloids.

(3) Kraft temperature- Temperature above which formation of micelles takes places.

(4) Critical micelle concentration (cmc) - concentration above which micelle formation takes place is known as cmc.

(5) PREPERATION OF COLLOIDS

(a) Chemical methods- By double decomposition, oxidation reaction or hydrolysis

OXIDATION

e.g. $SO_2 + 2H_2S \rightarrow 3S\ (SOL) + 2H_2O$

HYDROLYSIS

e.g. $FeCl_3 + 3H_2O \rightarrow \underset{(sol)}{Fe(OH)_3} + 3HCl$

(b) Bredig's arc method- For preparation of metallic sol. It involves dispersion as well as condensation.

(c) Peptization- Process of converting a precipitate into colloidal sol. By shaking it with dispersion medium in the presence of a small amount of electrolyte.

(6)PURIFICATION OF COLLIODAL SOLUTION :-

(a) Dialysis-it is a process of removing a dissolved substance from a colloidal solution by membrane.

(b)Electro dialysis-when dialysis is carried out with an electric field applied around the membrane.

(c) Ultra filtration- Use of special filters which are permeable to all ionic substances except colloidal particles.

(7)PROPERTIES OF COLLOIDAL SOLUTION:-

(1) They show colligative properties

(2) Brownian movement-zig-zag motion of colloidal particles

(3) Tyndall effect-scattering of light by colloidal particles by which path of beam becomes clearly visible. This effect is known as tyndall effect.

- Charge on colloidal particles – Colloidal particles carries electric charge and nature of charge is same on all particles.
- Electrophoresis - Movement of Colloidal particles towards opposite electrode in presence of external electric field.
- Coagulation – The process of setting of colloidal particles by the addition of small amount of electrolyte is called coagulation of the sol.
- Hardy Schulze Law – Coagulating value of a coagulating ion is directly proportional to the charge on the ion.
  Eg: $Na^+ < Ca^{++} < Al^{3+}$ for negatively charged sol.
  $Cl^- < CO^{2-}_3 < PO^{3-}_4 < [Fe(CN)_6]^{4-}$ for positive sol.
  Emulsion – Liquid – liquid colloidal system is known as Emulsion.
    - There are two types of Emulsion.
    - O/W type - Oil dispersed in water. Eg: milk, vanishing cream.
    - W/O type – Water dispersed in oil. Eg: Butter & Cream.
- Emulsifying Agent – The substance which stabilizes emulsion.

VERY SHORT ANSWER TYPE QUESTION

(1 marks)

1. What are the physical states of dispersed phase and dispersion medium of froth?

Ans - Dispersed phase is gas, dispersion medium is liquid.

2. What is the cause of Brownian movement among colloidal particles?

Ans - Due to collision between particles.

3. Arrange the solutions: True solution, colloidal solution, suspension in decreasing order of their particles size?

Ans – Suspension > colloidal > true solution.

4. Give an example of micelles system?

Ans – Sodium stearate ($C_{17}H_{35}COO^- Na^+$)

5. Why is it necessary to remove CO when ammonia is obtained by Haber's process?

Ans- CO acts as poison catalyst for Haber's process therefore it will lower the activity of solution therefore it is necessary to remove when NH_3 obtained by Haber's process.

6. How is adsorption of a gas related to its critical temperature?
Ans- Higher the critical temperature of the gas. Greater is the ease of liquefaction. i.e. greater Vander walls forces of attraction and hence large adsorption will occur.

7. What is meant by Shape Selective Catalyst?
Ans – On the Shape Selective Catalyst, the rate depends upon pore size of the catalyst and the shape & size of the reactant and products molecules.

8. Of the physiorption & chemisorptions, which type of adsorption has higher enthalpy of adsorption?
Ans - chemisorptions.

9. Write down the Example of Positive Sol?
Ans – Ferric hydro-oxide sol.

10. Write down the Example of Negative Sol?
Ans – Arsenic sulphide.

SHORT ANSWER TYPE QUESTION

(2 marks)

1. Differentiate between physical & chemical adsorption?
Ans –

Physical adsorption	**Chemical adsorption**
a) Forces between adsorbate & adsorbent are week Vander waal forces. b) Low heat of Adsorption.	a) Forces between adsorbate & adsorbent are strong chemical forces. b) High heat of Adsorption.

2. Differentiate between Lyophobic & Lyophilic colloids**?**
3. Ans –

Lyophilic colloids	**Lyophobic colloids**
a) These are easily formed by direct mixing. b) Particles of colloids are not easily visible even under ultra microscope. c) These are very stable.	a) These are easily formed by Special method. b) Particles of colloids are easily visible under ultra microscope. c) These are unstable.

4. Differentiate between multi molecular, macromolecular and associated colloids?
5. Ans**:-**

Multi molecular colloids	**Macromolecular colloids**	**Associated colloids**
a) They consist of aggregates of atoms or molecules which generally have diameter less than 1nm. b) They are usually lyophobic	a) They consist of large molecules. b) They are	a) Behave as colloidal size particles at higher conc. b) They have both lyophobic character & Lyophilic

	lyophobic	

6. What is difference between Sol. & Gel?
Ans – Both are colloidal solutions. Sol has solid as ‘dispersed phase & liquid as dispersion medium’. While ‘Gel’ has liquid as dispersed phase and solid as dispersion medium.

7. Action of Soap is due to Emulsification & Micelle formation? Comment.
Ans – soaps are sodium & potassium salts of higher fatty acids.
Eg: $C_{17}H_{35}COONa$ oil & Grease in dirt adhere firmly to clothing and is undisturbed by washing in tap water. Soap acts as an Emulsifying agent and brings the Greasy dirt into colloidal dispersion the hydrocarbon chain of soap molecule is soluble in oil or grease. It dissolves in grease and encapsulates. It to form micelle. The anionic ends of chain protrude from droplets and interact with water molecules, preventing coalescence of droplets.

SHORT ANSWER TYPE QUESTION

(3 marks)

8. Discuss the effect of pressure & temperature on the adsorption of gases on solids?
Ans – Effect of pressure on adsorption: - At constant temp the extent of adsorption of gas(x/m) in the solid increases with pressure. A graph between x/m and the pressure P of a gas at constant temp is called adsorption isotherm.

Freundlich adsorption isotherm -

i) At lower range of pressure, (x/m) is directly proportional to the applied pressure.
$X/m \propto p^I$

ii) At high pressure range, the extent of adsorption of a gas (x/m) is independent of the applied pressure i.e.
$X/m \propto p^o$

iii) At intermediate pressure range, the value of (x/m) is proportional to the fractional power of pressure i.e.
$X/m \propto p^{1/n}$
Where 1/n is fraction. Its value may be between 0 and 1
$X/m = kp^{1/n}$
$\text{Log}(x/m) = \log k + 1/n \log p$

Effect of temp on Adsorption – Adsorption is generally temp dependent. Mostly adsorption processes are exothermic and hence, adsorption decreases with increasing temp. However for an endothermic adsorption process adsorption increases with increase in Temperature.

1. Explain What is observe when
i) An electrolyte, NaCl is added to hydrate ferric oxide sol.
ii) Electric current is passed through a colloidal sol.
iii) When a beam of light is passed through a colloidal sol.

Ans –(i) The positively charged colloidal particles of $Fe(OH)_3$ get coagulated by the positively charged Cl^- ions provided by NaCl.

(ii) On passing direct current, colloidal particles move towards the positively charged electrode where they lose their charge and get coagulated.

(iii) Scattering of light by the colloidal particles takes place and the path of light becomes visible (Tyndall effect).

2. Describes some features of catalysis by Zeolites?

Ans – Features of catalysis by Zeolites:-

I) Zeolites are hydrated alumino silicates which have a three dimensional network structure containing water molecules in their pores.

II) To use them as catalysts, they heated so that water of hydration present in the pores is lost and the pores become vacant.

III) The size of pores varies from 260 to 740 pm. Thus, only those molecules can be adsorbed in these pores and catalyzed whose size is small enough to enter these pores. Hence, they act as molecular sieves or shape selective catalysts.

An important catalyst used in petroleum industries in ZSM-5. It converts alcohols into petrol by first dehydrating them to form a mixture of hydro carbons.

$$\text{Alcohols} \xrightarrow[Dehyderation]{ZSM-5} \text{Hydro carbons}$$

3. Comment on the statement that “colloid is not a substance but state of a substance”?

Ans – The given statement is true. This is because the statement may exist as a colloid under certain conditions and as a crystalloid under certain other conditions.e.g:NaCl in water behaves as a crystalloid while in benzene, behaves as a colloid (called associated colloid). It is the size of the particles which matters i.e. the state in which the substance exist. If the size of the particles lies in the range 1nm to 1000nm it is in the colloid state.

4. Write short notes on followings:-

(a) Tyndall effect
(b) Brownian Movement
(c) Hardy Schulze Rule

Ans- (a) Tyndall effect-scattering of light by colloidal particles by which path of beam becomes clearly visible. this effect is known as tyndall effect

(b) Brownian movement-zig-zag motion of colloidal particles.

(c) Hardy Sehulze Law – Coagulating value of a coagulating ion is directly proportional to the charge on the ion.

e.g: $Na^{+} < Ca^{++} < Al^{3+}$ for negatively changed sol.

$Cl^{-} < CO_3^{2-} < PO_4^{3-} < [Fe(CN)_6]^{4-}$ for positive sol.

Chapter:-6

General Principles & Process of Isolation of Elements

Important Points :

1. The chemical substances in the earth's crust obtained by mining are called Minerals.

2. Minerals, which act as source for metal, are called Ore.

3. The unwanted impurities present in ore are called Gangue.

4. The entire process of extraction of metal from its ore is called Metallurgy.

5. Removal of gangue from ore is called Concentration, Dressing or Benefaction of ore.

6. Concentration by Hydraulic washing is based on the difference in gravities of ore and gangue particles.

7. Concentration by Magnetic separation is based on differences in magnetic properties of ore components. If either of ore or gangue is capable of attracted by a magnet field, then such separation is carried out.

8. Concentration by Froth Flotation Process is based on the facts that sulphide ore is wetted by oil & gangue particles are wetted by water.

9. Concentration by Leaching is based on the facts that ore is soluble in some suitable reagent & gangue is insoluble in same reagent. e.g. Bauxite ore contains impurities of silica, iron oxide & TiO_2 .The powdered ore is treated with NaOH which dissolve Al & impurities remains insoluble in it.

$$Al_2O_3 + 2NaOH + 3\,H_2O \longrightarrow 2\,Na\,[Al(OH)_4].$$

10. Calcination involves heating of ore in absence of air below melting point of metal. In this process volatile impurities escapes leaving behind metal oxide.

$$Fe_2O_3.xH_2O \longrightarrow Fe_2O_3 + xH_2O$$

$$ZnCO_3 \longrightarrow ZnO + CO_2$$

$$CaCO_3.MgCO_3 \longrightarrow CaO + MgO + 2CO_2$$

11. Roasting involves heating of ore in presence of air below melting point of metal in reverberatory furnace. In this process volatile impurities escapes leaving behind metal oxide and metal sulphide converts to metal oxide.

$$2\,ZnS + 3\,O_2 \longrightarrow 2ZnO + 2SO_2$$

$$2PbS + 3\,O_2 \longrightarrow 2\,PbO + 2\,SO_2$$

$$2\,Cu_2S + 3\,O_2 \longrightarrow 2Cu_2O + 2\,SO_2$$

12. Reduction of metal oxide involves heating of metal in presence of suitable reagent Coke or CO_2.

13. Reactions taking place at different zones of blast furnace in extraction of iron:-

(i) Zone of reduction:- Temperature range 250°C-700°C

$$3Fe_2O_3 + CO \longrightarrow 2Fe_3O_4 + CO_2$$

$$Fe_3O_4 + CO \longrightarrow 3FeO + CO_2$$

$$FeO + CO \longrightarrow Fe + CO_2$$

(ii) Zone of slag formation:- Temperature range 800°C-1000°C

$$CaCO_3 \longrightarrow CaO + CO_2$$

$CaO + SiO_2 \longrightarrow CaSiO_3$, $P_4O_{10} + 10C \longrightarrow 4P + 10CO$,

$SiO_2 + 2C \longrightarrow Si + 2CO$, $MnO_2 + 2C \longrightarrow Mn + 2CO$

(iii) Zone of fusion: - Temperature range 1150°C-1350°C

$$CO_2 + C \longrightarrow 2CO$$

(iv) Zone of fusion: - Temperature range 1450°C-1950°C

$$C + O_2 \longrightarrow CO_2$$

14. FLOW SHEET FOR EXTRACTION OF IRON:-

Iron ore(Magnetite Fe_3O_4)

↓

Concentration is done by Gravity separation followed by magnetic separation

↓

Calcination &Roasting i.e. Ore + Air +Heat→Moisture,CO_2,SO_2, As_2O_3 removed And FeO oxidized to Fe_2O_3

↓

Smelting of charge i.e. mixture of ore, coke & $CaCO_3$ takes place in long BLAST FURNACE. Following reaction take place at different zones:-

(refer to point 13)

↓

Pig iron is obtained, which is remelted and cooled then cast iron is obtained

15. Pig Iron: - It contains Fe 93-95%, Carbon 2.5-5%, and Impurities 3%.

16. Cast Iron: - It contains Fe 99.5-99.8%, Carbon 0.1-0.2% Impurities 0.3%.

17. Spongy iron: - Iron formed in the zone of reduction of blast furnace is called spongy iron. It contains impurities of C, Mn , Si, etc.

18. FLOW SHEET FOR EXTRACTION OF COPPER:-

Copper Pyrites $CuFeS_2$

↓

Concentration is done by Froth floatation process

Powdered ore + water +pine oil +air→ Sulphide ore in the froth

↓

Roasting is presence of air. following reactions take place:-

$S + O2 \rightarrow SO_2$, $4As + 3O_2 \rightarrow 2As_2O_3$, $2CuFeS_2 + O_2 \rightarrow Cu_2S + 2FeS + SO_2$

↓

Smelting in small blast furnace of a mixture of Roasted ore, coke, and silica.

$2FeS + 3O_2 \rightarrow 2FeO + 2SO_2$, $FeO + SiO_2 \rightarrow FeSiO_3$(slag)

↓

A mixture of Cu_2S, FeS & silica is obtained from blast furnace known as Copper matte

↓

Bessemerisation of copper matte is done in Bessemer converter in presence of air. Following reactions take place:-

$$2FeS + 3O_2 \rightarrow 2FeO + 2\,SO_2,\ FeO + SiO_2 \rightarrow FeSiO_3\ \text{(slag)},$$
$$2Cu_2S + 3O_2 \rightarrow 2Cu_2O + 2SO_2,\ 2Cu_2O + 2Cu_2S \rightarrow 6Cu + SO_2$$

↓

Melted copper is cooled, and then SO_2 is evolved. such copper is known as BLISTER COPPER(98%Cu+2% impurities)

19. FLOW SHEET FOR EXTRACTION OF ALUMINIUM:-

Bauxite $Al_2O_3.2H_2O$

↓

Concentration of ore is done by leaching .Bauxite is treated with NaOH .Following reaction takes place:-
$Al_2O_3 + 2NaOH + 3\,H_2O \longrightarrow 2\,Na\,[Al\,(OH)_4]$ and impurities of Fe_2O_3, TiO2 &SiO_2 are removed.

↓

$Na\,[Al\,(OH)_4]$,then reacts with CO_2 then pure Alumina is obtained.
$$Na\,[Al(OH)_4] + 2CO_2 \rightarrow Al_2O_3.xH_2O + 2NaHCO_3$$

↓

Electrolytic reduction of pure alumina takes place in iron box (cathode) with cryolite (Na_3AlF_6) & fluorspar CaF_2.Graphite rods act as anode. Following reactions take place:-
At cathode:- $Al^{3+} + 3e^- \rightarrow Al$, At Anode:- $2O^{2-} \rightarrow O_2 + 4e^-$

↓

By this process 98.8% pure Aluminum is obtained.

20. Vapour phase refining is used for extraction of Nickel (MOND PROCESS) and Zirconium &Titanium (VAN ARKEL PROCESS).
21. Zone refining is used for extraction of Si, Ge, Ga, etc.
22. Chromatography method is based on selective distribution of various constituents of a mixture between two phases, a stationary phase and a moving phase. The stationary phase can be either solid or liquid on solid support.
22. Column chromatography is based on adsorption phenomenon. This method is useful for those elements, which are available in small amounts and the impurities are not much different in chemical properties from the element to be purified.

VERY SHORT ANSWER TYPE QUESTION (1 marks)

Q.1- What is slag?
A.1- It is easily fusible material, which is formed when gangue still present in roasted ore combines with the flux.

e.g. CaO (flux) + SiO_2 (gangue) $\rightarrow CaSiO_3$ (slag)

Q.2- Which is better reducing agent at 983K, carbon or CO?
A.2- CO, (above 983K CO being more stable & does not act as a good reducing agent but carbon does.)
Q.3- At which temperature carbon can be used as a reducing agent for FeO?
A.3- Above 1123K, carbon can reduce FeO to Fe.
Q.4- What is the role of graphite rods in electrometallurgy of aluminium?
A.4- Graphite rods act as anode, are attacked by oxygen to form CO_2 and so to be replace time to time.
Q.5- What is the role of cryolite in electrometallurgy of aluminium?
A.5- alumina cannot be fused easily because of high melting point. Dissolving of alumina in cryolite furnishes Al^{3+} ions, which can be electrolyzed easily.
Q.6- What are depressants?
A.6- It is possible to separate two sulphide ore by adjusting proportion of oil to water in froth flotation process by using a substance known as depressant.
e.g. NaCN is used to separate ZnS and PbS.
Q.7- Copper can be extracted by hydrometallurgy but not Zn. Why?
A.7- The E^0 of Zn is lower than that of Cu thus Zn can displace Cu^{2+} ion from its solution. On other hand side to displace Zn from Zn^{2+} ion, we need a more reactive metal than it.
Q.8- Give name and formula of important ore of iron .
A.8- Haematite – Fe_2O_3, Magnetite –Fe_3O_4, Iron pyrites FeS_2.
Q.9- Give name and formula of important ore of Copper .
A.9- Copper pyrites $CuFeS_2$, Malachite $CuCO_3 \cdot Cu(OH)_2$, Cuprite Cu_2O.
Q.10- Give name and formula of important ore of Zinc .
A.10- Zinc blende - ZnS, Calamine- $ZnCO_3$, Zincite – ZnO .

SHORT ANSWER TYPE QUESTION
(2 marks)

Q.1 Describe the method of refining of nickel.
A.1- In the Mond Process, Ni is heated in a stream of CO forming a volatile complex, which then decomposes at higher temperature to give Ni.
At 330-350K: - $Ni + 4CO \rightarrow Ni(CO)_4$
At 450-470K $Ni(CO)_4 \rightarrow Ni + 4CO$
Q.2- What is Zone Refining? Explain with example.
A.2- Zone refining is a method of obtaining a metal in very pure state. It is based on the principal that impurities are more soluble in molten state of metal than solidified state.

In this method, a rod of impure metal is moved slowly over circular heater. The portion of the metal being heated melts & forms the molten zone. As this portion of the rod moves out of heater, it solidified while the impurities pass into molten zone. The process is repeated to obtain ultrapure metal and end of rod containing impure metal cutoff.

Q.3 Write the principal of electro-refining.
A.3- In this method of purification impure metal is made Anode and pure metal is made the cathode. On passing electricity, pure metal is deposited at the cathode while the impurities dissolve in solution as anode mud. E.g. electro- refining of copper:-
At Cathode: - $Cu^{2+} + 2e^- \rightarrow Cu$

At Anode: - $Cu \rightarrow Cu^{2+} + 2e^-$

Q.4- Write difference between calcinations and roasting.

Q.5- Describe the method of refining of Zirconium and Titanium.

A.5- Van Arkel process is used for obtaining ultrapure metal. The impure metal is converted into volatile compound, which then decomposes electrically to get pure metal.

At 850K: - Zr impure) $+ 2 I_2 \rightarrow ZrI_4$

At 2075K:- $ZrI_4 \rightarrow Zr$ (pure) $+ 2 I_2$

Q.6- Out of C & CO, which is better reducing agent for ZnO?

A.6- Since free energy of formation of CO from C is lower at temperature above 1120K while that of CO_2 from carbon is lower above 1323K than free energy of formation 0f ZnO. However, the free energy of formation of CO_2 from CO is always higher than that of ZnO. Hence, C is better reducing agent of ZnO.

Q.7- The value of $\Delta_f G^0$ for Cr_2O_3 is -540kJ/mole & that of Al_2O_3 is -827kJ/mole. Is the reduction of Cr_2O_3 possible with aluminium?

A.7- The desired conversion is

$$4 Al + 2Cr_2O_3 \rightarrow 2Al_2O_3 + 4Cr$$

It is obtained by addition of following two reactions:-

$4Al + 3O_2 \rightarrow 2 Al_2O_3$ $\Delta_f G^0$=-827kJ/mole

$2Cr_2O_3 \rightarrow 4Cr + 3O_2$ $\Delta_f G^0$==+ 540 kJ/mole

Therefore, ΔG^0 for desired reaction is -827+540=-287, as a result reduction is possible.

Q.8:- Why copper matte is put in silica lined converter?

A.8:- Copper matte consists of Cu_2S and FeS. When blast of air is passed through molten matte in silica-lined converter, FeS present in matte is oxidized to FeO, which combines with silica to form slag.

(i) $2FeS + 3O_2 \rightarrow 2FeO + 2 SO_2$, (ii) $FeO + SiO_2 \rightarrow FeSiO_3$ (slag),

(III) $2Cu_2S + 3O_2 \rightarrow 2Cu_2O + 2SO_2$, (IV) $2Cu_2O + 2Cu_2S \rightarrow 6Cu + SO_2$

Q.9- What is meant by term chromatography?

A.9-Chromato means Colour and graphy means writing because the method was first used for separation of coloured substance. It is based on selective distribution of various constituents of a mixture between two phases, a stationary phase and a moving phase. The stationary phase can be either solid or liquid on solid support.

Q.10-Why is reduction of metal oxide easier if metal formed is in liquid state at temperature of reduction.

A.10- The entropy of a substance is higher in liquid state than solid state. In the reduction of metal oxide, the entropy change will be positive if metal formed is in liquid state. Thus, the value of ΔG^0 becomes negative and reduction occurs easily.

SHORT ANSWER TYPE QUESTION

(3 marks)

Q.1- Explain the following:-

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

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

(iii) Extraction of Cu from pyrites is difficult than that from its oxide ore through reduction.

A.1- (i) Zn is more powerful reducing agent in comparison to copper.Zn is also cheaper than Cu.

(ii) Partial roasting of sulphide ore forms some oxide. This oxide then reacts with remaining sulphide ore to give copper i.e. self-reduction occurs.

$2Cu_2S + 3O_2 \rightarrow 2Cu_2O + 2SO_2$,

$2Cu_2O + 2Cu_2S \rightarrow 6Cu + SO_2$.

(iii) Though carbon is good reducing agent for oxide but it is poor reducing agent for sulphides. The reduction of metal sulphide does not have large negative value.

Q.2- Explain the method for obtaining pig iron from magnetite.

A.2- Extraction of iron from Magnetite takes place in following steps:-

(i) Concentration of ore: - It is done by Gravity separation followed by magnetic separation process.

(ii) Calcination: - It involve heating when the volatile matter escapes leaving behind metal oxide.

$$Fe_2O_3.xH_2O \rightarrow Fe_2O_3 + xH_2O\ .$$

(iii) Roasting: - It involves heating of ore in presence of air, thus moisture,CO_2,SO_2, As_2O_3 removed And FeO oxidized to Fe_2O_3.

(iv) Smelting of roasted ore: - A mixture of ore, coke & $CaCO_3$ is smelted in long BLAST FURNACE. Following reaction takes place at different temperature zones:-

(i) Zone of reduction: - Temperature range 250^oC-700^oC

$$3Fe_2O_3+CO \longrightarrow 2Fe_3O_4+CO_2$$

$$Fe_3O_4+CO \longrightarrow 3FeO+ CO_2$$

$$FeO +CO \longrightarrow Fe+ CO_2$$

(ii) Zone of slag formation:- Temperature range 800^oC-1000^oC

$$CaCO3 \longrightarrow CaO+CO2$$

$CaO+SiO_2 \longrightarrow CaSiO_3$, $P_4O_{10}+10C \longrightarrow 4P+10CO$,

$SiO_2+2C \longrightarrow Si+2CO$, $MnO_2+2C \longrightarrow Mn+2CO$

(iii) Zone of fusion:- Temperature range 1150^oC-1350^oC

$$CO_2 + C \longrightarrow 2CO$$

(iv) Zone of fusion:- Temperature range 1450^oC-1950^oC

$$C +O_2 \longrightarrow CO_2$$

Thus, Pig iron is obtained from Blast Furnace.

Q.3- Describe the principles of extraction of copper from its ore .

Q.4- Name the principal ore of aluminium and describe how Al is extracted from its ore.

A.4- Important ores -(i) Bauxite $Al_2O_3.xH_20$ (ii) Corrundum Al_2O_3. Bauxite is commercially important ore of Al.

Extraction from Bauxite ore involves the following two stages:-

(i) Purification of bauxite to get pure alumina (Al_2O_3)

(ii) Electrolysis of pure alumina in molten cryolite

Step:-1 Bauxite is treated with NaOH .Following reaction takes place:-

$Al_2O_3 +2NaOH + 3H_2O \longrightarrow 2\ Na\ [Al(OH)_4]$ and impurities of Fe_2O_3,TiO_2 &SiO_2 are removed . Na $[Al(OH)_4]$,then reacts with CO_2 then pure Alumina is obtained.

$$Na\ [Al(OH)_4] + 2CO_2 \rightarrow Al_2O_3.xH_2O + 2NaHCO_3$$

Step:-2 Electrolytic reduction of pure alumina takes place in iron box (cathode) with cryolite (Na_3AlF_6) & fluorspar CaF_2.Graphide rods act as anode. Following reactions take place:-

At cathode:- $Al^{3+} + 3e^- \rightarrow Al$, At Anode:- $2O^{2-} \rightarrow O_2 + 4e^-$

By this process 98.8% pure Aluminum is obtained.

Q.5- Describe the principles of extraction of Zinc from zinc blende .

A.5- Important ores of Zn:-Zinc blende - ZnS, Calamine- $ZnCO_3$, and Zincite – ZnO. ZnS is commercially important ore of Zn.Various stages involved in the extraction of Zn from ZnS are as following:-

(i) Concentration of ore:-It is concentrated by Froth flotation process followed by gravity separation process.

(ii) Roasting: - The concentrated ore is roasted in presence of air. Following reactions take place:-

$$2ZnS + 3O_2 \rightarrow 2ZnO + 2SO_2$$

The mass obtained during roasting is porous and is called porous clinker.

(iii) Reduction of ZnO to Zn: - ZnO is made into bricketts with coke and clay and heated ai1163K.Zn formed distills off and is collected by rapid cooling of zinc vapours.

$$ZnO + C \rightarrow Zn + CO$$

Chapter- 7.

p-Block Elements

Points to remember:-

The general valence shell electronic configuration of p-block elements $ns^2\ np^{1-6}$

GROUP 15 ELEMENTS:-

Group 15 elements ; N, P, As, Sb & Bi

General electronic configuration: ns^2np^3

Physical Properties:-

- Dinitrogen is a diatomic gas while all others are solids.
- N & P are non-metals. As & Sb metalloids & Bi is a metals. This is due to decrease in ionization enthalpy & increase in atomic size.
- Electro negativity decreases down the group.

Chemical properties:-

- Common oxidation states : -3, +3 & +5.
- Due to inert pair effect, the stability of +5 state decreases down the group & stability of +3 state increases .
- In the case of Nitrogen all Oxidation states from +1 to +4 tend to disproportionate in acid solution , e.g.:- $3HNO_2 \rightarrow HNO_3 + H_2O + 2NO$

Anomalous behavior of Nitrogen :- due to its small size, high electronegativity, high ionization enthalpy and absence of d-orbital.

N_2 has unique ability to form pπ-pπ multiple bonds whereas the heavier element of this group do not form pπ –pπ because their atomic orbitals are so large & diffuse that they cannot have effective overlapping.

Nitrogen exists as diatomic molecule with triple bond between the two atoms whereas other elements form single bonds in elemental state.

N cannot form dπ-pπ due to the non-availability of d-orbitals whereas other elements can.

Trends In Properties:-

Stability - $NH_3>PH_3>AsH_3>SbH_3>BiH_3$

Bond Dissociation Enthalpy- $NH_3>PH_3>AsH_3>SbH_3>BiH_3$

Reducing character - $NH_3>PH_3>AsH_3>SbH_3>BiH_3$

Basic character- $NH_3>PH_3>AsH_3>SbH_3>BiH_3$

Acidic character- $N_2O_3>P_2O_3>As_2O_3>Sb_2O_3>Bi_2O_3$

Dinitrogen:-

Preparation

- Commercial preparation – By the liquefaction & fractional distillation of air.
- Laboratory preparation – By treating an aqueous solution NH_4Cl with sodium nitrate .
  $NH_4Cl + NaNO_2 \rightarrow N_2 + 2H_2O + NaCl$
- Thermal decomposition of ammonium dichromate also give N_2.
  $(NH_4)_2Cr_2O_7 \rightarrow N_2 + 4H_2O + Cr_2O_3$
- Thermal decomposition of Barium or Sodium azide gives very pure N_2.

PROPERTIES

At high temperature nitrogen combines with metals to form ionic nitride (Mg_3N_2) & with non-metals , covalent nitride.

AMMONIA PREPARATION

- In laboratory it is prepared by heating ammonium salt with NaOH or lime.
  $2NH_4Cl + Ca(OH)_2 \rightarrow 2NH_3 + 2H_2O + CaCl_2$
- In large scale it is manufactured by Haber 'process
  $N_2 + 3H_2 \rightarrow 2NH_3$
  $\Delta H^0 = -46.1 kJ/mol$
  Acc.to Lechatelier's principle the favourable conditions for the manufacture of NH_3 are:-
  Optimum temperature: 700 K
  High pressure: 200 atm

Catalyst: Iron Oxides

Promoter: K_2O & Al_2O_3

PROPERTIES

Ammonia is a colorless gas with pungent odour.

Highly soluble in water.

In solids & liquid states it exists as an associated molecule due to hydrogen bonding which accounts for high melting & boiling points of NH_3

Trigonal Pyramidal shape of NH_3 molecule.

Aqueous solution of ammonia is weakly basic due to the formation of OH^- ion .

$ZnSO_4 + 2NH_4OH \rightarrow Zn(OH)_2 + (NH_4)_2SO_4$

Ammonia can form coordinate bonds by donating its lone on nitrogen, ammonia forms complexes.

$CuSO_4 + 4NH_3 \rightarrow [Cu(NH_3)_4]_2SO_4$

Name	Formula	Oxidation state	Chemical nature
Nitrous oxide or Laughing gas	N_2O	+1	Neutral
Nitric oxide	NO	+2	Neutral
Dinitrogen trioxide	N_2O_3	+3	Acidic
Dinitrogen tetra oxide	N_2O_4or NO_2	+4	Acidic
Dinitrogen pentaoxide	N_2O_5	+5	Acidic

NITRIC ACID

PREPARATION: Ostwald's Process – it is based upon catalytic oxidation of ammonia by atmospheric oxidation . The main steps are

1) $4NH_3 + 5O_2 \xrightarrow[\text{500k, 9 Bar}]{\text{Pt}} 4NO + 6H_2O$

2) $2NO+O_2 \rightarrow 2NO_2$

3) $3NO_2 + H_2O \rightarrow 2HNO_3 +NO$

PROPERTIES:-

(i) Conc. HNO_3 is a strong oxidizing agent & attacks most metals gold & Pt. .
(ii) Cr & Al do not dissolve HNO_3 because of the formation of a positive film of oxide on the surface.
(iii) It oxidizes non-metals like I_2 to HIO_3, C to CO_2 , S to H_2SO_4
(iv) Brown ring test is used to detect NO_3^-.

PHOSPHOROUS:-

ALLOTROPIC FORMS: White , red α-black & β-black .

White phosphorous is more reactive red phosphorous because white P exists as discrete P_4 molecules . in red P several P_4molecules are linked to formed polymeric chain.

PHOSPHINE

Preparation:It is prepared in laboratory by heating white P with concentrated NaOH solution in an

Inert atmosphere of CO_2

$P_4+3NaOH+3H_2O\rightarrow PH_3+3NaH_2PO_2$

Phosphorous halides

Phosphorous forms two types of halides PX_3 & PX_5 (X=F,I,Br)

Trihalides have pyramidal shape and pentahalides have trigonal bipyramidal structure.

OXOACIDS OF PHOSPHOROUS

- **The acids in +3 oxidation state disproportionate to higher & lower oxidation.**

  $4H_3PO_3 \rightarrow 3H_3PO_4 + PH_3$

- **Acids which contains P-H bond have strong reducing properties.EX:-H_3PO_2 are ionisable and cause the basicity.**

- **Hydrogen atom which are attached with oxygen in P-OH form are ionisable**

GROUP-16 ELEMENTS (CHALCOGENS)

Group 16 Elements:O,S,Se,Te,Po

General electronic configuration:ns^2np^4

Element	Occurrence
Oxygen	Comprises 20.946% by volume of the atmosphere.
Sulphur	As sulphates such as gypsum $CaSO_4.2H_2O$,Epsom salt $MgSO_4.7H_2O$ and Sulphides Such as galena PbS, Zinc Blende ZnS, Copper Pyrites $CuFeS_2$
	As metal selenides and tellurides are in sulphide ores.
Se & Te	as a decay product of thorium and uranium minerals.

ATOMIC & PHYSICAL PROPERTIES

- **Ionisation enthalpy decreases from oxygen to polonium.**
- **Oxygen atom has less negative electron gain enthalpy than S because of the compact nature of the oxygen atom.However from the S onwards the value again becomes less negative upto polonium.**

- **Electronegativity gradually decreases from oxygen to polonium, metallic character increases from oxygen to polonium.**
- **Oxygen & S are non-metals, selenium and telerium are metalloids. Po is a radioactive metal.**
- **Oxygen is a diatomic gas while S,Se&Te are octa atomic S_8,Se_8&Te_8 molecules which has puckered ' ring' structure.**

CHEMICAL PROPERTIES

- **Common oxidation state:- -2,+2,+4 &+6.**
- **Due to inert effect,the stability of +6 decreases down the group and stability of +4 increases.**

Oxygen exhibits +1 state in O_2F_2,+2 in OF_2.

Anamolous behavior of oxygen-due to its small size,high electronegativity and absence of d-orbitals.

TREND IN PROPERTIES

Acidic character-$H_2O<H_2S<H_2Se<H_2Te$

Thermal stability-$H_2O>H_2S>H_2Se>H_2Te$

Reducing character-$H_2S<H_2Se<H_2Te$

Boiling point-$H_2S<H_2Se<H_2Te<H_2O$

Reducing property of dioxides-$SO_2>SeO_2>TeO_2$

Stability of halides-F>Cl>Br>I

HALIDES

DI HALIDES: sp^3 hybridisation but angular structure.

TETRA HALIDES:sp^3 hybridisation-see-saw geometry

HEXA HALIDES:sp^3d^2,octahedral SF_6

DIOXYGEN

Prepared by heating oxygen containing salts like chlorates, nitrates

$2KClO_3 \xrightarrow{-heat} 2KCl+3O_2$

OXIDES

A binary compound of oxygen with another element is called oxide. Oxides can be classified on the basis of nature

- **Acidic Oxides:- Non-metallic oxides. Aqueous solutions are acids. Neutralize bases to form salts.Ex:So_2, Co_2, N_2O_5 etc.**
- **Basic Oxides: Metallic oxides. Aqueous solutions are alkalies. Neutralize acids to form salts.Ex:Na_2O, K_2o etc.**
- **Amphoteric oxides:-some metallic oxides exhibit a dual behavior. Neutralize both acids & bases to form salts.**
  Ex:-Al_2O_3, SbO_2, SnO,etc……..

OZONE

PREPARATION

Prepared by subjecting cold, dry oxygen to silent electric discharge.
$3O_2\rightarrow 2O_3$

PROPERTIES

Due to the ease with which it liberates atoms of nascent oxygen, it acts as a powerful oxidizing agent. For eg:- it oxidises lead sulphide to lead sulphate and iodide ions to iodine.
$PbS + 4O_3\rightarrow PbSO_4+4O_2$

SULPHUR DIOXIDE

PREPARATION

Burning of S in air
$S+O_2\rightarrow SO_2$
Roasting of sulphide minerals
(Iron pyrites)
$4FeS_2+110_2\rightarrow 2Fe\ {}_2O_3+8SO_2$
(Zinc blend)$2ZnS+3O_2\rightarrow 2ZnO+2SO_2$

PROPERTIES

- **Highly soluble in water to form solution of sulphurous acid**
  $SO_2+H_2O\rightarrow H_2SO_3$

- SO_2 reacts with Cl_2 to form sulphuryl chloride
  $SO_2+Cl_2 \rightarrow SO_2Cl_2$
- It reacts with oxygen to form SO_3 in presence of V_2O_5 catalyst
  $2SO_2+O_2 \rightarrow 2SO_3$

- Moist SO_2 behaves as a reducing agent. It converts Fe(III) ions to Fe(II) ions& decolourises acidified potassium permanganate (VII) solution(It is the test for the SO_2 gas).

SULPHURIC ACID

PREPARATION

It is manufactured by contact process which involves 3 steps

1. Burning of S or Sulphide ores in air to generate SO_2.
2. Conversion of SO_2 to SO_3 in presence of V_2O_5 catalyst
3. Absorption of SO_3 in H_2SO_4 to give oleum.

PROPERTIES

1. In aqueous solution it ionizes in 2 steps

$H_2SO_4+H_2O \rightarrow H_3O^++HSO_4^-$

$HSO_4^-+H_2O \rightarrow H_3O^++SO_4^{2-}$

2. It is a strong dehydrating agent Eg:-charring action of sugar

$C12H22O11 \xrightarrow{H2SO4} 12C+11H_2O$

3. It is a moderately strong oxidizing agent.

$Cu+2H_2SO_4(conc.) \rightarrow CuSO_4+SO_2+2H_2O$

$C+2H_2SO_4(conc.) \rightarrow CO_2+2SO_2+2H_2O$

GROUP 17 ELEMENTS(HALOGENS)

Group 17 elements: F,Cl,Br,I,At

General electronic configuration:ns^2np^5

Element	Occurence
Fluorine	As insoluble fluorides(fluorspar CaF_2,Cryolite and fluoroapattie)
Cl, Br,I	Sea water contains chlorides, bromides and iodides of Sodium, potassium magnesium and calcium, but is mainly sodium chloride solution(2.5% by mass). Certain forms of marine life(various seaweeds)

ATOMIC & PHYSICAL PROPERTIES

i. Atomic & ionic radii increase from fluorine to iodine.

ii. Ionization enthalpy gradually decreases from fluorine to iodine due to increase in atomic size.

iii. Electron gain enthalpy of fluorine is less than that of chlorine. It is due to small size of fluorine & repulsion between newly added electron &electrons already present in its small 2p orbital.

iv. Electronegativity decreases from fluorine to iodine. Fluorine is the most electronegative element in the periodic table.

v. The color of halogens is due to absorption of radiations in visible region which results in the excitation of outer electrons to higher energy level.

vi. Bond dissociation enthalpy of fluorine is smaller than that of chlorine is due to electron-electron repulsion among the lone pair in fluorine molecules where they are much closer to each other than in case of chlorine. The trend: Cl-Cl>Br-Br>F-F>I-I.

CHEMICAL PROPERTIES

OXIDATION STATES:-1.However, chlorine, bromine &iodine exhibit +1, +3, +5, +7 oxidation states also.

Fluorine forms two oxides OF_2 and O_2F_2. These are essentially oxygen fluorides because of the higher electronegativity of fluorine than oxygen.

Anomalous behavior of fluorine- due to its small size, highest electronegativity, low F-F bond dissociation enthalpy and absence of d-orbitals.

TRENDS IN PROPERTIES

Oxidizing property – $F_2>Cl_2>Br_2>I_2$

Acidic strength- HF<HCl<HBr<HI

Stability & bond dissociation enthalpy- HF>HCl>HBr>HI

Stability of oxides of halogens- I>Cl>Br

Ionic character of halides –MF>MCl>MBr>MI

CHLORINE

PREPARATION

1. $MnO_2 + 4HCl \rightarrow MnCl_2 + Cl_2 + 2H_2O$
2. $4NaCl + MnO_2 + 4H_2SO_4 \rightarrow MnCl_2 + 4\,NaHSO_4 + 2H_2O + Cl_2$
3. $2KMnO_4 + 16HCl \rightarrow 2KCl + 2MnCl_2 + 8H_2O + 5Cl_2$

4. **DEACON'S PROCESS**

   $4HCl + O_2 \xrightarrow{CuCl_2} 2Cl_2 + 2H_2O$

5. By electrolysis of brine solution. Cl_2 is obtained at anode.

PROPERTIES

i. With cold and dilute Cl_2 produces a mixture of chloride and hypochlorite but with hot and concentrated alkalis it gives chloride and chlorate.

$2NaOH+Cl_2 \rightarrow NaCl+NaOCl+H_2O$

$6NaOH+3Cl_2 \rightarrow 5NaCl+NaClO_3+3H_2O$

ii. With dry slaked lime it gives bleaching powder.

$2Ca(OH)_2+2Cl_2 \rightarrow Ca(OH)_2+CaCl_2+2H_2O$

iii. It is a powerful bleaching agent; bleaching action is due to oxidation

$Cl_2+H_2O \rightarrow 2HCl+(O)$

Colored substance+(O)→colorless substance

iv. Action of concentrated H_2SO_4 on NaCl give HCl gas.

$NaCl+H_2SO_4 \xrightarrow{420K} NaHSO_4+HCl$

3:1 ratio of conc. HCl & HNO_3 is known as aquaregia & it is used for dissolving noble metals like Au and Pt.

OXOACIDS OF HALOGENS

Interhalogen compounds are prepared by direct combination of halogens.

Ex: ClF, ClF_3, BrF_5, IF_7

They are more reactive than halogens because X-X' is weaker than X-X bonds in halogens (except F-F).

TYPE	**STRUCTURE**
XX'_3	Bent T-shaped
XX'_5	Square pyramidal
XX'_7	Pentagonal bipyramidal

GROUP 18 ELEMENTS

GROUP 18 ELEMENTS: He, Ne, Ar,Kr,Xe &Rn

General electronic configuration:ns^2np^6

Atomic radii- large as compared to other elements in the period since it corresponds to Vander Waal radii.

Inert – due to complete octet of outermost shell, very high ionization enthalpy & electron gain enthalpies are almost zero.

The first noble compound prepared by Neil Bartlett was $XePtF_6$ &Xenon.

$O_2^+PtF_6^-$.led to the discovery of $XePtF_6$ since first ionization enthalpy of molecular oxygen (1175 $kJmol^{-1}$) was almost identical with that of xenon (1170$kJmol^{-1}$).

PROPERTIES

$Xe+F_2 \xrightarrow{673K,\ 1bar} XeF_2$

$Xe\ (g) + 2F_2\ (g) \xrightarrow{873k,\ 7bar} XeF_4(s)$

$Xe\ (g) + 3F_2\ (g) \xrightarrow{573k,\ 60\text{-}70\ bar} XeF_6(s)$

$XeF_6+MF \rightarrow M^+\ [XeF_7]^-$

$XeF_2+PF5 \rightarrow [XeF]^+[PF_6]^-$

$XeF_6+2H_2O \rightarrow XeO_2F_2+4HF$(partial hydrolysis)

SOLVED QUESTIONS

1 MARK QUESTIONS

1. Ammonia has higher boiling point than phosphine. Why?

   -Ammonia forms intermolecular H-bond.

2. Why does PCl_3 fume in moisture?

   In the presence of (H_2O), PCl_3 undergoes hydrolysis giving fumes of HCl .

   $PCl_3 + 3H_2O \rightarrow H_3PO_3 + 3HCl$

3. What Happens when H_3PO_3 is Heated ?

   It disproportionate to give orthophosphoric acid and Phosphine.

$4H_3PO_3 \rightarrow 3H_3PO_4 \ PH_3$

4. Why H_2S is acidic and H_2O is neutral ?

   The S – H bond is weaker than O – H bond because the size of S atom is bigger than that of O atom . Hence H_2S can dissociate to give H^+ Ions in aqueous solution.

5. Name two poisonous gases which can be prepared from chlorine gas?

Phosgene ($COCl_2$), tear gas (CCl_3NO_2)

6. Name the halogen which does not exhibit positive oxidation state .

   Flourine being the most electronegative element does not show positive oxidation state .

7. Iodine forms I_3^- but F_2 does not form F_3^- ions .why?

   Due to the presence of vacant d-orbitals , I_2 accepts electrons from I-ions to form I_3- ions , but because of d-orbitals F_2 does not accept electrons from F-ions to form F_3 ions.

8. Draw the structure of peroxos ulphuric acid.

9. Phosphorous forms PCl_5 but nitrogen cannot form NCl_5. Why?

   Due to the availability of vacant d-orbital in P.

2 MARK QUESTION (SHORT ANSWER TYPE QUESTION)

1. Why is HF acid stored in wax coated glass bottles?

This is because HF does not attack wax but reacts with glass. It dissolves SiO_2 present in glass forming hydrofluorosilicic acid.

$SiO_2 + 6HF \rightarrow H_2SiF_6 + 2H_2O$

2. What is laughing gas? Why is it so called? How is it prepared?

Nitrous oxide (N_2O) is called laughing gas, because when inhaled it produced hysterical laughter. It is prepared by gently heating ammonium nitrate.

$NH_4NO_3 \rightarrow N_2O+2H_2O$

3. Give reasons for the following:

(i) Conc.HNO_3 turns yellow on exposure to sunlight.

(ii) PCl_5 behaves as an ionic species in solid state.

(i)Conc HNO_3 decompose to NO_2 which is brown in colour & NO_2 dissolves in HNO_3 to it yellow.

(ii)It exists as $[PCl_4]^+$ $[PCl_6]^-$ in solid state.

4. What happens when white P is heated with conc. NaOH solution in an atmosphere of CO_2? Give equation.

Phosphorus gas will be formed.

$P_4+3NaOH+3H_2O \rightarrow PH_3+3NaH_2PO_2$

5. How is ozone estimated quantitatively?

When ozone reacts with an excess of potassium iodide solution

Buffered with a borate buffer (pH 9.2), Iodide is liberated which can be titrated against a standard solution of sodium thiosulphate . This is a quantitative method for estimating O_3 gas.

6. Are all the five bonds in PCl_5 molecule equivalent? Justify your answer.

PCl_5 has a trigonal bipyramidal structure and the three equatorial P-Cl bonds are equivalent, while the two axial bonds are different and longer than equatorial bonds.

7. NO_2 is coloured and readily dimerises.Why ?

NO_2 contains odd number of valence electrons.It behaves as a typical odd molecules .On dimerization; it is converted to stable N_20_4 molecule with even number of electrons.

8. Write the balanced chemical equation for the reaction of Cl_2 with hot and concentrated NaOH .Is this reaction a dispropotionation reaction? Justify:

$3Cl_2+6NaOH \rightarrow 5NaCl+NaClO_3+3H_2O$

Yes, chlorine from zero oxidation state is changed to -1 and +5 oxidation states.

9. Account for the following.

(i)SF_6 is less reactive than SF_4.

(ii) 0f the noble gases only xenon compounds are known.

Ans. (i)In SF_6 there is less repulsion between F atoms than In SF_4.

(II)Xe has low ionisation enthalpy & high polarising power due to larger atomic size.

10. With what neutral molecule is ClO^- Isoelectronic? Is that molecule a Lewis base?

ClF .Yes, it is Lewis base due to presence of lone pair of electron.

3 MARK QUESTIONS

1(i) why is He used in diving apparatus?

(ii)Noble gases have very low boiling points.Why?

(iii)Why is ICl more reactive than I_2?

(I)It is not soluble in blood even under high pressure.

(ii)Being monoatomic they have weak dispersion forces.

(ii)I-Cl bond is weaker than l-l bond

2. Complete the following equations.

(i)$XeF_4+H_2O \rightarrow$

(ii)$Ca_3P_2+H_2O \rightarrow$

(iii)AgCl(s) +NH_3 (aq)→

(i) $6XeF_4+12H_2O \rightarrow 4Xe+2XeO_3+24HF+3O_2$

(ii)$Ca_3P_2+6H_2O \rightarrow 3Ca(OH)_2+2PH_3$

(iii)$AgCl(s) +2NH_3(aq) \rightarrow [Ag(NH_3)_2]Cl(aq)$

3. (i)How is $XeOF_4$ prepared ?Draw its structure.

(ii)When HCl reacts with finely powdered iron, it forms ferrous chloride and not ferric chloride .Why?

(i)Partial hydrolysis of $XeOF_4$

$XeF_6+H_2O \rightarrow XeOF_4+2HF$

Structure -square pyramidal.

(ii) Its reaction with iron produces H_2

$Fe+2HCl \rightarrow FeCl_2+H_2$

Liberation of hydrogen prevents the formation of ferric chloride.

5 MARK QUESTION

1. Account for the following.

(i)Noble gas form compounds with F_2 &O_2 only.

(ii)Sulphur shows paramagnetic behavior.

(iii)HF is much less volatile than HCl.

(iv)White phosphorous is kept under water.

(v)Ammonia is a stronger base than phosphine.

(i)F_2&O_2 are best oxidizing agents.

(ii)In vapour state sulphur partly exists as S_2 molecule which has two unpaired electrons in the antibonding pi *orbitals like O_2 and, hence, exhibit paramagnetism.

(iii)HF is associated with intermolecular H bonding.

(iv) Ignition temperature of white phosphorous is very low (303 K). Therefore on explosure to air, it spontaneously catches fire forming P_4O_{10}. Therefore to protect it from air, it is kept under water.

(v)Due to the smaller size of N, lone pair of electrons is readily available.

2. When Conc. H_2SO_4 was added to an unknown salt present in a test tube, a brown gas (A) was evolved. This gas intensified when copper turnings were added in to test tube. On cooling gas (A) changed in to a colourless gas (B).

(a)Identify the gases 'A' and 'B'

(b)Write the equations for the reactions involved

The gas 'A' is NO_2 whereas 'B' is N_2O_4.

$NaNO_3 + H_2SO_4 \rightarrow NaHSO_4 + HNO_3$

Salt (conc.)

$Cu + 4HNO_3$ (Conc.) $\rightarrow Cu(NO_3)_2 + 2NO_2 + 2H_2O$

Blue Brown (A)

$2NO_2$ (on cooling) $\rightarrow N_2O_4$

Colourless(B)

3. Arrange the following in the increasing order of the property mentioned.

(i)HClO, $HClO_2$, $HClO_3$, $HClO_4$ (Acidic strength)

(ii)As_2O_3, ClO_2, GeO_3, Ga_2O_3 (Acidity)

(iii)NH_3, PH_3, AsH_3, SbH_3 (H-E-H bond angle) (iv)HF, HCl, HBr, HI (Acidic strength)

(v)MF, MCl, MBr, MI (ionic character)

(i)Acidic strength:$HClO<HClO_2<HClO_3<HClO_4$

(ii)Acidity: $Ga_2O_3<GeO_2<AsO_3<ClO_2$

(iii)Bond angle: $SbH_3<AsH_3<PH_3<NH_3$

(iv)Acidic strength: HF<HCl<HBr<HI

(v)Ionic character: MI<MBr<MCl<MF

ASSIGNMENTS

Very shot answer type questions:

1) PH_3 has lower boiling point than NH_3. Explain.

2) Why are halogens coloured.

3) What are chalcogens?

4) Which noble gas is Radioactive?

5) Explain why fluorine always exhibit an oxidation state of - 1 only.

6) Which compound led to the discovery of compounds of noble gas?

7) Name the most electronegative element.

8) Why is OF_6 compound not known?

9) Why N_2 is not reactive?

10) Ammonia acts as a ligand. Explain.

Short answer type questions:

1) White Phosphorous is more reactive than red phosphorous. Explain.

2) Why do noble gases have comparatively large atomic sizes?

3) Arrange in decreasing order of Ionic character

M – F, M – Cl, M – Br, M – I

4) Phosphinic acid behaves as a monoprotic acid

5) Arrange the following in the order of property indicated:

a) AS_2O_3, ClO_2, GeO_2, Ga_2O_3__Increasing acidity

b) H_2O, H_2S, H_2Se, H_2Te__Increasing acid strength.

6) Arrange in decreasing order of bond energy:

F_2, Cl_2, Br_2, I_2

7) Complete the following:

i) $HNO_3 + P_4O_{10} \rightarrow$

ii) $IO_3^- + I^- + H^+ \rightarrow$

8) Give the chemical reactions in support of following observations:

a) The +5 oxidation state of Bi is less stable than +3 oxidation state.

b) Sulphur exhibits greater tendency for catenation than selenium.

9) How would you account for following?

i) Enthalpy of dissociation of F_2 is much less than that of Cl_2.

ii) Sulphur in vapour state exhibits paramagnetism.

10) Draw structures of following:

a) Per-oxomonosulphuric acid H_2SO_5

b) XeF_4

Level – III

1. Complete and balance:

i) $F_2 + H_2O$ Cold $\rightarrow$

ii) $BrO^-_3 + F_2 + OH^- \rightarrow$

iii) $Li + N_2$ (cold) $\rightarrow$

iv) $NH_3 + NaOCl \rightarrow$

2) Despite lower electron affinity of F_2, it is stronger oxidising agent than Cl_2. Explain.

3) Give reasons:

a) Nitric oxide becomes brown when released in air.

b) PCl_5 is ionic in nature and exist in the solid state.

4) Which of the two is more covalent $SbCl_3$ or $SbCl_5$?

5) Addition of Cl_2 to KI solution gives a brown colour but excess of it turns colourless. Explain.

Chapter:-8 The d-and f-Block Elements

POINTS TO BE REMEMBERED: ---

1. The elements of periodic table belonging to group 3 to 12 are known as d-Block elements.
2. The general electronic configuration of these elements is (n -1)d^{1-10} ns $^{1-2}$
3. d- Block elements are collectively known as Transition Elements because properties of these elements vary in between s-Block and p-Block elements.
4. A transition element should have partially filled (n-1) d orbital.
5. Group 12 elements i.e. Zn, Cd, Hg have completely filled (n-1) d-orbital in atomic & ionic state & thus these elements are considered as Typical Transition Elements.
6. All these elements are metals. They are less electropositive than s-block elements & more electropositive than p-block elements.
7. The atomic radii decreases from group 3 to 6 (i.e. Sc to Cr) because of increase in effective nuclear charge gradually.
8. The atomic radii of group 7,8 9 &10 elements (i.e. Fe,Co,Ni) is almost same because pairing of electrons take place in (n-1)d orbital causing repulsion i.e. shielding of (n-1)d orbital.
9. Group 11 &12 elements i.e. Cu & Zn have bigger size due to strong shielding of completely filled (n-1)d orbital.
10. The transition elements show variable oxidation state due to small energy difference between (n-1)d &ns orbital as a result both (n-1)d &ns electrons take part in bond formation.
11. The highest oxidation state of an element is equal to number of unpaired electrons present in (n-1)d &ns orbital.
12. Transition elements have high enthalpy of atomization/ sublimation Because of large number of unpaired electrons in their atoms, they have stronger interatomic interaction and hence strong metallic bonding is present between atoms.
13. Most of transition elements are paramagnetic due to presence of unpaired electrons in (n-1) d orbital.
14. Most of transition elements are used as catalyst. It is due to (i) partially filled (n-1) d orbital (ii) Variable oxidation state (iii) Ability to change oxidation state frequently.
15. Most of transition elements form coloured compounds due to presence of unpaired electrons in (n-1) d orbital & thus they can undergo d-d transition.
16. Most of transition elements form complex compounds due to (i) small size (ii) high charge (iii) presence of vacant d-orbital of suitable energy.
17. Transition elements have lower value of Reduction Potential due to high ionization potential, high heat of sublimation & low enthalpy of hydration.
18. Transition elements form interstitial compounds because size of interstitial voids is similar to size of non- metals C, N, O, H.
19. Transition elements form alloys due to similar ionic radii.
20. The oxides of transition metals in lower oxidation state are BASIC, intermediate oxidation state are AMPHOTERIC, highest oxidation state are ACIDIC.

LANTHANOIDS: ---

1. The 14 elements after Lanthanum having atomic number 58 to 71 are collectively known as Lanthanoids.
2. The general electronic configuration of these elements is [Xe] $4f^{1-14}$, $5d^{0-1}$,$6s^2$.
3. Most common oxidation state of these elements is +3, but Ce shows +4, Eu +2, because they acquire stable configuration.
4. The size of Lanthanoids and its trivalent ion decreases from La to Lu due to poor shielding of 4f electrons. It is known as lanthanoids contraction.

ACTINOIDS:--

1. The 14 elements after Actinium having atomic number 90 to 113 are collectively known as Actinoids.

2. The general electronic configuration of these elements is [Rn] $5f^{1-14}$, $6d^{0-1}$,$7s^{2}$.
3. The size of actinoids and its trivalent ion decreases from Ac to Lw due to poor shielding of 5f electrons. It is known as actinoids contraction.
4. The elements after U (92) are man made known as transuranic elements.

POTASSIUM DICHROMATE:--

Preparation: - It takes place in three steps-

(i) Conversion of chromite ore to sodium chromate.
(ii) Conversion of sodium chromate to sodium dichromate.
(iii) Conversion of sodium dichromate to potassium dichromate

Following reaction take place:--

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

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

$$Na_2Cr_2O_7 + 2\ KCl \longrightarrow K_2Cr_2O_7 + 2\ NaCl$$

POTASSIUM PERMANGNATE:--

Preparation: --

It takes place in two steps:-

(i) Conversion of pyrolusite ore into potassium magnate
(ii) Conversion of potassium mangnate to potassium permaganate

Following reactions take place:-

$$2\ MnO_2 + 4\ KOH + O_2 \longrightarrow 2\ K_2MnO_4 + 2H_2O$$
$$3\ MnO_4^{\ 2-} + 4H^+ \longrightarrow 2\ MnO_4^- + MnO_2 + 2H_2O$$

QUESTION ANSWERS

(TWO MARK QUESTIONS)

Q.1-Explain briefly how +2 oxidation state becomes more and more stable in the first half of the first row transition elements with increasing atomic number.

A.1-In M^{2+} ions, 3d-orbitals get occupied gradually as the atomic number increases. Since, the number of empty d-orbitals decreases, the stability of cations increases from Sc^{2+} to Mn^{2+} .Mn^{2+} is most stable as all d-orbitals are singly occupied.

Q.2- Explain why transition elements have many irregularities in their electronic configurations?

A.2-In the transition elements, there is a little difference in the energy of (n-1) d-orbitals and ns-orbitals. Thus, incoming electron can occupy either of shell. Hence, transition elements exhibit many irregularities in their electronic configurations.

Q.3-What are different oxidation states exhibited by Lanthanides?

A.3-The common stable oxidation state of lanthanides is +3.However some members also show oxidation states of +2 & +4.

Q.4-How is the variability in oxidation states of transition metals different from that of the non-transition metals? Illustrate with examples.

A.4-The transition elements use its (n-1)d, ns and np orbital and the successive oxidation states differ by unity. For example, Mn shows all the oxidation states from +2 to +7. On other hand non transition elements use its ns, np and nd orbitals and the successive oxidation states differ by two units e.g. Sn^{2+}, Sn^{4+} etc.

Q.5- Why do transition elements show variable oxidation states?

A.5- The transition elements show variable oxidation state due to small energy difference between (n-1) d &ns orbital as a result both (n-1)d &ns electrons take part in bond formation.

Q.6-Why are Mn^{2+} compounds more stable than Fe^{2+} compounds towards oxidation to +3 state?

A.6-The electronic configuration of Mn^{2+} is [Ar] $3d^5$, i.e. all five d-orbitals are singly occupied. Thus this is stable electronic configuration and further loss of electron requires high energy .on other hand the electronic configuration of $Fe^{2+}$is [Ar] $3d^6$, i.e. Loss of one electron requires low energy.

Q.7-To what extent do the electronic configuration decide the stability of oxidation state in the first series of the transition elements? Illustrate your answer with an example.

A.7-In a transition series, the oxidation state which lead to exactly half filled or completely filled orbitals are more stable.e.g. the electronic configuration of Fe is [Ar] $3d^6$,$4s^2$. It shows various oxidation state but Fe(III) is more stable than Fe(II).

Q.8-What is meant by disproportionation? Give two examples.

A.8-Those reactions in which same substance undergoes oxidation as well as reduction are called disproportionation reactions.e.g.

$$2Cu^+ \rightarrow Cu^{2+} + Cu$$

$$3\ MnO_4^{2-} + 4\ H^+ \rightarrow 2\ MnO_4^- + MnO_2 + 2\ H_2O$$

Q.9- Which metal in the first series of transition metals exhibits +1 oxidation state most frequently and why?

A.9- Copper with configuration [Ar] $3d^{10}\ 4s^1$ exhibits +1 oxidation state. Copper loses $4s^1$ electron easily and achieved a stable configuration $3d^{10}$ by forming Cu^+.

Q.10- What are inner transition elements?

A.10- The f-block elements in which the last electron accommodated on (n-2) f-subshell are called inner transition elements. These include atomic numbers 58 to 71 and from 90 to 103.

Q.11- The paramagnetic character in 3d-transition series elements increases upto Mn and then decreases. Explain why?

A.11- In the 3d-transition series as we move from Sc (21) to Mn (25) the number of unpaired electrons increases and hence paramagnetic character increases. After Mn, the pairing of electrons in the d-orbital starts and the number of unpaired electrons decreases and hence, paramagnetic character decreases.

Q.12- Comment on the statement that elements of the first transition series possess many properties different from those of heavier transition metal

A.12-The following points justify that the given statement is true:-

(i) Ionization enthalpies of heavier transition elements are higher than the elements of 3d series. Consequently, heavier transition elements are less reactive in comparison to 3d-elements.

(ii) Melting points of heavier transition elements are higher than 3d-elements.

(iii) Higher oxidation states of heavier transition elements are stable whereas lower oxidation states are stable in 3d-elements.

Q.13-What are transition elements? Which d-block elements are not regarded as transition elements and why?

A.13- An element which has partially filled (n-1) d orbital is known as transition elements. Group 12 elements i.e. Zn, Cd, Hg have completely filled (n-1) d-orbital in atomic & ionic state & thus these elements are not considered as Transition Elements.

Q.14-What are interstitial compounds? Why are such compounds well known for transition metal?

A.14- Compounds of transition metal with relatively smaller non-metals are known as interstitial compounds. These compounds are well known for transition metals because size of C, N, O, and B is similar to size of interstitial voids of transition metal

Q.15-For the first row of transition metals the E^0 values are:-

E^0 values	V	Cr	Mn	Fe	Co	Ni	Cu
M^{2+}/M	-1.18	-0.91	-1.18	-0.44	-0.28	-0.25	+0.34

Explain the irregularity in the above values.

A.15-The E^0 (M^{2+}/M) values are not regular which can be explained from the irregular variation of ionization energy and sublimation energy of Mn due to half-filled orbitals.

(THREE MARK QUESTIONS)

Q.1- Decide giving reason which one of the following pairs exhibits the property indicated:

(i)Sc^{3+} or Cr^{3+} exhibits paramagnetism

(ii)V or Mn exhibits more number of oxidation states

(iii)V^{4+} or V^{5+} exhibits colour

A.1- (i) Sc=[Ar] $3d^14s^2$; Sc^{3+}=[Ar] ; it has no unpaired electron so diamagnetic
Cr=[Ar] $3d^54s^1$; Cr^{3+}=[Ar]$3d^3$; it has three unpaired electrons paramagnetic

(ii) V=[Ar] $3d^3 4s^2$ Mn=[Ar] $3d^5 4s^2$ Thus V exhibit oxidation states of +2, +3, +4, +5
Whereas Mn exhibit oxidation states of +2 to +7.

(iii) V^{4+}=[Ar] $3d^1$ → coloured V^{5+}=[Ar] → colourless

Q.2-(a) Describe the general trends in the following properties of the first series of the transition elements:-

(i) Stability of +2-oxidation state

(ii) Formation of oxometal ions

(b) Write steps involved in the preparation of $KMnO_4$ from K_2MnO_4

A.2- (a) i-The elements of first transition series show decreasing tendency to form divalent cation as we move left to right in the series. This trend is due to general increase in the first and second ionization energy. The greater stability of Mn^{2+} is due to half filled d^5 configuration and that of zinc is due to d^{10} configuration.

(ii) All metal except Sc from oxide of type MO which are basic. The highest oxidation number in all oxide, coincide with the group number and is attain in Sc_2O_3 to Mn_2O_7. Formation of oxoanions is due to high electro negativity and small size of oxygen atom.

2-(b) It takes place in two steps:-

(iii) Conversion of pyrolusite ore into potassium mangnate.
(iv) Conversion of potassium mangnate to potassium permanganate.

Following reactions take place:-

$$2\,MnO_2 + 4\,KOH + O_2 \longrightarrow 2\,K_2MnO_4 + 2H_2O$$

$$3\,MnO_4^{\,2-} + 4H^+ \longrightarrow 2\,MnO_4^- + MnO_2 + 2H_2O$$

Q.3-(a) Write the steps involve in the preparation of K2Cr2O7 from chromite ore.

(b) What is the effect of pH on dichromate ion solution?

A.3-(a):- It takes place in three steps-

(iv) Conversion of chromite ore to sodium chromate.
(v) Conversion of sodium chromate to sodium dichromate.
(vi) Conversion of sodium dichromate to potassium dichromate

Following reactions take place:--

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

$$2Na2CrO4 + 2\,H^+ \longrightarrow Na2Cr2O7 + 2\,Na^+ + H2O$$

$$Na2Cr2O7 + 2\,KCl \longrightarrow K2Cr2O7 + 2\,NaCl$$

(b) Dichromate ion is orange in acidic solution (pH<7) and turns yellow in basic solution. It is due to interconversion of dichromate ion to chromate ion. Following reactions take place:-

$$2\,CrO_4^{2-}\ (yellow) + 2\,H^+ \rightarrow Cr_2O_7^{2-}\ (orange) + H_2O$$

$$Cr_2O_7^{2-}\ (orange) + 2\,OH^- \rightarrow 2\,CrO_4^{2-}\ (yellow) + H_2O.$$

Q.4- (a) What is lanthanide contraction? What effect does it have on the chemistry of the elements, which follow lanthanoids?

(b) The chemistry of actinoid elements is not so much smooth as that of lanthanoids. Justify these statements by giving some examples from the oxidation state of these elements.

A.4- (a)The size of Lanthanoids and its trivalent ion decreases from La to Lu. It is known as lanthanoids contraction.

Cause: - It is due to poor shielding of 4f electrons.

Consequences of lanthanide contraction: - (i) Basic strength of hydroxide decreases from $La(OH)_3$ TO $Lu(OH)_3$. (ii) Because of similar chemical properties lanthanides are difficult to separate.

(b) Lanthanoids show limited number of oxidation states i.e. +2, +3, +4 (out of which +3 is most common) . This is because of a large energy gap between 4f, 5d and 6s subshell. The dominant oxidation state of actinides is also +3 but they show a number of other oxidation state also e.g. +4, +5, and +7. This is due to small energy difference between 5f, 6d and 7s orbitals.

Q.5- Give examples and suggest reasons for the following features of the transition metal chemistry:

(i) The lowest oxide of transition metal is basic, the highest is amphoteric/acidic.

(ii) A transition metal exhibits highest oxidation state in oxides and fluorides.

(iii) Of the d^4 species, Cr^{2+} is strongly reducing while manganese(III)is strongly oxidizing.

A.5-(i) The oxide of transition metals in lower oxidation states are generally basic while those in the higher oxidation states are acidic. Acidic character increases with increase in oxidation state is due to decrease in size of metal ion and increase in charge density.e.g. MnO (basic), Mn_3O_4 (amphoteric), Mn_2O_7 (acidic).

(ii) A transition metal exhibits higher oxidation states in oxides and fluorides because oxygen and fluorine are the most electronegative elements and thus easily can unpair electrons of metal atom.

(iii) Because oxidizing and reducing property depends on E^0 value. Since E^0 value of Cr^{3+}/Cr^{2+} is negative while that of Mn^{3+}/Mn^{2+} is positive, as a result Cr(II) act as reducing agent and Mn(III) is strong oxidizing.

Q.6-For M $^{2+}$/M and M $^{3+}$/M^{2+} systems ,the E^o values for some metals are as follows:

Cr^{2+}/Cr	-0.9V	Cr^{3+}/Cr^{2+}	-0.4V
Mn^{2+}/Mn	-1.2V	Mn^{3+}/Mn^{2+}	+ 1.5V
Fe^{2+}/Fe	-0.4V	Fe^{3+}/Fe^{2+}	+0.8V

Use this data to comment upon :-

(i)the stability of Fe^{3+} in acid solution as compared to Cr^{3+} or Mn^{3+} and

(ii)the ease with which iron can be oxidized as compared to a similar process for either chromium or manganese metal.

A.6- (i)E^o for Cr^{3+}/Cr^{2+} is -0.4V i.e. negative, this means Cr^{3+} ions in the solution cannot be reduced to Cr^{2+} easily i.e. Cr^{3+} is stable. As Mn^{3+}/Mn^{2+} is +1.5V i.e positive means Mn^{3+} can easily reduced to Mn^{2+} ions in comparison to Fe^{3+} ions. Thus relatively stability of these ions is:-

$$Mn^{3+} < Fe^{3+} < Cr^{3+}$$

(ii) The oxidation potentials for the given pairs will be +0.9V, +1.2V and 0.4V. Thus, the order of their getting oxidized will be in the order Mn>Cr>Fe.

Q.7-Account for the following statements:

(i)Cobalt (II) is stable in aqueous solution but in the presence of strong ligands and air, it can be oxidized to Co (III).

(ii)The d^1 configuration is very unstable in ions.

(iii)One among the lanthanides, Ce (III) can be easily oxidized to Ce (IV).

A.7- (i) Strong ligands force cobalt (II) to lose one more electron from 3d-subshell and thereby induced d^2sp^3 hybrisation.

(ii) The ion with d^1 configuration try to lose the only electron in order to acquire inert gas configuration.

(iii) The configuration of Ce is [Xe] $4f^1$, $5d^1$,$6s^2$. There is no much difference between the energy of 4f, 5d and 6s orbitals and thus, Ce can utilize electrons present in these orbitals and hence oxidation state of +4.

Q.8- Compare the chemistry of actinides with that of the lanthanoids with special reference to:

(i) electronic configuration
(ii) atomic and ionic sizes and
(iii) oxidation state
(iv) chemical reactivity

A.8-

Comparison of Lanthanoids and Actinoids

Properties	Lanthanoids	Actinoids
Electronic configuration	[Xe] $4f^{1-14}$, $5d^{0-1}$,$6s^2$	[Rn] $5f^{1-14}$, $6d^{0-1}$,$7s^{2.}$
Atomic/ionic sizes	Size decreases from La to Lu, and size is more than actinides.	Size decreases from Ac to Lw, and size is smaller than lanthanoids due to poorer shielding of 5f electrons
Oxidation states	Common oxidation is +3 where other oxidation states are +2, +4.It is due to a large energy gap between 4f, 5d and 6s subshell	Common oxidation is +3 where other oxidation states are +2, +4,+5 and+7 due to due to small energy difference between 5f, 6d and 7s orbitals

Chemical reactivity	The earlier member quite reactive but with increasing atomic number they behave like aluminum.	The actinides highly reactive ,especially in finely divided.
Complex formation	Less tendency to form complex due to less charge density.	More tendency to form complex due to high charge density.

Q.9-(a) What is actinoid contraction? What effect does it have on the chemistry of the elements, which follow actinides?

(b) Name an important alloy, which contains some of the lanthanide metals. Mention its uses.

A.9- (a) The size of actinoid and its trivalent ion decreases from Ac to Lw. It is known as l actinides contraction.

Cause: - It is due to poor shielding of 5f electrons.

Consequences of actinides contraction: - (i) Basic strength of hydroxide decreases from $Ac(OH)_3$ To $Lw(OH)_3$. (ii) Because of similar chemical properties l actinides are difficult to separate.

(b) An important alloy containing lanthanoid metals is mischmetal, which contains 95% lanthanide metal and 5% Fe along with traces of S, C, Ca and Al. It is used in Mg-based alloy to produce bullets, shells and lighter flint.

Q.10- Complete following reactions:-

(i) $MnO_4^- + H^+ + Fe^{2+} \rightarrow$ ------------+-------------+-------------

(ii) $MnO_4^- + C_2O_4^{2-} + H^+ \rightarrow$ ------------+-------------+-------------

(iii) $MnO_4^- + OH^- + I^- \rightarrow$ ------------+-------------+-------------

A.10-(i) $MnO_4^- + 8H^+ + 5Fe^{2+} \rightarrow Mn^{2+} + 5Fe^{3+} + 4H_2O$

(ii) $2MnO_4^- + 5C_2O_4^{2-} + 16H^+ \rightarrow 2Mn^{2+} + 10CO_2 + 8H_2O$

(iii) $2MnO_4^- + H_2O + I^- \rightarrow 2MnO_2 + 2OH^- + IO_3^-$

(FIVE MARK QUESTIONS)

Q.1-Explain giving reasons:

(i) Transition metals and many of their compounds show paramagnetic behaviour.
(ii) The enthalpies of atomisation of the transition metals are high.
(iii) The transition metals generally form coloured compounds.
(iv) Transition metals and their many compounds act as good catalyst.
(v)Transition metals have a strong tendency to form complexes.

A.1- (i)Transition metals and many of their compounds show paramagnetic behaviour due to presence of unpaired electrons in (n-1) d orbital.

(ii) The enthalpies of atomisation of the transition metals are high Because of large number of unpaired electrons in their atoms, they have stronger interatomic interaction and hence strong metallic bonding is present between atoms.

(iii) The transition metals generally form coloured compounds due to presence of unpaired electrons in (n-1) d orbital & thus they can undergo d-d transition.

(iv) Transition metals and their many compounds act as good catalyst It is due to (i) partially filled (n-1) d orbital (ii) Variable oxidation state (iii) Ability to change oxidation state frequently.

(v) Transition metals have a strong tendency to form complexes Most of transition elements form complex compounds due to (i) small size (ii) high charge (iii) presence of vacant d-orbital of suitable energy.

Q.2- Give reasons for the following:-

(i) Fe has higher melting point than Cu.
(ii) $[Ti(H_2O)_6]^{3+}$ is coloured while $[Sc(H_2O)_6]$ is colourless.
(iii)The 4d and 5d series of transition metals have more frequent metal-metal bonding in their compound than do the 3d metals.
(iv)Transition metals some time exhibit very low oxidation state such as +1and 0.

(v)Hg is not considered a transition metal.

A.2-(i) This is because Fe ($3d^6$, $4s^1$) has four unpaired electrons in 3d-subshell. While Cu ($3d^{10}$, $4s^1$) only one unpaired electron in 4s shell. Hence metallic bonding is stronger in Fe than those in Cu.

(ii) The oxidation state of Ti in $[Ti(H_2O)_6]^{3+}$ is +3 and its configuration is [Ar] $3d^1$ i.e one unpaired electron and hence it is coloured. Whereas the oxidation state of Sc in $[Sc(H_2O)_6]^{3+}$ is +3 and its configuration is [Ar] $3d^0$ i.e no unpaired electron and hence it is colourless.

(iii)In the same group of d-block elements, the 4d and 5d transition elements are larger size than that of 3d elements. Hence, the valence electrons are less tightly held and form metal-metal bond more frequently.

(iv)+1 oxidation state is shown by elements like Cu because after loss of one electron, it acquire stable configuration. Zero oxidation state is shown in metal carbonyl, because $\prod$ -electrons donated by CO are accepted into the empty orbital.

(v)The characteristic properties of transition metal are due to partially filled d-orbitals.Hg has completely filled d-orbital, as a result it doesn't show properties of transition metals and hence is not considered as transition metal.

Q.3-(a) write electronic configuration of element having atomic number 101.

(b) Which element show maximum oxidation state in 3d transition series?

(c) What is mischmetal?

(d) Explain why Cu^+ ion is not stable in aqueous solution?

(e) Name the transition metal which is well known to exhibit +4 oxidation state?

A.3-(a) [Rn] $5f^{13}$,$6d^0$, $7s^2$.

(b) Mn, Which shows +7 oxidation state in $KMnO_4$.

(c) It is an important alloy, which contains 95% lanthanide metal and 5% Fe along with traces of S, C, Ca and Al. It is used in Mg-based alloy to produce bullets, shells and lighter flint.

(d) Water is a good complexing agent and thus Cu forms complex by losing one more electron from 3d orbital.

(e)Cerium (Z=58)

Q.4-(a) Write the preparation of potassium dichromate from iron chromite. What happens when potassium dichromate reacts with (i) Hydrogen sulphide (ii) $FeSO_4$?

(b) Why do Zr and Hf exhibit almost similar properties?

(c)Why is $La(OH)_3$ stronger base than $Lu(OH)_3$.

A.4- (a) Preparation:- It takes place in three steps-

(i) Conversion of chromite ore to sodium chromate.

(ii) Conversion of sodium chromate to sodium dichromate.

(iii) Conversion of sodium dichromate to potassium dichromate

Following reaction takes place:--

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

$$2Na_2CrO_4 + 2\,H^+ \longrightarrow Na_2Cr_2O_7 + 2\,Na^+ + H_2O$$

$$Na_2Cr_2O_7 + 2\,KCl \longrightarrow K_2Cr_2O_7 + 2\,NaCl$$

Reactions: - (i) $Cr_2O_7{}^{2-} + 8\,H^+ + 3\,H_2S \rightarrow 2Cr^{3+} + 7\,H_20 + 3S$

(ii) $Cr_2O_7{}^{2-} + 14\,H^+ + 6\,Fe^{2+} \rightarrow 2Cr^{3+} + 7\,H_20 + 6\,Fe^{3+}$.

(b) Because both have similar ionic size

(c)Due to lanthanoid contraction size of La^{3+} is smaller than Lu^{3+} as a result Lu-O bond will stronger than La-O bond.

Q.5- Give reasons for the following:-

(i) Transition metals have high enthalpy of hydration.

(ii) Zn, Cd and Hg are not regarded as transition metal.

(iii) d block elements exhibit a large number of oxidation state than f block elements.

(iv)The second and third members in each group of transition element have similar atomic radii.

(v) $K_2[PtCl_6]$ is well known compound whereas the corresponding Ni compound is not known.

A.5-(i) Transition metal ions are smaller and have higher charge, therefore have high enthalpy of hydration.

(ii) Group 12 elements i.e. Zn, Cd, Hg have completely filled (n-1) d-orbital in atomic & ionic state & thus these elements are not considered as transition elements.

(iii)The difference in the energy of (n-1) d orbital and ns orbital is very small and thus both sub-shells are used for bond formation. Whereas in f block elements (n-2)f orbitals lie underneath and hence are not available for bond formation.

(iv) The second and third members in each group of transition element have similar atomic radii due to lanthanoid contraction. It arises due to poor shielding of d and f electron.

(v)The oxidation state of Pt in is +4 which is stable for Pt. The +4 oxidation state for Ni is very difficult to achieve because the sum of first four ionization energies is very high. Hence ,the corresponding Ni(II) compound is known.

UNIT 9: CO-ORDINATION COMPOUNDS

1	CO-ORDINATION COMPOUND	1. Nomenclature of co-ordination compounds
		2. Hybridisation co-ordination complexes
		3. Isomerization
		4. crystal field theory in octahedral complexes

POINTS TO REMEMBER:

1. Coordination compounds

Coordination compounds are compounds in which a central metal atom or ion is linked to a number of ions or neutral molecules by coordinate bonds or which contain complex ions. Examples- $K_4[Fe(CN)_6]$; $[Cu(NH_3)_4]SO_4$; $Ni(CO)_4$

2. The main postulates of Werner's theory of coordination compounds

i) In coordination compounds metals show two types of linkages or valencies- Primary and Secondary.

ii) The primary valencies are ionisable and are satisfied by negative ions.

iii) The secondary valencies are non- ionisable and are satisfied by neutral molecules or negative ions. The secondary valence is equal to the C.N and is fixed for a metal.

iv) The ions or groups bound by secondary linkages to the metal have characteristic spatial arrangements corresponding to different coordination nos.

3.Difference between a double salt and a complex

Both double salts as well as complexes are formed by the combination of two or more stable compounds in stoichiometric ratio. However, double salts such as carnallite, $KCl.MgCl_2.6H_2O$, Mohr's salt, $FeSO_4.(NH_4)_2SO_4.6H_2O$, potash alum, $K_2SO_4Al_2(SO_4)_3.24H_2O$, etc. dissociate into simple ions completely when dissolved in water. However, complex ions such as $[Fe(CN)_6]^{4-}$ of $K_4[Fe(CN)_6]$, do not dissociate into Fe^{2+} and CN^- ions.

IMPORTANT TERMINOLOGY

(i) Coordination entity: It constitutes the central metal ion or atom bonded to a fixed number of ions or molecules represented within a square bracket.

(ii) Central atom/ ion: In a coordination entity, the atom/ion to which a fixed number of ions/groups are bound in a definite geometrical arrangement around it, is called the central atom or ion.

iii) **Ligands**: The neutral or negative ions bound to the central metal or ion in the coordination entity. These donate a pair/s of electrons to the central metal atom /ion. Ligands may be classified as-

a) **Monodentate /Unidentate**: Ligands bound to the central metal atom/ion through a single donor atom. Ex- Cl^- ; H_2O ; NH_3 ; NO_2^-.

b) **Didentate**: The Ligands which bind to the central metal atom/ion through two donor atoms. Ex- $C_2O_4{}^{2-}$ (ox); $H_2NCH_2CH_2NH_2$(en)

c) **Polydentate**: The Ligands which bind to the central metal atom/ion through two or more donor atoms present in a single ligand. Ex- $(EDTA)^{4-}$

d) **Chelating ligands**: Di- or polydentate ligands that uses two or more donor atoms to bind to a single metal ion to form ring- like complexes. (Ox); (EDTA)

e) **Ambidentate ligand**: A ligand that can ligate through two different atoms, one at a time. Ex-NO_2^- ; SCN^-

v) **Coordination number**: The no. of ligand donor atoms to which the metal is directly bonded through sigma bonds only. It is commonly 4 or 6.

vi) **Counter ions**: The ionisable groups written outside the square bracket. Ex- K^+ in $K_4[Fe(CN)_6]$ OR Cl^- in $[Co(NH_3)_6]Cl_3$

vii) **Coordination Polyhedron**: The spatial arrangement of the ligand atoms which are directly attached to the central metal atom/ion. They are commonly Octahedral, Square-planar or Tetrahedral

Oxidation number: The charge that the central atom would carry if all the ligands are removed along with their pairs of electrons shared with the central atom. It is represented in parenthesis.

viii) **Homoleptic complexes**: Complexes in which a metal is bonded to only one kind of donor groups. Ex- $[Co(NH_3)_6]^{3+}$

ix) **Heteroleptic complexes**: Complexes in which a metal is bonded to more than one kind of donor groups. Ex- $[Co(NH_3)_4Cl_2]^+$

5. NOMENCLATURE OF MONONUCLEAR COORDINATION COMPOUNDS

The following rules are used-

i The cation is named first in both positively and negatively charged coordination entities.

ii The ligands are named in an alphabetical order before the name of the central atom/ion

iii The name of the anionic ligands end in –o, those of neutral and cationic ligands are the same except aqua for H_2O, ammine for NH_3, carbonyl for CO and nitrosyl for NO. these are placed within enclosing marks .

iv When the prefixes mono, di, tri, etc., are used to indicate the number of the individual ligands in the coordination entity. When the names of the ligands include a numerical prefix, then the terms, bis, tris , tetrakis are used, the ligand to which they refer being placed in parenthesis.

v Oxidation state of the metal in cation, anion, or neutral coordination entity is

indicated by roman numeral in parenthesis.

vi If the complex ion is a cation , the metal is same as the element.

vii The neutral complex molecule is named similar to that of the complex cation.

6.NAMES OF SOME COMMON LIGANDS

NEGATIVE LIGANDS		CHARGE	NEUTRAL LIGANDS		CHARGE
CN^-	Cyano	-1	NH_3	Ammine	0
Cl^-	Chlorido	-1	H_2O	Aqua/aquo	0
Br^-	Bromido	-1	NO	Nitrosyl	0
F^-	Fluoride	-1	CO	Carbonyl	0
SO_4^{2-}	Sulphato	-2	PH_3	Phosphine	0
$C_2O_4^{2-}$	Oxalato	-4	$CH_2\text{-}NH_2$ | CH_2NH_2	(1,2-Ethane diamine)	0
NH_2^-	Amido	-1	POSITIVE LIGANDS		
NH^{2-}	Imido	-2	$NH_2\text{-}NH_3^+$	Hydrazinium	+1
ONO^-	Nitrito	-1	NO^+	Nitrosonium	+1
NO_2^-	Nitro	-1	NO_2^+	Nitronium	+1
NO_3^-	Nitrato	-1			
SCN^-	Thiocyanato	-1			
NCS^-	Isothiocyanato	-1			
$CH_2(NH_2)COO^-$	Glycinato	-1			
-OH	Hydroxo	-1			

ISOMERISM IN COORDINATION COMPOUNDS

Two or more substances having the same molecular formula but different spatial arrangements are called isomers and the phenomenon is called isomerism. Coordination compounds show two main types of isomerism-

A) Structural Isomerism B) Stereoisomerism

STRUCTURAL ISOMERISM:- It arises due to the difference in structures of coordination compounds. It is further subdivided into the following types-

1) **Ionisation isomerism:** This form of isomerism arises when the counter ion in a complex salt is itself a potential ligand and can displace a ligand which can then become the counter ion. An example is provided by the ionization isomers $[Co(NH_3)_5SO_4]Br$ and $[Co(NH_3)_5Br]SO_4$.

2) **Hydrate or solvate isomerism**: This form of isomerism is known as ‗hydrate isomerism‘ in case where water is involved as a solvent. This is similar to ionisation isomerism. Solvate isomers 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. An example is provided by the aqua complex $[Cr(H_2O)_6]Cl_3$ (violet) and its solvate isomer $[Cr(H_2O)_5Cl]Cl_2.H_2O$ (grey-green).

3) **Linkage Isomerism**: Linkage isomerism arises in a coordination compound containing ambidentate ligand. A simple example is provided by complexes containing the thiocyanate ligand, NCS_-, which may bind through the nitrogen to give M–NCS or through sulphur to give M–SCN.

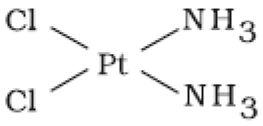
4) **Coordination isomerism:** It arises from the interchange of ligands between cationic and anionic entities of different metal ions present in a complex .
Example $[Co(NH_3)_6][Cr(CN)_6]$ & $[Cr(NH_3)_6][Co(CN)_6]$

STEREOISOMERISM: Stereo isomers have the same chemical formula and chemical bonds but they have different spatial arrangement. They are of two kinds

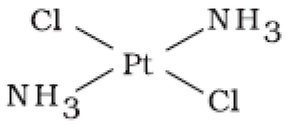
A. Geometrical isomerism

B. Optical isomerism

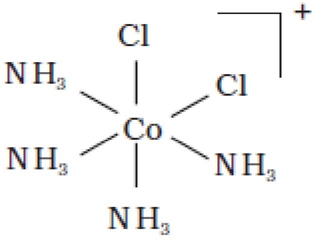
GEOMETRICAL ISOMERISM- This type of isomerism arises in heteroleptic complexes due to different possible geometric arrangements of the ligands. Important examples of this behaviour are found with coordination numbers 4 and 6. In a square planar complex of formula $[MX_2L_2]$ (X and L are unidentate), the two ligands X may be arranged adjacent to each other in a cis isomer, or opposite to each other in a trans isomer [MABXL]-Where A,B,X,L are unidentates Two cis- and one trans- isomers are possible.



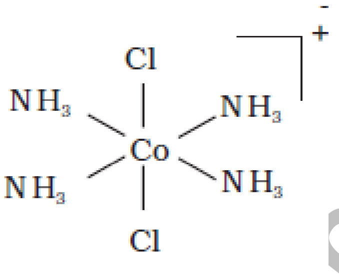
cis



trans

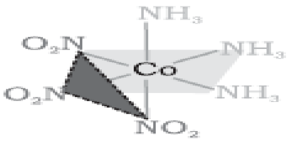


cis

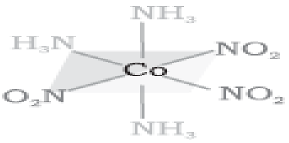


trans

Another type of geometrical isomerism occurs in octahedral coordination entities of the type [Ma_3b_3] like [$Co(NH_3)_3(NO_2)_3$]. If three donor atoms of the same ligands occupy adjacent positions at the corners of an octahedral face, we have the facial (fac) isomer. When the positions are around the meridian of the octahedron, we get the meridional (mer) isomer.

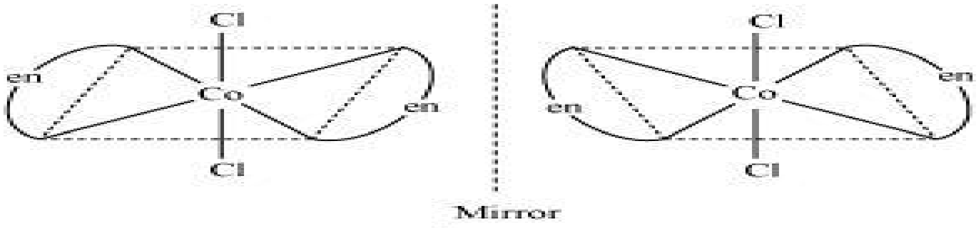


fac–

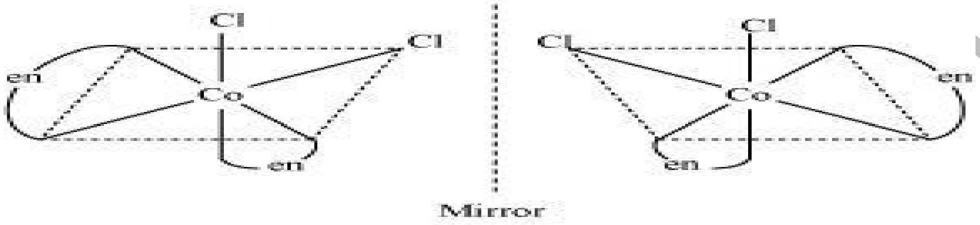


mer–

b) **OPTICAL ISOMERISM:** Optical isomers are mirror images that cannot be superimposed on one another. These are called as enantiomers. The molecules or ions that cannot be superimposed are called chiral. The two forms are called dextro (d) and laevo (l) depending upon the direction they rotate the plane of polarised light in a polarimeter (d rotates to the right, l to the left). Optical isomerism is common in octahedral complexes involving didentate ligands. In a coordination entity of the type [$CoCl_2(en)_2$]$^{2+}$, only the cis-isomer shows optical activity



Trans $[CoCl_2(en)_2]^+$ isomer-optically inactive
(Superimposable mirror images)



Cis $[CoCl_2(en)_2]^+$ isomer-optically active
(Non-superimposable mirror images)

TYPES OF HYBRIDISATION

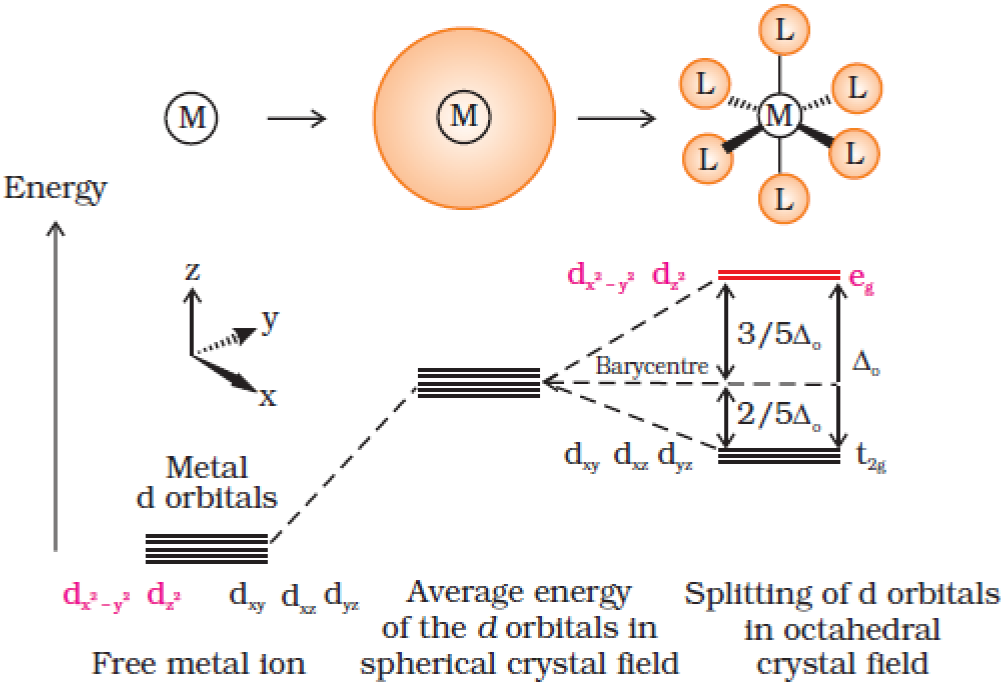
Coordination number	Type of hybridisation	Acquired geometry
4	sp^3	Tetrahedral
4	dsp^2	Square planar
5	sp^3d	Trigonal bipyramidal
6	sp^3d^2	Octahedral
6	d^2sp^3	Octahedral

8.CRYSTAL FIELD THEORY:

1. The metal-ligand bond is ionic arising purely from electrostatic interactions between the metal ion and the ligand.
2. Ligands are treated as point charges or dipoles in case of anions and neutral molecules.
3. In an isolated gaseous metal atom or ion the five d-orbitals are degenerate.
4. Degeneracy is maintained if a spherically symmetrical field of negative charges surrounds the metal /ion.
5. In a complex the negative field becomes asymmetrical and results in splitting of the

d-orbitals.

A) CRYSTAL FIELD SPLLITING IN OCTAHEDRAL COORDINATION ENTITIES



d orbital splitting in an octahedral crystal field

1. For d^4 ions, two possible patterns of electron distribution arise:
(i) If $\Delta_o < P$, the fourth electron enters one of the e_g orbitals giving the

configuration $t^3{}_{2g}\, e^1{}_g$. Ligands for which $\Delta_o < P$ are known as weak

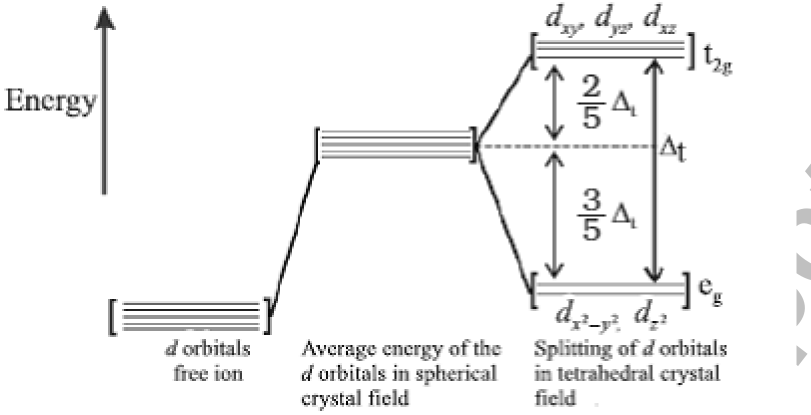
field ligands and form high spin complexes.

(ii) If $\Delta o > P$, it becomes more energetically favourable for the fourth electron to occupy a t_{2g} orbital with configuration $t^4{}_{2g}\, e^0{}_g$. Ligands which produce this effect are known as strong field ligands and form low spin complexes.

B) CRYSTAL FIELD SPLLITING IN TETRAHEDRAL COORDINATION ENTITIES

1. The four surrounding ligands approach the central metal atom/ion along the planes between the axes.
2. The t_{2g} orbitals are raised in energy (2/5) $_t$.
3. The two e_g orbitals are lowered in energy (3/5) $_t$
4. The splitting is smaller as compared to octahedral field splitting, $_t$=(4/9) $_{0.}$

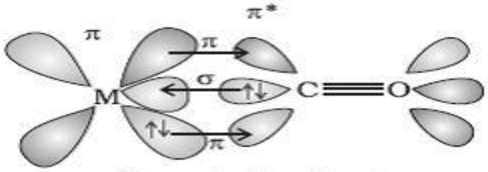
5. Pairing of electrons is rare and thus complexes have generally high spin configurations.



BONDING IN METAL CARBONYLS

The metal-carbon bond in metal carbonyls possess both σ and π character. The M–C σ bond

is formed by the donation of lone pair of electrons on 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 antibonding π* orbital of carbon monoxide. The metal to ligand bonding creates a synergic effect which strengthens the bond between CO and the metal .



Synergic bonding

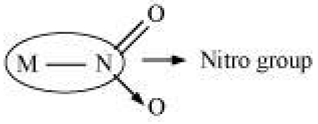
SOLVED QUESTIONS

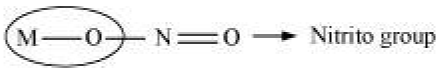
1 MARK QUESTIONS

1. What are ambidentate ligands? Give two examples for each.

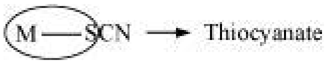
ANS. Ambidentate ligands are ligands that can attach themselves to the central metal atom through two different atoms. For example:

(a)





(The donor atom is N) (The donor atom is oxygen)

(b) 

(The donor atom is S) (The donor atom is N)

Q2. Using IUPAC norms write the formula for the following: Tetrahydroxozincate(II)
<u>**ANS.**</u> $[Zn(OH)_4]^{2-}$

Q3. Using IUPAC norms write the formula for the following: Hexaamminecobalt(III) sulphate
<u>**ANS.**</u> $[Co(NH_3)_6]_2\ (SO_4)_3$

Q4. Using IUPAC norms write the formula for the following: Pentaamminenitrito-O-cobalt(III)
<u>**ANS.**</u> $[Co(ONO)\ (NH_3)_5]^{2+}$

Q5. Using IUPAC norms write the systematic name of the following: $[Co(NH_3)_6]Cl_3$

<u>**ANS.**</u> Hexaamminecobalt(III) chloride

Q6. Using IUPAC norms write the systematic name of the following: $[Pt(NH_3)_2Cl(NH_2CH_3)]Cl$

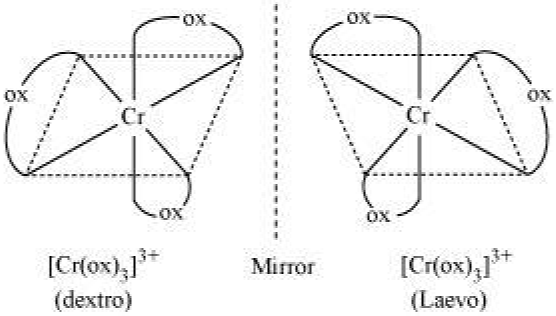
<u>**ANS.**</u> Diamminechlorido(methylamine) platinum(II) chloride

Q7. Using IUPAC norms write the systematic name of the following: $[Co(en)_3]^{3+}$

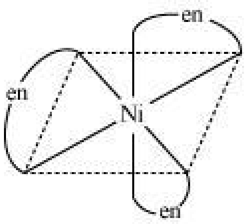
<u>**ANS.**</u> Tris(ethane-1, 2-diammine) cobalt(III) ion

Q8. Draw the structures of optical isomers of: c$[Cr(C_2O_4)_3]^{3-}$

<u>ANS</u> .



Q9. What is meant by the chelate effect? Give an example.
<u>**ANS.**</u> When a ligand attaches to the metal ion in a manner that forms a ring, then the metal-ligand association is found to be more stable. e.g. $[Ni\ (en)_3]^{2+}$



2 / 3 MARK QUESTIONS

Q1. What is spectrochemical series? Explain the difference between a weak field ligand and a strong field ligand.

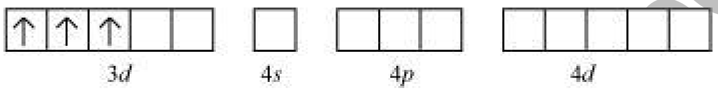
ANS. A spectrochemical series is the arrangement of common ligands in the increasing order of their crystal-field splitting energy (CFSE) values.

$I^- < Br^- < S^{2-} < SCN^- < Cl^- < N^{3-} < F^- < OH^- < C_2O_4^{2-} \sim H_2O < NCS^- \sim H^- < CN^- < NH_3 < en \sim SO_3^{2-} < NO_2^- < phen < CO$

Q2. $[Cr(NH_3)_6]^{3+}$ is paramagnetic while $[Ni(CN)_4]^{2-}$ is diamagnetic. Explain why?

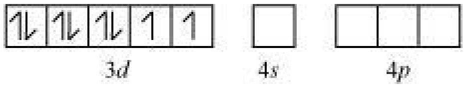
ANS. Cr is in the +3 oxidation state i.e., d^3 configuration. Also, NH_3 is a weak field ligand that does not cause the pairing of the electrons in the 3d orbital.

Cr^{3+} :

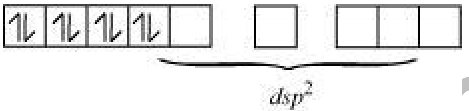


Therefore, it undergoes d^2sp^3 hybridization and the electrons in the 3d orbitals remain unpaired. Hence, it is paramagnetic in nature.
In $[Ni(CN)_4]^{2-}$, Ni exists in the +2 oxidation state i.e., d^8 configuration.

Ni^{2+}:



CN^- is a strong field ligand. It causes the pairing of the 3d orbital electrons. Then, Ni^{2+} undergoes dsp^2 hybridization.



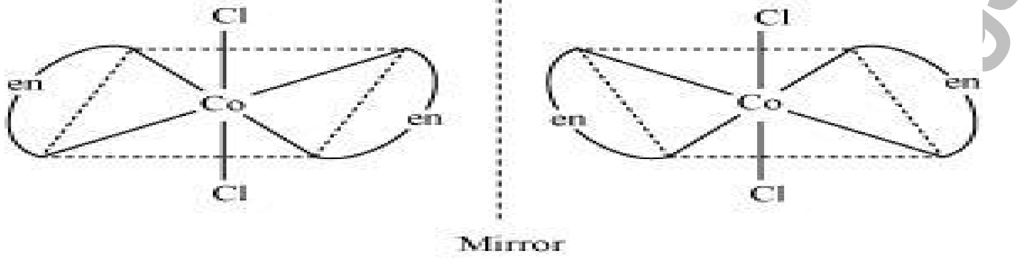
Q3. A solution of $[Ni(H_2O)_6]^{2+}$ is green but a solution of $[Ni(CN)_4]^{2-}$ is colourless. Explain.
ANS. In $[Ni(H_2O)_6]^{2+}$, $H_2\ddot{O}$ is a weak field ligand. Therefore, there are unpaired electrons in Ni^{2+}. In this complex, the d electrons from the lower energy level can be excited 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. As there are no unpaired electrons, it is diamagnetic.

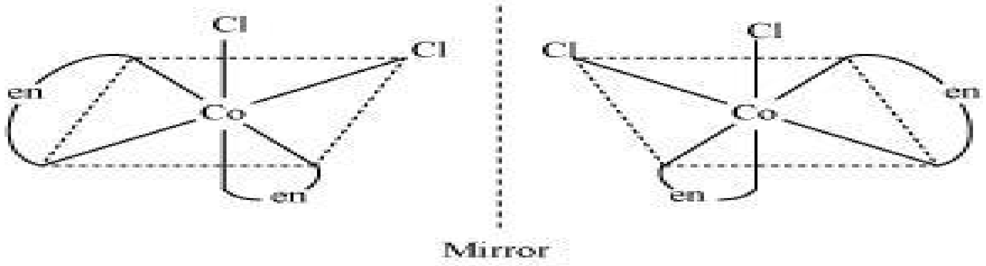
Q2. Draw all the isomers (geometrical and optical) of:

(i) $[CoCl_2(en)_2]^+$
(ii) $[Co(NH_3)Cl(en)_2]^{2+}$
(iii) $[Co(NH_3)_2Cl_2(en)]^+$

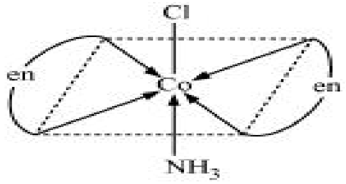
<u>ANS.</u> **(i)** $[CoCl_2(en)_2]^+$



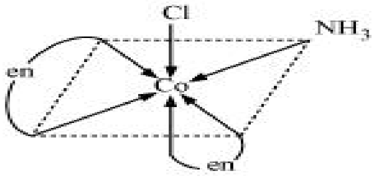
Trans $[CoCl_2(en)_2]^+$ isomer-optically inactive
(Superimposable mirror images)



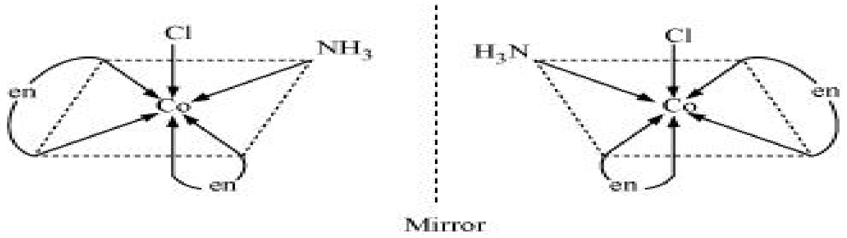
Cis $[CoCl_2(en)_2]^+$ isomer-optically active
(Non-superimposable mirror images)



Trans



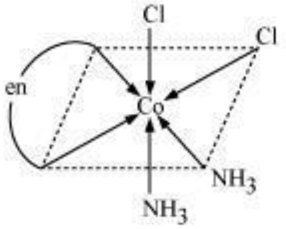
Cis

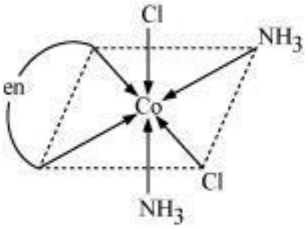


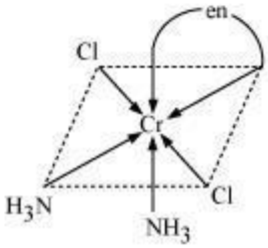
In total, three isomers are possible.

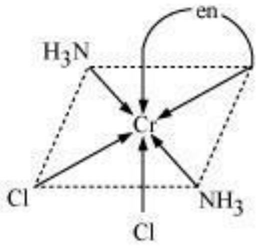
Trans-isomers are optically inactive.

Cis-isomers are optically active.





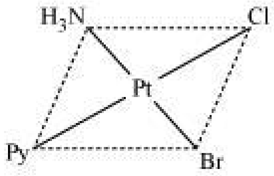


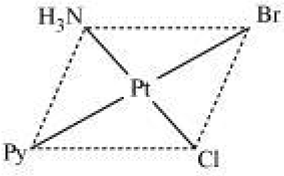


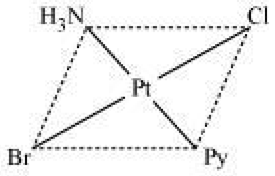
(iii) $[Co(NH_3)_2Cl_2(en)]^+$

Q3. Write all the geometrical isomers of $[Pt(NH_3)(Br)(Cl)(py)]$ and how many of these will exhibit optical isomers?

ANS. $[Pt(NH_3)(Br)(Cl)(py)]$







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.

Q4. What is meant by stability of a coordination compound in solution? State the factors which govern stability of complexes.

ANS. The stability of a complex in a solution refers to the degree of association between the two species involved in a state of equilibrium. Stability can be expressed quantitatively in terms of stability constant or formation constant.

$$M + 3L \longleftrightarrow ML_3$$

$$\text{Stability constant, } \beta = \frac{[ML_3]}{[M]\,[L]^3}$$

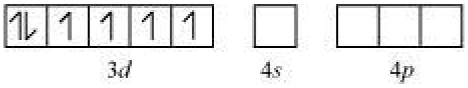
For this reaction, the greater the value of the stability constant, the greater is the proportion of ML_3 in the solution.

3 MARKS QUESTIONS

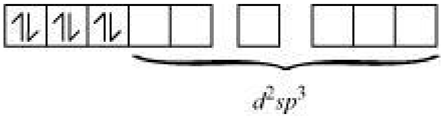
Q1. (a) Discuss the nature of bonding in the following coordination entities on the basisof valence bond theory:

(i) $[Fe(CN)_6]^{4-}$ (ii) $[FeF_6]^{3-}$ (iii) $[Co(C_2O_4)3]^{3-}$ (iv) $[CoF_6]^{3-}$

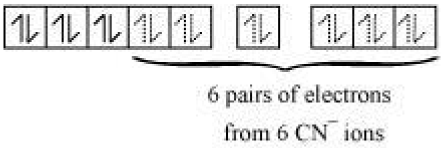
ANS. (i) $[Fe(CN)_6]^{4-}$In the above coordination complex, iron exists in the +II oxidation state.Fe^{2+} : Electronic configuration is $3d^6$ Orbitals of Fe^{2+} ion:



As CN^- is a strong field ligand, it causes the pairing of the unpaired 3d electrons.Since there are six ligands around the central metal ion, the most feasible hybridization is d^2sp^3. d^2sp^3 hybridized orbitals of Fe^{2+} are:



6 electron pairs from CN^- ions occupy the six hybrid d^2sp^3orbitals.Then,

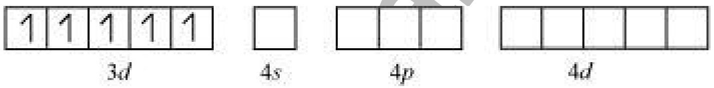


Hence, the geometry of the complex is octahedral and the complex is diamagnetic (as there are no unpaired electrons).

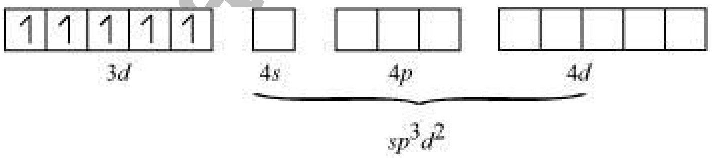
(ii) $[FeF_6]^{3-}$

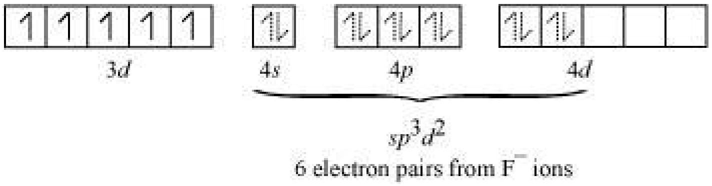
In this complex, the oxidation state of Fe is +3.

Orbitals of Fe^{+3} ion:



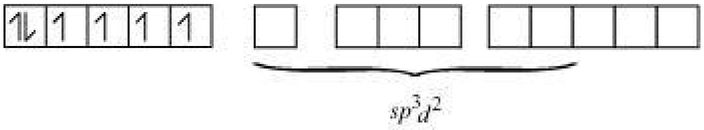
There are 6 F^- ions. Thus, it will undergo d^2sp^3 or sp^3d^2 hybridization. As F^- is a weak field ligand, it does not cause the pairing of the electrons in the 3d orbital. Hence, the most feasible hybridization is sp^3d^2.sp^3d^2 hybridized orbitals of Fe are:



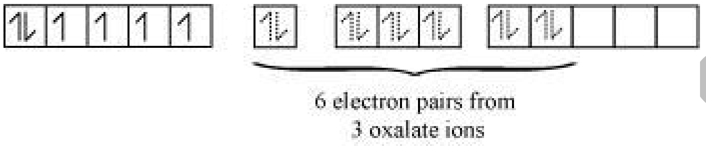


Hence, the geometry of the complex is found to be octahedral.

(iii) $[Co(C_2O_4)_3]^{3-}$
Cobalt exists in the +3 oxidation state in the given complex.Orbitals of Co^{3+} ion:Oxalate is a weak field ligand. Therefore, it cannot cause the pairing of the 3d orbital electrons. As there are 6 ligands, hybridization has to be either sp^3d^2 or d^2sp^3 hybridization.sp^3d^2 hybridization of Co^{3+}:



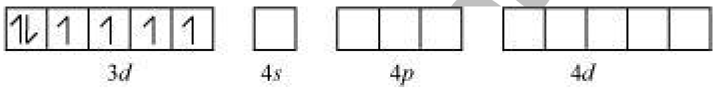
The 6 electron pairs from the 3 oxalate ions (oxalate anion is a bidentate ligand) occupy these sp^3d^2 orbitals.



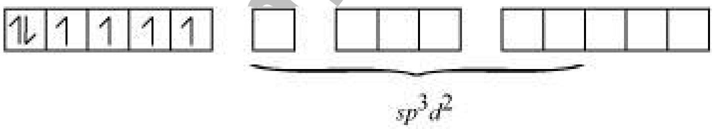
Hence, the geometry of the complex is found to be octahedral.

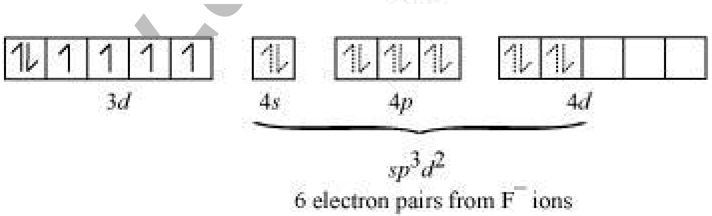
(iv) $[CoF_6]^{3-}$Cobalt exists in the +3 oxidation state.

Orbitals of Co^{3+} ion:



Again, fluoride ion is a weak field ligand. It cannot cause the pairing of the 3d electrons. As a result, the Co^{3+} ion will undergo sp^3d^2 hybridization.sp^3d^2 hybridized orbitals of Co^{3+} ion are:





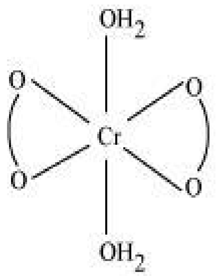
Hence, the geometry of the complex is octahedral and paramagnetic.

Q3. Write down the IUPAC name for each of the following complexes and indicate the oxidation state, electronic configuration and coordination number. Also give stereochemistry and magnetic moment of the complex:

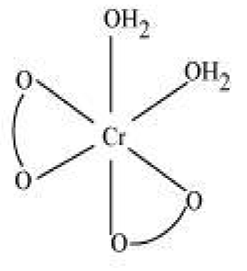
(i) $K[Cr(H_2O)_2(C_2O_4)_2].3H_2O$ (ii) $[Co(NH_3)_5Cl]Cl_2$ **ANS.** **(i)** Potassium diaquadioxalatochromate (III) trihydrate.

Oxidation state of chromium = 3 Electronic configuration: $3d^3$: t_{2g}^3
Coordination number = 6 Shape: octahedral

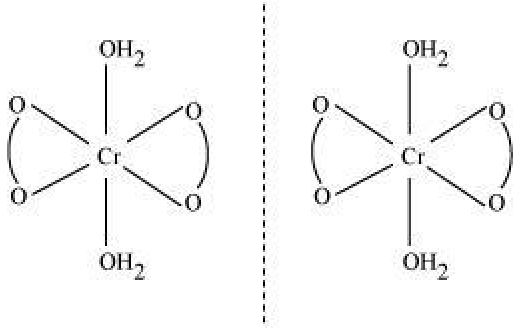
Stereochemistry:



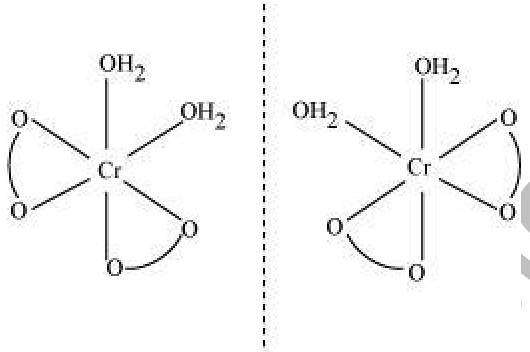
Trans



Cis



Trans is optically inactive



Cis is optically active

Magnetic moment, μ $= \sqrt{n(n+2)}$

$= \sqrt{3(3+2)}$

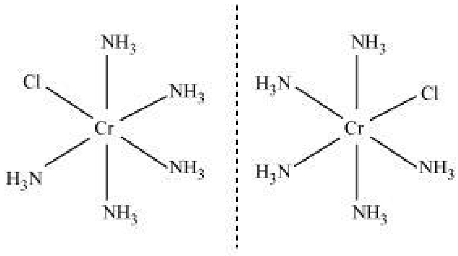
$= \sqrt{15}$

~ 4BM

(ii) $[CO(NH_3)_5Cl]Cl_2$
IUPAC name: Pentaamminechloridocobalt(III) chloride
Oxidation state of Co = +3
Coordination number = 6
Shape: octahedral.

Electronic configuration: d^6: t_{2g}^6.

Stereochemistry:



2 isomers

Magnetic Moment = 0

LEVEL 1

1.Why do tetrahedral complex not show geometrical isomerism?

2. Why does the colour changes on heating $[Ti(H_2O)_6]^{3+}$.

3. $[Fe(H_2O)_6]^{3+}$ is strongly paramagnetic whereas $[Fe(CN)_6]^{3-}$ is weakly paramagnetic. Explain.

4. What happens when potassium ferrocyanide solution is added to a ferric salt solution?

LEVEL 2

5. A coordination compound has a formula ($CoCl_3$. $4NH_3$). It does not liberate NH_3but precipitates chloride ion as AgCl. Give the IUPAC name of the complex and write its structural formula.

6. Write the correct formula for the following co-ordination compounds. $CrCl_3$ $6H_2O$ (Violet, with 3 Chloride ions/ Unit formula) $CrCl_3$. $6H_2O$ (Light green colour with 2 Chloride ions/ unit formula)

7. Give the electronic configuration of the d-orbitals of Ti in $[Ti (H_2O)_6]^{3+}$ ion in an octahedral crystal field.

8. Co(II) is stable in aqueous solution but in the presence of strong ligands and air, it can get oxidized to Co(III). (Atomic Number of cobalt is 27). Explain.

9. Give a chemical test to distinguish between $[Co(NH_3)_5Br]SO_4$ and $[Co(NH_3)_5SO_4]Br$. Name the type of isomerism exhibited by these compounds.

10. What is the coordination entity formed when excess of aqueous KCN is added to an aqueous solution of copper sulphate? Why is that no precipitate of copper sulphate is obtained when H_2S (g) is passed through this solution?

LEVEL 3

11. Aqueous copper sulphate solution (blue in colour) gives a green precipitate with aqueous potassium fluoride, a bright green solution with aqueous potassium chloride. Explain these experimental results.

12. A metal complex having the composition $[Cr(NH_3)_4Cl_2]Br$ has been isolated in two forms, A and B. The form A reacts with $AgNO_3$ solution to give a white precipitate readily soluble in dilute aqueous ammonia whereas B give a pale yellow precipitate soluble in concentrated ammonia solution. Write the formulae of A and B and write their IUPAC names.

13. Explain the following

i. All octahedral complexes of Ni^{2+}must be outer orbital complexes.

ii. NH_4^+ ion does not form any complex.

iii. $(SCN)^{-1}$ ion is involved in linkage isomerism in co-ordination compounds.

14. A metal ion M^{n+} having d^4 valence electronic configuration combines with three didentate ligands to form complexes. Assuming $\Delta_o > P$ Draw the diagram showing d orbital splitting during this complex formation. Write the electronic configuration of the valence electrons of the metal M^{n+} ion in terms of t_{2g} and e_g. What type of the hybridization will M^{n+} ion have? Name the type of isomerism exhibited by this complex.

15. The coordination no. of Ni^{2+} is 4.

$NiCl_2$ + KCN(excess) → A(a cyano complex)

A + Conc HCl(excess) → B (a chloro complex)

i) Write IUPAC name of A and B

ii) Predict the magnetic nature of A and B

iii) Write hybridization of Ni in A and B

16. Explain the following
i. $Cu(OH)_2$ is soluble in ammonium hydroxide but not in sodium hydroxide solution. ii.

EDTA is used to cure lead poisoning

iii. Blue coloured solution of $[CoCl_4]^{2-}$ changes to pink on reaction with $HgCl_2$.

1 MARK QUESTIONS

Q1. Write the formula for the following coordination compound:
Tetraamineaquachloridocobalt(III) chloride

Q2. Write the IUPAC name of the following coordination compound:
$[CoCl_2(en)_2]Cl$

Q3. Why is geometrical isomerism not possible in tetrahedral complexes having two different types of unidentate ligands coordinated with the central metal ion ?

Q4. Out of the following two coordination entities which is chiral (optically active)?
(a) *cis*-$[CrCl_2(ox)_2]^{3-}$ (b) *trans*-$[CrCl_2(ox)_2]^{3-}$

Q5. The spin only magnetic moment of $[MnBr_4]^{2-}$ is 5.9 BM. Predict the geometry of the complex ion?

Q6. $[NiCl_4]^{2-}$ is paramagnetic while $[Ni(CO)_4]$ is diamagnetic though both are tetrahedral. Why?

2 MARKS QUESTIONS

Q1. Draw structures of geometrical isomers of $[Fe(NH_3)_2(CN)_4]^-$

Q2. Indicate the type of isomerism exhibited by the following complex and draw the structures for these isomers:
$[Co(en)_3]Cl_3$

Q3. Give evidence that $[Co(NH_3)_5Cl]SO_4$ and $[Co(NH_3)_5SO_4]Cl$ are ionization isomers.

Q4. Calculate the overall complex dissociation equilibrium constant for the $[Cu(NH_3)_4]^{2+}$ ion, given that β_4 for this complex is 2.1×10^{13}.

Q5. What is meant by unidentate ligand? Give two examples.

Q6. What is meant by didentate ligand? Give two examples.

Q7. What is meant by ambidentate ligands? Give two examples.

Q8. Draw the structures of optical isomers of:
$[Cr(C_2O_4)_3]^{3-}$

Q9. Discuss the nature of bonding in metal carbonyls.

Q10. What is meant by the *chelate effect*? Give an example.

Q11. Draw the structures of:
(i) $Ni(CO)_4$ (ii) $Fe(CO)_5$

3 MARKS QUESTIONS

Q1. Discuss the nature of bonding in the following coordination entities on the basis of valence bond theory:
(i)$[Fe(CN)_6]^{4-}$ (ii) $[FeF_6]^{3-}$ (iii) $[Co(C_2O_4)_3]^{3-}$
Also predict their magnetic behaviour.

Q2. What is crystal field splitting energy? Draw figure to show the splitting of *d* orbitals in an octahedral crystal field. How does the magnitude of Δ_o decide the actual configuration of *d* orbitals in a coordination entity?

Q3. Discuss briefly giving an example in each case the role of coordination compounds in:

(i) biological systems (iii) analytical chemistry

(ii) medicinal chemistry .

UNIT-10

HALOALKANES , HALOARENES

1- Important terms and concept

$R\text{-}H + X_2 \longrightarrow R\text{-}X + H - X$

(i) Halogen derivative of alkenes called halo alkenes e.g. $R - CH_3$

(ii)Halogen derivative of arenes called halo arenes e.g. $R - C_6H_5$

2- (a) Vicinal di halides – where the two halogens are attached on the adjacent carbon atom. e.g. CH_2Cl
|
CH_2Cl

(b) geminal dihalide- where two halogen atoms are attached to the same carbon atom eg CH_3CHBr_2

2. Important Reactions
   (i) Nucleophilic substitution
   (ii) Eletrophilic substitution
   (iii) Elimination reaction
   (iv) Carbylamine reaction
   (v) Reimer Tiemann reaction
   (vi) Wurtz reaction
   (vii) Wurtz fittig reaction

Nucleophillic substitution → it involves the substitution of an atom or group by another atom or group

$A – B + C \rightarrow A – C + B$

It must be remembered that A – B and A – C both are covalent compounds.

(i) In aliphatic system

$R – X + OH^- \rightarrow R – OH + X^-$

$R – X + \overset{-}{O}C_2H_5 \rightarrow R\text{-}O\text{-}C_2H_5 + X^-$

Decreasing order of Basicity $CH_3 > NH_2 > O^-R > OH^- > I^- > Br^- > Cl^-$

In general

$R - X + :B^- \rightarrow R - B + X^-$

$: B^- \rightarrow OH^-, RO^-, CN^-, RCOO^-, NO_3^-, SH^-, RS^-$

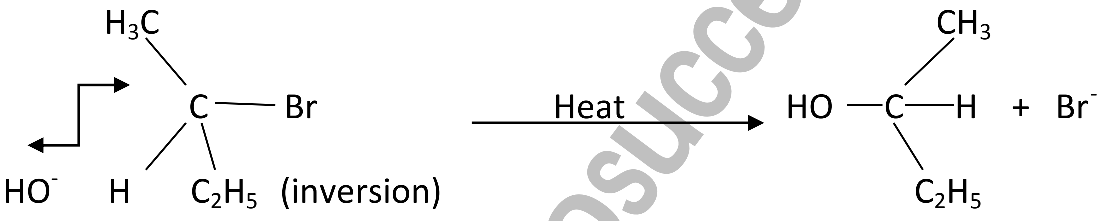
Bimolecular Nucleophillic substitution SN^2

(i) It takes place in one step.

(ii) Most of the SN^2 reaction are second order but some time when Nucleophillic reagent is present in excess quantity the reaction is of Ist order but still proceeds by SN^2

(iii) It is bimolecular

(iv) It leads to inversion of configuration. The attack of Nucleophillic occur from direction opposite to the leaving group.



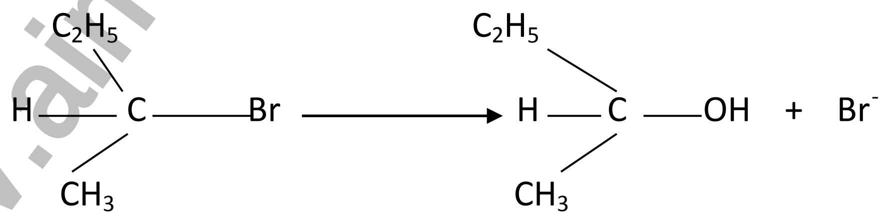
SN^1 → (i) It takes place in two steps.

(ii) All are Ist order.

(iii) Unimolecular

(iv) It leads racemisation

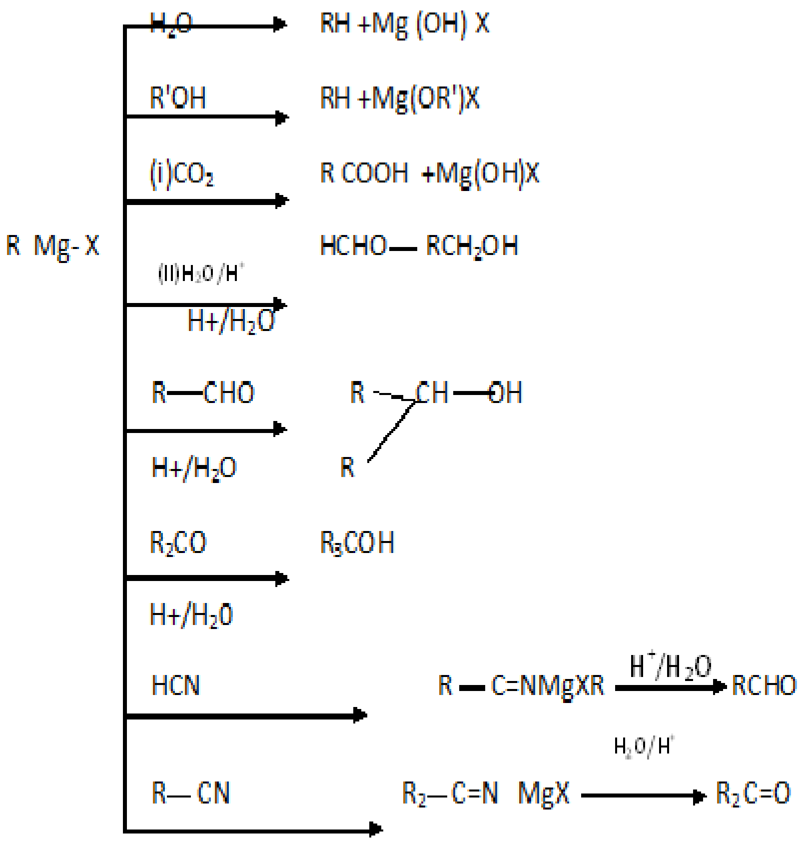
(v) Retention of configuration



The preservation of spatial arrangement of bonds at an asymmetric centre during the chemical reaction.

Stereochemistry of SN^1 reaction

If an alkyl halide is optically active then the product is racemic mixture, here the attack of Nucleophile from the both side [50:50 mix of the two enantiomers.



e.g. Nitration – how Electrophillic produce.

$HNO_3 + 2H_2SO_4 \rightarrow NO^{+}_2\ H_3O+ +2HSO^{-}_4$

OR

$BF_3 + HNO_3 \rightarrow NO_2^{+} + HO\text{-}BF_3^{-}$

Elimination reaction

Two groups or atoms attached to two adjacent carbon atom and simultaneous formation of multiple bonds between these carbon atom.[Reverse of addition]

Two types (i) β. Elimination -

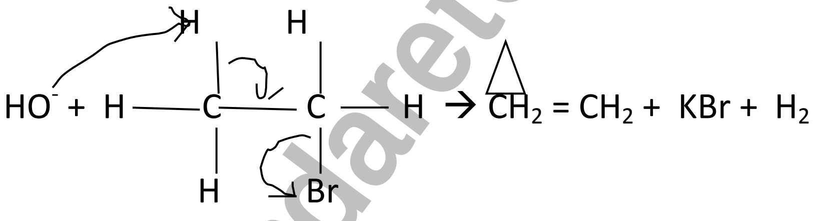
E_1 → Two step eliminate

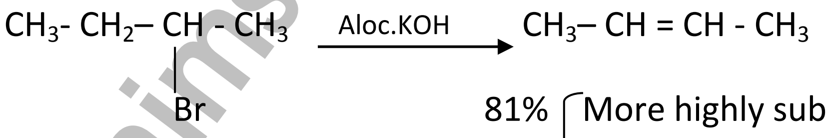
E_2 → One step eliminate

(ii)α- elimination

Saytzaff's Rule

(i)





$$CH_3\text{-}\ CH_2\text{–}\ \underset{\displaystyle Br}{\underset{|}{CH}}\ \text{-}\ CH_3 \xrightarrow{\text{Aloc.KOH}} CH_3\text{–}\ CH = CH\ \text{-}\ CH_3$$

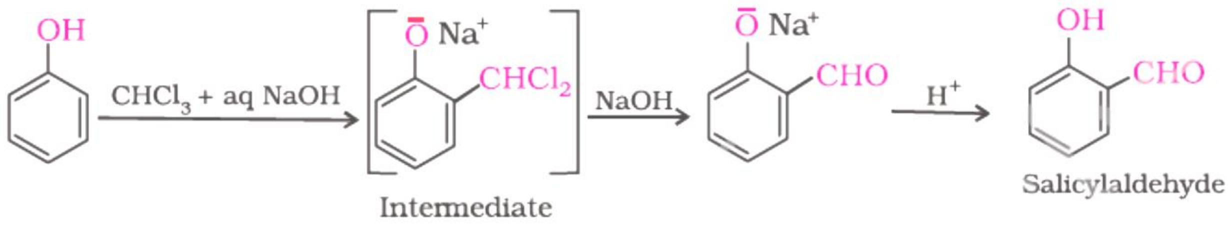
81% More highly substitutedAlkenes,

More stable

Some important name reaction

1. Carbylamines reaction.
   $R - NH_2 + CHCl_3 + 3\ KOH \longrightarrow R.NC + 3KCl + 3H_2O$
   $C_6H_5NH_2 + CHCl_3 + 3\ KOH \rightarrow C_6H_5NC + 3KCl + 3H_2O$

2. Reimer Tiemann Reaction



3. **Haloform reaction**

$CH_3CH_2OH \rightarrow 4I_2 + 6\ Na\ OH \rightarrow CHI_3 + HCOONa + 5NaI + 5H_2O$

$CH_3CHOHCH_3 + 4I_2 + 6\ Na\ OH \rightarrow CHI_3 + CH_3COONa + 5NaI + 5H_2O$

$CH_3COC_6H_5 + 3I_2 + 4NaOH \rightarrow CHI_3 + C_6H_5COONa + 3NaI + 3H_2O$

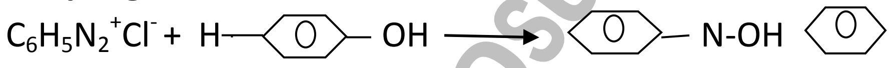
4. **Wurtz reaction**

R – X + 2Na +RX $\xrightarrow{ether}$ R – R +2 NaX

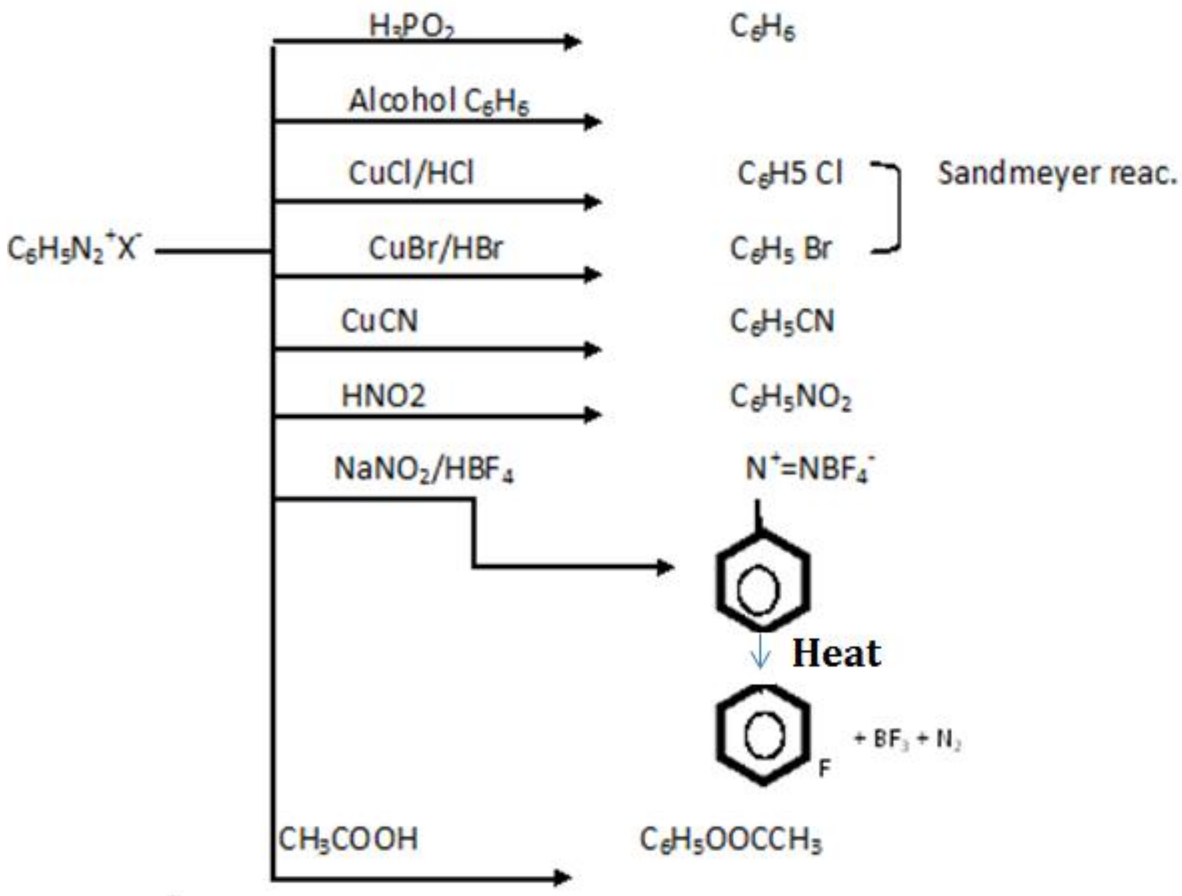
WurtzFITTIG REACTION

$C_6H_5Br + 2Na + Br + C_2H_5 \xrightarrow{ether} C_6H_5C_2H_5 + 2\ NaBr$

Coupling reac.



Diazonium Salt



CONCEPTUAL QUESTIONS

Q1. Why haloalkanes are more reactive than haloarenes.

Ans. In haloarenes, there is double bond character b/w carbon and halogen due to resonance effect which makes them less reactive.

(ii) In benzene, carbon being sp^2hybridisedwhich is smaller in size than sp^3 present in haloalkanes. So C-Cl bond in aryl halides is shorter and stronger.

Q2. Why do haloalkenes under go nucleophillic substitution whereas haloarenes under go electophillic substitution .

Ans.Due to more electro negative nature of halide atom in haloalkanes carbon atom becomes slightly positive and is easily attacked by nucleophillic reagents.

While in haloarenes due to resonance, carbon atom becomes slightly negative and attacked by electrophillic reagents.

Q3.When an alkyl halide is treated with ethanolic solution of KCN, the major product is alkyl cyanide where as if alkyl halide is treated with AgCN, the major product is alkyl isocyanide.

Ans.KCN is ionic they can attach through C or N but C-C bond is strong than C-N bond. So alkyl cyanide is the major product but AgCN is covalent so more electronegative N can attach to C and forms isocyanides.

Q4.How do 1^0, 2^0, 3^0 alcohols differ in terms of dehydrogenation?

Ans.1^0alcohol $\xrightarrow{Cu,300^0c}$ aldehyde

2^0alcohol $\xrightarrow{Cu,300^0c}$ ketone

3^0alcohol $\xrightarrow{Cu,300^0C}$ alkene

Q5. Why are the reaction of alcohol /phenol with acid chloride carried out in the presence of pyridine?

Ans. Because esterification reaction is reversible and presence of base (pyridine) neutralises HCl produced during reaction thus promoting forward reaction .

Q6 Explain why o-nitrophenol is more acidic than o-methoxy phenol ?

Ans. -NO_2 group is electron with drawing group, e^- density on O decreases and loss of H^+ is easy whereas –OCH_3 group is electron releasing group, which increases e^- density on O , which makes difficult to the loss of H^+, hence are less acidic .

Q7. Aryl halides cannot be prepared by the action of sodium halide in the presence H_2SO_4 .Why?

Ans. Due to resonance the carbon- oxygen bond in phenols has partial double bond and it is stronger than carbon oxygen single bond.

Q8. Why Grignard reagent should be prepared under anhydrous conditions?

Ans. Grignard reagent react with H_2O to form alkanes , therefore they are prepared under anhydrous condition.

Q9. Why is Sulphuric acid not used during the reaction of alcohols with KI ?

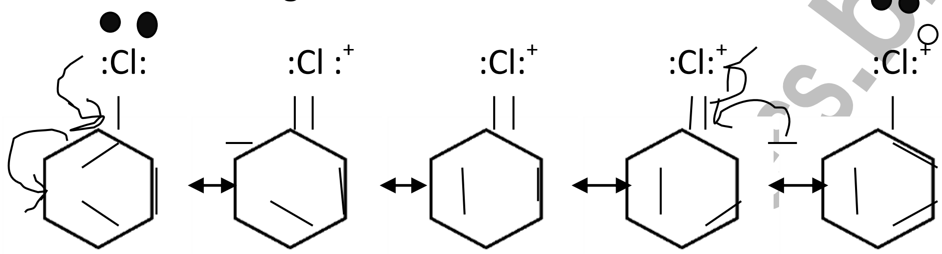
Ans. It is because HI formed will get oxidized to I_2 by concentrated Sulphuric acid which is an oxidizing agent.

Q10. p- dichlorobenzene has highest m.p. than those of ortho and m-isomers.?

Ans. p- dichlorobenzene is symmetrical, fits into crystal lattice more readily and has higher melting point.

Q11. Although chlorine is an electron- withdrawing group, yet it is ortho and para directing in electrophillic aromatic substitution reactions. Why?

Ans. Chlorobenzene is resonance hybrid, there is –ve charge at 0 and para positions, electrophillic substitution reaction will take place at 0 and para position due to +R effect.+R effect is dominating over – I effect..



Q12. The treatment of alkyl chlorides with aqueous KOH lead to the formation of alcohols but in presence of alcoholic KOH alkenes are major products. Explain?

Ans. In aqueous KOH,OH^- is nucleophile which replaces another nucleophile.

$$R\text{-}X + KOH \longrightarrow R\text{-}OH + KX$$

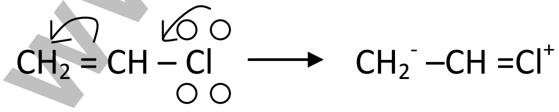
Where as in alcoholic KOH

$$C_2H_5OH + KOH \longrightarrow C_2H_5O^- + K^+$$

$$CH_3CH_2\text{-}Cl + \text{alcoholic KOH} \longrightarrow CH_2{=}CH_2 + C_2H_5OH$$

Q13. Explain why vinyl chloride is unreactive in nucleophillic substitution reaction?

Ans. Vinyl chloride is unreactive in nucleophillic substitution reaction because of double bond character between C=Cl bond which is difficult to break.



$$CH_2 = CH - Cl \longrightarrow CH_2^- - CH = Cl^+$$

Q14. Arrange the following compounds according to reactivity towards nucleophillic substitution reaction with reagents mentioned :-

(i) 4- nitrochlorobenzene, 2,4 dinitrochlorobemzene, 2,4,6, trinitrochlorobenzene with CH_3ONa

Ans- 2,4,6, trinitrochlorobenzene>2,4 dinitrochlorobemzene>4- nitrochlorobenzene

Q15. Which compound will react faster in SN^2 reaction with OH^{---}?

Ans-(a) CH_3Br and CH_3I (SN^2)

CH_3I will react faster than CH_3Br

(b) $(CH_3)_3C\text{-}Cl$ or CH_3Cl (SN^2)

CH_3Cl will react faster than 3^0 halide

Q16. Arrange in order of boiling points.

(a) Bromobenzene, Bromoform, chloromethane,Dibromo-methane
(b) 1-chloropropane, Isopropyle chloride, 1-Chlorobutane.

Ans. (a) chloromethane < Bromobenzene < Dibromo-methane< , Bromoform

(b), Isopropyle chloride <1-chloropropane <1-Chlorobutane

(As Branching increases , boiling point decreases)

Q 17. Predict the reactivity in SN_1

(a) $C_6H_5CH_2Br$, $C_6H_5CH(C_6H_5)Br$, $C_6H_5CH(CH_3)Br$, $C_6H_5C(CH_3)(C_6H_5)Br$

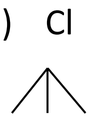
Ans. $3^0 > 2^0 > 1^0$ (SN_1)

$C_6H_5C(CH_3)(C_6H_5)Br > C_6H_5(C_6H_5)Br > C_6H_5CH(CH_3)Br > C_6H_5CH_2Br$

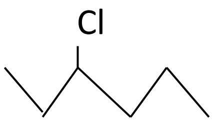
(3^0) (2^0) (2^0) (1^0)

Q18. Which compound undergoes SN_1 reaction first ?

(a)



and



(b)

(a) ANS. $3^0 > 2^0 > 1^0 (SN_1)$

(b)(2^0)

react faster than

VERY SHORT ANSWER TYPE QUESTION

[1 MARKS]

Q.1. Write the formula & chemical name of DDT?

Q.2. An alkyl halide having molecular formula C_4H_9Cl is optically active. What is its structure?

Q.3. Why is vinyl chloride less reactive than ethyl chloride?

Q.4. Write the structural isomers of $C_3H_6Cl_2$ which can exhibit enantiomerism?

Q.5. Write down the structure of the following compounds;

(a) 1- chloro-4-ethyl cyclohexane

(b)1,4-dibromo but-2-ene

(c) 4-tert, butyl-3-iodoheptane

(d)1-bromo-4-secbutyl-2-methylbenzene

Q.6. Which compound $(CH_3)_3$- C-Cl or ; CH_3Cl will react faster in s_n^2 reaction with –OH?

Q.7. A hydrocarbon C_5H_{10} does not react with chlorine in dark but it gives a single monobromo compound in bright sunlight. Identify the compound.

Q.8. Why is sulphuric acid not used during the reaction of alchohols with KI?

Q.9. Out of $C_6H_5CH_2Cl$ &$C_6H_5CH_2Cl$ $_6H_5$ which is more easily hydrolysed with aq. KOH& why ?

Q.10. Chloroform is stored in dark coloured & sealed bottle. Why?

Short answer type questions

Q,1. Give the IUPAC names of the following compounds?

A) $ClCH_2C = CCH_2BR$ b) $(CCl_3)_3CCl$

C)$CH_3CH(Cl)CH(Br)CH_3$

Q.2. Starting from methyl iodine, how will you prepare:

A) nitromethane

B) Methyl nitrite

Q.3. How can iodoform be prepared from ethanol?

Q.4.Predict the product of the following reactions;

Q.5.Write the reaction involved in:

A) The isocyanide test

B) iodoform test

Q.6. Rearranging the following in order of increasing case of dehydro halogenation $CH_3CH_2CH_2Cl$, $CH_3CHCLCH_3$, $CH_3 – C- Cl(CH_3)2$.

Q.7.How will you distinguish between

(i) $CH_3NH_2$and $(CH_3)_2NH$

(ii) ethanol & 1-propanol

Q.8. Give the uses of (a) CCl_4 (b) iodoform

Q.9. Propose the mechanism of the following reaction:

$$CH_3\text{-}CH_2\text{-}Br + CH_3O \longrightarrow CH_3\text{-}CH_2\text{-}OCH_3 + Br$$

Q.10. Which will have a higher boiling point 1-chloropentane or 2-chloro-2-methylbutane?

Q.11.How will you bring the following conversion?

(a) Propene to Propyne

(b) Toluene toBenzyle Alcohol

(c) Aniline to Phenylisocyanide

Q.12.What happen when;

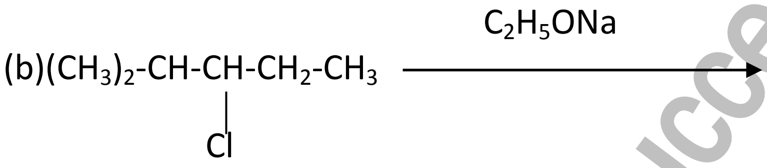
(a) n-butyl chloride is treated with alc.KOH.

(b) ethyl chloride is treated with aq.KOH.

(c) methyl chloride is treated with KCN.

Q.13Complete the following reaction;

(a)$Cl_2CH\text{-}CH\text{-}Cl_2 + Zn \xrightarrow{\triangle}$



(b)$(CH_3)_2\text{-}CH\text{-}\underset{\displaystyle Cl}{\underset{|}{CH}}\text{-}CH_2\text{-}CH_3 \xrightarrow{C_2H_5ONa}$

(c)$C_6H_5ONa + C_2H_5Cl \longrightarrow$

3 MARKS QUESTIONS

1. How can we produce nitro benzene from phenol?

A. (I) First convert phenol to benzene by heating with Zn dust.

(II) Nitration of benzene with conc. nitric acid in presence of conc. sulphuric acid.

2. Alcohols reacts with halogen acids to form haloalkenes but phenol does not form halobenzene. Explain

Ans.The C—O bond in phenol acquires partial double bond character due to resonance and hence be cleaved by X^- ions to form halobenzenes. But in alcohols a pure C — O bond is maintained and can be cleaved by X^- ions.

3. Explain why o-nitrophenol is more acidic than o-methoxy phenol?

A. Due to — R and — I effect of — NO_2 group, e– density on O^{-2} if O — H bond decreases and loss of H^+ is easy. -I effect, in o-methoxy phenol due to + R effect, –OCH_3 increases. e– density on O^{-2} of O — H group, and hence loss of H+ is difficult.(both –ve charge repel each other).

4. Of benzene and phenol, which is more easily nitrated and why?
A. Nitration is an electrophilic substitution reaction. The — OH group in phenol increases the e– density at o- and p- position as follows: Since phenol has a higher electron density due to electron releasing nature of -OH group, compared to benzene, therefore nitration is easy in phenol than benzene

5. How will you account for the following? Ethers possess a net dipole moment even if they are symmetrical in structure?
A. Because of greater electronegativity of o- atom than carbon C – O bonds are polar. C – O bond are inclined to each other at an angle of 110° (or more), two dipoles do not cancel out each other.

6. How do 1°, 2° and 3° alcohols differ in terms of their oxidation reaction and dehydrogenation ?
A. (I) Oxidation reaction :
1° alcohol → aldehyde → carboxylic acid
2° alcohol → ketone → carboxylic acid (acid with loss of 1 carbon atom)
3° alcohol → resistant to oxidation
(II) Hydrogenation reaction : give
1° alcohol → aldehyde
2° alcohol → ketone
3° alcohol → alkene
3° alcohols prefer to undergo dehydration and form alkene.
7.(i) How is diethyl ether prepared from ethyl alcohol ?

A. Ethyl alcohol is first treated with sodium to form sodium ethoxide.

$C_2H_5OH + Na \rightarrow C_2H_5O– Na + H_2$

Sodium ethoxide is then treated with ethyl halide to form di ethyl ether. SN^2

$C_2H_5O\ Na + C_2H_5X \rightarrow C_2H_5\ O\ C_2H_5 + NaX$ (Williamson synthesis)

(II) Complete the reaction:

(a) $CH_3OCH_3 + PCl_5$?

(b) $C_2H_5OCH_3 + HCl$?

(c) $(C_2H_5)_2\ O + HCl$

A. (a) CH_3Cl (b) $CH_3Cl + C_2H_5OH$ (c) $C_2H_5Cl + C_2H_5OH$

8. Why are reactions of alcohol/phenol and with acid chloride in the presence of pyridine?

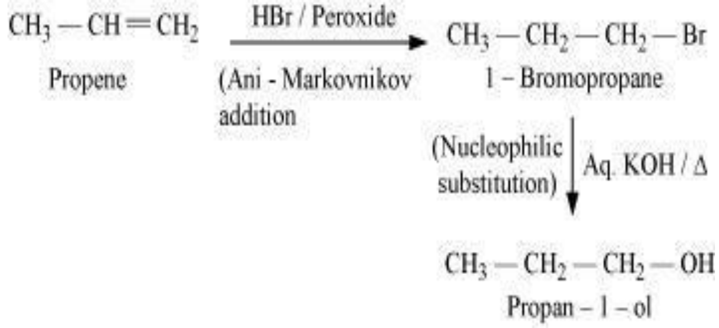
A. Because esterification reaction is reversible and presence of base (pyridine) neutralises HCl produced during reaction thus promoting forward reaction.

LONG ANSWER

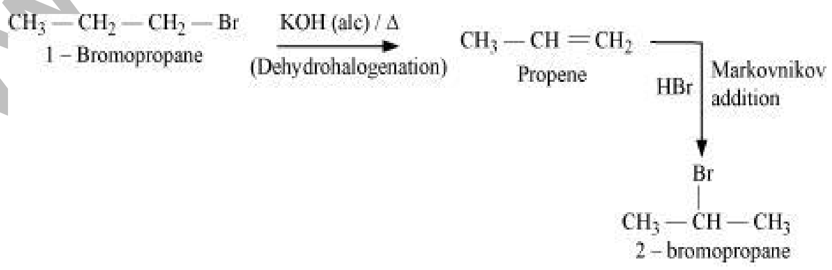
Q1) How the following conversions can be carried out?

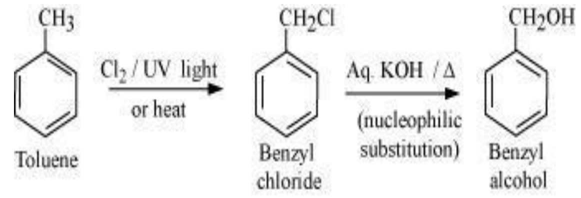
(i) Propene to propan-1-ol
(ii) 1-Bromopropane to 2-bromopropane
(iii) Toluene to benzyl alcohol
(iv) Benzene to 4-bromonitrobenzene
(v) Benzyl alcohol to 2-phenylethanoic acid

1

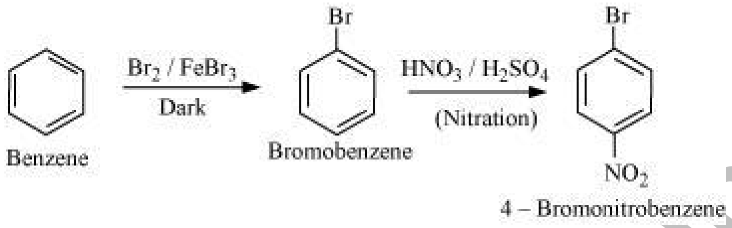


2



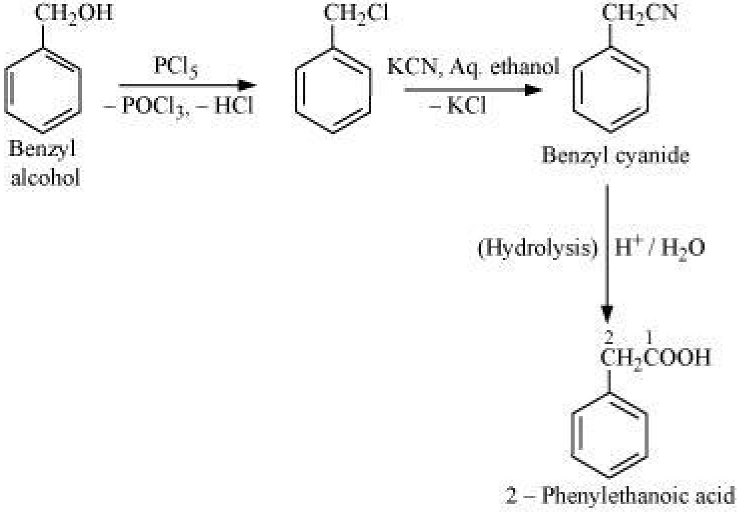


3



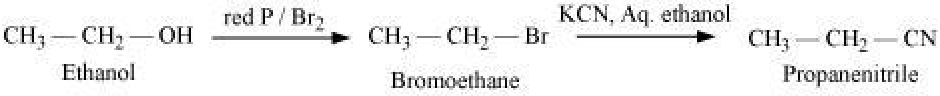
4

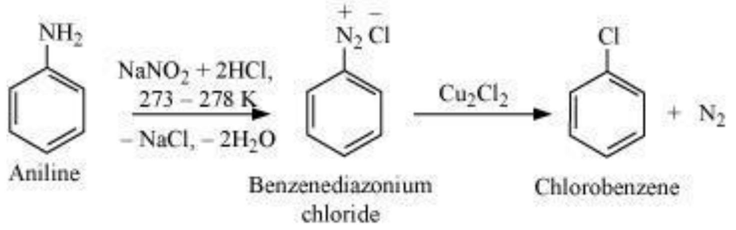
5

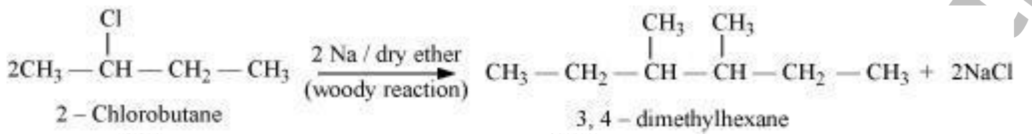


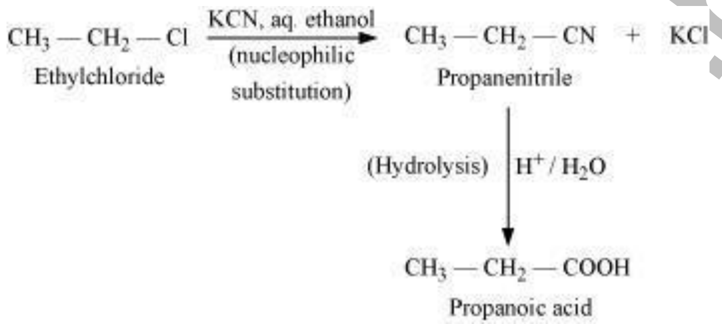
Q2) How the following conversions can be carried out?

(vi) Ethanol to propanenitrile
(vii) Aniline to chlorobenzene
(viii) 2-Chlorobutane to 3, 4-dimethylhexane
(ix) 2-Methyl-1-propene to 2-chloro-2-methylpropane
(x) Ethyl chloride to propanoic acid









Q3) How the following conversions can be carried out?

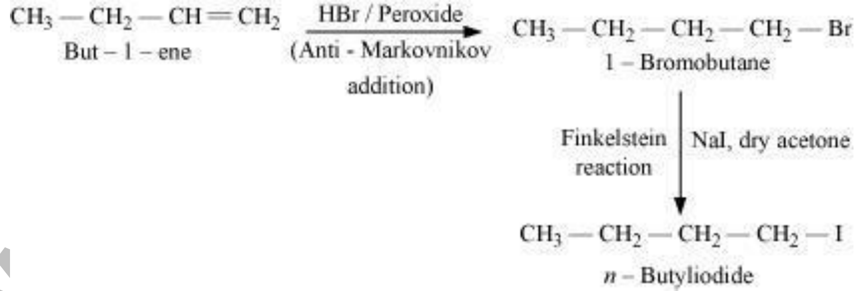
(xi) But-1-ene to n-butyliodide

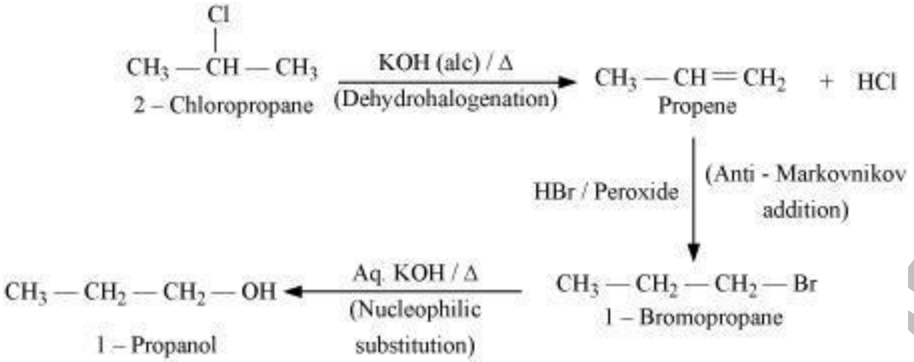
(xii) 2-Chloropropane to 1-propanol

(xiii) Isopropyl alcohol to iodoform

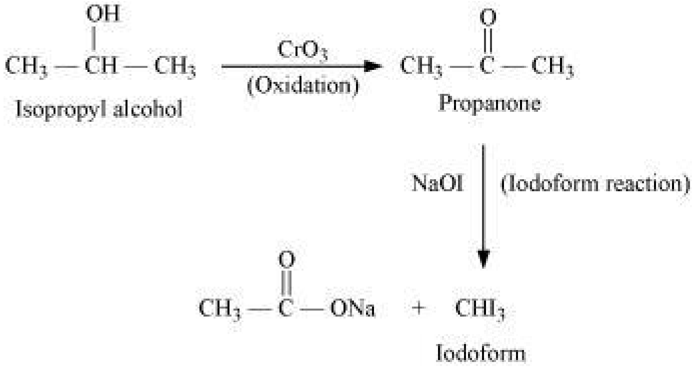
(xiv) Chlorobenzene to p-nitrophenol

(xv) 2-Bromopropane to 1-bromopropane

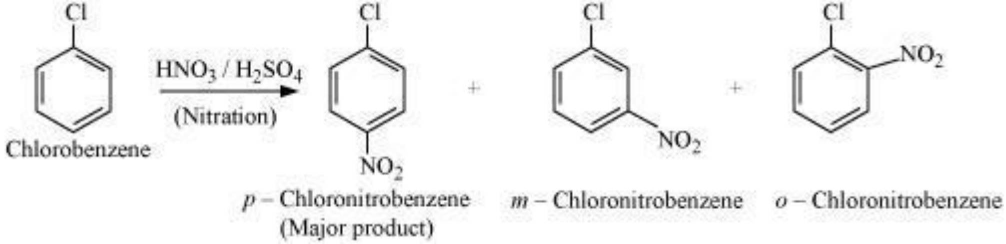




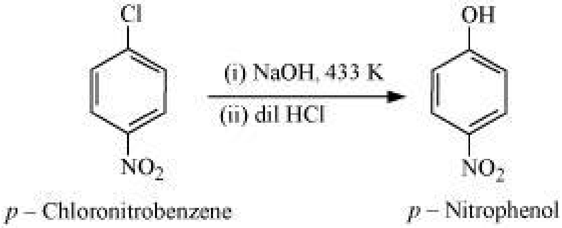
Cl
CH3 — CH — CH3
2 – Chloropropane
KOH (alc) / Δ
(Dehydrohalogenation)
CH3 — CH = CH2 + HCl
Propene
HBr / Peroxide
(Anti - Markovnikov addition)
CH3 — CH2 — CH2 — Br
1 – Bromopropane
Aq. KOH / Δ
(Nucleophilic substitution)
CH3 — CH2 — CH2 — OH
1 – Propanol



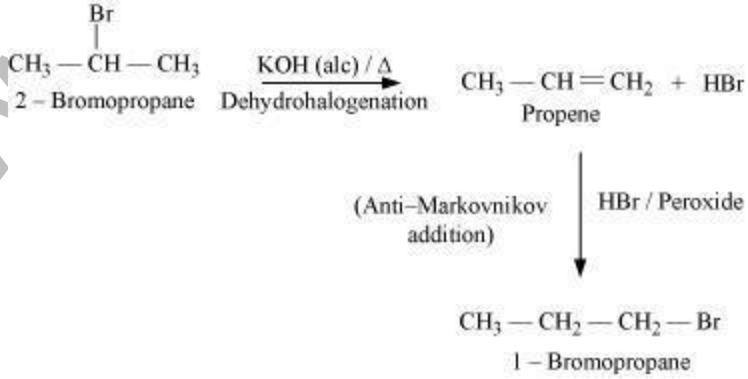
OH
CH3 — CH — CH3
Isopropyl alcohol
CrO3
(Oxidation)
O
CH3 — C — CH3
Propanone
NaOI
(Iodoform reaction)
O
CH3 — C — ONa + CHI3
Iodoform



Cl
Chlorobenzene
HNO3 / H2SO4
(Nitration)
Cl
NO2
p – Chloronitrobenzene
(Major product)
+
Cl
NO2
m – Chloronitrobenzene
+
Cl
NO2
o – Chloronitrobenzene



Cl
NO2
p – Chloronitrobenzene
(i) NaOH, 433 K
(ii) dil HCl
OH
NO2
p – Nitrophenol



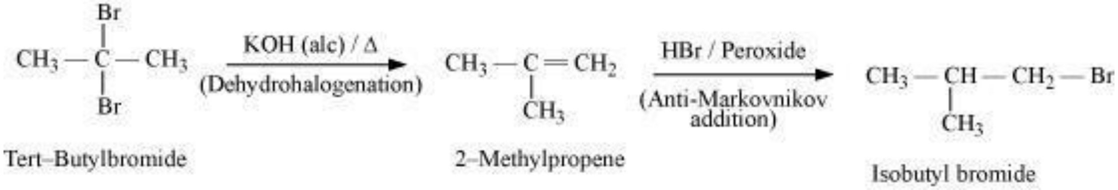
Br
CH3 — CH — CH3
2 – Bromopropane
KOH (alc) / Δ
Dehydrohalogenation
CH3 — CH = CH2 + HBr
Propene
(Anti–Markovnikov addition)
HBr / Peroxide
CH3 — CH2 — CH2 — Br
1 – Bromopropane

Q4) How the following conversions can be carried out?

(xvi) Chloro Ethane To Butane
(xvii) Benzene to diphenyl
(xviii) tert-Butyl bromide to isobutyl bromide
(xix) Aniline to phenylisocyanide

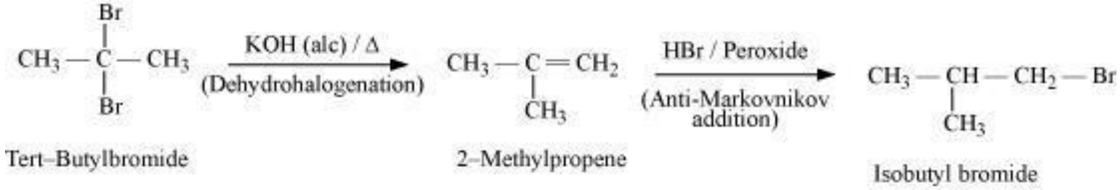
$$CH_3-CH_2-Cl \xrightarrow[\text{(Wurtz reaction)}]{\text{2 Na / dry ether}} CH_3-CH_2-CH_2-CH_3 + 2NaCl$$

Chloroethane Butane



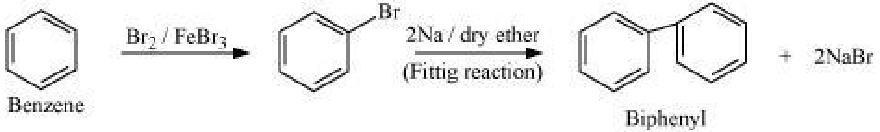
$$CH_3-\overset{Br}{\underset{Br}{C}}-CH_3 \xrightarrow[\text{(Dehydrohalogenation)}]{\text{KOH (alc) / }\Delta} CH_3-\underset{CH_3}{C}=CH_2 \xrightarrow[\text{(Anti-Markovnikov addition)}]{\text{HBr / Peroxide}} CH_3-\underset{CH_3}{CH}-CH_2-Br$$

Tert–Butylbromide 2–Methylpropene Isobutyl bromide



$$CH_3-\overset{Br}{\underset{Br}{C}}-CH_3 \xrightarrow[\text{(Dehydrohalogenation)}]{\text{KOH (alc) / }\Delta} CH_3-\underset{CH_3}{C}=CH_2 \xrightarrow[\text{(Anti-Markovnikov addition)}]{\text{HBr / Peroxide}} CH_3-\underset{CH_3}{CH}-CH_2-Br$$

Tert–Butylbromide 2–Methylpropene Isobutyl bromide

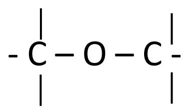
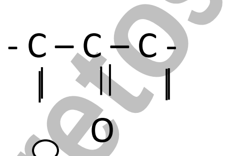
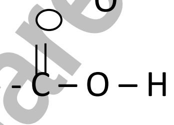
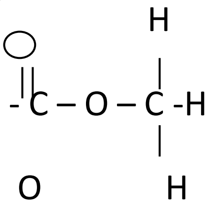
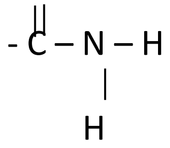


Benzene Biphenyl

$$CH_3-CH_2-OH \xrightarrow{\text{red P / }Br_2} CH_3-CH_2-Br \xrightarrow{\text{KCN, Aq. ethanol}} CH_3-CH_2-CN$$

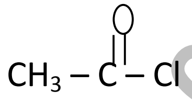
Ethanol Bromoethane Propanenitrile

UNIT-11 ALCOHOLS PHENOLS AND ETHERS

Family	Functional group	Example
Alcohol	R – O – H	CH_3OH methanol
Phenol	Ar – O – H	C_6H_5OH Phenol
Ether	 $-\overset{\vert}{\underset{\vert}{C}}-O-\overset{\vert}{\underset{\vert}{C}}-$	methylether$CH_3\,OCH_3$
Aldehyde	- CHO	Acetaldehyde CH_3CHO
Ketone	 $-\underset{\vert}{C}-\underset{\underset{O}{\Vert}}{C}-\underset{\vert}{C}-$	Acetone CH_3COCH_3
Carboxylic acid	 $-\overset{\overset{O}{\Vert}}{C}-O-H$	Acetic acid CH_3COOH
Ester	 $-\overset{\overset{O}{\Vert}}{C}-O-\overset{\overset{H}{\vert}}{\underset{\underset{H}{\vert}}{C}}-H$	Ester $CH_3-COOCH_3$ Methyl / acetate
Amide	 $-\overset{\overset{O}{\Vert}}{C}-\underset{\underset{H}{\vert}}{N}-H$	acetamide CH_3CONH_2

Acid Anhydride $(RCO)_2O$ $CH_3COOCOCH_3$ acetic anhydride

Acid chloride RCOCl acetylchloride



$CH_3 - \overset{O}{\overset{\|}{C}} - Cl$

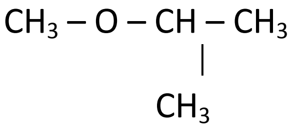
IUPAC Name

$CH_3 - O - CH_2 - CH_2 - CH_3$ 1-Methoxypropane

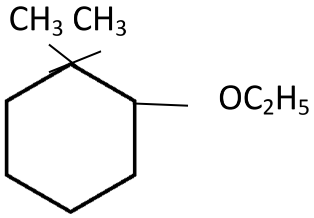
$C_6H_5OCH_3$ Methoxy benzene

[Anisole]

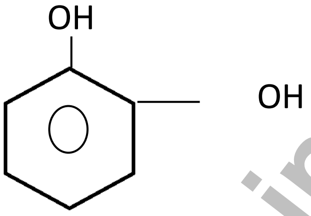
$C_6H_5O(CH_2)_6 - CH_3$ 1- Phenoxy heptanes



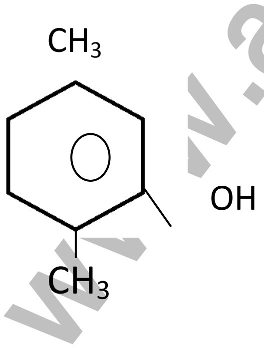
$CH_3 - O - \underset{\underset{CH_3}{|}}{CH} - CH_3$ 2- Methoxy propane



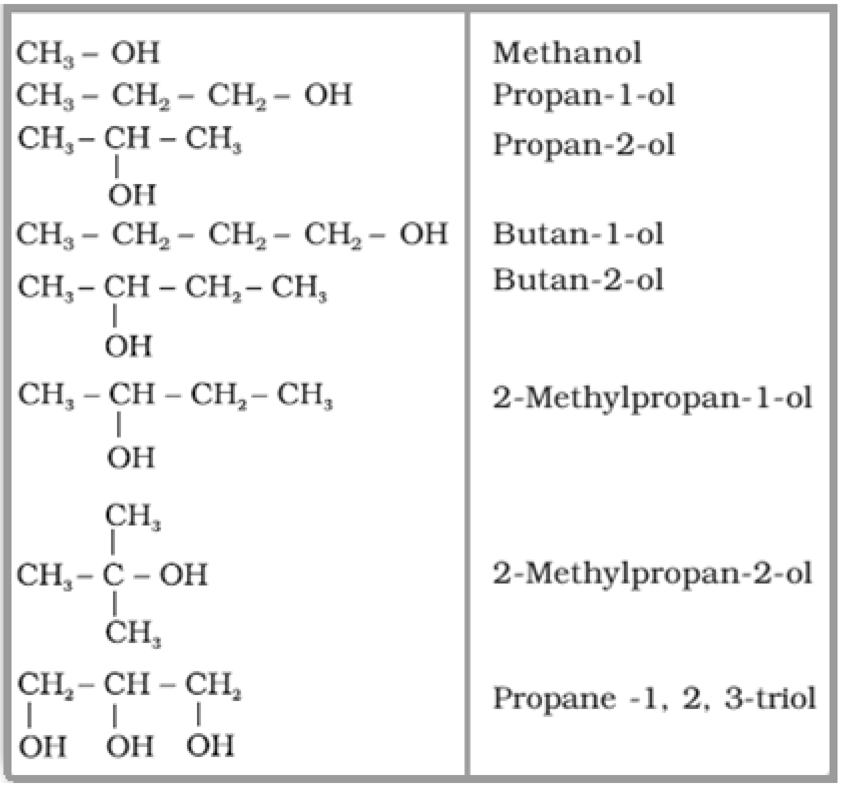
2- ethoxy – 1, 1- dimethyl cyclohexane



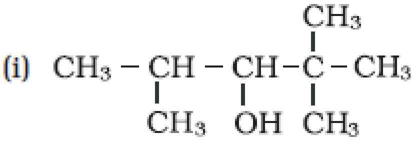
Benzene – 1,2 – diol



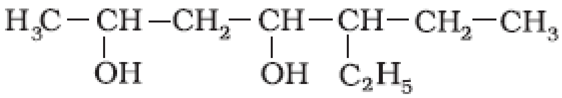
2,5 – Dimethyl phenol



CH_3-OH	Methanol
$CH_3-CH_2-CH_2-OH$	Propan-1-ol
$CH_3-\underset{\underset{OH}{\mid}}{CH}-CH_3$	Propan-2-ol
$CH_3-CH_2-CH_2-CH_2-OH$	Butan-1-ol
$CH_3-\underset{\underset{OH}{\mid}}{CH}-CH_2-CH_3$	Butan-2-ol
$CH_3-\underset{\underset{OH}{\mid}}{CH}-CH_2-CH_3$	2-Methylpropan-1-ol
$CH_3-\overset{\overset{CH_3}{\mid}}{\underset{\underset{CH_3}{\mid}}{C}}-OH$	2-Methylpropan-2-ol
$\underset{\underset{OH}{\mid}}{CH_2}-\underset{\underset{OH}{\mid}}{CH}-\underset{\underset{OH}{\mid}}{CH_2}$	Propane -1, 2, 3-triol

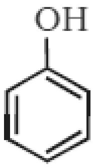
(i) 
$CH_3-\underset{\underset{CH_3}{\mid}}{CH}-\underset{\underset{OH}{\mid}}{CH}-\overset{\overset{CH_3}{\mid}}{\underset{\underset{CH_3}{\mid}}{C}}-CH_3$

2,2,4-Trimethylpentan-3-ol

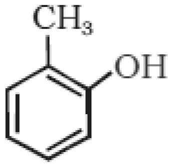
(ii) 
$H_3C-\underset{\underset{OH}{\mid}}{CH}-CH_2-\underset{\underset{OH}{\mid}}{CH}-\underset{\underset{C_2H_5}{\mid}}{CH}-CH_2-CH_3$

5-Ethylheptane-2,4-diol

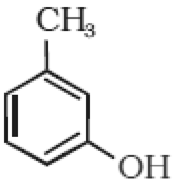
IUPAC names of phenols



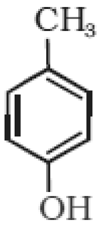
Phenol



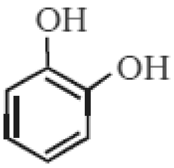
2-Methylphenol



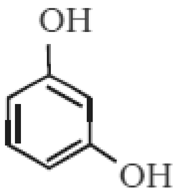
3-Methylphenol



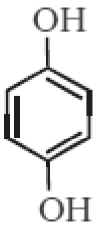
4-Methylphenol



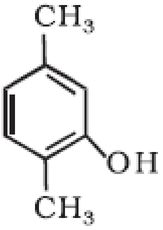
Benzene-1,2-diol



Benzene-1,3-diol

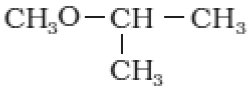
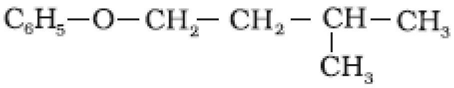
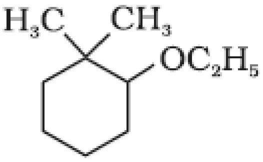


Benzene-1,4-diol



2,5-Dimethylphenol

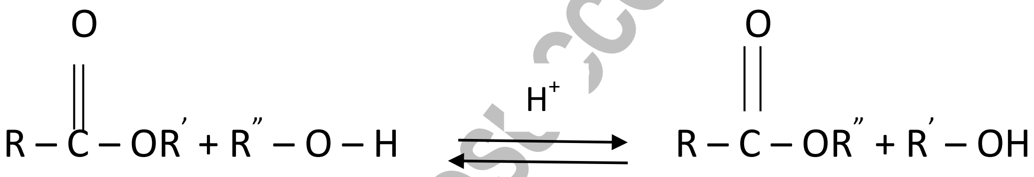
IUPAC names of some ethers

Compound	IUPAC name
CH_3OCH_3	Methoxymethane
$C_2H_5OC_2H_5$	Ethoxyethane
$CH_3OCH_2CH_2CH_3$	1-Methoxypropane
$C_6H_5OCH_3$	Methoxybenzene (Anisole)
$C_6H_5OCH_2CH_3$	Ethoxybenzene
$C_6H_5O(CH_2)_6-CH_3$	1-Phenoxyheptane
 $CH_3O-\underset{\large CH_3}{\underset{\vert}{CH}}-CH_3$	2-Methoxypropane
 $C_6H_5-O-CH_2-CH_2-\underset{\large CH_3}{\underset{\vert}{CH}}-CH_3$	3- Methylbutoxybenzene
$CH_3-O-CH_2-CH_2-OCH_3$	1,2-Dimethoxyethane
	2-Ethoxy- -1,1-dimethylcyclohexane

Name reaction

(1) Reimer Tiemann. Reaction –
(2) Transesterification
(3) Williamson synthesis
(4) Kolbe reaction
(5) Friedel craft

Transesterification : When an ester treated with excess of another alcohol [other than the one from which ester has been derived] in presence of corresponding sod. or pot. alkoxide or an acid H_2SO_4 / HCl as catalyst i.e. also cleavage by an alcohol , calcolysis



$$R-\overset{\overset{O}{\|}}{C}-OR' + R''-O-H \overset{H^+}{\rightleftharpoons} R-\overset{\overset{O}{\|}}{C}-OR'' + R'-OH$$

Williamson synthesis:- Reaction with alkyl halide with sodium alkoxide or sod. Phenoxide called Williamson synthesis.

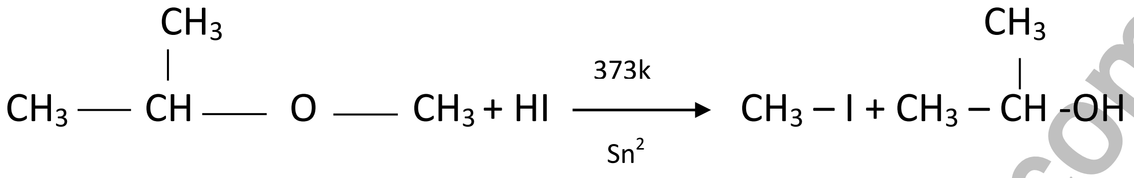
$R-X + R^1-O-Na \longrightarrow R-O-R' + NaX$

$CH_3I + CH_3CH_2ONa \longrightarrow CH_3O.CH_2-CH_3 + NaI$

$CH_3CH_2-I + PhONa \longrightarrow PhOH + NaI$

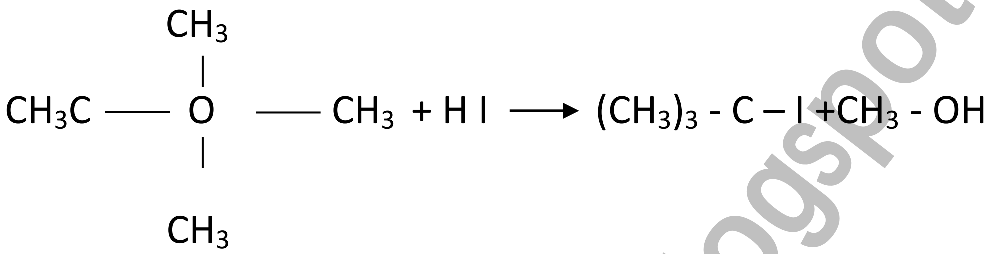
Both simple and mixed ether can be produced.

Depending upon structure and cleavage of unsymmetrical ethers by halogen acid may occur either by SN^2 or SN^1 mechanism e.g. (i)



$$CH_3-\overset{CH_3}{\overset{|}{CH}}-O-CH_3+HI\xrightarrow[Sn^2]{373k}CH_3-I+CH_3-\overset{CH_3}{\overset{|}{CH}}-OH$$

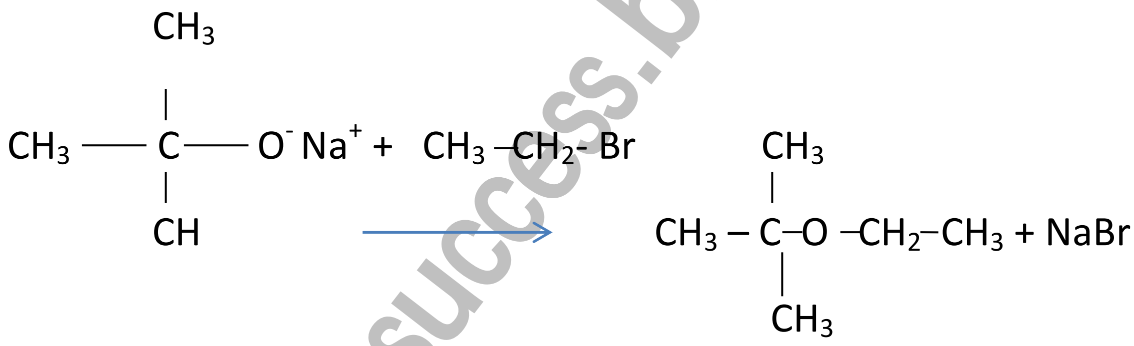
(3)



$$CH_3C-\underset{\underset{CH_3}{|}}{\overset{CH_3}{\overset{|}{O}}}-CH_3+HI\longrightarrow(CH_3)_3-C-I+CH_3-OH$$

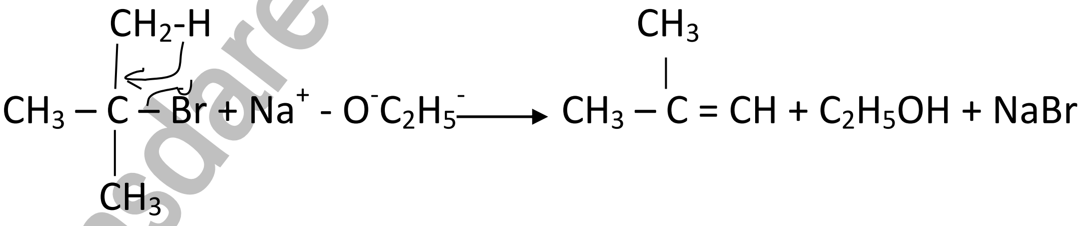
LIMITATIONS OF WILLIAMSON SYNTHESIS

(i)

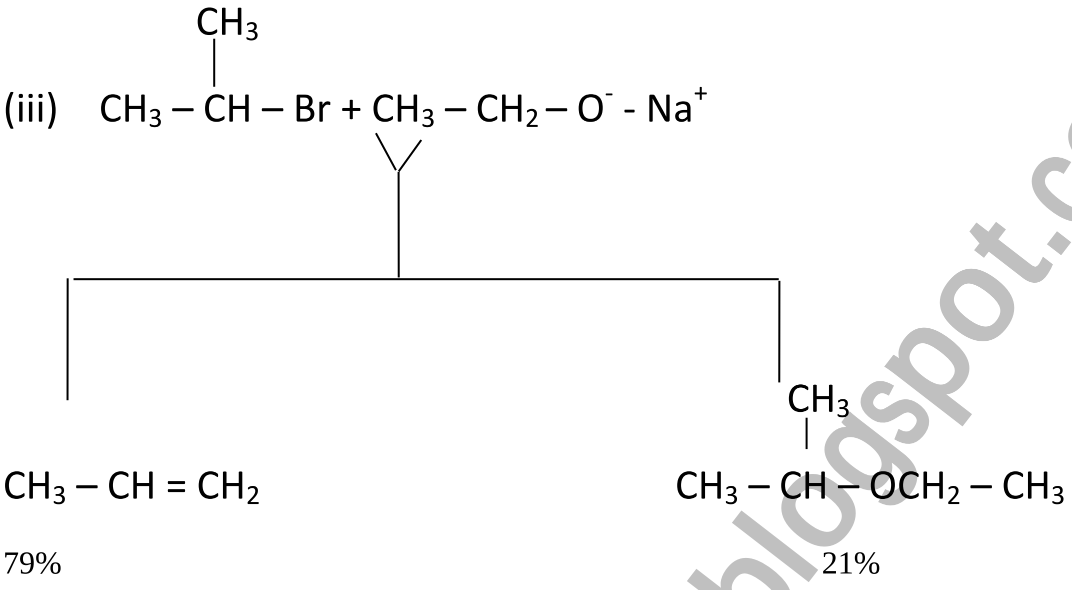


$$CH_3-\underset{\underset{CH}{|}}{\overset{CH_3}{\overset{|}{C}}}-O^-Na^++CH_3-CH_2-Br\longrightarrow CH_3-\underset{\underset{CH_3}{|}}{\overset{CH_3}{\overset{|}{C}}}-O-CH_2-CH_3+NaBr$$

(ii)



$$CH_3-\underset{\underset{CH_3}{|}}{\overset{CH_2-H}{\overset{|}{C}}}-Br+Na^+-O^-C_2H_5^-\longrightarrow CH_3-\overset{CH_3}{\overset{|}{C}}=CH+C_2H_5OH+NaBr$$

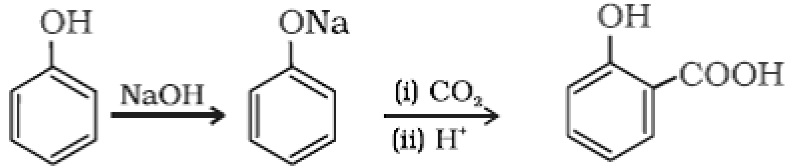


(iii) $CH_3-\overset{CH_3}{\overset{|}{C}H}-Br + CH_3-CH_2-O^- - Na^+$

$CH_3-CH=CH_2$ 79%

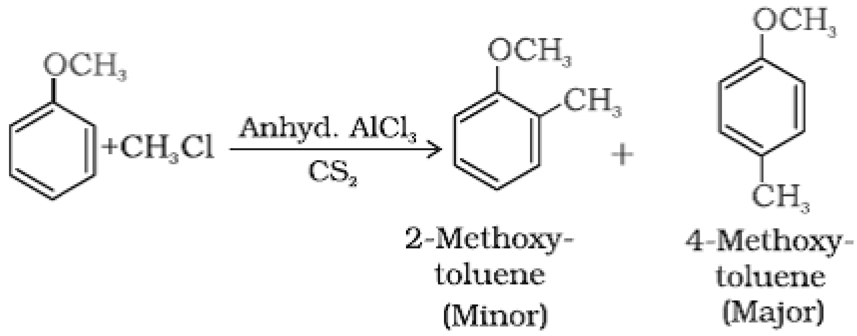
$CH_3-\overset{CH_3}{\overset{|}{C}H}-OCH_2-CH_3$ 21%

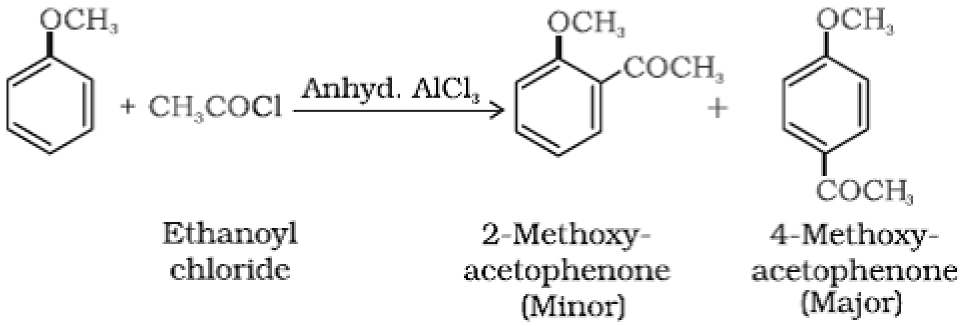
Kolbe reaction



2-Hydroxybenzoic acid
(Salicylic acid)

Friedel craft reaction





DISTINCTION BETWEEN PAIR OF COMPOUNDS

When 1^0,2^0, and 3^0 alcohol treated with lucas reagent [con, HCl + an hydrous $ZnCl_2$] at room temp

- (i) If turbidity appears immediately alcohol is 3^0.
- (ii) If turbidity appears in five minutes alcohol is2^0.
- (iii) 1^0 alcohol does not react with L.R. at room temp.

(II) All those compound like alcohol, aldehyde Ketones which on oxidation giving CH_3 - CO^- Group undergoes iodoform test.

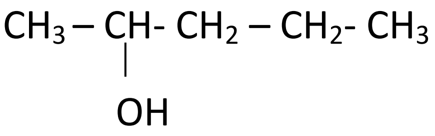
e.g. (i) CH_3CH_2—OH

(II) CH_3– CHO

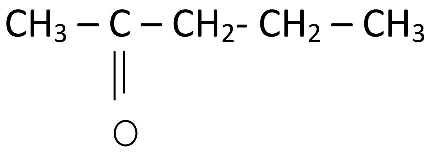
(III) (CH_3) – CH – OH

(IV) CH_3-COCH_3

(V) $C_6H_5-CO-CH_3$

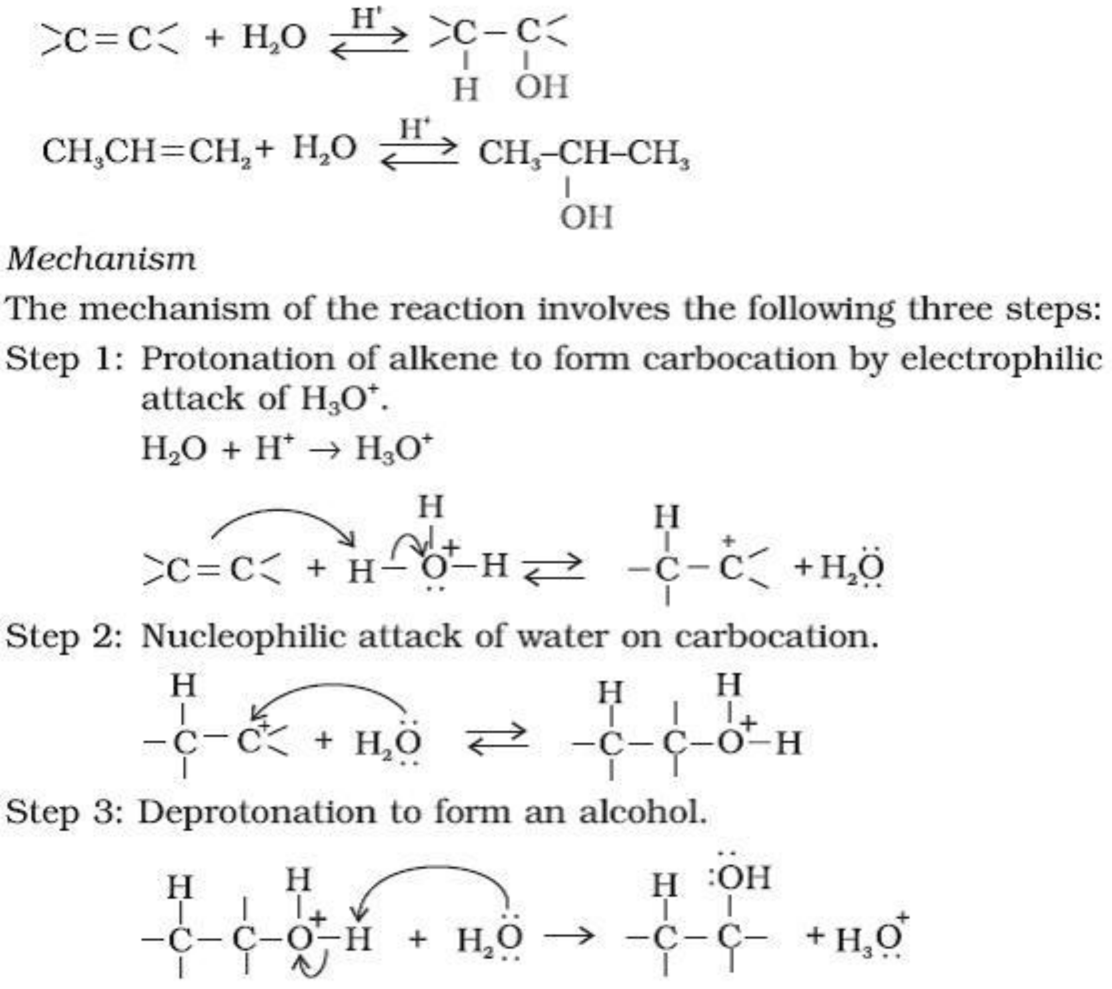
(VI) 

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

(VII) 

$CH_3-\underset{\displaystyle O}{\underset{\|}{C}}-CH_2-CH_2-CH_3$

Important mechanism



$$>C=C< + H_2O \overset{H^+}{\rightleftharpoons} >\underset{H}{\underset{|}{C}}-\underset{OH}{\underset{|}{C}}<$$

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

Mechanism

The mechanism of the reaction involves the following three steps:

Step 1: Protonation of alkene to form carbocation by electrophilic attack of H_3O^+.

$H_2O + H^+ \rightarrow H_3O^+$

$$>C=C< + H-\overset{H}{\overset{|}{\overset{+}{\underset{..}{O}}}}-H \rightleftharpoons -\overset{H}{\overset{|}{\underset{|}{C}}}-\overset{+}{C}< + H_2\ddot{O}$$

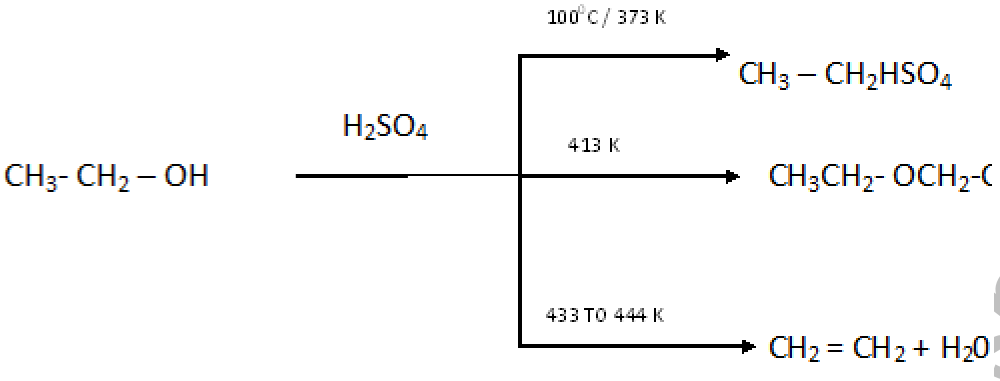
Step 2: Nucleophilic attack of water on carbocation.

$$-\overset{H}{\overset{|}{\underset{|}{C}}}-\overset{+}{C}< + H_2\ddot{O} \rightleftharpoons -\overset{H}{\overset{|}{\underset{|}{C}}}-\overset{|}{\underset{|}{C}}-\overset{H}{\overset{|}{\overset{+}{O}}}-H$$

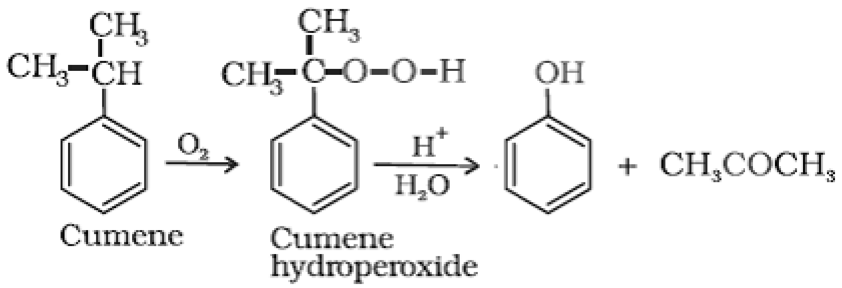
Step 3: Deprotonation to form an alcohol.

$$-\overset{H}{\overset{|}{\underset{|}{C}}}-\overset{|}{\underset{|}{C}}-\overset{H}{\overset{|}{\overset{+}{O}}}-H + H_2\ddot{O} \rightarrow -\overset{H}{\overset{|}{\underset{|}{C}}}-\overset{:\ddot{O}H}{\overset{|}{\underset{|}{C}}}- + H_3\ddot{O}^+$$

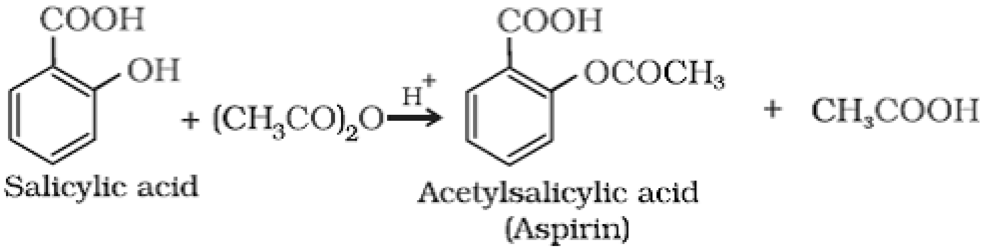
Important reaction



(2) Preparation of phenol from Cumene

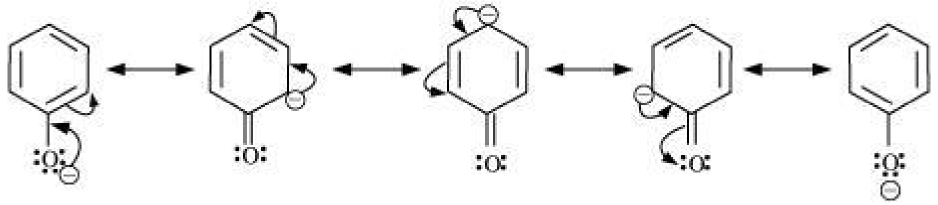


(3)Preparation of aspirin



Explain phenol is acidic?

Phenpxide ion is resonance stabilised



If electron with drawing group are attached into the benzene ring it enchance acidic character and vice versa.

2,4,6 trinitrophenol > 2,4, dinitrophenol > 4-nitrophenol > phenol

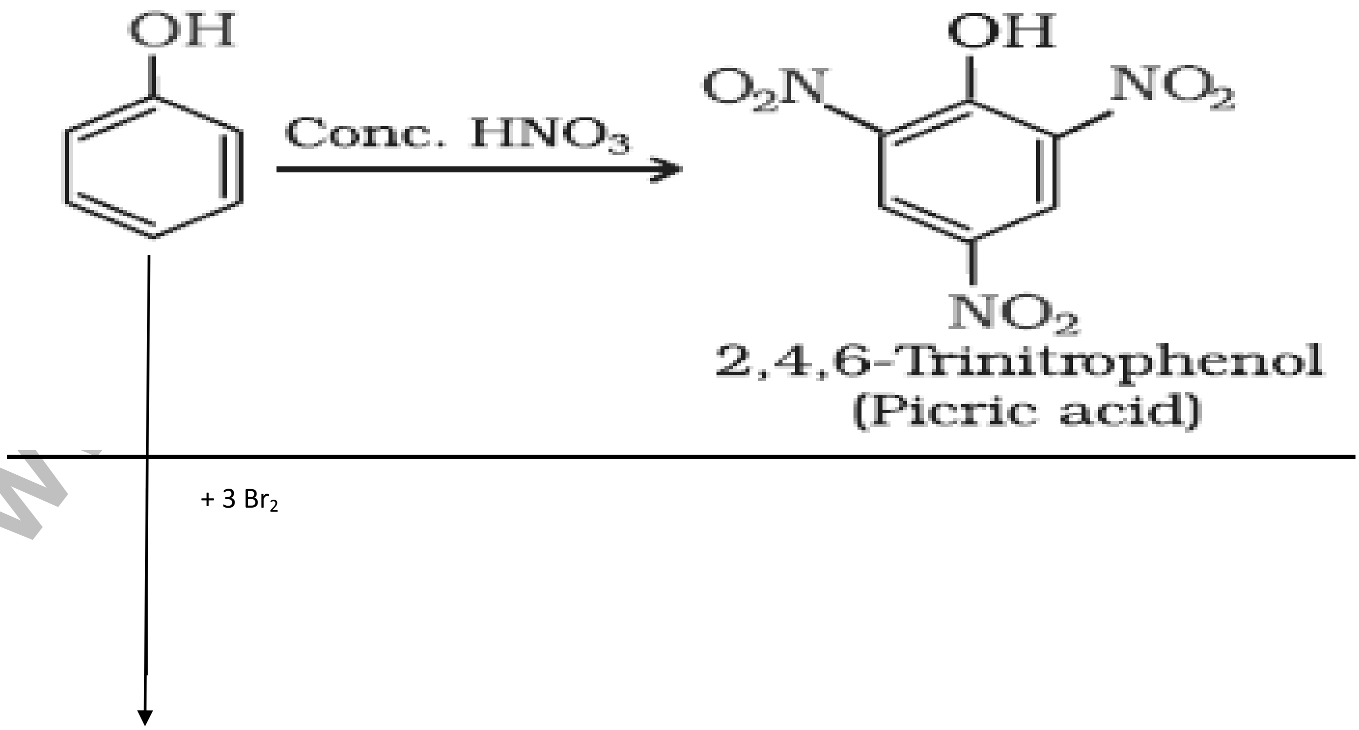
Phenol > m- cresol > P cresol > O cresol

m-methoxyphenol > phenol > O methoxy phenol > P methoxy phenol.

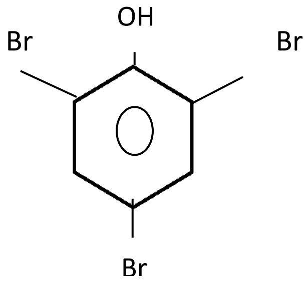
O chloro phenol > O bromophenol > O iodo phenol > O fluoro phenol

FORMATION OF PICRIC ACID

(I)



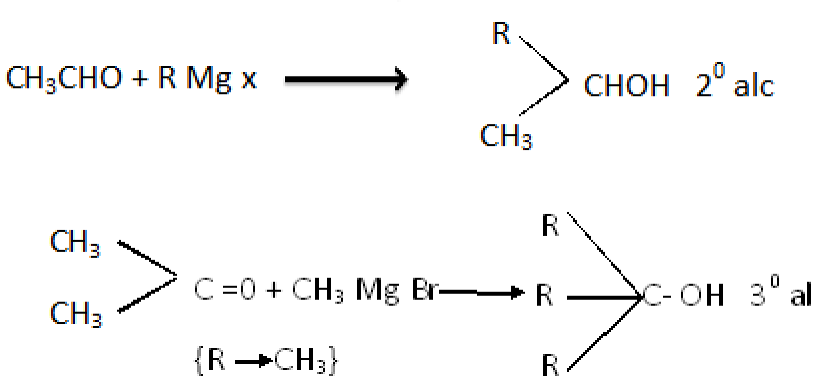
2,4,6-Trinitrophenol
(Picric acid)



2,4,6 tribromo phenol (white ppt)

(I)Phenol gives violet colour with $FeCl_3$ solution .

PREPARATION OF $1^0,2^0,3^0$ ALCOHOLS



$$HCHO + R\,Mg\,x \longrightarrow R\text{-}CH_2OH \quad 1^0\ \text{alc}$$

$$CH_3CHO + R\,Mg\,x \longrightarrow \begin{matrix} R \\ CH_3 \end{matrix}\!\!>CHOH \quad 2^0\ \text{alc}$$

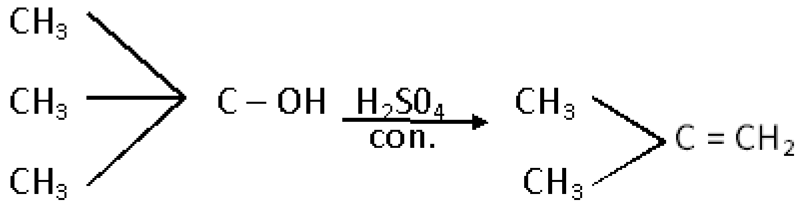
$$\begin{matrix} CH_3 \\ CH_3 \end{matrix}\!\!>C=0 + CH_3\,Mg\,Br \longrightarrow \begin{matrix} R \\ R \\ R \end{matrix}\!\!-\!C\text{-}OH \quad 3^0\ \text{al}$$

$\{R \rightarrow CH_3\}$

CONCEPTUAL QUESTIONS

Q1) Preparation of ethers by acid dehydration of secondry or 3^0 alcohols is not a suitable method?

Ans:- The formation of ethers by dehydration of alcohol is a bimolecular reaction (SN_2) group is hindered. as a result elimination dominates substitution as 3^0 carbocation is more stable. Hence ,in place of others , alkenes are formed.



Q2) Phenols do not give protonation reactions readily. Why?

Ans:- The lone pair on oxygen of O-H in phenol is being shared with benzene ring through resonance.Thus,lone pair is not fully present on oxygen and hence phenols do not undergo protonatian reactions.

Q3) Ortho- nitrophenol is more acidic than ortho –methoxy phenol ? why?

Ans:- NO$_2$ group is electron with drawing which increases acidic charcter due to easily ease

REASONING QUESTIONS

Q1. Explain why propanol has higher boiling point than that of the hydrocarbon, butane?

ANS. The molecules of Butane are held together by weak van der Waal's Forces of attraction while those of propanol are held together by stronger intermolecular hydrogen bonding.

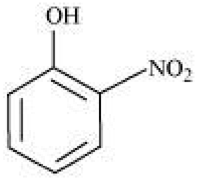
Q2. Alcohols are comparatively more soluble in water than hydrocarbons of comparable molecular masses. Explain this fact.

ANS. Alcohols can form hydrogen bonds with water and break the hydrogen bonds already existing between water molecules Therefore they are soluble in water. Whereas hydrocarbons cannot form hydrogen bonds with water and hence are insoluble in water.

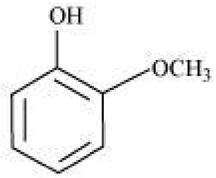
Q3. While separating a mixture of ortho and para nitrophenols by steam distillation, name the isomer which will be steam volatile. Give reason.

ANS. O-nitrophenol is steam volatile due to intramolecular hydrogen bonding and hence can be separated by steam distillation from p-nitrophenol which is not steam volatile because of inter-molecular hydrogen bonding.

Q4. Explain why is ortho nitrophenol more acidic than ortho methoxyphenol?



o – Nitrophenol

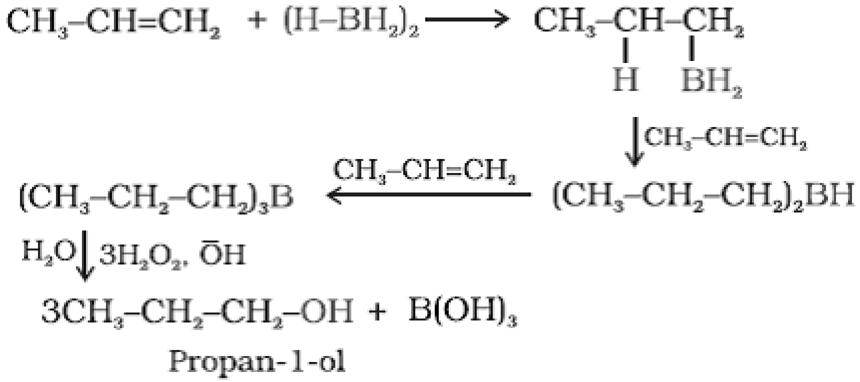


o – Methoxyphenol

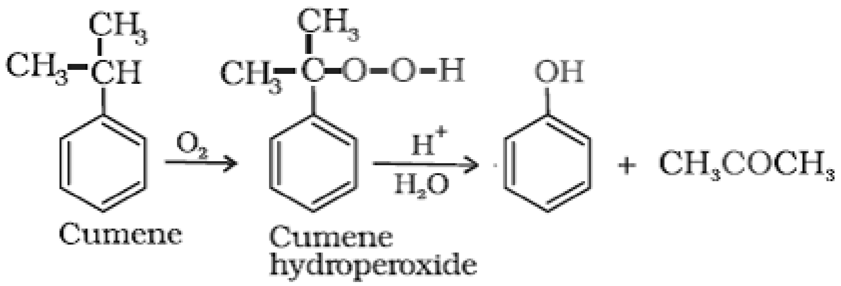
Ans. The nitro-group is an electron-withdrawing group. The presence of this group in the ortho position decreases the electron density in the O−H bond. As a result, it is easier to lose a proton. Also, the o-nitrophenoxide ion formed after the loss of protons is stabilized by resonance. Hence, ortho nitrophenol is a stronger acid. On the other hand, methoxy group is an electron-releasing group. Thus, it increases the electron density in the O−H bond and hence, the proton cannot be given out easily.Therefore ortho-nitrophenol is more acidic than ortho-methoxyphenol.

Q5. Preparation of ethers by acid dehydration of secondary or tertiary alcohols is not a suitable method. Give reason.
ANS. The formation of ethers by dehydration of alcohol is a bimolecular reaction (S_N2) involving the attack of an alcohol molecule on a protonated alcohol molecule. In the method, the alkyl group should be unhindered. In case of secondary or tertiary alcohols, the alkyl group is hindered. As a result, elimination dominates substitution.

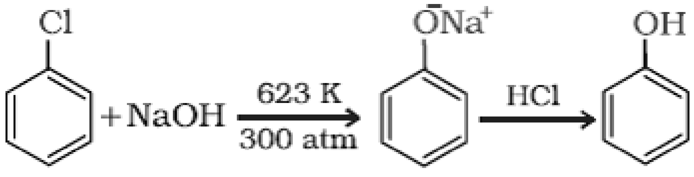
Q3. What is meant by hydroboration-oxidation reaction? Illustrate it with an example
ANS. Diborane $(BH_3)_2$ reacts with alkenes to give trialkyl boranes as addition product. This is oxidised to alcohol by hydrogen peroxide in the presence of aqueous sodium hydroxide.



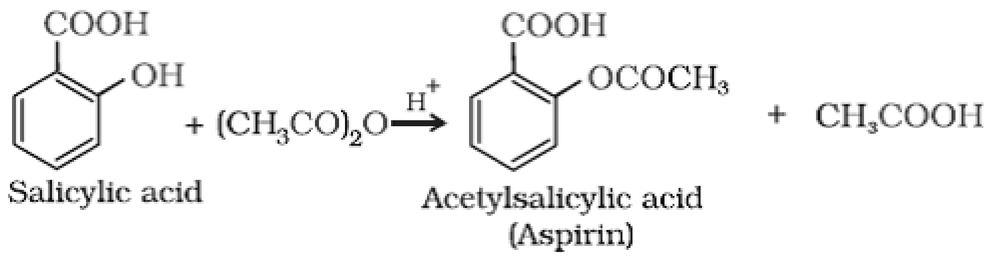
Q4. Give the equations of reactions for the preparation of phenol from cumene.



Q6. Write chemical reaction for the preparation of phenol from chlorobenzene. ANS. Chlorobenzene is fused with NaOH at 623K and 320 atmospheric pressure. Phenol is obtained by acidification of sodium phenoxide so produced.



Q7. How is aspirin (Acetylsalicylic acid) prepared from salicylic acid? ANS. Acetylation of salicylic acid produces aspirin.



Salicylic acid

Acetylsalicylic acid
(Aspirin)

Q8. Which out of propan-1-ol and propan-2-ol is stronger acid? ANS Propan-1-ol is stronger acid than propan-2-ol. The acidic strength of alcohols is in the order $1_0>2_0>3_0$.

Q9. What is denaturation of an alcohol?

ANS. The commercial alcohol is made unfit for drinking by mixing in it some copper sulphate (to give it a colour) and pyridine (a foul smelling liquid). It is known as denaturation of alcohol.

Q10. Give IUPAC name of $CH_3OCH_2OCH_3$

ANS. Dimethoxymethane

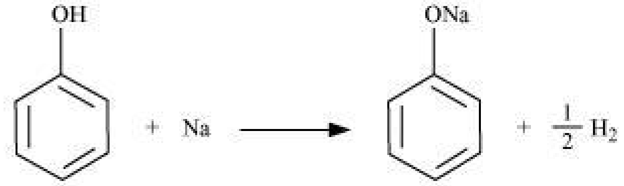
Q11. Diethyl ether does not react with sodium. Explain.

ANS. Diethyl ether does not contain any active hydrogen.

2 MARKS QUESTIONS

Q1. Give two reactions that show the acidic nature of phenol. Compare acidity of phenol with that of ethanol.

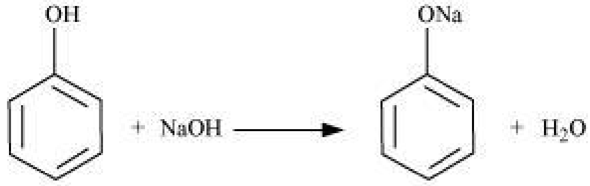
ANS. The acidic nature of phenol can be represented by the following two reactions: (i) Phenol reacts with sodium to give sodium phenoxide, liberating H_2.



(Phenol

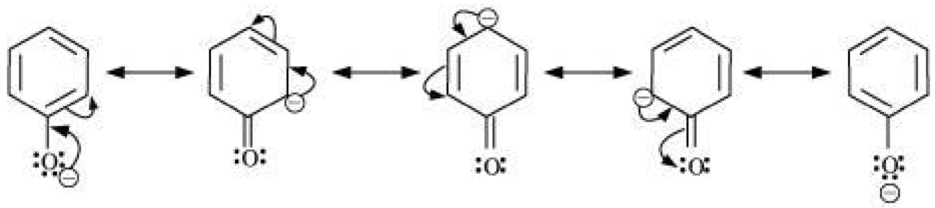
Sodium phenoxide

(i) Phenol reacts with sodium hydroxide to give sodium phenoxide and water as by-products



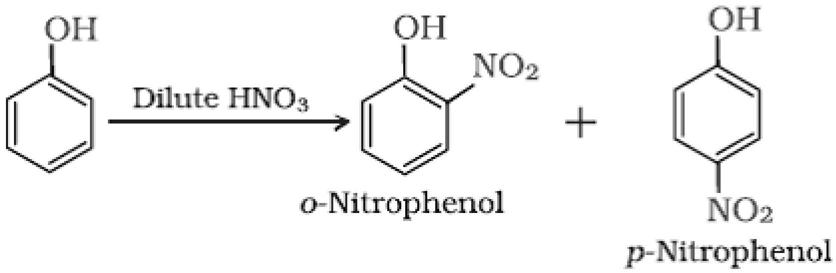
Sodium phenoxide

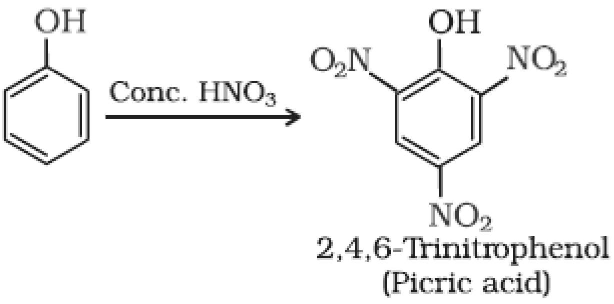
The acidity of phenol is more than that of ethanol. This is because after losing a proton, the phenoxide ion undergoes resonance and gets stabilized whereas ethoxide ion does not.



Q2. How does phenol react with dilute and conc. HNO_3 ?

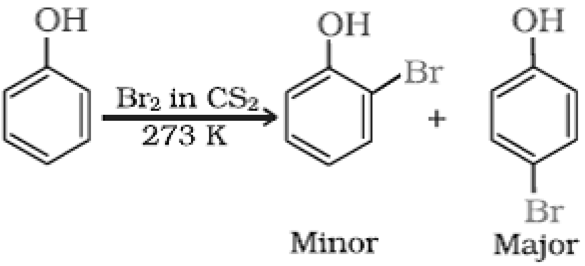
ANS. (i) With dilute nitric acid at low temperature (298 K), phenol yields a mixture of ortho and para nitrophenols. (ii) With concentrated nitric acid, phenol is converted to 2,4,6-trinitrophenol. The product is commonly known as picric acid.



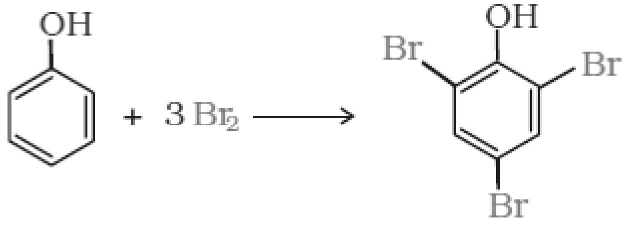


Q3. How does phenol react with Br_2 in CS_2 and Bromine water?

ANS. (i) When the reaction is carried out in solvents of low polarity such as $CHCl_3$ or CS_2 and at low temperature, monobromophenols are formed.



(ii) When phenol is treated with bromine water, 2,4,6-tribromophenol is formed as white precipitate.



2,4,6-Tribromophenol

Q4. How do you account for the fact that unlike phenol, 2, 4-dinitrophenol and 2, 4, 6-trinitrophenol are soluble in aqueous solution of sodium carbonate?
ANS 2, 4-Dinitrophenol and 2, 4, 6-trinitrophenol are stronger acids then carbonic acid (H_2CO_3) due to the presence of electron withdrawing – NO_2 groups. Hence, they react with Na_2CO_3 to form their corresponding salts and dissolve in aq. Na_2CO_3 solution.

Q5. (i) Why is the Dipole moment of methanol higher than that of phenol? (ii) . Explain why phenols do not undergo substitution of the –OH group like alcohols.
ANS. (i) Due to electron withdrawing effect of phenyl group, the C—O bond in phenol is less polar, whereas in case of methanol the methyl group has electron releasing effect and hence C—O bond in it is more polar. (ii) C—O bond in phenols has partial double bond character due to resonance and hence is difficult to cleave.

Q6. Account for the following:
a. Boiling point of the C_2H_5OH is more than that of C_2H_5Cl
b. The solubility of alcohols in water decreases with increase in molecular mass.

ANS. a. Because of hydrogen bonding. b. With increase in molecular mass the non-polar alkyl group becomes more predominant.

Q7. Answer the following

a. What is the order of reactivity of 1_0, 2_0 and 3_0 alcohols with sodium metal?
b. How will you account for the solubility of lower alcohols in water?

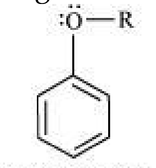
Ans: a. $1_0>2_0>3_0$.
b. Here—OH group is predominant and the alcohol molecules can form hydrogen bonds with water molecules.

Q8. Give reasons: i)Nitration of phenol gives ortho- and para- products only. ii)Why do alcohols have higher boiling points than the haloalkanes of the same molecular mass?
ANS (1) -OH group increases the electron density more at ortho and para positions through its electron releasing resonance effect. (2) Alcohols are capable of forming intermolecular H-bonds.

Q9. Account for the following: i) Phenols has a smaller dipole moment than methanol ii) Phenols do not give protonation reactions readily.
ANS a. In phenol the electron withdrawing inductive effect of –OH group is opposed by electron releasing the resonance effect of –OH. b. The lone pair on oxygen of –OH in phenol is being shared with benzene ring through resonance. Thus, lone pair is not fully present on oxygen and hence phenols do not undergo protonation reactions.

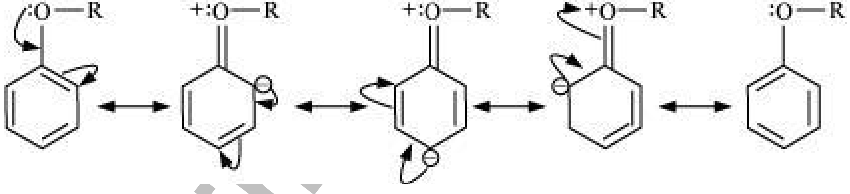
Q10. Explain the fact that in aryl alkyl ethers (i) The alkoxy group activates the benzene ring towards electrophilic substitution and (ii) It directs the incoming substituents to ortho and para positions in benzene ring.

ANS. (i)



Aryl alkyl ether

In aryl alkyl ethers, due to the +R effect of the alkoxy group, the electron density in the benzene ring increases as shown in the following resonance structure.



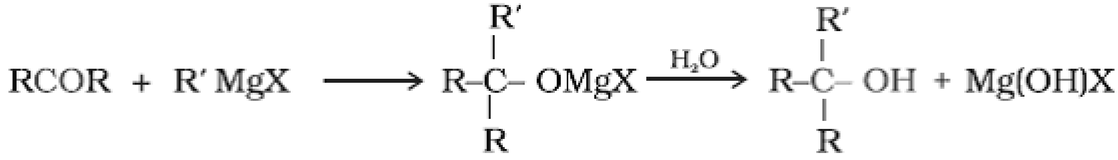
Thus, benzene is activated towards electrophilic substitution by the alkoxy group. (ii) It can also be observed from the resonance structures that the electron density increases more at the ortho and para positions than at the meta position. As a result, the incoming substituents are directed to the ortho and para positions in the benzene ring.

3 MARKS QUESTIONS

Q1. How are primary, secondary and tertiary alcohols prepared from Grignard Reagents?
ANS.

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

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



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

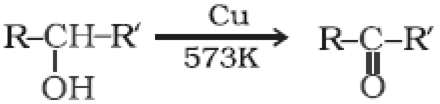
.

The reaction produces a primary alcohol with methanal, a secondary alcohol with other aldehydes and tertiary alcohol with ketones.

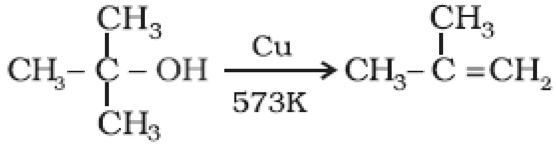
Q2. Give the equations of oxidation of primary, secondary and tertiary alcohols by Cu at 573 K.

ANS.

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



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



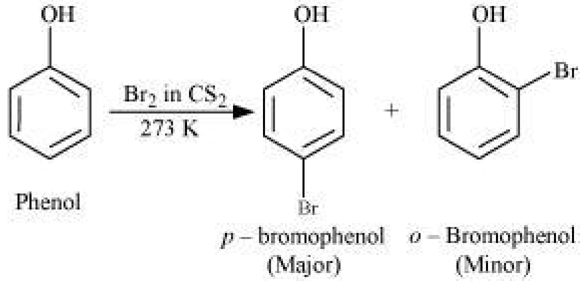
$$CH_3\!-\!\underset{CH_3}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}\!-\!OH \xrightarrow[573K]{Cu} CH_3\!-\!\overset{CH_3}{\overset{|}{C}}=CH_2$$

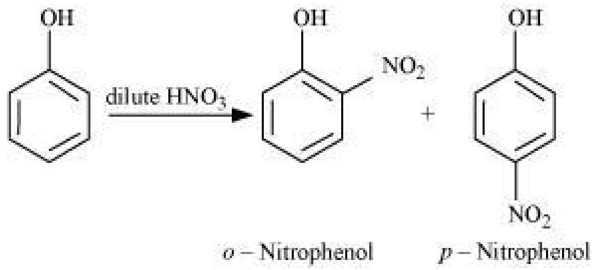
Q3. Give equations of the following reactions: (i) Oxidation of propan-1-ol with alkaline $KMnO_4$ solution. (ii) Bromine in CS_2 with phenol. (iii) Dilute HNO_3 with phenol.

ANS. (i)

$$\underset{\text{Propan-1-ol}}{CH_3CH_2CH_2OH} \xrightarrow{\text{alk KmnO}_4} \underset{\text{Propanoic acid}}{CH_3CH_2COOH}$$

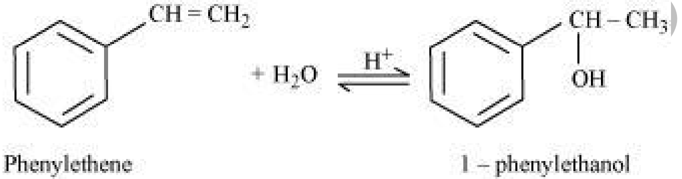
(





Q4. Show how will you synthesize:

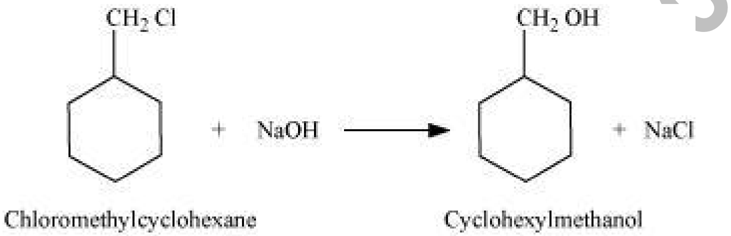
(i) 1-phenylethanol from a suitable alkene.
(ii) (ii) cyclohexylmethanol using an alkyl halide by an SN2 reaction.
(iii) (iii) pentan-1-ol using a suitable alkyl halide?
(iv) ANS. (i) By acid-catalyzed hydration of ethylbenzene (styrene), 1-phenylethanol can be



synthesized.

(v)

(ii) When chloromethylcyclohexane is treated with sodium hydroxide, cyclohexylmethanol is obtained.



(iii) When 1-chloropentane is treated with NaOH, pentan-1-ol is produced.

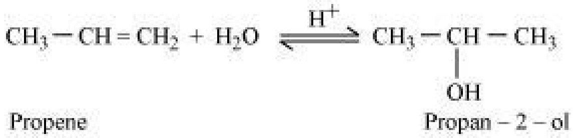
$$CH_3CH_2CH_2CH_2CH_2Cl + NaOH \longrightarrow CH_3CH_2CH_2CH_2CH_2OH + NaCl$$

(iv) 1-Chloropentane Pantan-1-ol

Q5. How are the following conversions carried out?

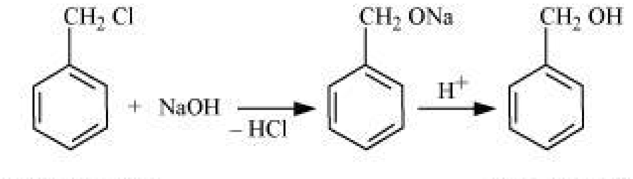
(i) Propene → Propan-2-ol
(ii) (ii) Benzyl chloride → Benzyl alcohol
(iii) (iii) Ethyl magnesium chloride → Propan-1-ol.

ANS. (i)If propene is allowed to react with water in the presence of an acid as a catalyst, then propan-2-ol is obtained.



$$\underset{\text{Propene}}{CH_3-CH=CH_2} + H_2O \xrightleftharpoons{H^+} \underset{\text{Propan – 2 – ol}}{CH_3-\underset{OH}{\underset{|}{CH}}-CH_3}$$

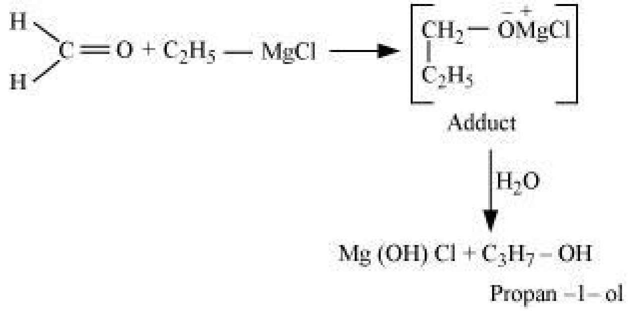
(ii)(ii) If benzyl chloride is treated with NaOH (followed by acidification) then benzyl alcohol is produced.



Benzyl chloride

Benzyl alcohol

(iii)When ethyl magnesium chloride is treated with methanal, an adduct is the produced which gives propan-1-ol on hydrolysis.



Q6. Name the reagents used in the following reactions:

(i) Oxidation of a primary alcohol to carboxylic acid.
(ii) (ii) Oxidation of a primary alcohol to aldehyde.
(iii) Bromination of phenol to 2,4,6-tribromophenol.

ANS. (i) Acidified potassium permanganate
(ii) Pyridinium chlorochromate (PCC)
(iii) Bromine water

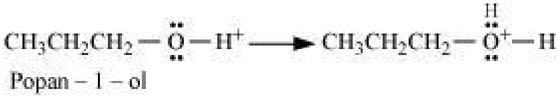
Q7. How is 1-propoxypropane synthesised from propan-1-ol? Write mechanism of this reaction.

ANS. 1-propoxypropane can be synthesized from propan-1-ol by dehydration. Propan-1-ol undergoes dehydration in the presence of protic acids (such as H_2SO_4, H_3PO_4) to give 1-propoxypropane.

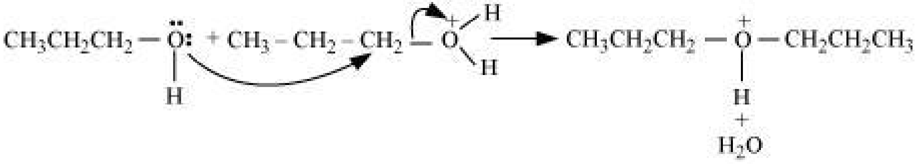
$$\underset{\text{Propane-1-ol}}{2CH_3CH_2CH_2-OH} \xrightarrow{H^+} \underset{\text{1-Propoxypropane}}{CH_3CH_2CH_2-O-CH_2CH_2CH_3}$$

The mechanism of this reaction involves the following three steps:

Step 1: Protonation



Step 2: Nucleophilic attack



Step 3: Deprotonation

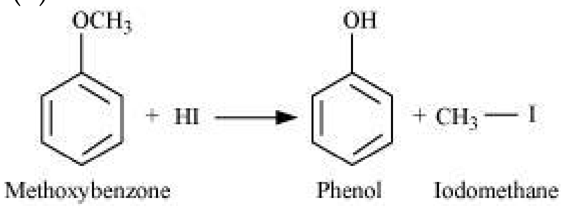
Q8. Write the equation of the reaction of hydrogen iodide with:

(i) 1-propoxypropane (ii) Methoxybenzene and (iii) Benzyl ethyl ether

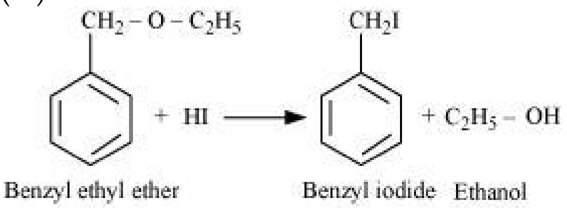
ANS. (i)

$$\underset{\text{1-Propoxypropane}}{C_2H_5CH_2-O-CH_2C_2H_5} + HI \xrightarrow{373K} \underset{\text{Propan-1-ol}}{CH_3CH_2CH_2-OH} + \underset{\text{1-Iodopropane}}{CH_3CH_2CH_2-I}$$

(ii)



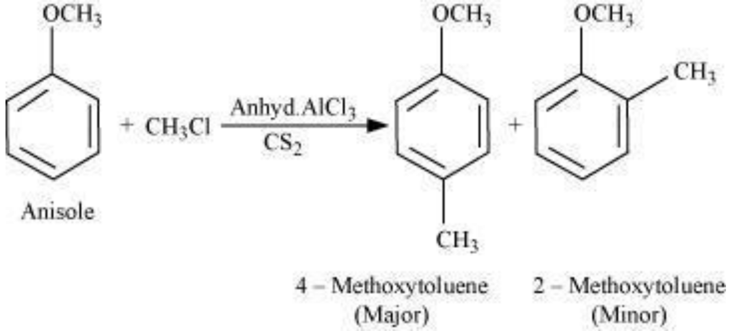
(iii)



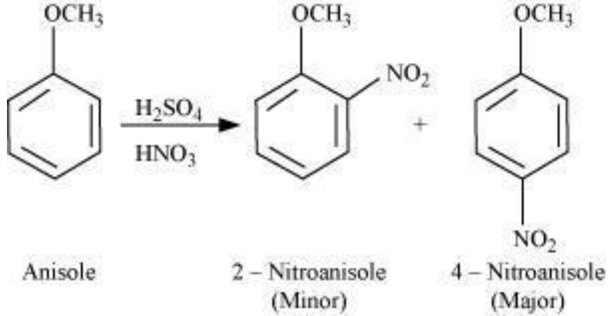
5 MARKS QUESTIONS

Q1. Write equations of the following reactions:
(i) Friedel-Crafts reaction−alkylation of anisole.
(ii) Nitration of anisole.
(iii) Bromination of anisole in ethanoic acid medium.
(iv) Friedel-Craft's acetylation of anisole.
(v)Reaction of phenol with Zn dust.

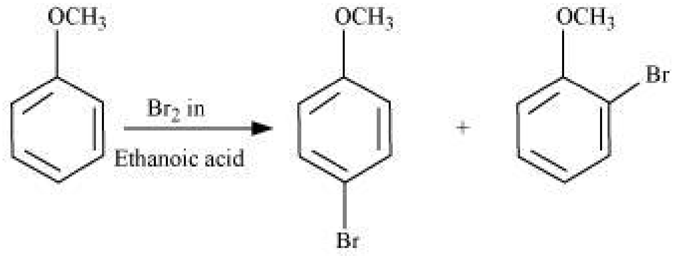
ANS. (i)



(ii)



(iii)

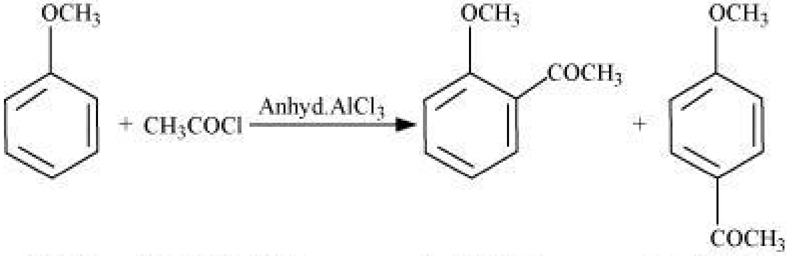


Anisole

p – Bromoanisole (Major)

o – Nitroanisole (Minor)

(iv)



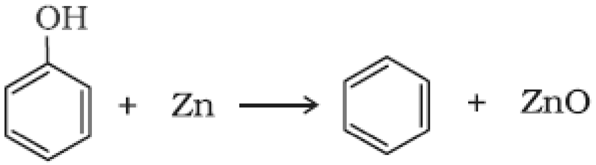
Anisole

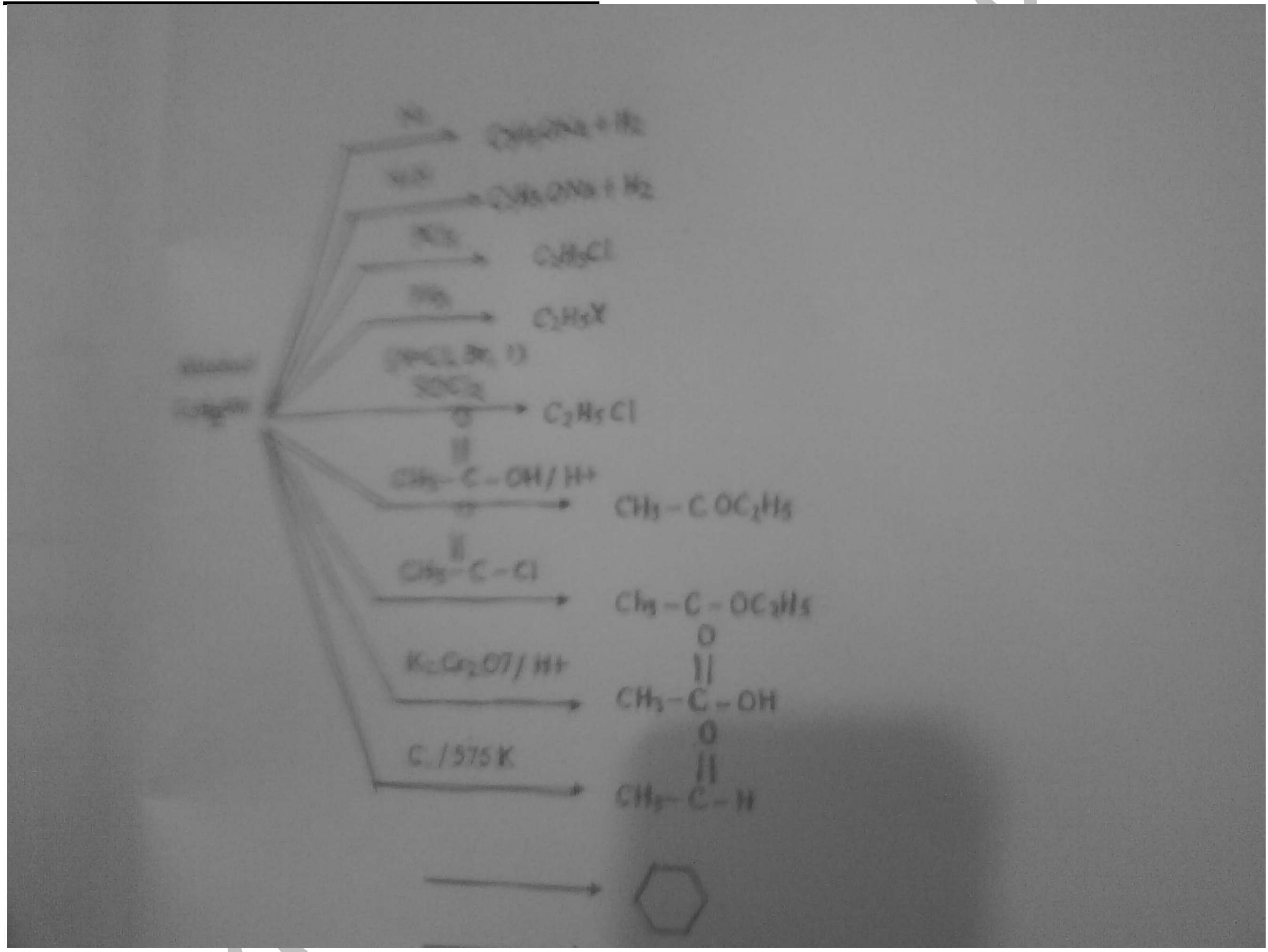
Ethanoyl chloride

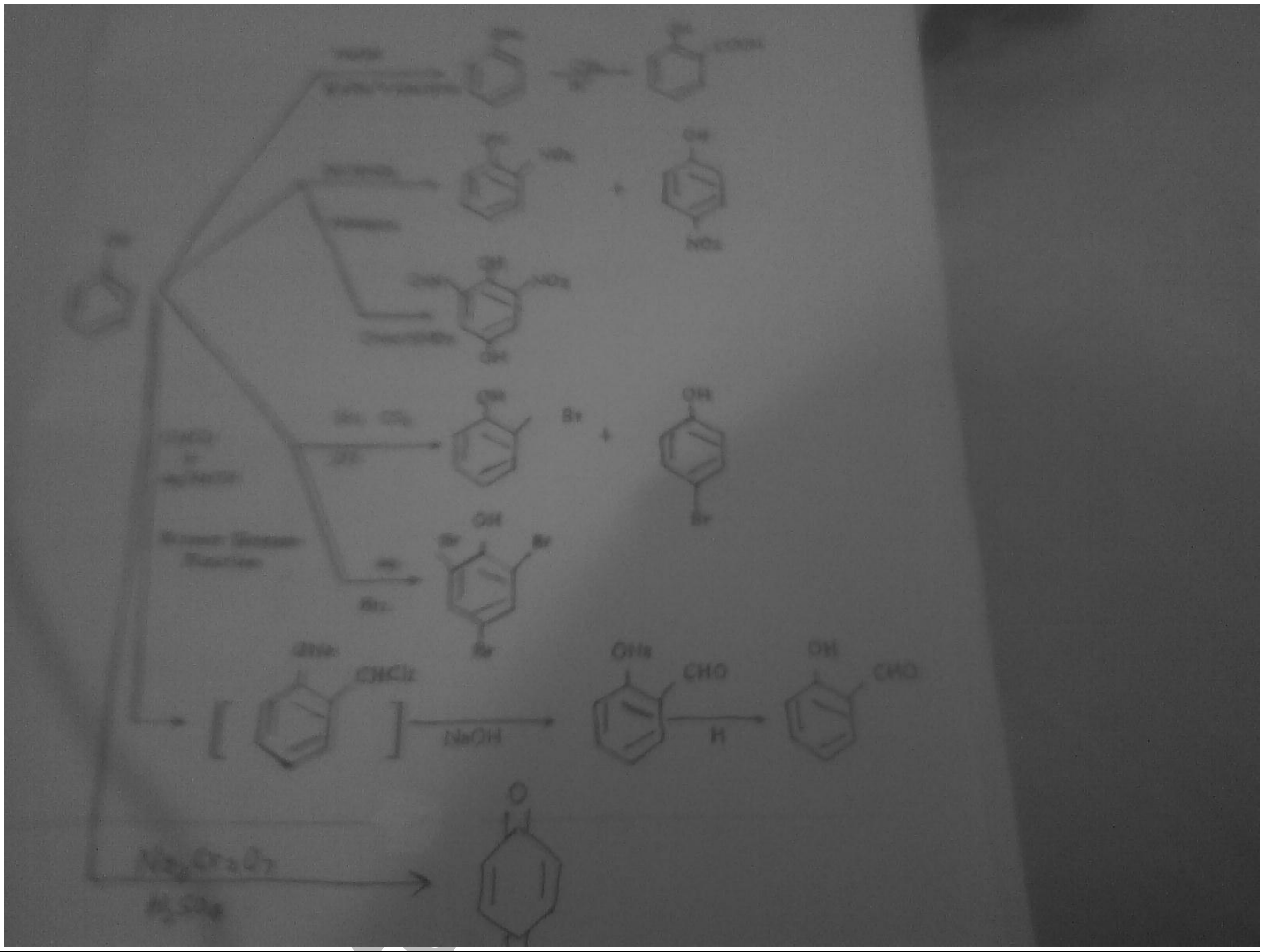
2 – Methoxy – acetophenone (Minor)

4 – Methoxy – acetophenone (Major)

(v)


OH
+ Zn
+ ZnO


Na
C2H5ONa + H2
NaH
C2H5ONa + H2
PCl5
C2H5Cl
PX3
C2H5X
(X=Cl, Br, I)
SOCl2
C2H5Cl
O
CH3-C-OH / H+
CH3-C OC2H5
O
CH3-C-Cl
CH3-C-OC2H5
K2Cr2O7/H+
O
CH3-C-OH
C. / 575 K
O
CH3-C-H

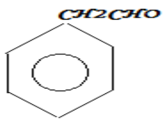

OH
COOH
NO2
OH
NO2
Br
Br
OH
Br
Br
Br
CHCl3
aq NaOH
Reimer Tiemann Reaction
CHCl2
NaOH
OH
CHO
OH
CHO
O
Na2Cr2O7
H2SO4

UNIT 12

ALDEHYDES, KETONES AND CARBOXYLIC ACIDS

The π Electron cloud of >C=O is unsymmetrical. On the other hand, due to same electronegativity of the two carbon atoms, the π-electron of the >C=C< bond is symmetrical.

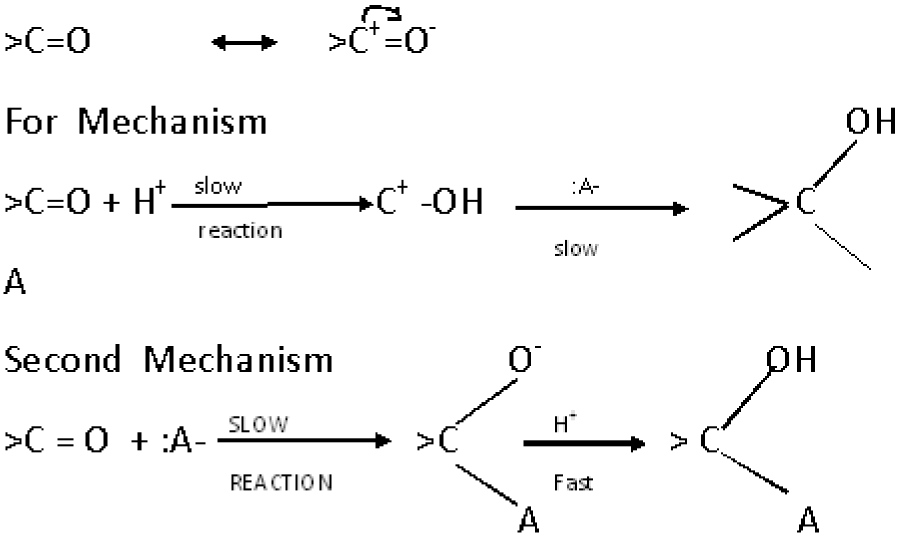
Nature of carbonyl group:- The Pi electron cloud of >C=O is unsymmetrical therefore, partial positive charge develop over carbon of carbonyl group while negative charge develop over oxygen of carbonyl group and dipole moment is approximate 2.6D.

FORMULA	NAME OF THE CORRESPONDING ACID	COMMON NAME	IUPAC NAME
HCHO	HCOOH(formic acid)	Formaldehyde	Methanal
CH_3CHO	CH_3COOH(Acetic acid)	Acetaldehyde	Ethanal
CH_3CH_2CHO	CH_3CH_2COOH(Propanoic acid)	Propionaldehyde	Propanal
$CH_3CH_2CH_2CHO$	$CH_3CH_2CH_2COOH$(Butyric acid)	Butyraldehyde	Butanal
$CH_3CH(CH_3)CHO$	$CH_3CH(CH_3)COOH$(Isobutyric acid)	Isobutyraldehyde	2-Methylpropanal
$CH_3CH_2CH(CH_3)CHO$	$CH_3CH_2CH(CH_3)COOH$(α-Methylbutyic acid)	α-Methylbutyraldehyde	2-Methylbutanal
$CH_3CH(CH_3)CH_2CHO$	$CH_3CH(CH_3)CH_2COOH$ (β-Methylbutyric acid)	B-Methylbutyraldehyde	3-Methylbutanal
			2-Phenylethanal

FORMULA	COMMON NAME	IUPAC NAME
CH_3COCH_3	Dimethyl Ketone or acetone	Propanone
$CH_3COCH_2CH_3$	Ethyl methyl Ketone	Butan-2-one or
1 2		Butanone
$CH_3COCH_2CH_2CH_3$	Methyl n-propyl Ketone	Pentan-2-one
1 2 3		
$CH_3CH_2COCH_2CH_3$	Diethyl Ketone	Pentan-3-one

Addition to C=O bonds

The structure of the carbonyl group in aldehydes and Ketones is , not entirely adequately represented by >C=O, nor by the alternative $>C^+-O^-$. The real structure or resonance hybrid lies somewhere between the following structure:



Reactivity of aldehyde and Ketones is as $HCHO>RCHO>RCOR>RCOOR>RCONH_2$.

POINTS TO REMEMBER

Aldehydes, Ketones and Carboxylic acids are important classes of organic compounds containing carbonyl groups.

They are highly polar molecules.

They boil at higher temperatures than the corresponding hydrocarbons and weakly polar compounds such as ethers.

Lower members are soluble in water because they can form H-bond with water.

Higher members are insoluble in water due to large size of their hydrophobic group.

Aldehydes are prepared by-

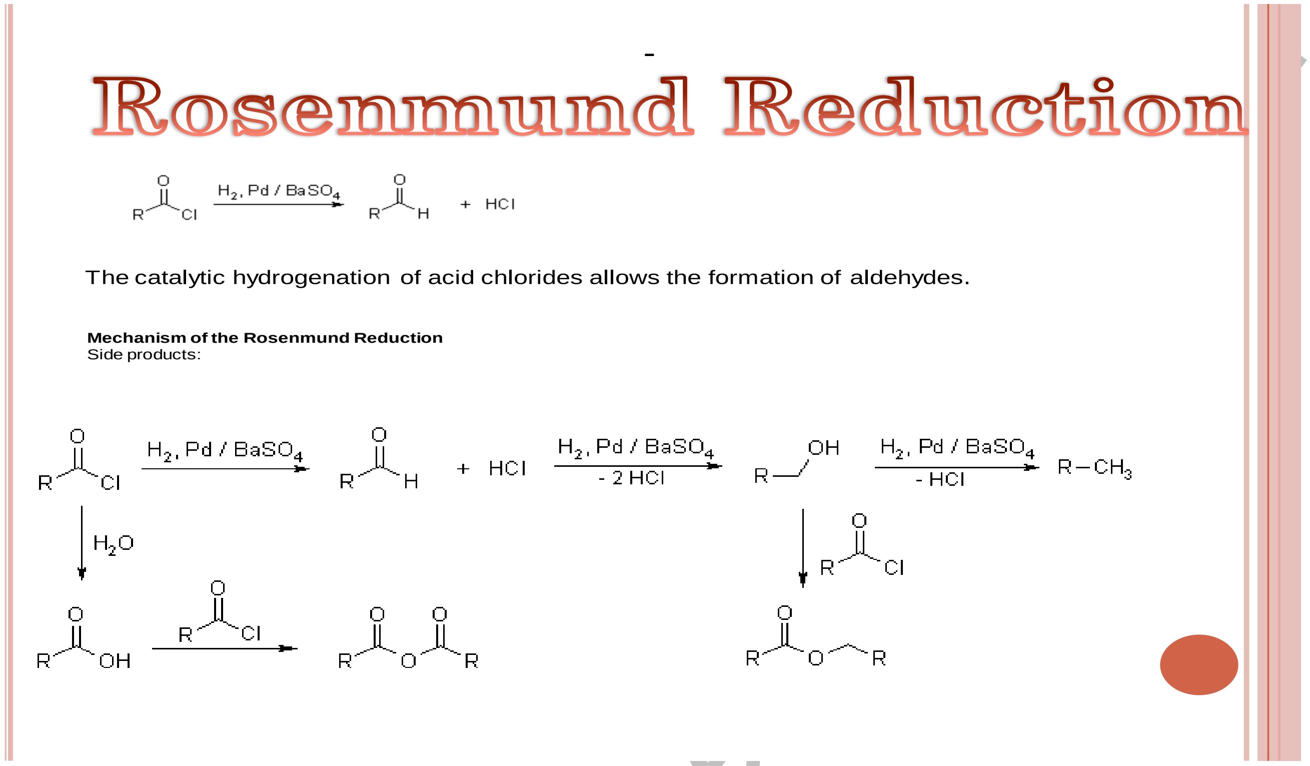
a. Dehydrogenation of primary alcohols
b. Controlled oxidation of primary alcohols.
c. Controlled and selective reduction of acyl halides
Aromatic aldehydes can be prepared by-
a. Oxidation of toluene with chromyl chloride or CrO_3 in the presence of acetic anhydride
b. Formylation of arenes with carbon monoxide and Hydrochloric acid in the

presence of anhydrous aluminium chloride / Cuprous chloride
c. Hydrolysis of benzal chloride

Ketones are prepared by-
a. oxidation of secondary alcohols
b. Hydration of alkenes
c. Reaction acyl chlorides with dialkylcadmium
d. By friedel crafts reaction

Carboxylic acids are prepared by –
a. oxidation of primary alcohols, aldehydes and alkenes
b. hydrolysis of nitriles
c. Treatment of grignard reagent with carbondioxide.

NAME REACTIONS 1
.
ROSENMUND REDUCTION:



Rosenmund Reduction

The catalytic hydrogenation of acid chlorides allows the formation of aldehydes.

Mechanism of the Rosenmund Reduction

Side products:

. **ROSENMUND REDUCTION**:

Acyl chlorides when hydrogenated over catalyst, palladium on barium sulphate yield aldehydes

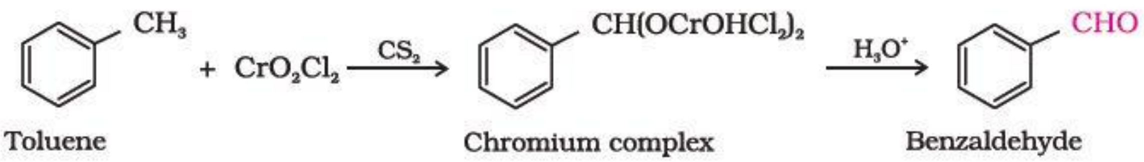
Benzoyl chloride Benzaldehyde 2

2. STEPHEN REACTION

Nitriles are reduced to corresponding imines with stannous chloride in the presence of Hydrochloric acid, which on hydrolysis give corresponding aldehyde.

$RCN + SnCl_2 + HCl \rightarrow RCH{=}NH \xrightarrow{H_3O} R\,CHO.$

ETARD REACTION On treating toluene with chromyl chlorideCrO_2Cl_2, the methyl group is oxidized to a chromium complex, which on hydrolysis gives corresponding benzaldehyde.



This reaction is called **Etard reaction**.

CLEMMENSEN REDUCTION The carbonyl group of aldehydes and ketone is reduced to –CH_2 group on treatment with zinc amalgam and conc. Hydrochloric acid.

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

Alkanes –

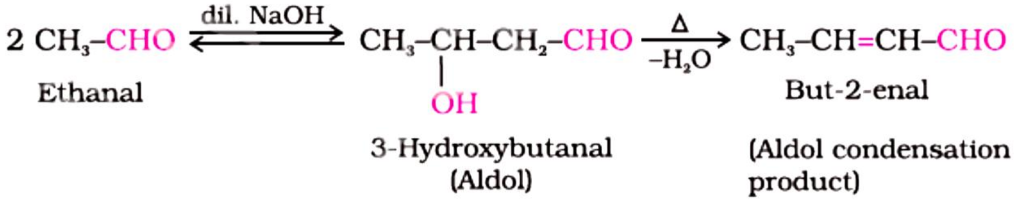
WOLFF- KISHNER REDUCTION

On treatment with hydrazine followed by heating with sodium or potassium hydroxide in high boiling solvent like ethylene glycol

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

ALDOL CONDENSATION

Aldehydes and ketones having at least one α-hydrogen condense in the presence of dilute alkali as catalyst to form β-hydroxy alddilehydes (aldol) or β-hydroxy ketones (ketol).

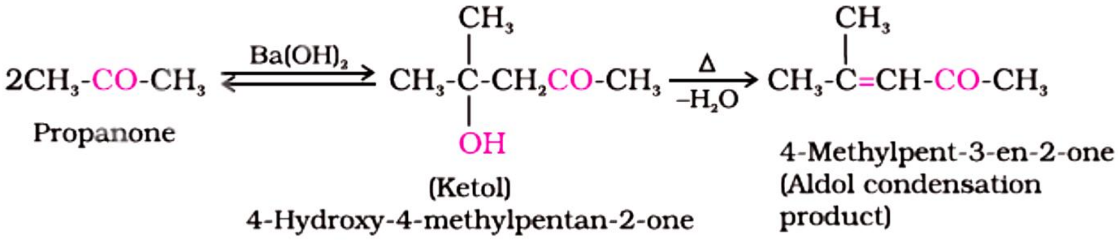


$$2\ CH_3{-}CHO \underset{}{\overset{\text{dil. NaOH}}{\rightleftharpoons}} CH_3{-}\underset{OH}{\underset{|}{C}H}{-}CH_2{-}CHO \xrightarrow[-H_2O]{\Delta} CH_3{-}CH{=}CH{-}CHO$$

Ethanal

3-Hydroxybutanal (Aldol)

But-2-enal (Aldol condensation product)



$$2CH_3{-}CO{-}CH_3 \overset{Ba(OH)_2}{\rightleftharpoons} CH_3{-}\overset{CH_3}{\underset{OH}{C}}{-}CH_2CO{-}CH_3 \xrightarrow[-H_2O]{\Delta} CH_3{-}\overset{CH_3}{C}{=}CH{-}CO{-}CH_3$$

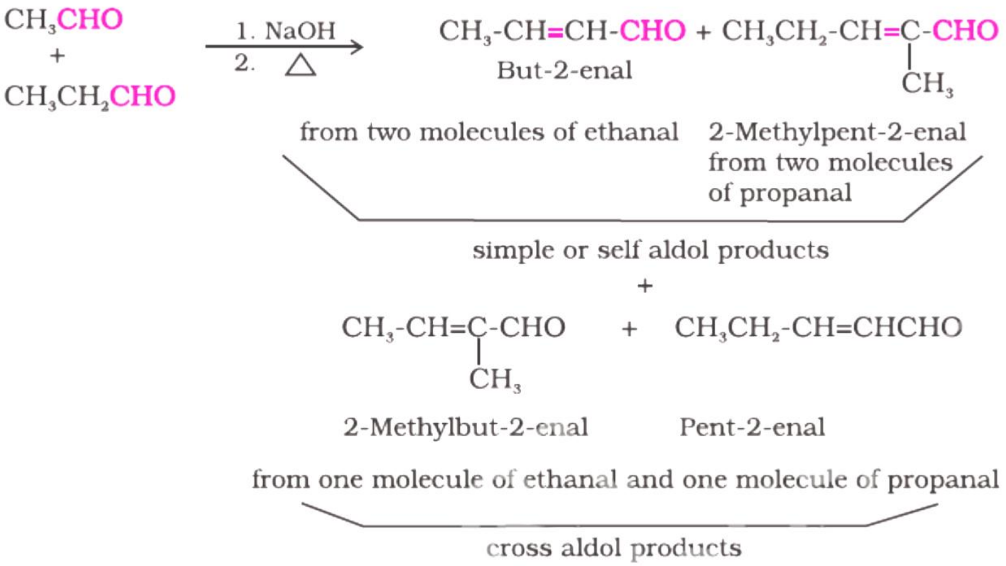
Propanone

(Ketol) 4-Hydroxy-4-methylpentan-2-one

4-Methylpent-3-en-2-one (Aldol condensation product)

CROSS- ALDOL CONDENSATION

When aldol condensation is carried out between two different aldehydes and / or ketones, a mixture of self and cross-aldol products are obtained.



$$CH_3CHO + CH_3CH_2CHO \xrightarrow[2.\ \Delta]{1.\ NaOH} CH_3{-}CH{=}CH{-}CHO + CH_3CH_2{-}CH{=}\underset{CH_3}{C}{-}CHO$$

But-2-enal from two molecules of ethanal

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

simple or self aldol products

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

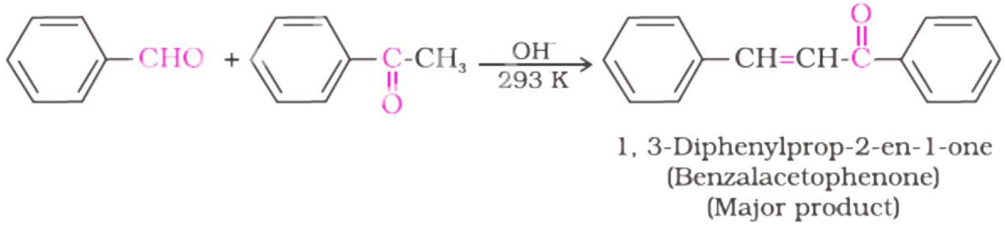
2-Methylbut-2-enal

Pent-2-enal

from one molecule of ethanal and one molecule of propanal

cross aldol products

Ketones can also be used as one component in the cross aldol reactions.



1, 3-Diphenylprop-2-en-1-one (Benzalacetophenone) (Major product)

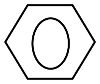
CANNIZARO REACTION

Aldehydes which do not have an α-hydrogen atom, undergo self oxidation and reduction (dispropotionation) reaction on treatment with concentrated alkali,to yield carboxylioc acid salt and an alcohol respectively.

$$\text{H-CHO} + \text{H-CHO} + \text{Conc.KOH} \longrightarrow CH_3OH + HCOOK$$

Formaldehyde

Methanol Pot. Formate



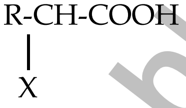
$$\text{-CHO} + \text{NaOH (con.)} \longrightarrow C_6H_5CH_2OH + C_6H_5COONa$$

Benzaldehyde Benzyl alcohol Sodium benzoate

CARBOXYLIC ACIDS

1. **HELL-VOLHARD-ZELINSKY REACTION (HVZ)**

Carboxylic acids having an α – hydrogen are halogenated at the α –position on treatment with chlorine or bromine in the presence of small amount of red phosphorus to give α – halocarboxylic acids.



$$RCH_2\text{-COOH} \xrightarrow[\text{ii } H_2O]{\text{i } X_2/\text{ Red phosphorus}} \text{R-}\underset{\substack{|\\X}}{\text{CH}}\text{-COOH}$$

X=Cl,Br

α –halocarboxylic acids

2. **ESTERIFICATION**

Carboxylic acids react with alcohols or phenols in the presence of a mineral acid such as conc.H_2SO_4 as catalyst to form esters.

$$\underset{\text{Carboxylic acid}}{RCOOH} + \underset{\text{alcohol}}{R'OH} \overset{H^+}{\rightleftharpoons} \underset{\text{Ester}}{RCOOR'} + H_2O$$

DECARBOXYLATION:

Carboxylic acids lose carbondioxide to form hydrocarbons when their sodium salts are heated with sodalime NaOH and CaO in the ratio 3: 1 .

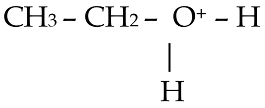
$$RCOONa \xrightarrow{\text{NaOH and CaO} / \Delta} \text{R-H} + Na_2CO_3$$

MECHANISMS

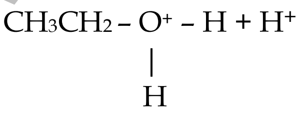
.

1. $$CH_3CH_2OH \xrightarrow[\text{443 K}]{\text{Con } H_2SO_4} CH_2 = CH_2 + H_2O$$

(i) $H_2SO_4 \rightleftharpoons H^+ + HSO_4^-$



(ii) $$CH_3CH_2 - O - H + H^+ \longrightarrow CH_3 - CH_2 - \underset{\substack{|\\H}}{O^+} - H$$



(iii) $$CH_3CH_2 - \underset{\substack{|\\H}}{O^+} - H + H^+ \longrightarrow CH_3CH_2^+ + H_2O$$

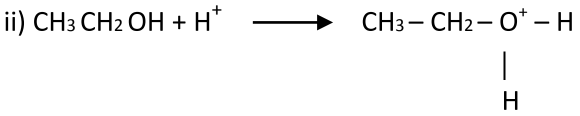
(iv) $CH_3CH_2^+ \longrightarrow CH_2 = CH_2 + H^+$

(v) $H^+ + HSO_4^- \longrightarrow H_2SO_4$

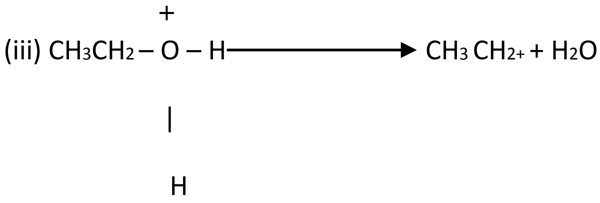
2 $2CH_3CH_2OH \xrightarrow[413\ K]{Con\ H_2SO_4} CH_3CH_2OCH_2CH_3 + H_2O$

Mechanism:-

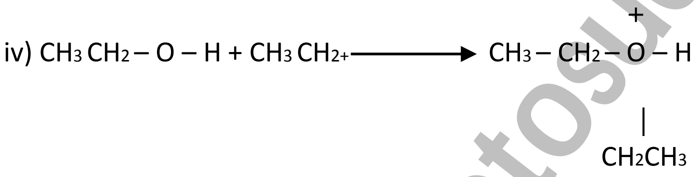
i) $H_2SO_4 \longrightarrow H^+ + HSO_4^-$



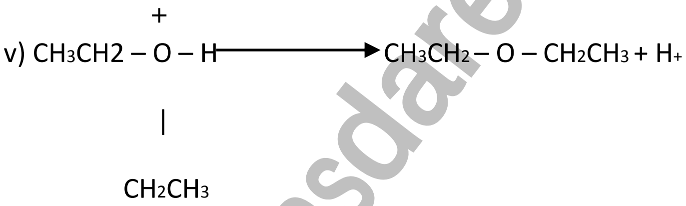
ii) $CH_3CH_2OH + H^+ \longrightarrow CH_3-CH_2-\underset{\displaystyle H}{\underset{|}{O^+}}-H$



(iii) $CH_3CH_2-\underset{\displaystyle H}{\underset{|}{\overset{+}{O}}}-H \longrightarrow CH_3CH_2^+ + H_2O$



iv) $CH_3CH_2-O-H + CH_3CH_2^+ \longrightarrow CH_3-CH_2-\underset{\displaystyle CH_2CH_3}{\underset{|}{\overset{+}{O}}}-H$



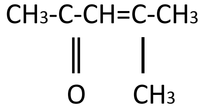
v) $CH_3CH2-\underset{\displaystyle CH_2CH_3}{\underset{|}{\overset{+}{O}}}-H \longrightarrow CH_3CH_2-O-CH_2CH_3 + H^+$

vi) $HSO_4^- + H^+ \longrightarrow H_2SO_4$

NOMENCLATURE

a. $CH_3CH\ CH_3\ CH_2CH_2CHO$
   4-Methylpentanal
b. $CH_3CH_2COCH\ C_2H_5\ CH_2CH_2Cl$
   6-chloro-4-ethylhexan-3-one
c. $CH_3CH=CHCHO$
   But-2-enal

d. $CH_3COCH_2COCH_3$
   Pentane.2,4-dione .
e. $OHCC_6H_4CHO$
   Benzene-1,4-di carbaldehyde
f. $CH_3CH_2CHC_6H_5CHO$
   2-Phenylbutanal
2. Draw the structures of the following compound;
   4-Methypent-3-en-2-one



$$\underset{\underset{O}{\|}}{CH_3\text{-}C}\text{-}CH{=}\underset{\underset{CH_3}{|}}{C}\text{-}CH_3$$

DISTINGUISH

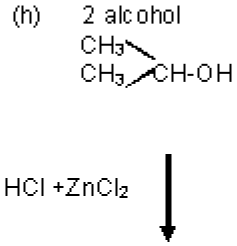
Q1:-Distinguish between the following:-
(a)Phenol and alcohol
(b)Benzaldehyde and Propanal
(c)Acetic acid and formic acid
(d)Benzophenone and acetophenone
(e)Ethanal and propanal
(f)Propanol and ethanol
(g)Pentanone-2 and pentanone-3
(h)2 Alcohal and 3 alcohol
(i)1,2,3 amine
(j)Benzoic acid and benzene
(k)Phenol and benzoic acid
(l)Aniline and ethyl amine
(m)Aniline and nitrobenzene
(n)Benzaldehyde and acetophenone
(o)Methanol and benzaldehyde
(p)Chloro benzene and benzyl chloride

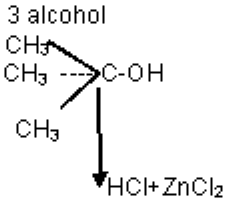
ANSWERS

(a)	Phenol	Alcohol
	It gives $FeCl_3$ test (voilet colour)	It doesn't give this test
(b)	Benzaldehyde	Propanal
	It gives tollen's	It also give tollen's reagent test
	It doesn't give fehling solution test	It gives fehling solution test
(c)	Acetic acid	Formic acid
	It doesn't gives tollen's reagent	It gives tollen's test

	It doesn't give fehling's test	It gives fehling test
(d)	Benzophenone	Acetophenone
	It doesn't give iodoform test	It gives iodoform test
(e)	Ethanal	Propanal
	It gives iodoform test	It doesn't gives iodoform test
(f)	Propanol	Ethanol
	It doesn't give iodoform test	It gives iodoform test
(g)	pentanone-2	pentanone-3
	It gives iodoform test	It doesn't gives iodoform test

(h)





It takes 5 minutes	turbidity is formed within no seconds

(i) 1 amine

$C_2H_5NH_2 + C_6H_5SO_2Cl \longrightarrow C_6H_5NH\text{-}SO_2\text{-}C_6H_5$

(benzene sulphonyl chloride) soluble in alkali

2 amine

$C_2H_5\text{-}\underset{\displaystyle C_2H_5}{\underset{|}{N}}H + C_6H_5SO_2Cl \rightarrow C_2H_5\text{-}\underset{\displaystyle C_2H_5}{\underset{|}{N}}\text{-}SO_2C_6H_5$

Insoluble in KOH

3 amine

$C_2H_5\text{-}\underset{\displaystyle C_2H_5}{\underset{\backslash}{N}}\text{-}C_2H_5 + C_6H_5SO_2Cl\text{--->}X$ (No reaction)

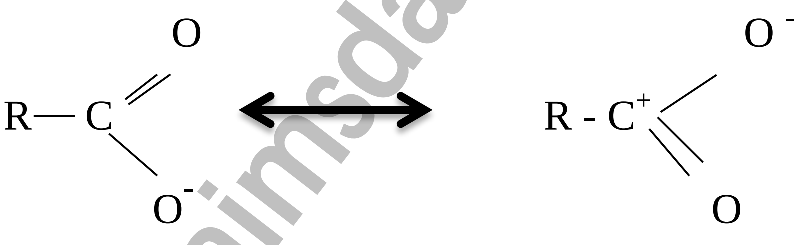
(J)	Benzoic acid	Benzene
	add $NaHCO_3$	no effervescence obtained
	Effervescence obtained(CO_2)	
(k)	Phenol	Benzoic acid
	It gives voilet colour with $FeCl_3$ test	It doesn't give voilet colour with $FeCl_3$
	It doesn't give effervescenes of CO_2	Effervescence of CO_2 evolve when $NaHCO_3$ is added

(l)	Aniline It gives azo-dye test (orange dye)	Ethyl amine It doesn't give azo-dye
(m)	Aniline It gives azo-dye test	Nitrobenzene It doesn't
(n)	Benzaldehyde It gives tollen's test It doesn't give iodoform test	Acetophenone It doesn't It gives iodoform test
(o)	Methanal It gives fehling solution test	Benzaldehyde It doesn't
(p)	Chloro benzene	Benzyl choride

Q1) Although phenoxide ion has more no. of resonating structures than carboxylate ion , even though carbxylic acid is a stronger acid why ?

Ans:- The phenoxide ion has non equivalent resonance structures in which –ve charge is at less electronegative C atom and +ve charge as at more electronegative O-atom.

In carboxylate ion –Ve charge is delocalized on two electronegative O-atoms hence resonance is more effective and a stronger acid.



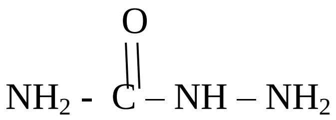
Q.2 Why Carboxylic acid have higher boiling point than alcohols as alcohol forms strongest inter molecular hydrogen bonding?

Ans As Carboxylic acid forms a dimer due to which their surface area increases and forms strong intermolecular H-bonding

- It having more boiling point than alcohols.

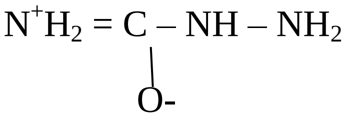
Q.3 There are two-NH_2 group in semicarbazide . However only one is involved in formation of semicarbazones. Why?

Ans.



$NH_2-\overset{O}{\overset{\|}{C}}-NH-NH_2$

Due to resonance one NH_2 group undergoes or involved in resonance and hence can't participate in the formation of semicarbazone.



$N^+H_2=\underset{O^-}{\underset{|}{C}}-NH-NH_2$

Lone pair of NH_2 group is not involved in resonance and is available for nucleophillic attack.

Q.4 Why does solubility decreases with increasing molecular mass in carboxylic acid?

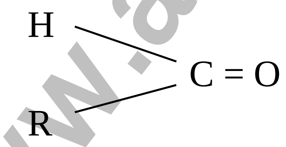
Ans. Because of increase in alkyl chain length which is hydrophobic in nature.

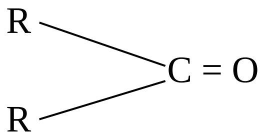
Hence solubility decreases.

Q.5 Why are aldehydes are more reactive than ketones when undergo nucleophillic addition reaction?

Ans (a) + I effect:- The alkyl group in Ketones due to their e-releasing character decrease the +Ve charge on C-Atom and thus reduce its reactivity.

(a) Steric hindrance:- Due to steric hindrance in ketones they are less reactive.





Q.6 Why PCC cannot oxidize methanol to methanoic acid and while $KMnO_4$ can?

Ans This is because PCC is a mild oxidising agent and can oxide methanol to methanal only.

While $KMnO_4$ being strong oxidising agent oxidises it to methanoic acid.

Q.7 During preparation of esters from a carboxylic acid and an alcohol in the presence of acid catalyst water or ester formed should be removed as soon as it is formed.

Ans The formation of esters from a carboxylic acid and an alcohol in the presence of acid catalyst is a reversible reaction.

$$R - COOH + R'OH \overset{H_2SO_4}{\rightleftharpoons} R - COOR' + H_2O$$

To shift the equilibrium in forward direction, the water or ester formed should be removed as fast as it is formed.

Q.8 Why HCOOH does not give HVZ reaction while CH_3COOH does?

Ans CH_3COOH contains α-hydrogens and hence give HVZ reaction but HCOOH does not contain α-hydrogen and hence does not give HVZ reaction.

Q.9 Suggest a reason for the large difference in the boling point of butanol and butanal although they have same solubility in water.

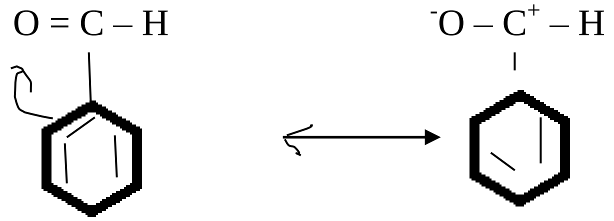
Ans Because Butanol has strong intermolecular H-bonding while butanal has weak dipole-dipole interaction.

However both of them form H-bonds with water and hence are soluble.

Q.10 Would you expect benzaldehyde to be more reactive or less reactive in nucleophillic addition reaction than propanol. Explain.

Ans C-atom of Carbonyl group of benzaldehyde is less electrophilic than C-atom of Carbonyl group in propanol.

Polarity of Carbonyl group is in benzaldehyde reduced due to resonance making it less reactive in nucleophillic addition reactions.



Q.11 Why does methanal not give aldol condensation while ethanol gives?

Ans This is because only those compounds which have α-hydrogen atoms can undergo aldol reaction ethanol possess α-hydrogen and undergoes aldol condensation Methanal has no alpha hydrogen atoms hence does not undergo aldol condensation.

Q.12 Why does methanal undergo cannizaro's reaction?

Ans because it does not possesses α-hydrogen atom.

Q.13 Which acid is stronger and why?

F_3C-C_6H_4COOH and $CH_3C_6H_4COOH$

Ans CF_3- has strong (-I)effect

Whereas, CH_3- has strong (+I)effect

Due to greater stability of $F_3CC_6H_4COO$ ion over CH_3— C_6H_4COO ion CF_3 C_6H_4COOH is much stronger acid than CH_3-C_6H_4COOH.

Q.14 Explain why O-hydroxy benzaldehyde is a liquid at room temperature while p- hydroxy benzaldehyde is a high melting solid.

Ans Due to intramolecular H-bonding in O-hydroxy benzaldehyde exists as discrete molecule whereas due to intermolecular H-bonding p-hydroxy benzaldehyde exist as associated molecules.

To break this intermolecular H-bonds a large amount of energy is needed. Consequently p-isomer has a much higher m.p. and b.p. than that of o-isomer.

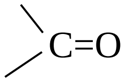
As a result o-hydroxy benzaldehyde is liquid.

Q.15 Why is the boiling point of an acid anhydride higher than the acid from which it is derived?

Ans Acid anhydrides are bigger in size than corresponding acids have more surface area and more van der Waals Force of attraction hence have higher boiling point.

Q.16 Why do Carboxylic acids not give the characteristic reactions of a carbonyl group?

Ans Due to resonance, It doesn’t give the characteristics reactions of carbonyl group. It does not have free



C=O group.

Q.17 Cyclohexanone forms cyanohydrin in good yield but 2,2,6 trimethyl cyclohexanone does not. Why?

Ans In 2,2,6 trimethyl cyclohexanone there is stearic hinderance of 3 methyl groups,

It does not form cynohydrin in good yield.

Q.18 Why is carboxyl group in benzoic acid meta directing?

Ans In benzoic acid the Carboxyl group is meta directing because it is electron-withdrawing

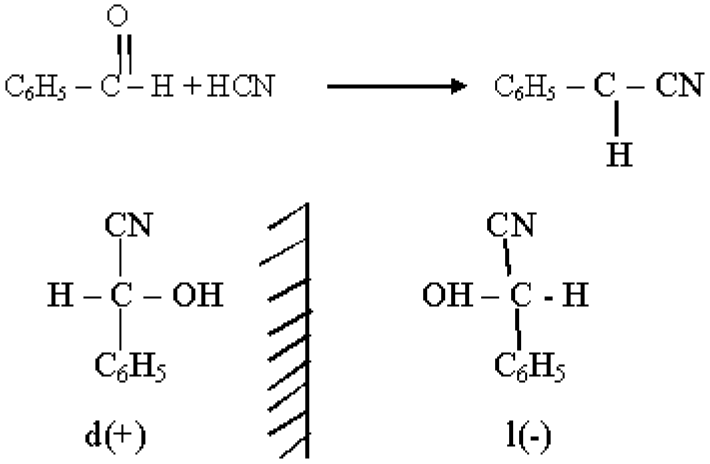
There is +ve charge on ortho and para positions

Electrophillic substitution takes place at meta-position.

Q.19 Treatment of Benzaldehyde with HCN gives a mixture of two isomers which cannot be separated even by careful fractional distillation. Explain why?

Ans It is because we get two optical isomers which have same physical properties

Cannot be Separated by Fractional distillation.

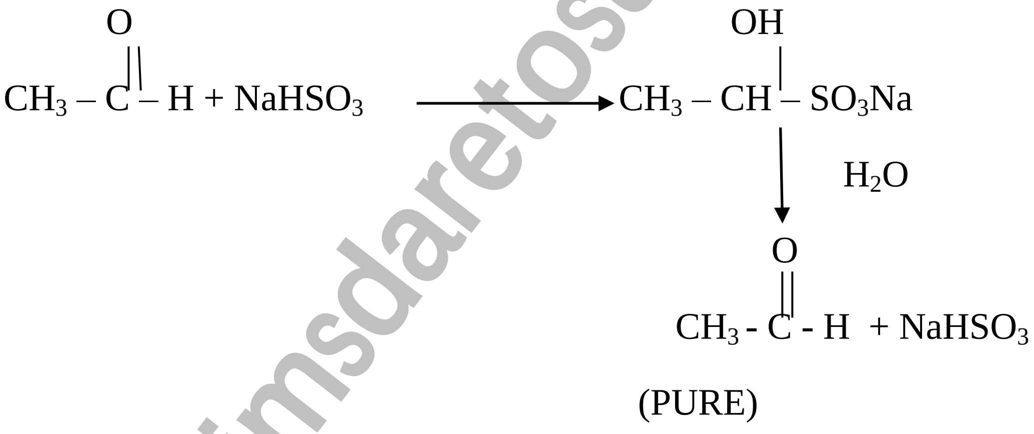


$$C_6H_5-\overset{\overset{O}{||}}{C}-H + HCN \longrightarrow C_6H_5-\underset{\underset{H}{|}}{C}-CN$$

Q.20 Sodium Bisulphite is used for the purification of aldehydes and Ketones. Explain.

Ans Aldehydes and Ketones form addition compounds with $NaHSO_3$ whereas impurities do not.

On hydrolysis we get pure aldehydes and Ketones back.



$$CH_3-\overset{\overset{O}{||}}{C}-H + NaHSO_3 \longrightarrow CH_3-\overset{\overset{OH}{|}}{CH}-SO_3Na \xrightarrow{H_2O} CH_3-\overset{\overset{O}{||}}{C}-H + NaHSO_3$$

(PURE)

Q.21 Why pH of reaction should be carefully controlled while preparing ammonia derivatives of carbonyl compound?

Ans In strongly acidic medium ammonia derivatives being basic will react with acids and will not react with carbonyl compound. In basic medium, OH^- will attack carbonyl group.

pH of a reaction should be carefully controlled.

Q.22 Why formic acid is stronger acid than acetic acid?

Ans Due to +I effect, CH_3- group in acetic acid increases e- density on carbon atom which makes it Weak acid.While in formic acid no such pushing group is present, hence is more stronger acid than acetic acid.

Q.23 Why is oxidation of alcohols to get aldehydes carried out under controlled conditions?

Ans It is because aldehydes get further oxidised to acids, oxidation of alcohols to aldehydes needs to be controlled.

Q.24 Why the oxidation of toluene to benzaldehyde with CrO_3 is carried out in the presence of acetic anhydride.

Ans If acetic anhydride is not used we will get benzoic acid.Acetic anhydride used to prevent oxidation of benzaldehyde to benzoic acid.

Q.25 Melting point of an acid with even no. of carbon atoms is higher than those of its neighbour with odd no. of carbon atoms.

Ans They fit into crystal lattice more readily than odd ones that is why they have higher lattice energy and higher melting point.

Q.26 Why do aldehydes have lower boiling point than corresponding alcohols?

Ans Aldehydes have lower boiling point as they are not associated with intermolecular whereas alcohols are associated with intermoleculer H-bonding

Aldehydes have lower B.p.

Q.27 Why do aldehydes behave like polar compounds?

Ans Due to presence of

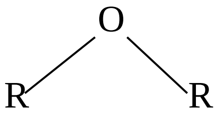
>C=O group which is polar.

Q.28 Most aromatic acids are solids while acetic acid and others of this series are liquids. Explain why?

Ans Aromatic acids have higher molecular mass, More Vander waals forces of attraction as compared to aliphatic acids They are solids.

Q.29 ethers possess a dipole moment ever if the alkyl radicals in the molecules are identical. Why?

Ans It is because ethers are bent molecules, dipole do not get cancelled.



Q.30 Why does acyl chlorides have lower boiling point than corresponding acids?

Ans Acyl chlorides are not associated with intermolecular H-bonding

They have lower boiling point.

Q.31 Why ethers are stored in coloured bottles?

Ans They are stored in coloured bottles because in presence of sunlight they react with oxygen to form peroxides which may cause explosion.

Q.32 Why formaldehyde cannot be prepared by Rosenmund's reduction?

Ans Because the formyl chloride thus formed is unstable at room temperature.

Cannot be prepared by Rosenmund reduction.

-Q1 An organic compound (A) {$C_8H_{16}O_2$} was hydrolysed with dilute sulphuric acid to give a carboxylic acid (B)and an alcohol (C). Oxidation of (C)with chromic acid produced (B).(C) on dehyration gives but-1-ene .Identity A,B,C

Ans-: $CH_3CH_2CH_2COOCH_2CH_2CH_2CH_3 + H_2O \xrightarrow[H_2SO_4]{}$ $CH_3CH_2CH_2COOH$

(A) Butyl Butanoate

(B)

+

$CH_3CH_2CH_2\ CH_2OH$

(C)

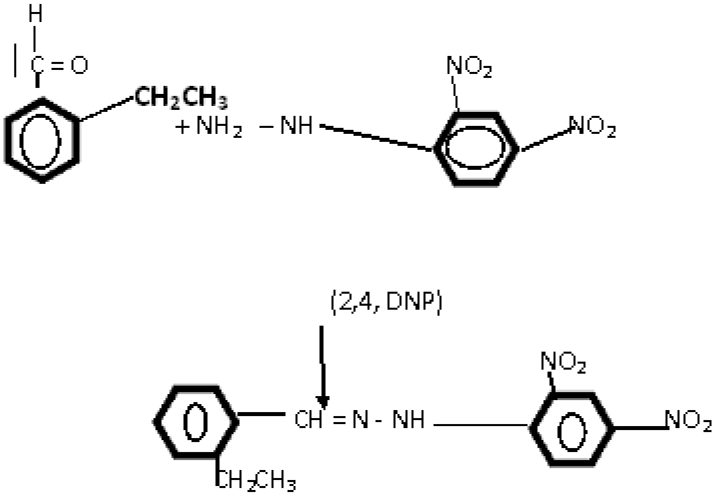
$CH_3CH_2CH_2\ CH_2OH \xrightarrow{K_2Cr_2O_7} CH_3CH_2CH_2COOH$

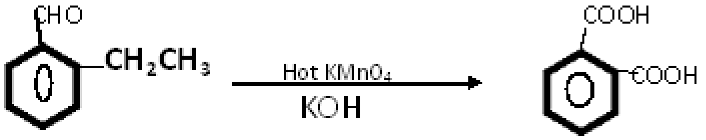
(C) (B)

$CH_3CH_2CH_2\ CH_2OH \xrightarrow[H_2SO_4]{Conc.} CH_3CH_2CH = CH_2$ (bute – 1-ene)

Q2 -:An organic compound with the molecular formula $C_9H_{10}O$ forms 2,4 DNP derivative reduces tollens reagent and undergoes cannizaro reaction . on vigorous oxidation ,it gives 1,2 benzenecarboxylic acid . identify the compound .

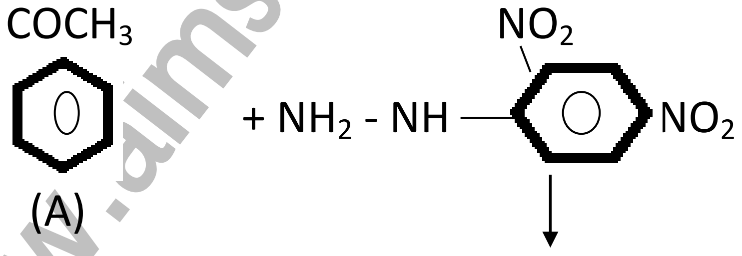
Ans.

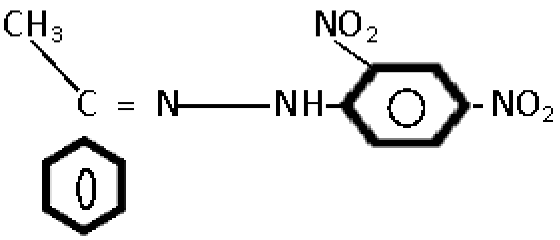




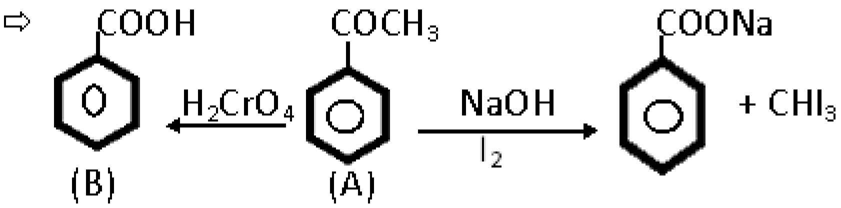
Ans

Q3 an organic compound (a) with molecular formula C_8H_8O forms an orange-red precipitate with 2,4 DNP reagent and gives yellow precipitate on heating with iodine in the presence of sodium hydroxide. It neither reduces tollen's or fehling's reagent , nor does it decolourise bromine water or baeyer's reagents .On drastic oxidation with chromic acid .it gives a carboxylic acid (B) having molecular formula $C_7H_6O_2$. Identify the compounds (A) and (B).





(2,4,DNP derivative)



Q4 two moles of organic compound A on treatment with a strong base gives two compounds B and C. Compound B on dehydration with cu gives A while acidification of C yields carboxylic acid D having molecular formula of CH_2O_2 .Identify the compoundsA,B,C,D

Ans:- $2HCHO \xrightarrow[\text{KOH}]{\text{Conc.}} HCOOK + CH_3OH$

(A) (C) (B)

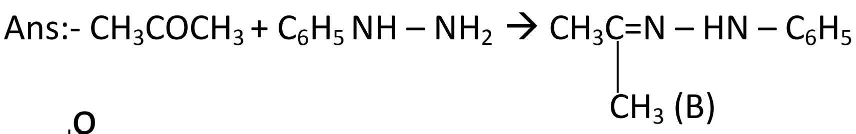
$CH_3OH \xrightarrow[\text{573 K}]{\text{Cu}} HCHO$

(B) (A)

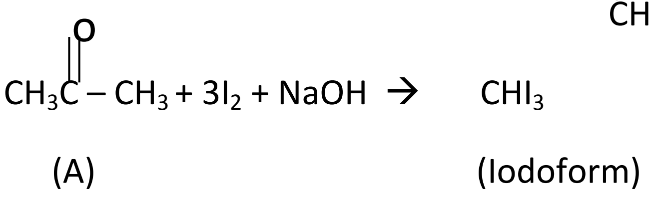
$HCOOK + HCl \longrightarrow HCOOH + KCl$

(C) (D)

Q5 An aliphatic compound ‘A’ with a molecular formula of C_3H_6O reacts with phenylhydrazine to give compound ‘B’ . Reaction of ‘A’ with I_2 in alkaline medium on warming gives a yellow precipitate ‘C’. Identify the component A, B, C



$$\text{Ans:- } CH_3COCH_3 + C_6H_5\,NH-NH_2 \rightarrow CH_3\underset{\underset{CH_3\ (B)}{|}}{C}=N-HN-C_6H_5$$

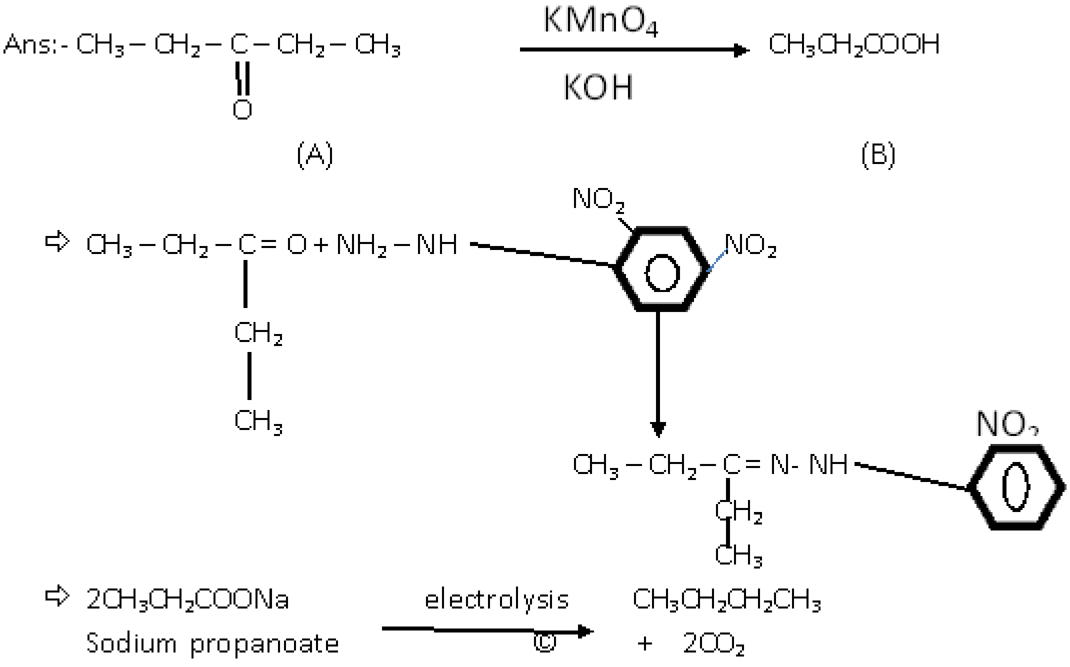


$$CH_3\overset{\overset{O}{\|}}{C}-CH_3 + 3I_2 + NaOH \rightarrow \quad CHI_3$$

(A) (Iodoform)

(C)

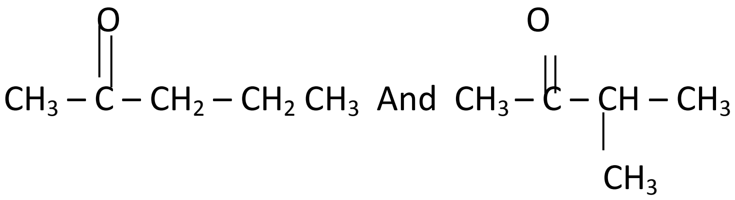
Q6 A component ‘A’ with molecular formula $C_5H_{10}O$ gave a positive 2,4 DNP test but a negative tollen’s reagents test . It was oxidised to carboxylic acid ‘B’ with molecular formula $C_3H_60_2$ when treated with alkaline $KMnO_4$ under vigorous condition . Sodium salt of ‘B’ gave hydrocarbon ‘C’ on kolbe electrolysis reduction. Identify A, B, C and D.



Q7 An organic compound ‘A’ has the molecular formula $C_5H_{10}O$ .It does not reduce Fehling’s solution but forms a bisulphite compound .It also gives positive Iodoform test. What are possible structure of ‘A’ ?Explain your reasoning.

Ans-:It does not reduce Fehling’s solution but forms bisulphite compound so it is a ketone therefore it gives positive Iodoform test therefore it is methyl ketone .

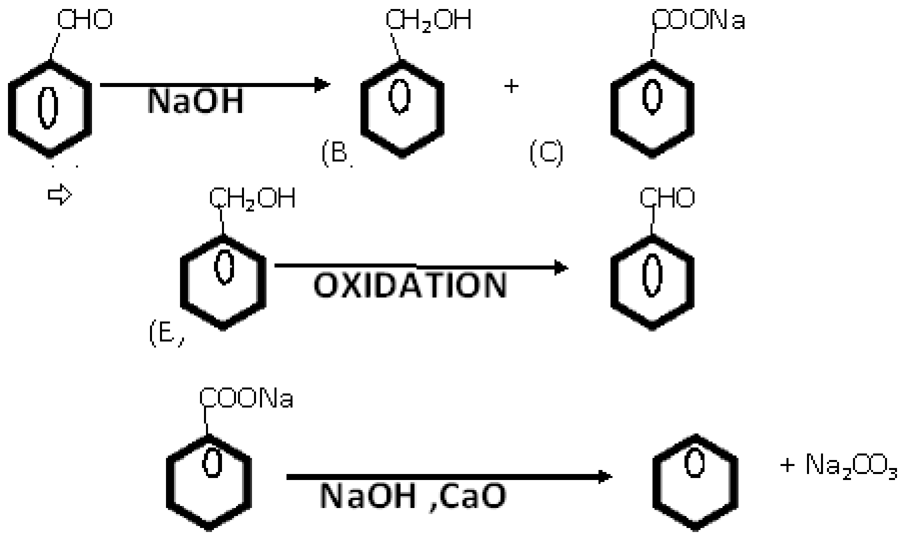
The possible structure are-:



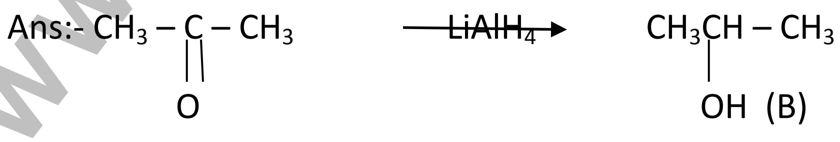
$CH_3-\overset{\overset{O}{\|}}{C}-CH_2-CH_2CH_3$ And $CH_3-\overset{\overset{O}{\|}}{C}-\underset{\underset{CH_3}{|}}{CH}-CH_3$

Q8An organic compound ‘A’ which has characterstic odour , on treatment with NaOH forms

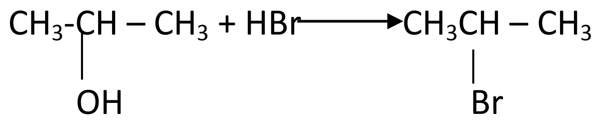
two compounds ‘B’ and ‘C’. Compound ‘B’ has the molecular formula C_7H_8O which on oxidation gives back compound ‘A’. Compound ‘C’ is the sodium salt of an acid which when heated with soda lime yields an aromatic hydrocarbon ‘D’. Deduce A,B,C,D



Q9. An organic compound ‘A’ is resistant to oxidation forms an oxidation forms a compound B(C_3H_80) on reduction . B reacts with HBr to form a bromide ‘C’ which on treatment with alcoholic KOH forms an alkene ‘D’ (C_3H_6). Deduce A,B,C,D.

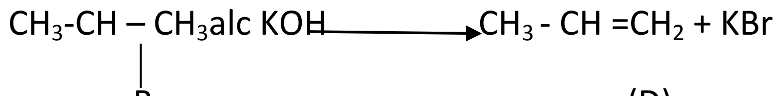


Ans:- $CH_3-\underset{\underset{O}{\|}}{C}-CH_3 \xrightarrow{LiAlH_4} CH_3\underset{\underset{OH}{|}}{C}H-CH_3$ (B)



$$CH_3\text{-}\underset{\substack{|\\ OH}}{CH}-CH_3 + HBr \longrightarrow CH_3\underset{\substack{|\\ Br}}{CH}-CH_3$$

(A) (C)



$$CH_3\text{-}\underset{\substack{|\\ Br}}{CH}-CH_3 \xrightarrow{\text{alc KOH}} CH_3\text{ - }CH=CH_2 + KBr$$

(D)

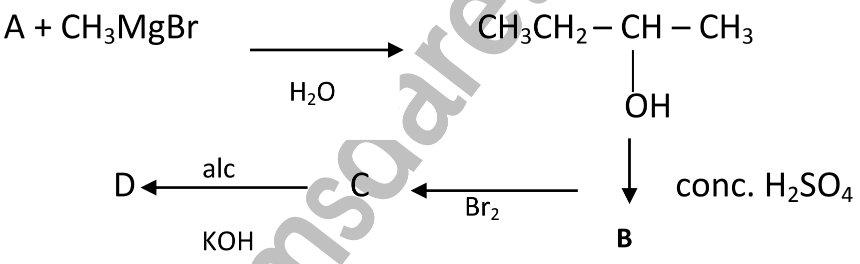
Q10 Eherial solution of an organic compound ‘A’ when heated with magnesium gave ‘B’ on treatment with ethanal followed by acid hydrolysis gave 2-propanol .Identify the compound A . What is B known as?

Ans:- CH_3 Br + Mg CH_3 MgBr

(a) (b)

$$CH_3CHO + CH_3MgBr \quad CH_3-\underset{\substack{|\\ OH}}{CH}-CH_3 + Mg(OH)Br$$

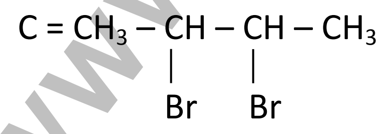
Q11 Identify A,B,C,D



$$\begin{tikzcd} A + CH_3MgBr \arrow[rr, "H_2O"'] & & CH_3CH_2-\underset{\substack{|\\ OH}}{CH}-CH_3 \arrow[d, "\text{conc. } H_2SO_4"] \\ D & C \arrow[l, "alc"', "KOH"] & B \arrow[l, "Br_2"'] \end{tikzcd}$$

A = CH_3CH_2CHO

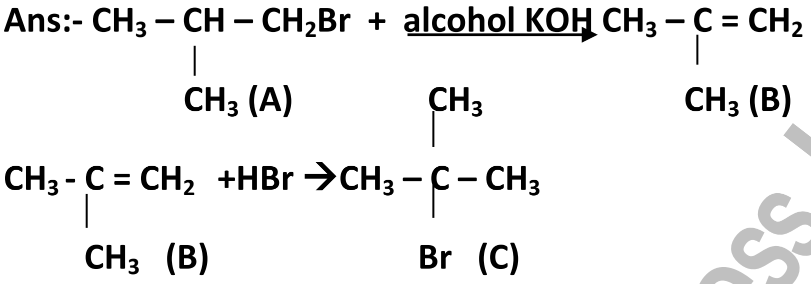
B = $CH_3CH = CH - CH_3$



$$C = CH_3-\underset{\substack{|\\ Br}}{CH}-\underset{\substack{|\\ Br}}{CH}-CH_3$$

D) $CH_3-C=C-CH_3$

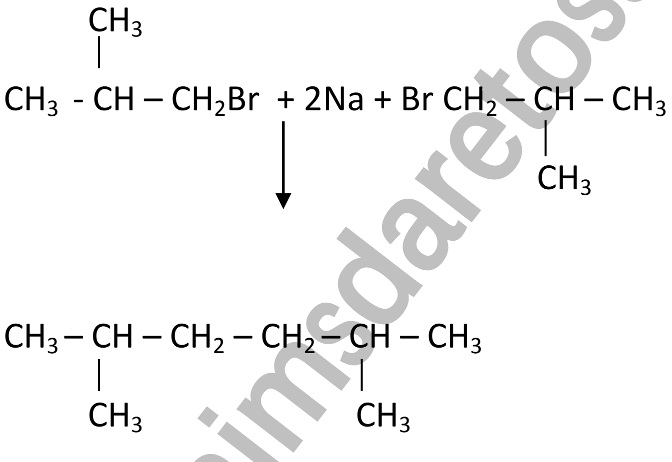
Q12 Primary alkyl halide C_4H_9Br (A) reacted with alcoholic KOH to give compound (B) is reacted with HBr to give (c) which is an isomer of (A). When (A) is reacted with sodium metal it gives compound (D) C_8H_{18} that was different from the compound formed when n-butyl bromide is reacted with sodium . Give the formula of A and write equation s.



Ans:- $$CH_3-\underset{\underset{CH_3\ (A)}{|}}{CH}-CH_2Br + \xrightarrow{\text{alcohol KOH}} CH_3-\underset{\underset{CH_3\ (B)}{|}}{C}=CH_2$$

$$CH_3-\underset{\underset{CH_3\ \ (B)}{|}}{C}=CH_2 + HBr \rightarrow CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{Br\ \ (C)}{|}}{C}}-CH_3$$

C is the isomer of A

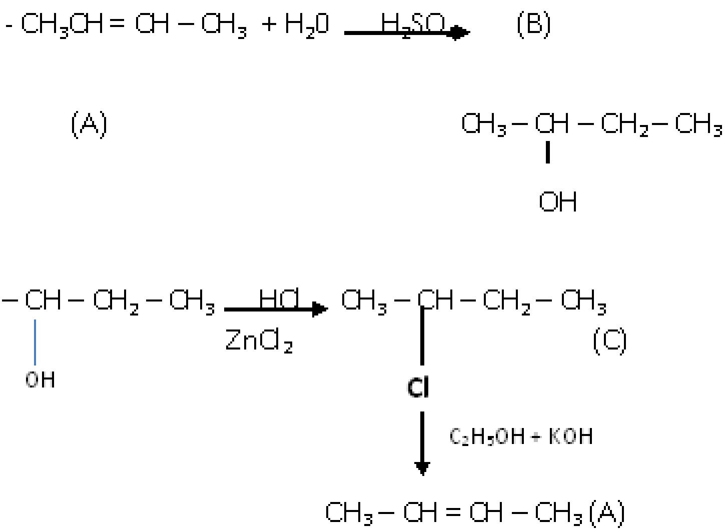


$$CH_3-\overset{\overset{CH_3}{|}}{CH}-CH_2Br + 2Na + Br\,CH_2-\underset{\underset{CH_3}{|}}{CH}-CH_3$$
$$\downarrow$$
$$CH_3-\underset{\underset{CH_3}{|}}{CH}-CH_2-CH_2-\underset{\underset{CH_3}{|}}{CH}-CH_3$$

(C_8H_{18})

Q13 An organic compound 'A' having molecular formula C_4H_8 on treatment with dil.H_2SO_4 gives B . B on treatment with conc. HCL and anhydrous $ZnCl_2$ gives C and on treatment with sodium ehoxide gives back A.Identify A,B,C.

Ans:-



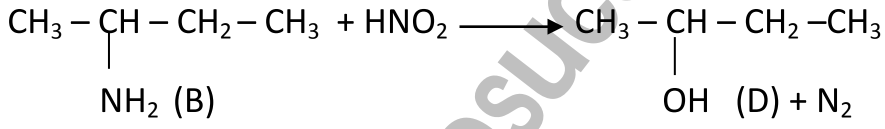
$$CH_3CH=CH-CH_3 + H_20 \xrightarrow{H_2SO_4} \underset{(B)}{CH_3-\underset{OH}{\underset{|}{CH}}-CH_2-CH_3}$$

(A)

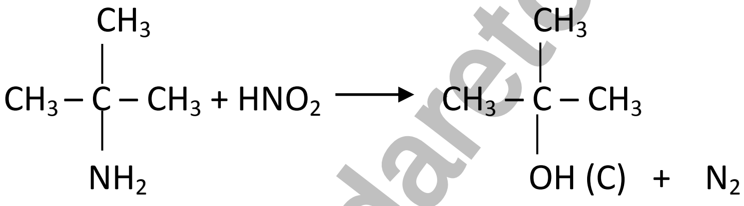
$$CH_3-\underset{OH}{\underset{|}{CH}}-CH_2-CH_3 \xrightarrow[ZnCl_2]{HCl} CH_3-\underset{Cl}{\underset{|}{CH}}-CH_2-CH_3 \;(C) \xrightarrow{C_2H_5OH + KOH} CH_3-CH=CH-CH_3\,(A)$$

Q14 . Two isomeric compound A and B having molecular formula $C_{15}H_{11}N$, both lose N_2 on treatment with $HNO_2$and gives compound C and D. C is resistant to oxidation but immediately responds to oxidation to lucas reagent after 5 minutes andgives a positive Iodoform test. Identify A and B .

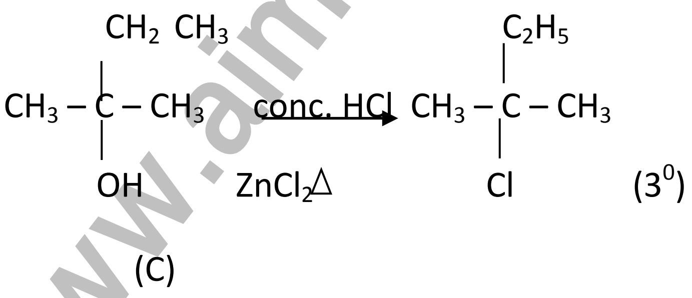
Ans:-



$$CH_3-\underset{NH_2\ (B)}{\underset{|}{CH}}-CH_2-CH_3 + HNO_2 \longrightarrow CH_3-\underset{OH\ \ (D)}{\underset{|}{CH}}-CH_2-CH_3 + N_2$$



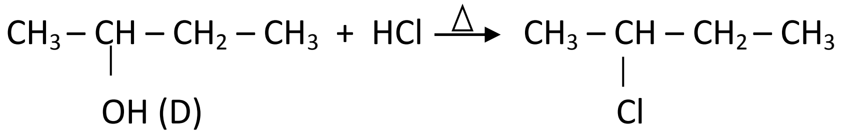
$$CH_3-\overset{CH_3}{\overset{|}{\underset{NH_2}{\underset{|}{C}}}}-CH_3 + HNO_2 \longrightarrow CH_3-\overset{CH_3}{\overset{|}{\underset{OH\ (C)}{\underset{|}{C}}}}-CH_3 + N_2$$



$$CH_3-\overset{CH_2\ CH_3}{\overset{|}{\underset{OH}{\underset{|}{C}}}}-CH_3 \xrightarrow[ZnCl_2\Delta]{conc.\ HCl} CH_3-\overset{C_2H_5}{\overset{|}{\underset{Cl}{\underset{|}{C}}}}-CH_3 \quad (3^0)$$

(C)

But ‘D’ respond to lucas reagent in 5 minutes.



$$CH_3-\underset{\displaystyle OH\ (D)}{CH}-CH_2-CH_3 + HCl \xrightarrow{\Delta} CH_3-\underset{\displaystyle Cl}{CH}-CH_2-CH_3$$

$$CH_3-CH(OH)-CH_2-CH_3 + I_2 + NaOH \longrightarrow CHI_3 + CH_3-CH_2COONa$$

Q15. An organic compound 'A' having molecular formula $C_2H_5O_2N$ on reduction gives a compound 'B' with molecular formula C_2H_7N. Which gives 'B' positive idoform test . Identify A,B and C.

Ans:-

$$\begin{tikzcd}
\underset{(A)}{CH_3-CH_2NO_2} + Sn/HCl \arrow[r] & CH_3-CH_2NH_2\ (B) \arrow[d, "HNO_2"] \\
 & (C)\ CH_3CH_2OH \arrow[d, "I_2/NaOH"] \\
 & CHI_3\ (IODOFORM)
\end{tikzcd}$$

Q16 An organic compound 'A' having molecular formula C_3H_5N on reduction gave another compound 'B'. The compound B on treatment with HNO_2 gave propyl alcohol. B on warming with $CHCl_3$ and alcoholic caustic potash give the offensive smelling C .Identify A,B,C

Ans:- $\underset{(A)}{C_2H_5CN} + 2H_2 \longrightarrow \underset{(B)}{CH_3CH_2CH_2NH_2} \xrightarrow{HNO_2} CH_3CH_2CH_2OH$

$\underset{(B)}{CH_3CH_2\,CH_2NH_2} + CHCl_3 + 3KOH \rightarrow \quad \rightarrow \underset{(C)}{CH_3CH_2NC}$

Q17 Iodomethane reacts with KCN to form a major product A .Compound 'A' on reduction in presence of $LiAlH_4$ forms a higher amine 'B'. Compound B on treatment with $CuCl_2$ forms a blue colour complex C . Identify A, B, C

Ans . $$\begin{tikzcd} CH_3I + KCN \arrow[r] & CH_3 - CN \arrow[r] & CH_3CH_2NH_2\ (B) \arrow[d, "CuCl_2"] \\ & & {[Cu(CH_3CH_2NH_2)_4]Cl_2} \end{tikzcd}$$

Bluecomplex

Q18. An aliphatic compound A with molecular formula C_2H_3Cl on treatment with AgCN gives two isomeric compounds of unequal amount with the molecular formula C_3H_3N .The minor of these two products on complete reduction with H_2 in the presence of Ni gives a compound 'B' with molecular formula C_3H_9N.Identify the compounds.

Ans:- $CH_2 = CH - Cl + AgCN \rightarrow CH_2 = CH - CN + CH_2 = CH - N- C$

(A) (MINOR) (MAJOR)

$CH_2 = CH - C = N \xrightarrow[H_2]{Ni} CH_3 - CH_2 - CH_2 - NH_2$

B

Q19. A compound 'X' having molecular formula C_3H_7NO reacts with Br_2 in presence of KOH to give another compound Y. the compound Y reacts with HNO_2 to form ethanol N_2 gas. Identify X, Y,

Ans:- $$\begin{tikzcd} CH_3CH_2CONH_2 + Br_2 + 4\ KOH \arrow[r] & CH_3CH_2NH_2 \arrow[d, "HN0_2"] \\ & CH_3CH_2OH + N_2\ (g) \end{tikzcd}$$

(X) (Y)

Q20. A compound 'A' of molecular formula $C_3H_7O_2N$ reaction with Fe and conc, HCl gives a compound 'B' OF molecular formula C_3H_9N. Compound 'B' on treatment WITH $NaNO_2$ and HCl gives another compound 'C' of molecular formula C_3H_8O.The compound 'C' gives effervescences with Na on oxidation with CrO_3.The compound 'C' gives a saturated aldehyde containing three carbon atom deduce A,B,C.

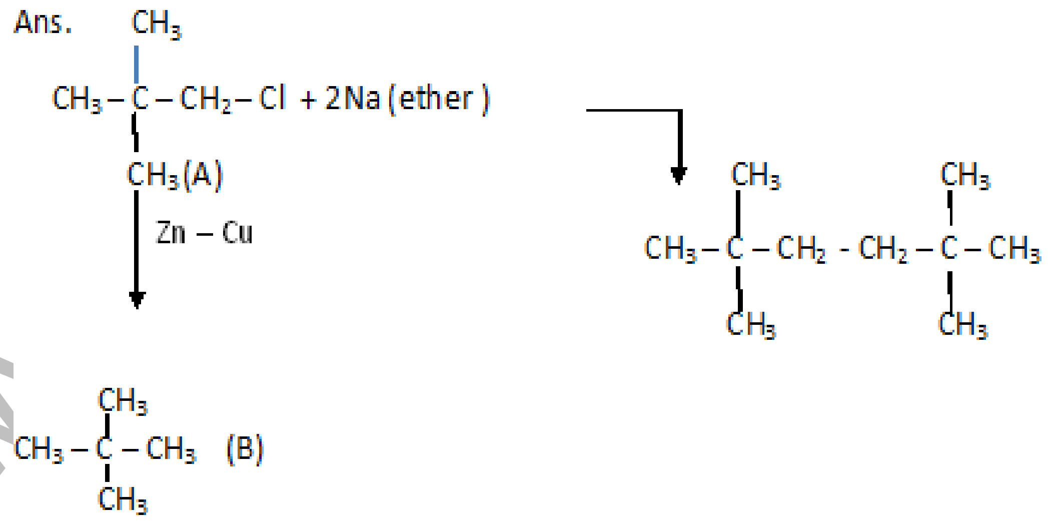
Ans:-
$$\begin{tikzcd} CH_3CH_2CH_2NO_2 \arrow[r, "Fe/HCl"] & CH_3CH_2CH_2NH_2 \quad (B) \arrow[d, "NaN0_2/HCl"] \\ (A) & CH_3CH_2CH_2OH \quad (C) \arrow[d, "Na"] \\ & CH_3CH_2CH_2ONa \end{tikzcd}$$

Sodium propoxide

$$CH_3CH_2CH_2OH \xrightarrow[CrO_3]{} CH_3CH_2CHO$$

(C)

Q22 A Chloro compound 'A' on reduction with Zn – Cu and alcohol gives the hydro carbon (B) with five carbon atom.When 'A' is dissolved in ether and treated with sodium 2,2,5,5 tetramethyl hexane is formed structure of A and B?



Ans.

$$CH_3-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3\,(A)}{C}}-CH_2-Cl + 2Na\,(ether) \longrightarrow CH_3-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}-CH_2-CH_2-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}-CH_3$$

$$(A) \xrightarrow{Zn-Cu} CH_3-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}-CH_3 \quad (B)$$

IDENTIFY A,B,C

Q1. $CH_3COOH \xrightarrow[NH_3]{\Delta} A \xrightarrow[NaOBr]{} B \xrightarrow[NaNO_2]{HCl} C$

Q2. $C_6H_5NO_2 \xrightarrow{Fe/HCl} A \xrightarrow{NaNO_2/HCl} B \xrightarrow{H_2O/H^+} C$

Q3.. $C_6H_5NO_2 \xrightarrow{Fe/HCl} A \xrightarrow{NaNO_2/HCl} B \xrightarrow{C_6H_5OH} C$

Q4,$CH_3CH_2Br \xrightarrow{KCN} A \xrightarrow{LiAlH_4} B \xrightarrow{HNO_3} C$

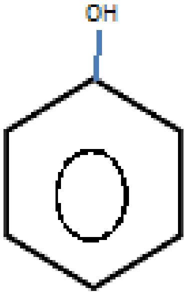
Q5... $C_6H_5N^+_2Cl^- \xrightarrow{CuCN} A \xrightarrow{H_2O\ /\ H^+} B \xrightarrow{NH_3} C$

Q6.$CH_3CH_2I \xrightarrow{NaCN} A \xrightarrow{OH^-} B \xrightarrow{NaOH} C$

Q7. $C_6H_5NH_2 + (CH_3CH_2)_2O \longrightarrow A$

Q8. $C_6H_5N_2^+Cl^- \xrightarrow[HBF_4]{NaNO_2/Cu\ \Delta} A$

Q9. $A \xrightarrow[Br_2]{NaOH} B \xrightarrow[HNO_2]{} C \xrightarrow[Red\ P/\ I_2]{} D\ (CH_3I)$

Q10. $A \xrightarrow[Dil\ HNO_3]{} B \xrightarrow[Sn/HCl]{} C \xrightarrow[NaNO_2 + HCl]{}$ 

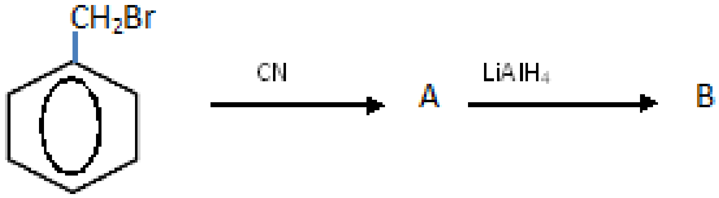
Q11. $A \xrightarrow[KOH]{} B \xrightarrow[HNO_2]{Br_2} C \xrightarrow{} C_2H_5NH_2$

Q12. $A \xrightarrow[AgCN]{} B \xrightarrow[Sn/HCl]{} C$

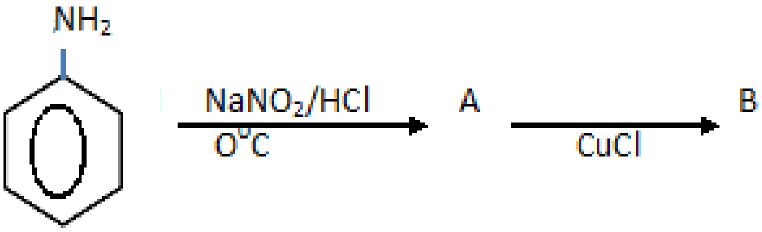
Q13. $CH_3CN \xrightarrow{H^+/H_2O} A \xrightarrow{LiAlH_4} B$

Q14. $R_2CO \xrightarrow{NH_3} A \xrightarrow{Ni/H_2} B$

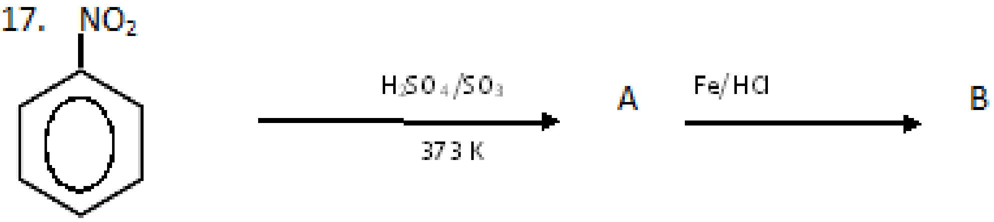
Q15.



Q16.

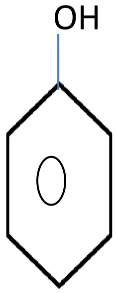


Q17.

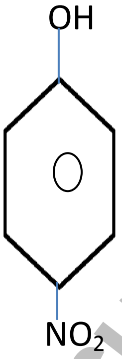


ANSWERS

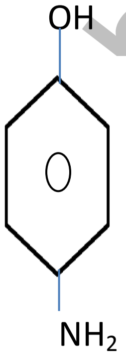
1) A= CH_3CONH_2 , B = CH_3NH_2 , C = CH_3OH
2) A = $C_6H_5NH_2$, B =$C_6H_5N_2^+Cl^-$, (C) C_6H_5OH
3) A = CH_3CH_2CN , B =CH_3CH_2-CH_2NH_2 , C = $CH_3CH_2CH_2OH$
4) A= $C_6H_5NH_2$, B= $C_6H_5N_2^+Cl^-$, C= $CH_3CH_2CH_2OH$
5) A = C_6H_5CN , B = C_6H_5COOH , C= $C_6H_5CONH_2$
6) A= CH_3CH_2CN, B = $CH_3CH_2CONH_2$, C = $CH_2CH_2NH_2$
7) A) $C_6H_5NHCOCH_3$ + CH_3COOH
8) $C_6H_5NO_2$ = A
9) A = CH_3CONH_2 , B = CH_3NH_2 , C = CH_3OH
10) A)



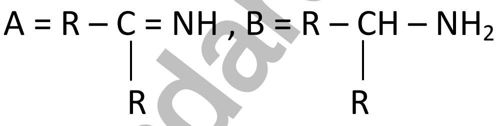
, B)



, C)

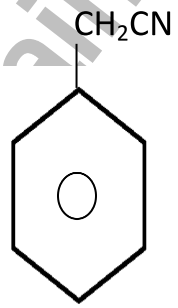


11) A= $CH_3CH_2COONH_4$, B= $CH_3CH_2CONH_2$, C= $CH_3CH_2NH_2$
12) A = CH_3Cl , B = CH_3NC
13) A = CH_3COOH , B = CH_3CH_2OH
14)

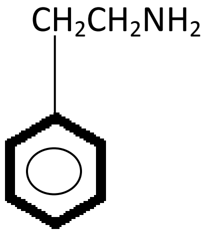


A = $R - \underset{\substack{| \\ R}}{C} = NH$, B = $R - \underset{\substack{| \\ R}}{CH} - NH_2$

15)

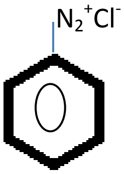


(A)

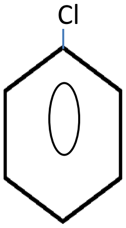


(B)

16)

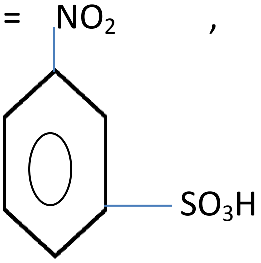


(A)



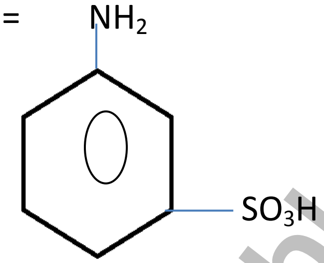
(B)

17) A =



,

B =



1 MARK QUESTIONS

1. Name the reaction and the reagent used for the conversion of acid chlorides to the corresponding aldehydes.

Ans. Name : Rosenmund's reaction Reagent : H_2 in the presence of Pd (supported over $BaSO_4$) and partially poisoned by addition of Sulphur or quinoline.

2. Suggest a reason for the large difference in the boiling points of butanol and butanal, although they have same solubility in water.

Ans. The b.p. of butanol is higher than that of butanal because butanol has strong intermolecular H-bonding while butanal has weak dipole-dipole interaction. However both of them form H-bonds with water and hence are soluble.

3. What type of aldehydes undergo Cannizaro reaction ?

Ans. Aromatic and aliphatic aldehydes which do not contain α-hydrogens.

4. Out of acetophenone and benzophenone, which gives iodoform test ? Write the reaction involved. (The compound should have CH_3CO-group to show the iodoform test.)

Ans. Acetophenone ($C_6H_5COCH_3$) contains the grouping (CH_3CO attached to carbon) and hence gives iodoform test while benzophenone does not contain this group and hence does not give iodoform test.

$$C_6H_5COCH_3 + 3\,I_2 + 4\,NaOH \rightarrow CHI_3 + C_6H_5COONa + 3\,NaI + 3\,H_2O$$

$C_6H_5COC_6H_5 \xrightarrow{I_2/NaOH}$ No reaction

5. Give Fehling solution test for identification of aldehyde group (only equations). Name the aldehyde which does not give Fehling's soln. test.

A. $R - CHO + 2\,Cu^{2+} + 5\,OH^- \rightarrow RCOO^- + Cu_2O + 3\,H_2O$

Benzaldehyde does not give Fehling soln. test. (Aromatic aldehydes do not give this test.)

6. What makes acetic acid a stronger acid than phenol?

Ans. Greater resonance stabilization of acetate ion over phenoxide ion.

7. Why HCOOH does not give HVZ (Hell Volhard Zelinsky) reaction but CH_3COOH does?

Ans. CH_3COOH contains alpha hydrogens and hence give HVZ reaction but HCOOH does not contain alpha-hydrogen and hence does not give HVZ reaction

. 8. During preparation of esters from a carboxylic acid and an alcohol in the presence of an acid catalyst, water or the ester formed should be removed as soon as it is formed.

Ans. The formation of esters from a carboxylic acid and an alcohol in the presence of acid catalyst in a reversible reaction.

$$\underset{\text{Carboxylic acid}}{RCOOH} + \underset{\text{alcohol}}{R'OH} \xrightleftharpoons{H_2SO_4} \underset{\text{Ester}}{RCOOR'} + H_2O$$

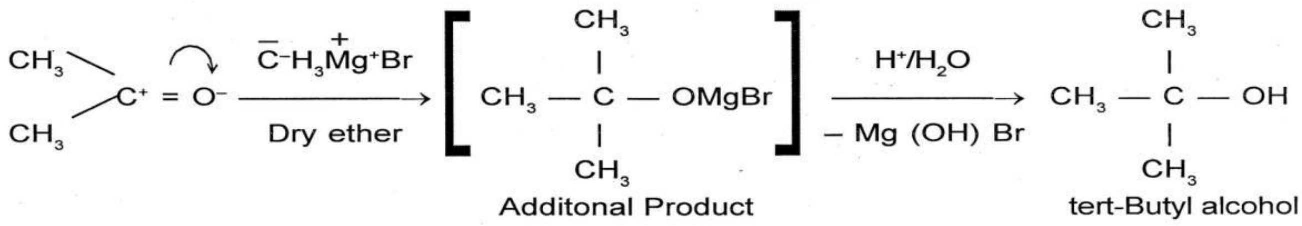
To shift the equilibrium in the forward direction, the water or ester formed should be removed as fast as it is formed

9. Arrange the following compounds in increasing order of their acid strength. Benzoic acid, 4-Nitrobenzoic acid, 3, 4-dinitrobenzoic acid, 4-methoxy benzoic acid.

Ans. 4-methoxybenzoic acid < benzoic acid < 4-nitrobenzoic acid <

4, dinitrobenzoic acid.

10. How is tert-butyl alcohol obtained from acetone? A.



2 / 3 MARKS QUESTIONS

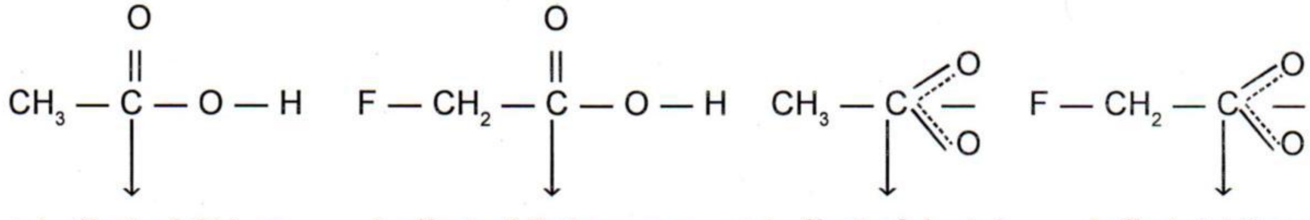
1. Arrange the following compounds in increasing order of their boiling points. Explain by giving reasons.
   CH_3CHO, CH_3CH_2OH, CH_3OCH_3, $CH_3CH_2CH_3$.
   A. The molecular masses of all these compounds are comparable :

CH_3CHO (44), CH_3CH_2OH (46), CH_3COCH_3 (46), $CH_3CH_2CH_3$ (44).

CH_3CH_2OH exists as associated molecule due to extensive intermolecular hydrogen bonding and hence its boiling point is the highest (351 K). Since dipole-dipole interaction are stronger in CH_3CHO than in CH_3OCH_3, hence boiling point of CH_3CHO (293 K) is much higher than that of CH_3OCH_3 (249 K). Further, molecules of $CH_3CH_2CH_3$ have only weak Vander Waals forces while the molecules of CH_3OCH_3 have little stronger dipole-dipole interactions and hence the boiling point of CH_3OCH_3 is higher (249 K) than that of $CH_3CH_2CH_3$ (231 K). Thus the overall increasing order of boiling points is :

$$CH_3CH_2CH_3 < CH_3OCH_3 < CH_3CHO < CH_3CH_2OH$$

2. Which acid of each pair shown here would you expect to be stronger?
   CH_3CO_2H or FCH_2CO_2H



Thus due to lesser electron density in the O — H bond and greater stability of FCH_2COO^- ion over CH_3COO^- ion FCH_2COOH is a stronger acid than CH_3COOH.

3. Which acid is stronger and why?

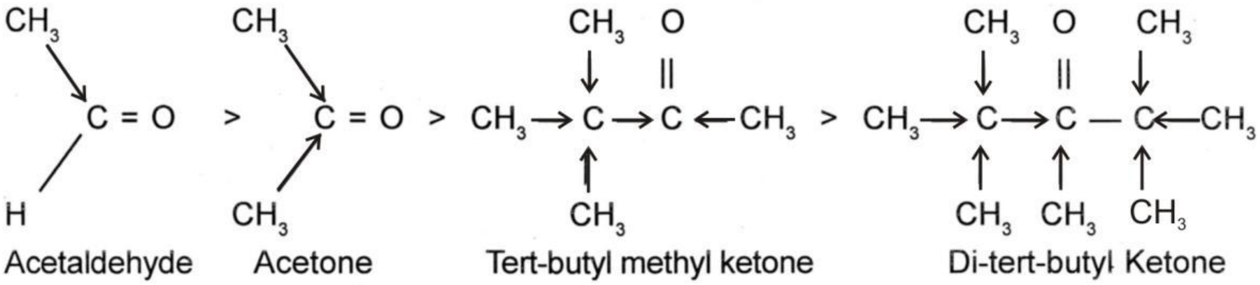
$F_3C - C_6H_4 - COOH$,	$CH_3 - C_6H_4 - COOH$
Ans. CF_3 has a strong(– I) effect. It stabilises the carboxylate ion by dispersing the – ve charge.	CH_3 has a weak (+ I) effect. It stabilises the carboxylate ion by intensifying the – ve charge.

Therefore due to greater stability of $F_3C - C_6H_4 - COO^-$ ion over $CH_3 - C_6H_4COO^-$ ion, $F_3C - C_6H_4 - COOH$ is a much stronger acid than $CH_3 - C_6H_4 - COOH$.

4. Arrange the following compounds in increasing order of their reactivity towards HCN. Explain it with proper reasoning. Acetaldehyde, Acetone, Di-tert-butyl ketone, Methyl tert-butyl ketone.

Ans. Addition of HCN to the carboxyl compounds is a nucleophilic addition reaction.

The reactivity towards HCN addition decreases as the + I effect of the alkyl groups increases and/or the steric hindrance to the nucleophilic attack by CN^- at the carboxyl carbon increases. Thus the reactivity decreases in the order.



———————— + I effect increases————————

———————— Steric hindrance increases————————

———————— Reactivity towards HCN addition decreases ————————

In other words, reactivity increases in the reverse order, i. e. , Ditert-butyl Ketone < tert-Butyl methyl Ketone < Acetone < Acetaldehyde

5.Explain why o-hydroxybenzaldehyde is a liquid at room temperature while p-hydroxybenzaldehyde is a high melting solid.

Ans. Due to interamolecular H-bonding ortho-hydroxy benzaldehyde exists as discrete molecule whereas due to intermolecular H-bonding, p-hydroxybenzaldehyde exists as associated molecules. To break these intermolecular H-bonds, a large amount of energy is needed. Consequently, p-hydroxybenzaldehyde has a much higher m. pt. and b. pt. than that of o-hydroxy benzaldehyde. As a result, o-hydroxy benzaldehyde is a liquid at room temperaturewhile p-hydroxy benzaldehyde is a high melting solid.

5 MARKS QUESTIONS

1. Arrange the following compounds in order ot their property as indicated-
   i) Acetaldehyde,Acetone, di-tert-butyl ketone, Methyl tert-butyl ketone reactivity towards HCN

   - di-tert-butyl ketone < Methyl tert-butyl ketone <Acetone <Acetaldehyde

-aldehydes are more reactive towards nucleophilic addition across the >C=O due to steric and electronic reasons.

-Sterically the presence of two relatively large substituents in ketones hinders the approach of nucleophile to carbonyl carbon than in aldehydes having only one such substituent.

–Electronically, the presence of two alkyl groups reduces the electrophilicity of the carbonyl carbon in ketones.

ii) $CH_3CH_2CHBrCOOH$,$CH_3CHBrCH_2COOH$, CH_3 CH_2COOH, $CH_3CH_2CH_2COOH$ acid strength

-$CH_3CH_2COOH < CH_3CH_2CH_2COOH < CH_3CHBrCH_2COOH < CH_3CH_2CHBrCOOH$

-Electron withdrawing groups like –Br increases the acidity of carboxylic aids by stabilizing the conjugate base through delocalisation of negative charge by negative inductive effect. The closer the electron withdrawing group to the –COOH group, greater is the stabilising effect.

-Electron donating groups decrease the acidity by destabilizing the conjugate base. Greater the number of –CH_3 groups, greater the destabilizing effect and lower the acidity.

iii) Benzoic acid, 4-Nitrobenzoic acid, 3,4-Dinitrobenzoic acid, 4-Methoxybenzoic acid (acid strength)

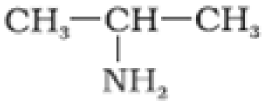
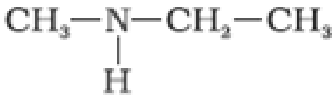
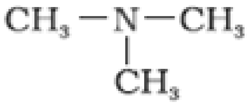
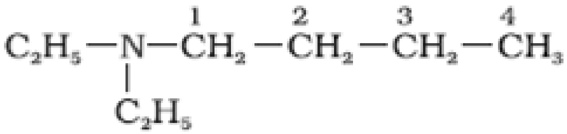
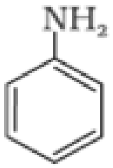
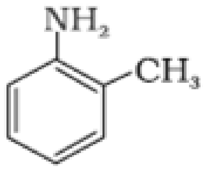
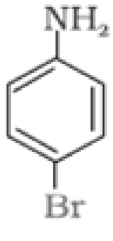
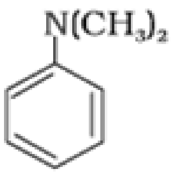
4- Methoxybenzoic acid< Benzoic acid <4-Nitrobenzoic acid < 3,4-Dinitrobenzoic acid

- Benzoic acid is a stronger acid than aliphatic carboxylic acid due to stabilization of the conjugate base due to resonance.
- Presence of electron withdrawing group-NO_2 on the phenyl ring of aromatic carboxylic acid increases their acidity while electron donating groups-OCH_3 decreases their acidity.

UNIT 13:
AMINES

2.	Amines	1. Ammonolysis of alkylhalids, Gabriel Phthalimide synthesis, Hoffmann Bromamide, Degradation. 2. Basic character of Amines(pK_b) and comparisons in gaseous and aqueous phase. 3. Carbylamine Reaction, Hinsberg's Test. 4. Electrophilic substitution. 5. Diazonium salts –reactions

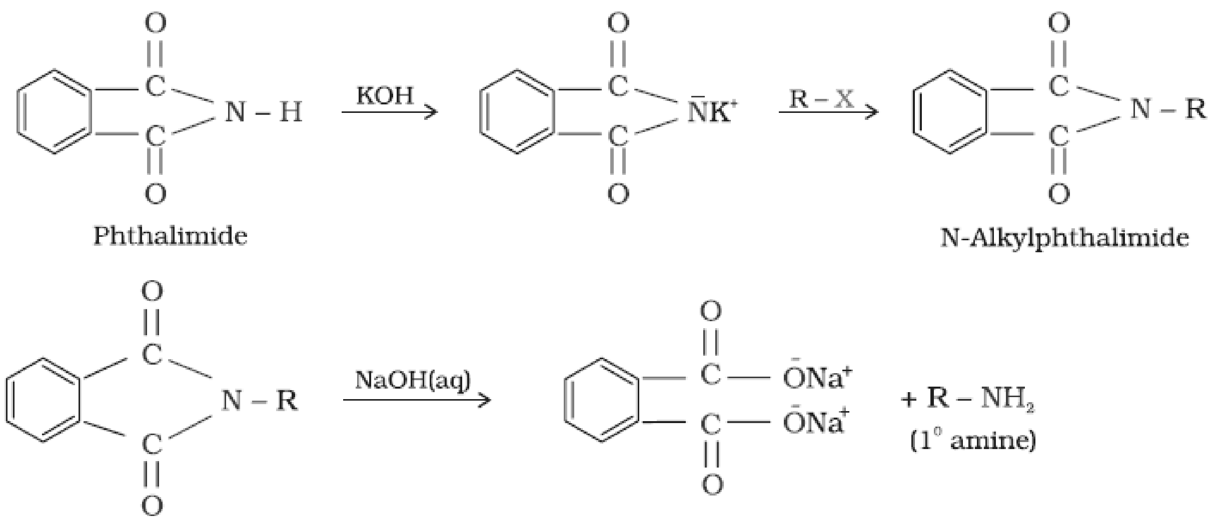
IUPAC NOMENCLATURE

Amine	IUPAC name
$CH_3–CH_2–NH_2$	Ethanamine
$CH_3–CH_2–CH_2–NH_2$	Propan-1-amine
 $CH_3-\underset{\displaystyle NH_2}{\underset{\mid}{CH}}-CH_3$	Propan-2-amine
 $CH_3-\underset{\displaystyle H}{\underset{\mid}{N}}-CH_2-CH_3$	N-Methylethanamine
 $CH_3-\underset{\displaystyle CH_3}{\underset{\mid}{N}}-CH_3$	N,N-Dimethylmethanamine
 $C_2H_5-\underset{\displaystyle C_2H_5}{\underset{\mid}{N}}-\overset{1}{C}H_2-\overset{2}{C}H_2-\overset{3}{C}H_2-\overset{4}{C}H_3$	N,N-Diethylbutan-1-amine
$NH_2-\overset{1}{C}H_2-\overset{2}{C}H=\overset{3}{C}H_2$	Prop-2-en-1-amine
$NH_2-(CH_2)_6-NH_2$	Hexane-1,6-diamine
	Aniline or Benzenamine
	2-Aminotoluene
	4-Bromobenzenamine or 4-Bromoaniline
	N,N-Dimethylbenzenamine

NAME REACTIONS

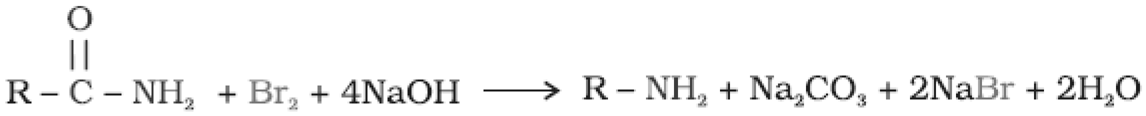
1. Gabriel phthalimide synthesis

Gabriel synthesis is used for the preparation of primary amines. Phthalimide on treatment with ethanolic potassium hydroxide forms potassium salt of phthalimide which on heating with alkyl halide followed by alkaline hydrolysis produces the corresponding primary amine. Aromatic primary amines cannot be prepared by this method because aryl halides do not undergo nucleophilic substitution with the anion formed by phthalimide.



2. Hoffmann bromamide degradation reaction

Hoffmann developed a method for preparation of primary amines by treating an amide with bromine in an aqueous or ethanolic solution of sodium hydroxide. The amine so formed contains one carbon less than that present in the amide.



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

3. Carbylamine reaction

Aliphatic and aromatic primary amines on heating with chloroform and ethanolic potassium hydroxide form isocyanides or carbylamines which are foul smelling substances. Secondary and tertiary amines do not show this reaction. This reaction is known as carbylamine reaction or isocyanide test and is used as a test for primary amines.

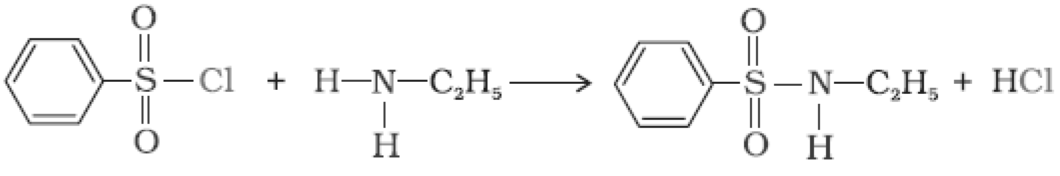
$$R-NH_2 + CHCl_3 + 3KOH \xrightarrow{Heat} R-NC + 3KCl + 3H_2O$$

4. Hinsberg Test:

Benzenesulphonyl chloride ($C_6H_5SO_2Cl$), which is also known as Hinsberg's reagent, reacts with primary and secondary amines to form sulphonamides.

(a) The reaction of benzenesulphonyl chloride with primary amine

yields N-ethylbenzenesulphonyl amide.

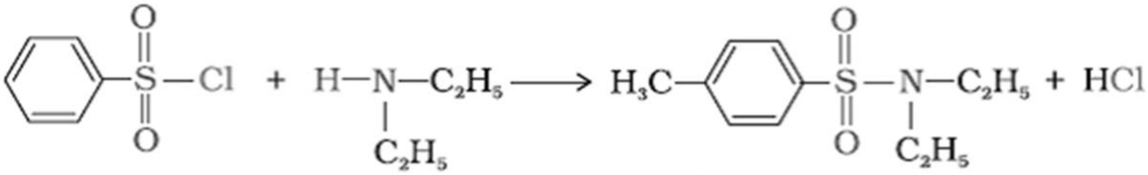


N-Ethylbenzenesulphonamide
(soluble in alkali)

The hydrogen attached to nitrogen in sulphonamide is strongly acidic due to the presence of strong electron withdrawing sulphonyl group. Hence, it is soluble in alkali.

(b) In the reaction with secondary amine, N,N-diethylbenzenesulphonamide

is formed.



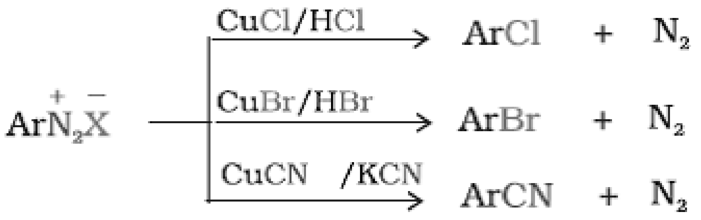
N,N-Diethylbenzenesulphonamide

Since N, N-diethylbenzene sulphonamide does not contain any hydrogen atom attached to nitrogen atom, it is not acidic and hence insoluble in alkali.

(c) Tertiary amines do not react with benzenesulphonyl chloride. This property of amines reacting with benzenesulphonyl chloride in a different manner is used for the distinction of primary, secondary and tertiary amines and also for the separation of a mixture of amines.

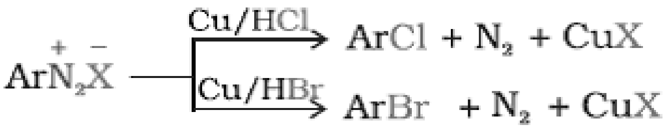
5. Sandmeyer Reaction

The Cl^-, Br^- and CN^- nucleophiles can easily be introduced in the benzene ring of diazonium salts in the presence of Cu(I) ion.



6. Gatterman Reaction

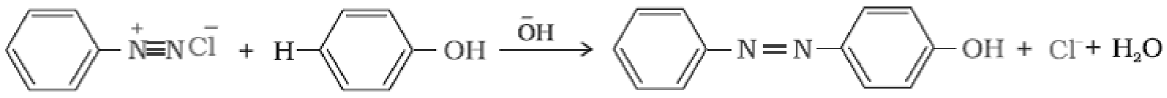
Chlorine or bromine can be introduced in the benzene ring by treating the diazonium salt solution with corresponding halogen acid in the presence of copper powder.



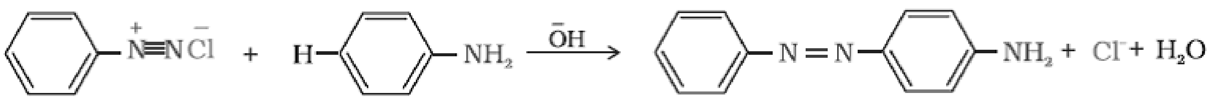
7. Coupling reactions

The azo products obtained have an extended conjugate system having both the aromatic rings joined through the –N=N– bond. These compounds are often coloured and are used as dyes. Benzene diazonium chloride reacts with phenol in which the phenol molecule at its para position is coupled with the diazonium salt to form p-hydroxyazobenzene. This type of reaction is known as coupling reaction.

Similarly the reaction of diazonium salt with aniline yields p-aminoazobenzene.



p-Hydroxyazobenzene (orange dye)



p-Aminoazobenzene
(yellow dye)

DISTINCTION BETWEEN PAIRS OF COMPOUNDS

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

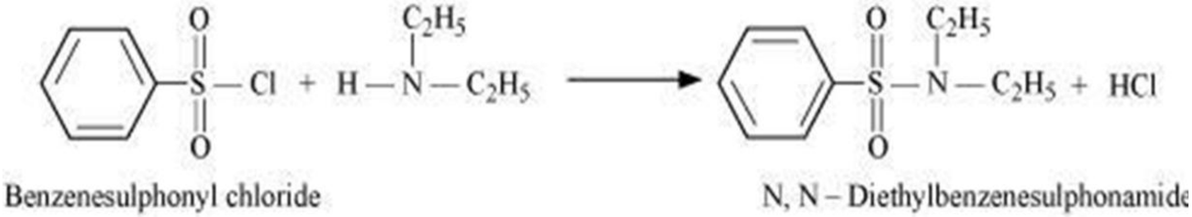
(v) Aniline and N-methylaniline.

ANS. (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.

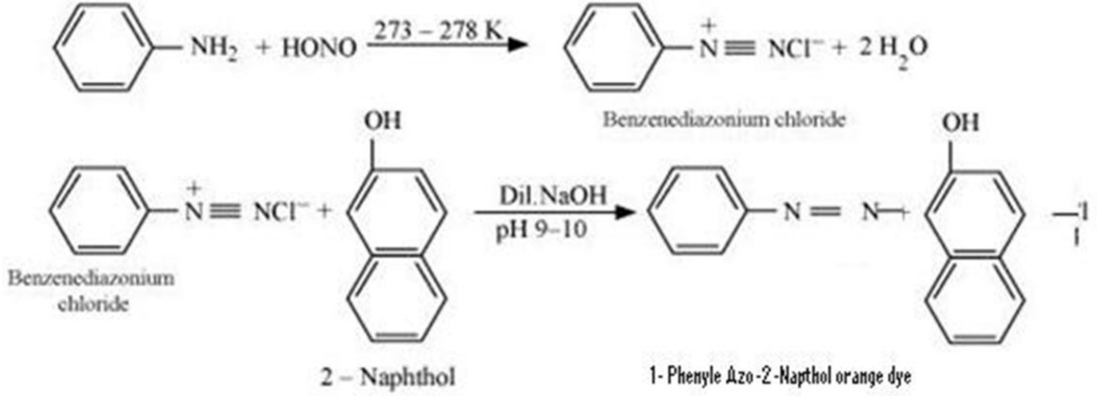
$$\underset{\text{Methylamine}(1^0)}{CH_3-NH_2} + CHCl_3 + 3KOH \xrightarrow{\Delta} \underset{\substack{\text{Methyl isocyanide}\\ \text{(foul smell)}}}{CH_3-NC} + 3KCl + 3H_2$$

$$(CH_3)_2NH + CHCl_3 + 3KOH \xrightarrow{\Delta} \text{No reaction}$$

(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.



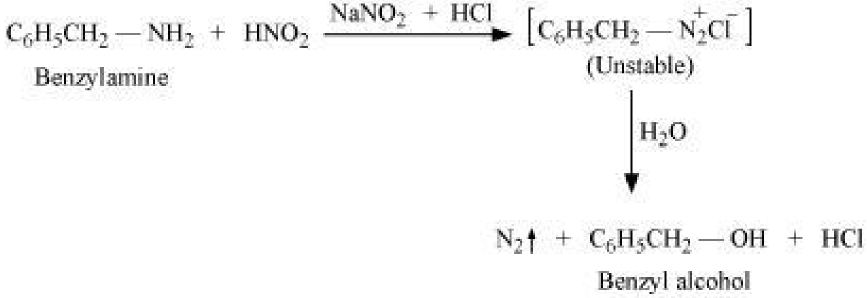
(iii) Ethylamine and aniline can be distinguished using the azo-dye test. A dye is obtained when aromatic amines react with HNO_2 ($NaNO_2$ + dil.HCl) at 0-5°C, followed by a reaction with the alkaline solution of 2-naphthol. The dye is usually yellow, red, or orange in colour. Aliphatic amines give a brisk effervescence due (to the evolution of N_2 gas) under similar conditions.



$$CH_3CH_2-NH_2 + HONO \xrightarrow{0\text{-}5^\circ C} C_2H_5OH + N_2\uparrow + H_2O$$

(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.



$$C_6H_5CH_2-NH_2 + HNO_2 \xrightarrow{NaNO_2 + HCl} [C_6H_5CH_2-\overset{+}{N_2}\overset{-}{Cl}] \xrightarrow{H_2O} N_2\uparrow + C_6H_5CH_2-OH + HCl$$

Benzylamine; (Unstable); Benzyl alcohol

On the other hand, aniline reacts with HNO_2 at a low temperature to form stable diazonium salt. Thus, nitrogen gas is not evolved.

(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.

$$\underset{\text{Benzylamine}(1^0)}{C_6H_5-NH_2} + CHCl_3 + 3KOH \xrightarrow{\Delta} \underset{\substack{\text{Benzyl isocyanide}\\ \text{(foul smell)}}}{C_6H_5-NC} + 3KCl + 3H_2O$$

$$\underset{\text{N-Methylaniline}}{C_6H_5NHCH_3} + CHCl_3 + 3KOH \xrightarrow{\Delta} \text{No reaction}$$

REASONING QUESTIONS

Q1. Account for the following:

(i) pKb of aniline is more than that of methylamine.

(ii) Ethylamine is soluble in water whereas aniline is not.

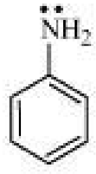
(iii) Methylamine in water reacts with ferric chloride to precipitate hydrated ferric oxide.

(iv) Although amino group is o– and 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.

Ans. (i) pK_b of aniline is more than that of methylamine:

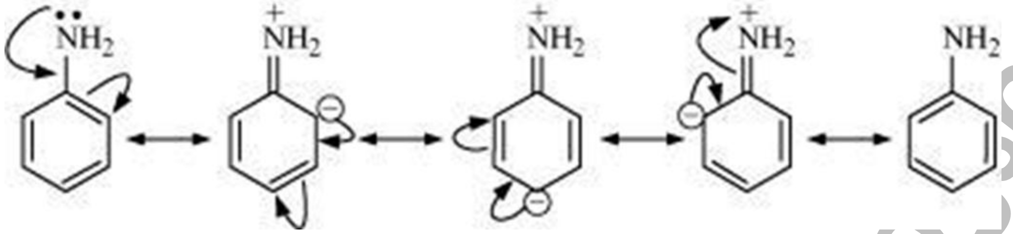


Aniline

$CH_3-\ddot{N}H_2$

Methylamine

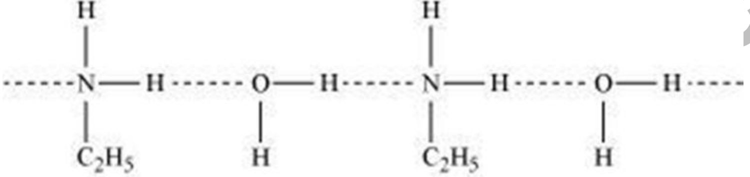
Aniline undergoes resonance and as a result, the electrons on the N-atom are delocalized over the benzene ring. Therefore, the electrons on the N-atom are less available to donate.



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, pK_b 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 $-C_6H_5$ group. Hence, aniline is insoluble in water.

(iii) Methylamine in water reacts with ferric chloride to precipitate hydrated ferric oxide:

$CH_3 \longrightarrow NH_2$ $\qquad$ $H-OH$

Methylamine $\qquad$ 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.

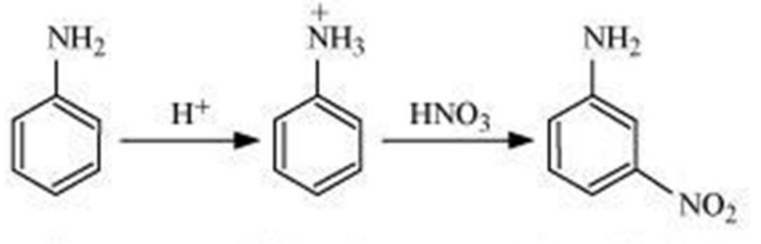
$$FeCl_3 \longrightarrow Fe^{3+} + 3Cl^-$$

Then, OH^- ion reacts with Fe^{3+} 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).

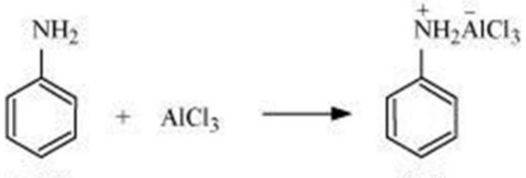


Aniline Anilinium ion *m*-Nitroaniline (47%)

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).

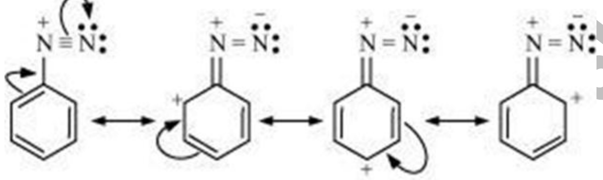


Aniline Salt

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:

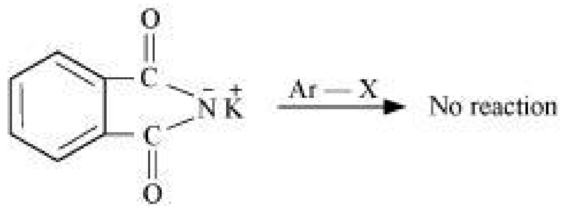
The diazonium ion undergoes resonance as shown below:



This resonance accounts for the stability of the diazonium ion. Hence, diazonium salts of aromatic amines are more stable than those of aliphatic amines.

Q2. Why aromatic primary amines cannot be prepared by Gabriel phthalimide synthesis?

Ans. Gabriel phthalimide synthesis is used for the preparation of aliphatic primary amines. It involves nucleophilic substitution (S_N2) of alkyl halides by the anion formed by the phthalimide. But aryl halides do not undergo nucleophilic substitution with the anion formed by the phthalimide.



Hence, aromatic primary amines cannot be prepared by this process.

Q3. Give possible explanation for each of the following:

(i) Why are amines less acidic than alcohols of comparable molecular masses?

(ii) Why do primary amines have higher boiling point than tertiary amines?

(iii) Why are aliphatic amines stronger bases than aromatic amines?

Ans. (i) Amines undergo protonation to give amide ion.

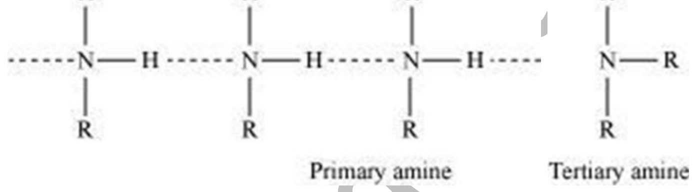
$$R-NH_2 \longrightarrow \underset{\text{Amide ion}}{R-\overset{-}{N}H} + H^+$$

Similarly, alcohol loses a proton to give alkoxide ion.

$$\underset{\text{Alcohol}}{R-OH} \longrightarrow \underset{\text{Alkoxide ion}}{R-\overset{-}{O}} + H^+$$

In an amide ion, the negative charge is on the N-atom whereas in alkoxide ion, the negative charge is on the O-atom. Since O is more electronegative than N, O can accommodate the negative charge more easily than N. As a result, the amide ion is less stable than the alkoxide ion. Hence, amines are less acidic than alcohols of comparable molecular masses.

(ii) In a molecule of tertiary amine, there are no H−atoms whereas in primary amines, two hydrogen atoms are present. Due to the presence of H−atoms, primary amines undergo extensive intermolecular H−bonding.



As a result, extra energy is required to separate the molecules of primary amines. Hence, primary amines have higher boiling points than tertiary amines.

(iii) Due to the −R effect of the benzene ring, the electrons on the N- atom are less available in case of aromatic amines. Therefore, the electrons on the N-atom in aromatic amines cannot be donated easily. This explains why aliphatic amines are stronger bases than aromatic amines.

SOLVED QUESTIONS

1 MARK QUESTIONS

Q1. Give the IUPAC name of the compound and classify into primary, secondary or tertiary amines.

$(CH_3)_2CHNH_2$ 1-Methylethanamine (1^0 amine)

Q2. Give the IUPAC name of the compound and classify into primary, secondary or tertiary amines.

$CH_3(CH_2)_2NH_2$

Propan-1-amine (1^0 amine)

Q3. Give the IUPAC name of the compound and classify into primary, secondary or tertiary amines.

$CH_3NHCH(CH_3)_2$

N−Methyl-2-methylethanamine (2^0 amine)

Q4. Give the IUPAC name of the compound and classify into primary, secondary or tertiary amines.

$(CH_3)_3CNH_2$

2-Methylpropan-2-amine (1^0 amine)

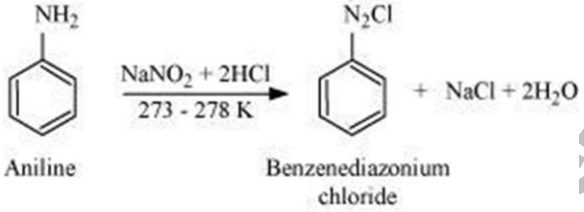
Q5. Give the IUPAC name of the compound and classify into primary, secondary or tertiary amines.

$C_6H_5NHCH_3$

N−Methylbenzamine or N-methylaniline (2^0 amine)

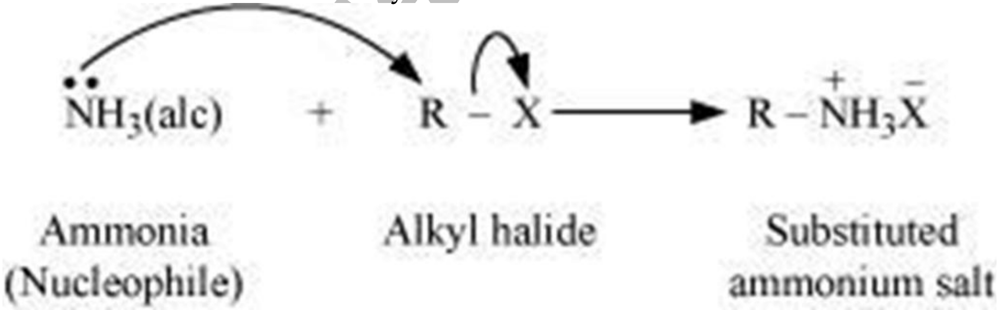
Q6. Write short notes on diazotization

Aromatic primary amines react with nitrous acid (prepared in situ from $NaNO_2$ and a mineral acid such as HCl) at low temperatures (273-278 K) to form diazonium salts. This conversion of aromatic primary amines into diazonium salts is known as diazotization. For example, on treatment with $NaNO_2$ and HCl at 273−278 K, aniline produces benzenediazonium chloride, with NaCl and H_2O as by-products.



Q7. Write short notes on ammonolysis

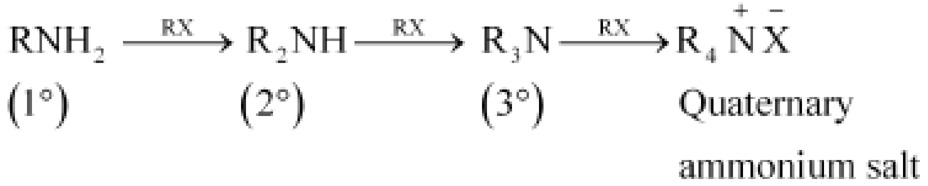
When an alkyl or benzyl halide is allowed to react with an ethanolic solution of ammonia, it undergoes nucleophilic substitution reaction in which the halogen atom is replaced by an amino ($-NH_2$) group. This process of cleavage of the carbon-halogen bond is known as ammonolysis.



When this substituted ammonium salt is treated with a strong base such as sodium hydroxide, amine is obtained.

$$R-\overset{+}{N}H_3\overset{-}{X} + NaOH \longrightarrow \underset{\text{Amine}}{R-NH_2} + H_2O + NaX$$

Though primary amine is produced as the major product, this process produces a mixture of primary, secondary and tertiary amines, and also a quaternary ammonium salt



$$\underset{(1^\circ)}{RNH_2} \xrightarrow{RX} \underset{(2^\circ)}{R_2NH} \xrightarrow{RX} \underset{(3^\circ)}{R_3N} \xrightarrow{RX} R_4\overset{+}{N}\overset{-}{X}$$

Quaternary ammonium salt

Q8. Write short notes on acetylation.

Acetylation (or ethanoylation) is the process of introducing an acetyl group into a molecule. Aliphatic and aromatic primary and secondary amines undergo acetylation reaction by nucleophilic substitution when treated with acid chlorides, anhydrides or esters. This reaction involves the replacement of the hydrogen atom of $-NH_2$ or $> NH$ group by the acetyl group, which in turn leads to the production of amides. To shift the equilibrium to the right hand side, the HCl formed during the reaction is removed as soon as it is formed. This reaction is carried out in the presence of a base (such as pyridine) which is stronger than the amine.

$$C_2H_5NH_2 + CH_3COCl \xrightarrow{\text{pyridine}} C_2H_5NHCOCH_3 + HCl$$

Q9.Why are amines basic in character?

ANS. Like ammonia, the nitrogen atom in amines RNH_2 is trivalent and bears an unshared pair of electrons. Thus it acts like a Lewis base and donates the pair of electrons to electron-deficient species which further increases due to +I effect of alkyl radical.

Q10. Arrange the following in decreasing order of their basic strength:

$C_6H_5NH_2$, $C_2H_5NH_2$, $(C_2H_5)_2NH$, NH_3

The decreasing order of basic strength of the above amines and ammonia

follows the following order:

$(C_2H_5)_2NH > C_2H_5NH_2 > NH_3 > C_6H_5NH_2$

SOLVED EXAMPLES (2 Marks)

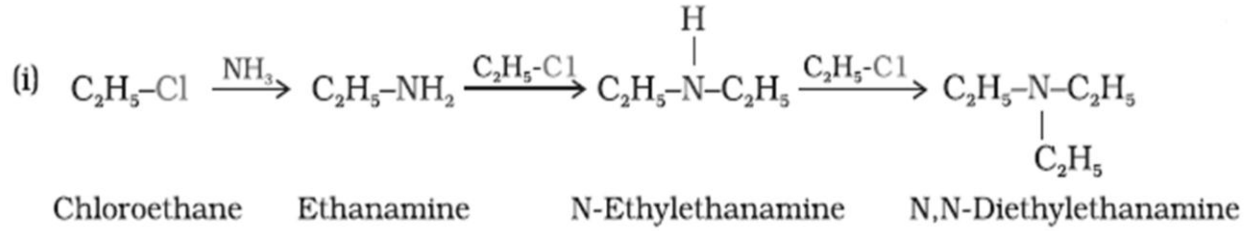
Q1. Write chemical equations for the following reactions:

(i) Reaction of ethanolic NH_3 with C_2H_5Cl.

(ii) Ammonolysis of benzyl chloride and reaction of amine so formed

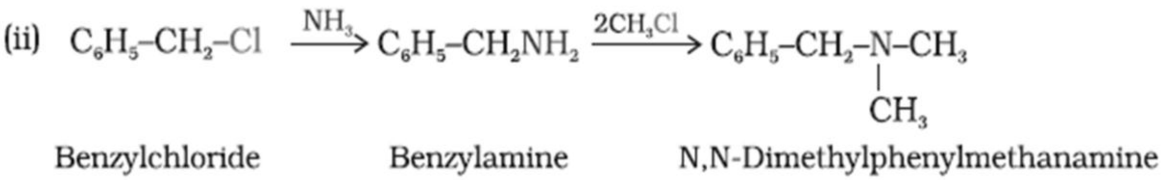
with two moles of CH_3Cl

Ans.



$$\text{(i)}\; C_2H_5{-}Cl \xrightarrow{NH_3} C_2H_5{-}NH_2 \xrightarrow{C_2H_5{-}Cl} C_2H_5{-}\overset{\displaystyle H}{\overset{|}{N}}{-}C_2H_5 \xrightarrow{C_2H_5{-}Cl} C_2H_5{-}\underset{\displaystyle C_2H_5}{\underset{|}{N}}{-}C_2H_5$$

Chloroethane Ethanamine N-Ethylethanamine N,N-Diethylethanamine



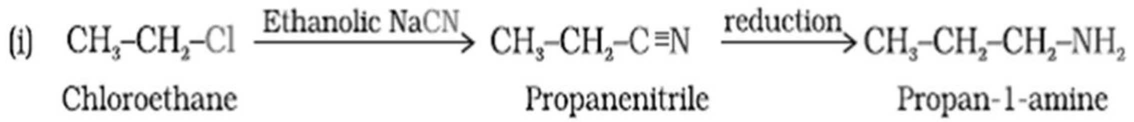
$$\text{(ii)}\; C_6H_5{-}CH_2{-}Cl \xrightarrow{NH_3} C_6H_5{-}CH_2NH_2 \xrightarrow{2CH_3Cl} C_6H_5{-}CH_2{-}\underset{\displaystyle CH_3}{\underset{|}{N}}{-}CH_3$$

Benzylchloride Benzylamine N,N-Dimethylphenylmethanamine

Q2. Write chemical equations for the following conversions:

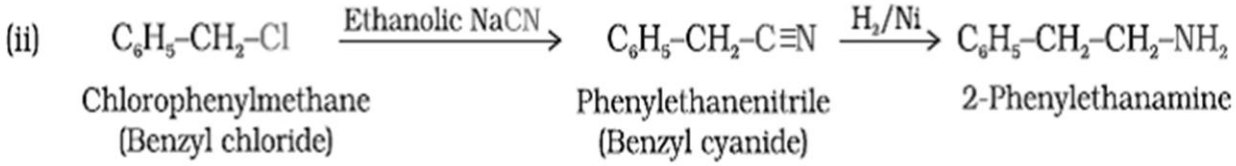
(i) CH_3 –CH_2 –Cl into CH_3 –CH_2 –CH_2 –NH_2

(ii) C_6H_5–CH_2 –Cl into C_6H_5 –CH_2 –CH_2 –NH_2



$$\text{(i)}\; CH_3{-}CH_2{-}Cl \xrightarrow{\text{Ethanolic NaCN}} CH_3{-}CH_2{-}C{\equiv}N \xrightarrow{\text{reduction}} CH_3{-}CH_2{-}CH_2{-}NH_2$$

Chloroethane Propanenitrile Propan-1-amine



$$\text{(ii)}\; C_6H_5{-}CH_2{-}Cl \xrightarrow{\text{Ethanolic NaCN}} C_6H_5{-}CH_2{-}C{\equiv}N \xrightarrow{H_2/Ni} C_6H_5{-}CH_2{-}CH_2{-}NH_2$$

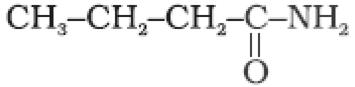
Chlorophenylmethane (Benzyl chloride) Phenylethanenitrile (Benzyl cyanide) 2-Phenylethanamine

Q3.Write structures and IUPAC names of

(i) The amide which gives propanamine by Hoffmann bromamide reaction.

(ii) the amine produced by the Hoffmann degradation of benzamide.

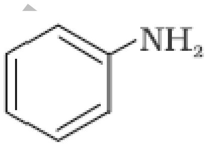
Ans. (i) Propanamine contains three carbons. Hence, the amide molecule must contain four carbon atoms. Structure and IUPAC name of the starting amide with four carbon atoms are given below:



$$CH_3{-}CH_2{-}CH_2{-}\underset{\displaystyle O}{\underset{\|}{C}}{-}NH_2$$

(Butanamide)

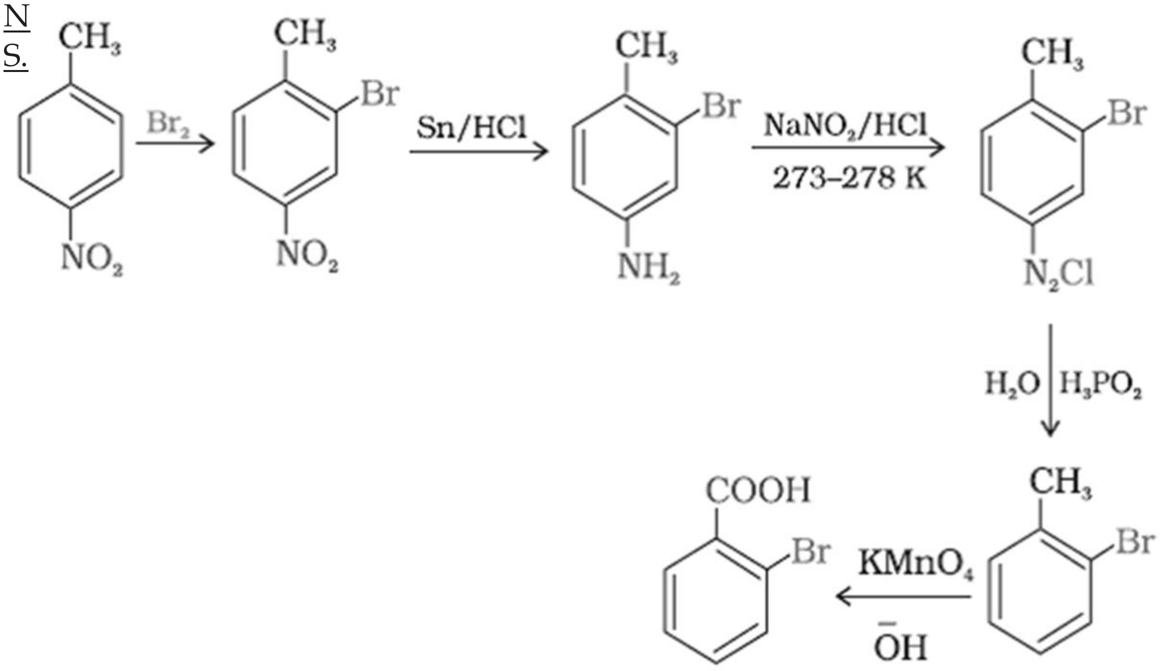
(ii) Benzamide is an aromatic amide containing seven carbon atoms. Hence, the amine formed from benzamide is aromatic primary amine containing six carbon atoms.



(Aniline or benzenamine)

Q4. How will you convert 4-nitrotoluene to 2-bromobenzoic acid?

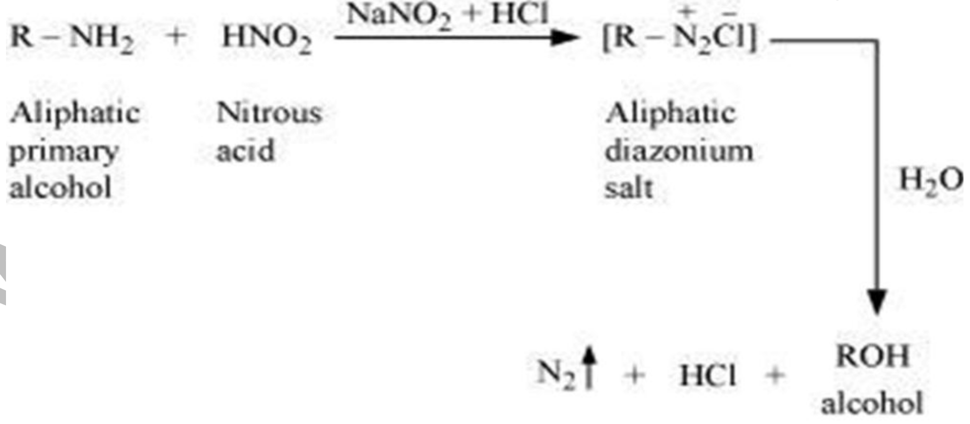
ANS.



Q5. Write the reactions of (i) aromatic and (ii) aliphatic primary amines with nitrous acid.

ANS. (i) Aromatic amines react with nitrous acid (prepared in situ from $NaNO_2$ and a mineral acid such as HCl) at 273 − 278 K to form stable aromatic diazonium salts i.e., NaCl and H_2O.

(ii) Aliphatic primary amines react with nitrous acid (prepared in situ from $NaNO_2$ and a mineral acid such as HCl) to form unstable aliphatic diazonium salts, which further produce alcohol and HCl with the evolution of N_2 gas.

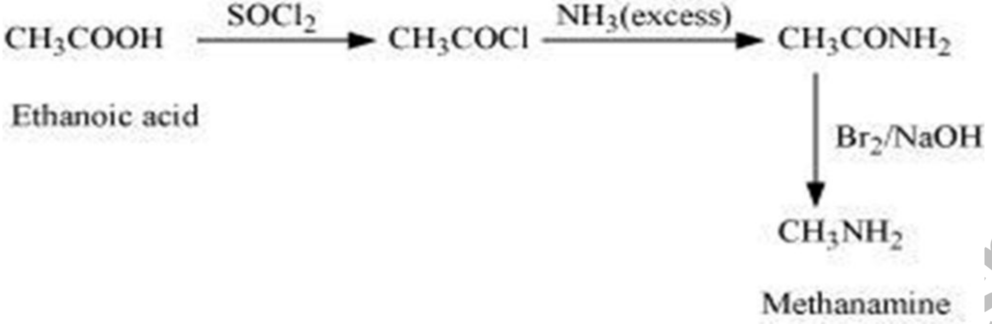


Q6. How will you convert:

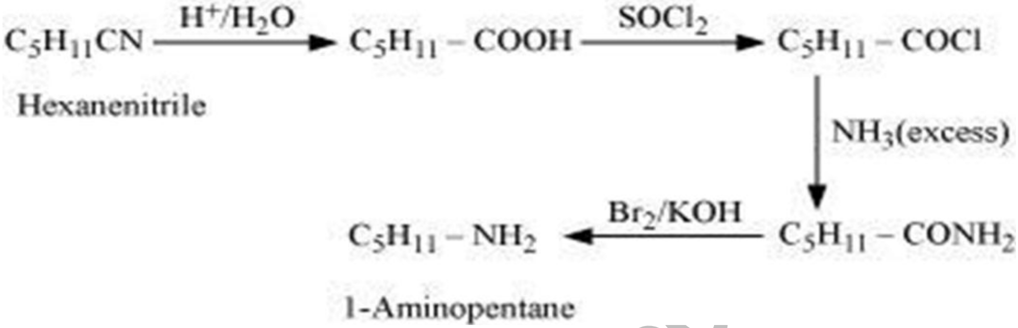
(i) Ethanoic acid into methanamine

(ii) Hexanenitrile into 1-aminopentane

ANS. (i)



(ii)

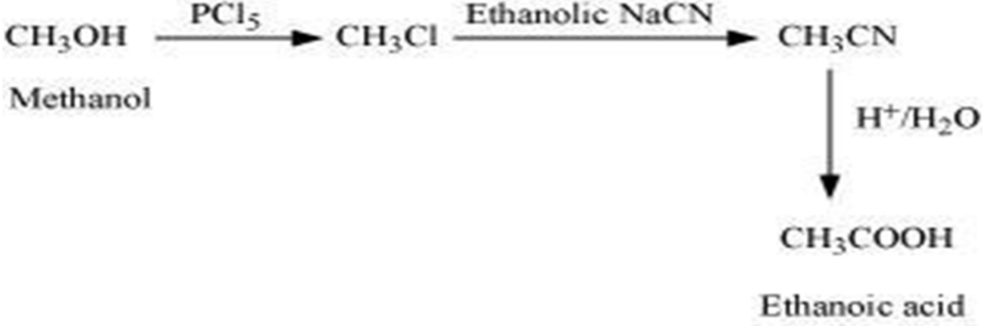


Q7. How will you convert:

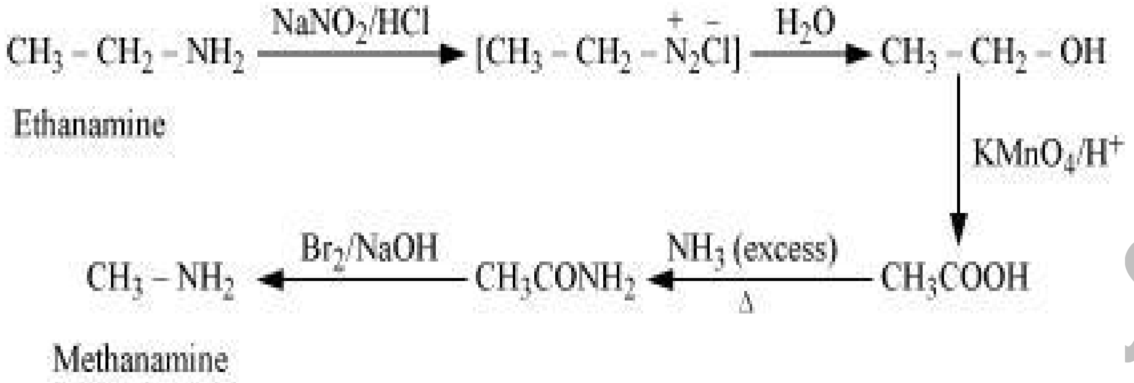
(i) Methanol to ethanoic acid

(ii) Ethanamine into methanamine

Ans. (i)



(ii)

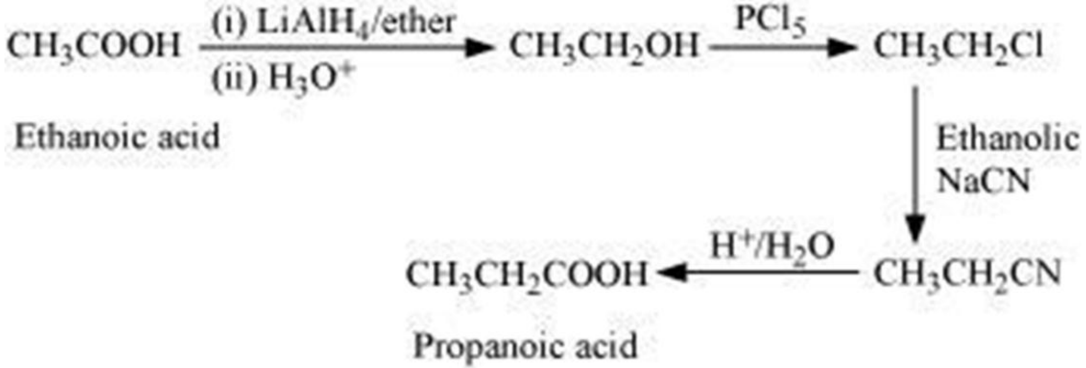


Q8. How will you convert

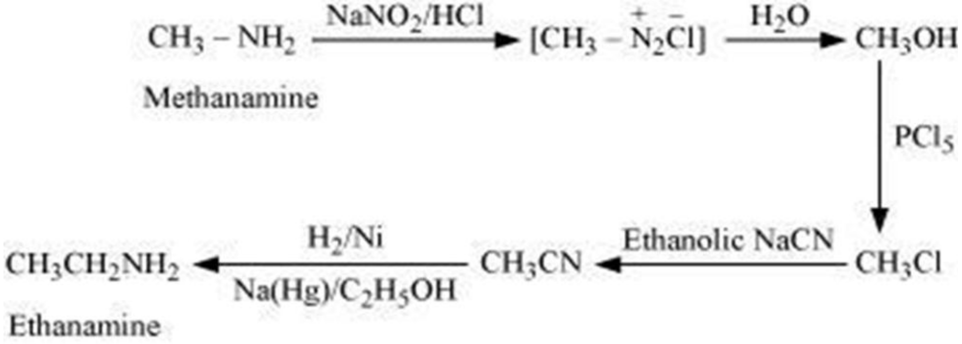
(i) Ethanoic acid into propanoic acid

(ii) Methanamine into ethanamine

<u>Ans.</u> (i)



(ii)

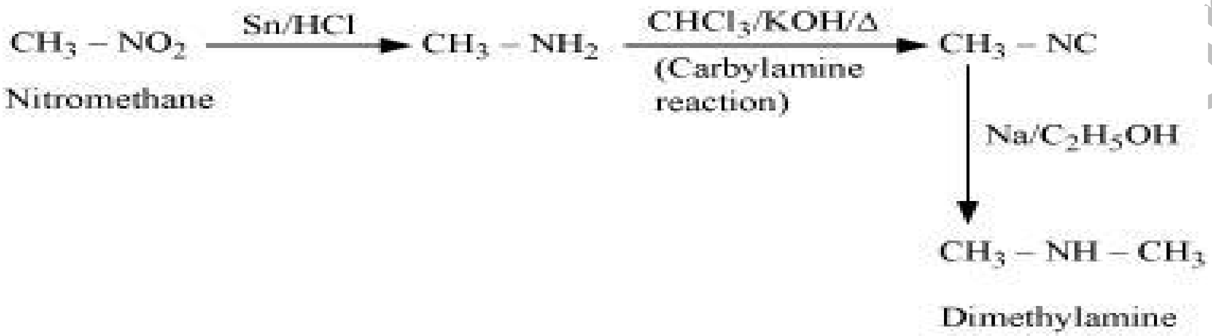


Q9. How will you convert

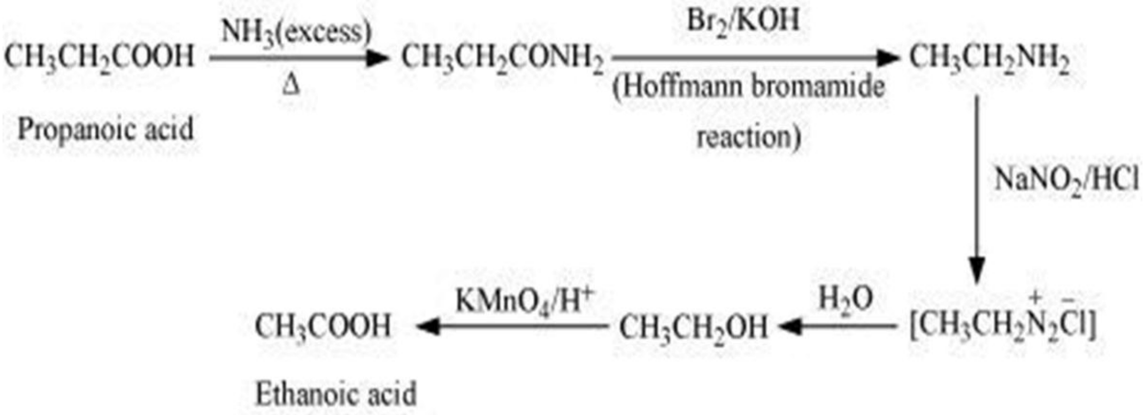
(i) Nitromethane into dimethylamine

(ii) Propanoic acid into ethanoic acid?

(i)

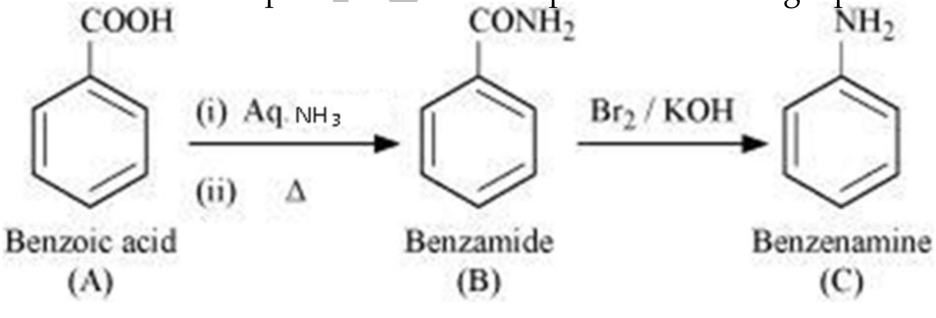


(ii)



Q10. An aromatic compound ‗A‘ on treatment with aqueous ammonia and heating forms compound ‗B‘ which on heating with Br_2 and KOH forms a compound ‗C‘ of molecular formula C_6H_7N. Write the structures and IUPAC names of compounds A, B and C.

Ans. It is given that compound ‗C‘ having the molecular formula, C_6H_7N is formed by heating compound ‗B‘ with Br_2 and KOH. This is a Hoffmann bromamide degradation reaction. Therefore, compound ‗B‘ is an amide and compound ‗C‘ is an amine. The only amine having the molecular formula, C_6H_7N is aniline, ($C_6H_5NH_2$).The given reactions can be explained with the help of the following equations:



3 MARKS QUESTIONS

Q1. Arrange the following:

(i) In decreasing order of the pKb values:
$C_2H_5NH_2$, $C_6H_5NHCH_3$, $(C_2H_5)_2NH$ 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:

Aniline, p-nitroaniline and p-toluidine

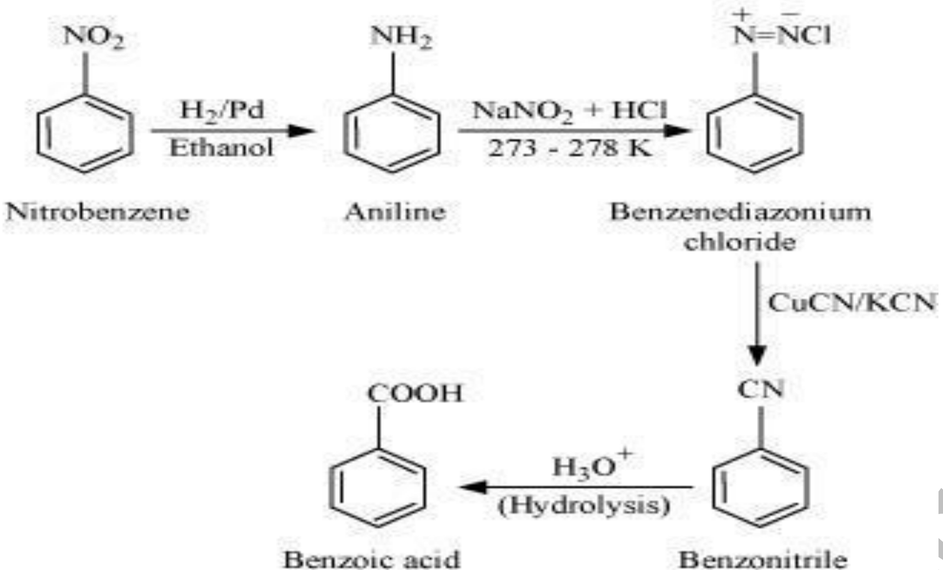
ANS. (i) The order of increasing basicity of the given compounds is as follows:
$C_6H_5NH_2 < C_6H_5NHCH_3 < C_2H_5NH_2 < (C_2H_5)_2NH$
We know that the higher the basic strength, the lower is the pK_b values.
$C_6H_5NH_2 > C_6H_5NHCH_3 > C_2H_5NH_2 > (C_2H_5)_2NH$
(ii)The increasing order of the basic 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) The increasing order of the basic strengths of the given compounds is :
p-Nitroaniline < Aniline < p-Toluidine

Q2. Arrange the following
(i) In decreasing order of basic strength in gas phase:
$C_2H_5NH_2$, $(C_2H_5)_2NH$, $(C_2H_5)_3N$ and NH_3
(ii) In increasing order of boiling point:
C_2H_5OH, $(CH_3)_2NH$, $C_2H_5NH_2$
(iii) In increasing order of solubility in water:
$C_6H_5NH_2$, $(C_2H_5)_2NH$, $C_2H_5NH_2$.

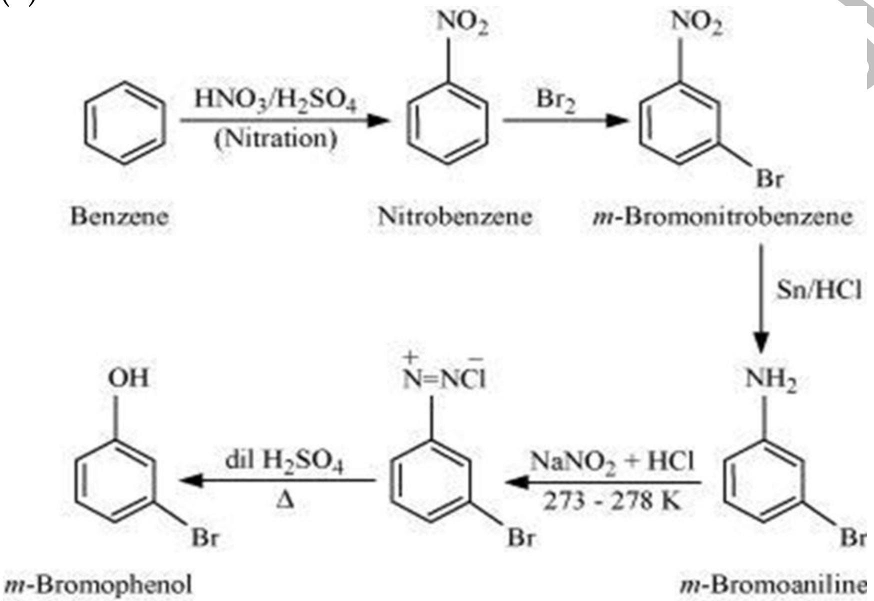
Ans. (i) The given compounds can be arranged in the decreasing order of their basic strengths in the gas phase as follows:
$(C_2H_5)_3N > (C_2H_5)_2NH > C_2H_5NH_2 > NH_3$
(ii) The given compounds can be arranged in the increasing order of their boiling points as follows:
$(CH_3)_2NH < C_2H_5NH_2 < C_2H_5OH$
(iii) 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 $(C_2H_5)_2NH$.

Q3. Accomplish the following conversions:
(i) Nitrobenzene to benzoic acid
(ii) Benzene to m-bromophenol
(iii) Benzoic acid to aniline

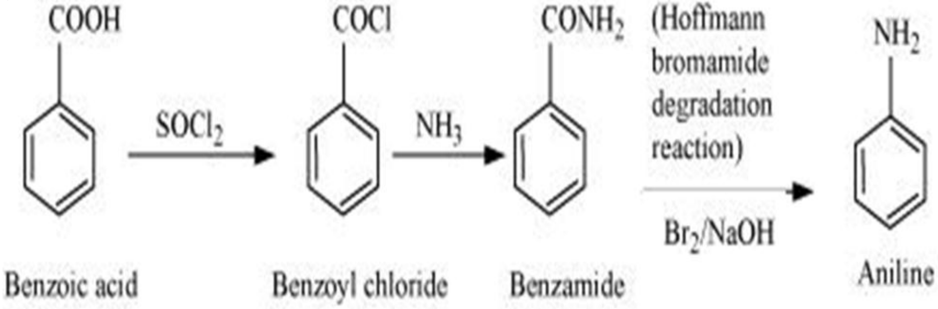
Ans. (i)



(ii)

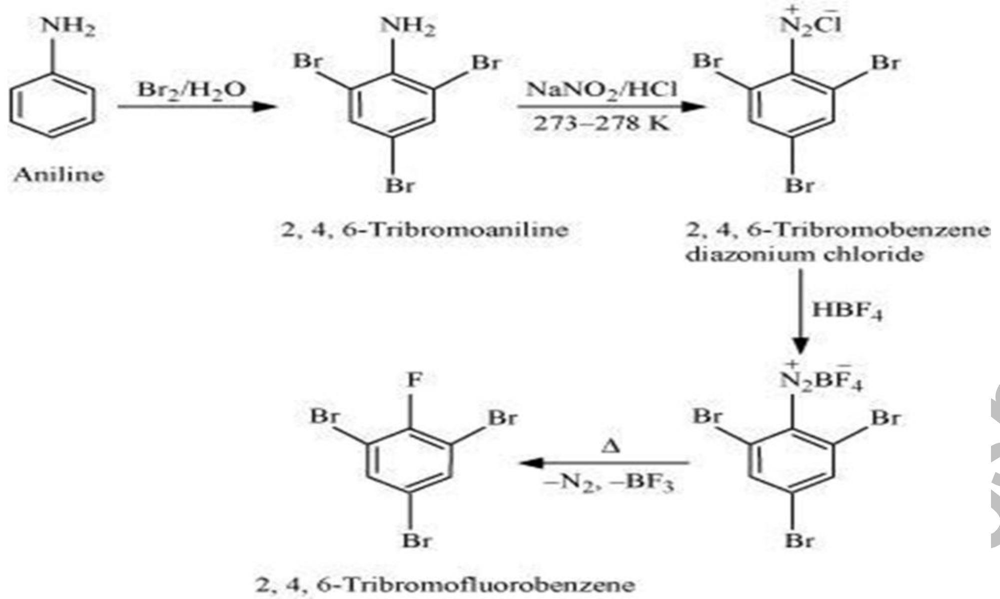


(iii)

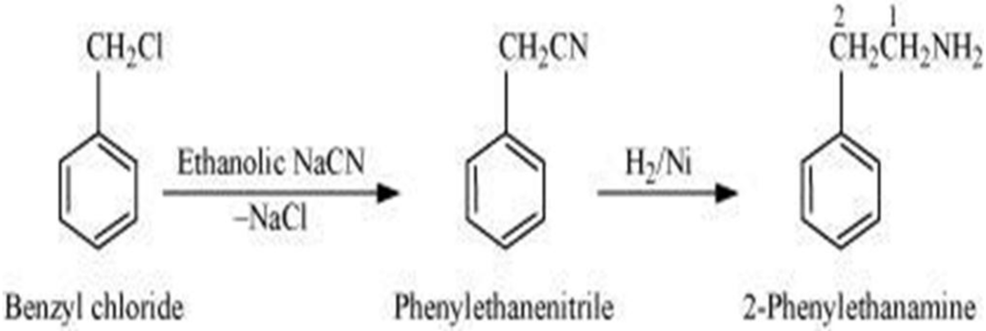


Q4. Accomplish the following conversions:
(i) Aniline to 2,4,6-tribromofluorobenzene
(ii) Benzyl chloride to 2-phenylethanamine
(iii) Chlorobenzene to p-chloroaniline

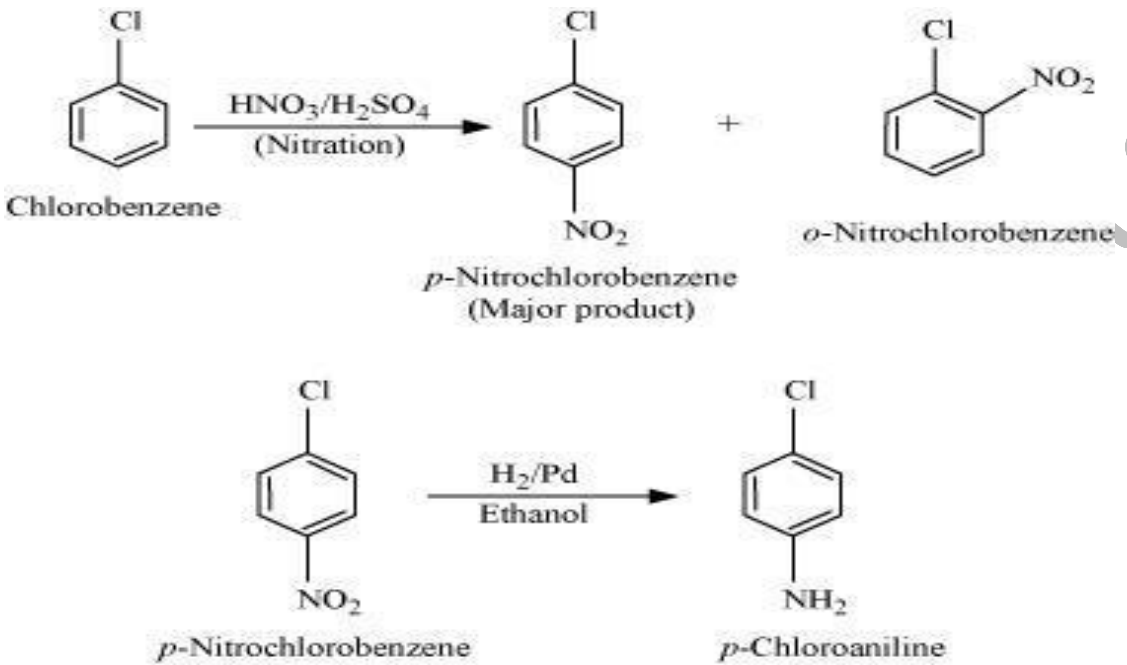
Ans. (i)


NH₂
Br₂/H₂O
Aniline
NH₂
Br
Br
Br
2, 4, 6-Tribromoaniline
NaNO₂/HCl
273–278 K
N₂Cl
Br
Br
Br
2, 4, 6-Tribromobenzene diazonium chloride
HBF₄
N₂BF₄
Br
Br
Br
Δ
–N₂, –BF₃
F
Br
Br
Br
2, 4, 6-Tribromofluorobenzene

(ii)

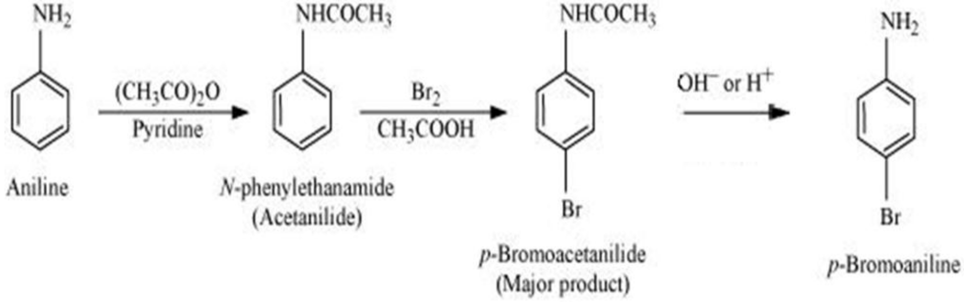

CH₂Cl
Ethanolic NaCN
–NaCl
Benzyl chloride
CH₂CN
H₂/Ni
Phenylethanenitrile
2 1
CH₂CH₂NH₂
2-Phenylethanamine

(iii)

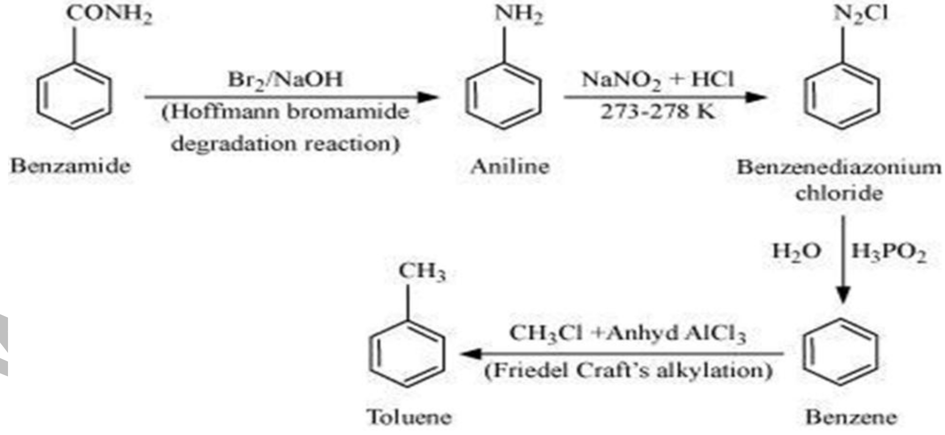


Q5. Accomplish the following conversions:
(i) Aniline to p-bromoaniline
(ii) Benzamide to toluene
(iii) Aniline to benzyl alcohol.

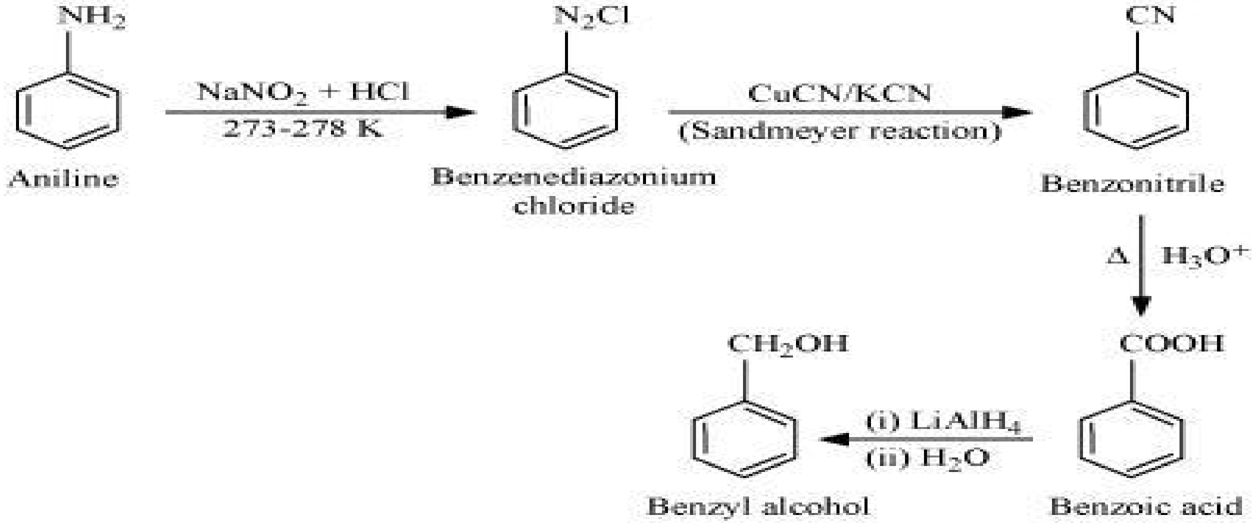
<u>ANS.</u> (i)



(ii)



(iii)



5 MARKS QUESTIONS

Q1. Give the structures of A, B and C in the following reactions:

(i)

$$CH_3CH_2I \xrightarrow{NaCN} A \xrightarrow[\text{Partial hydrolysis}]{OH^-} B \xrightarrow{NaOH, Br_2} C$$

(ii)

$$C_6H_5N_2Cl \xrightarrow{CuCN} A \xrightarrow{H_2O/H^+} B \xrightarrow[\Delta]{NH_3} C$$

(iii)

$$CH_3CH_2Br \xrightarrow{KCN} A \xrightarrow{LiAlH_4} B \xrightarrow[0^0 C]{HNO_2} C$$

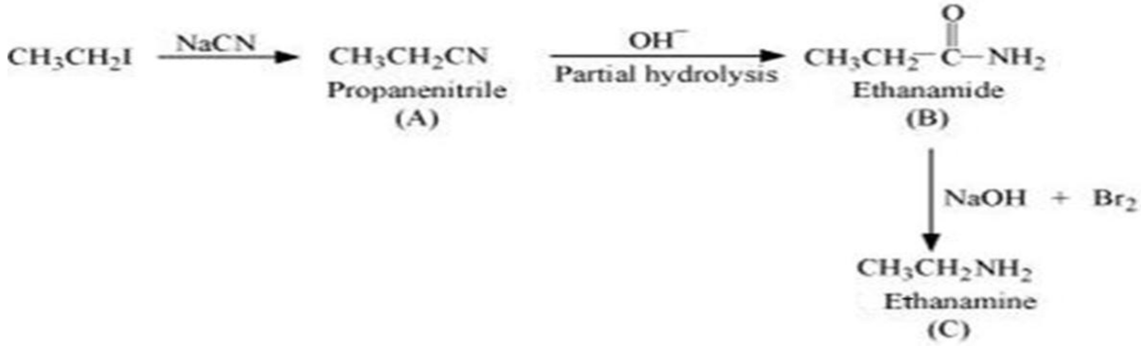
(iv)

$$C_6H_5NO_2 \xrightarrow{Fe/HCl} A \xrightarrow[273K]{NaNO_2+HCl} B \xrightarrow[\Delta]{H_2O/H^+} C$$

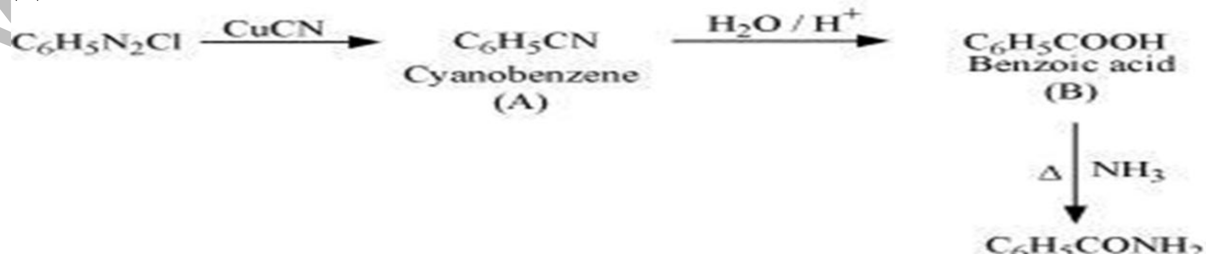
(v)

$$CH_3COOH \xrightarrow[\Delta]{NH_3} A \xrightarrow{NaOBr} B \xrightarrow{NaNO_2/HCl} C$$

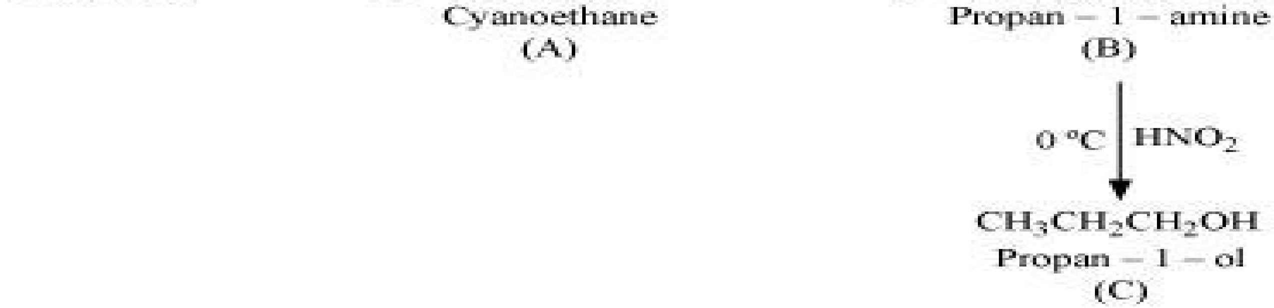
ANS. (i)



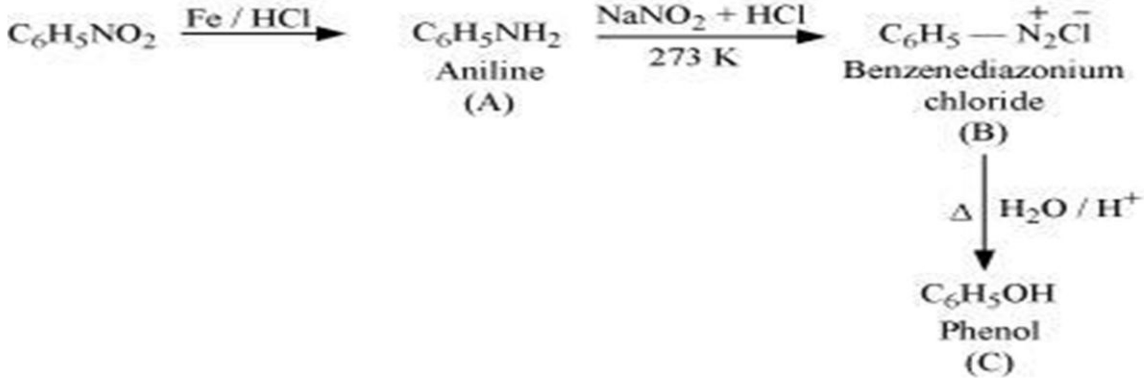
(ii)



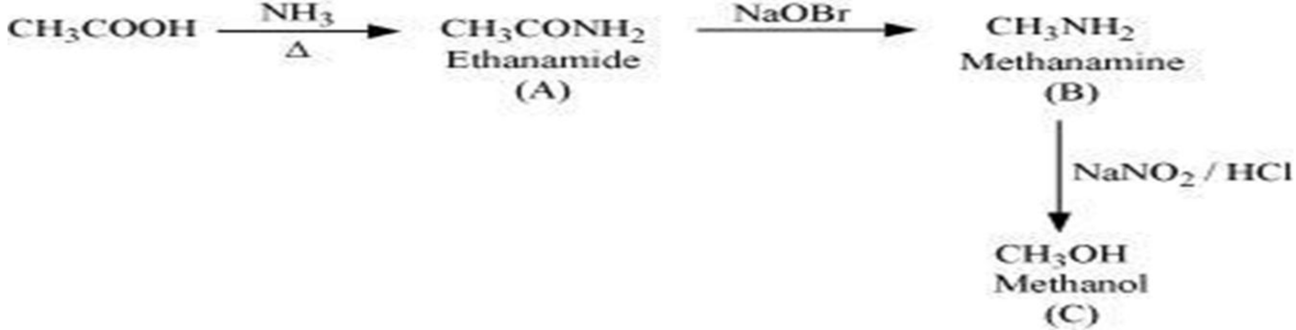
(iii)



(iv)



(v)



Q2. Complete the following reactions:

(i)

$$C_6H_5NH_2 + CHCl_3 + \text{alc.KOH} \rightarrow$$

(ii)

$$C_6H_5N_2Cl + H_3PO_2 + H_2O \rightarrow$$

(iii)

$C_6H_5NH_2 + H_2SO_4(\text{conc.}) \rightarrow$

(iv)

$C_6H_5N_2Cl + C_2H_5OH \rightarrow$

(v)

$C_6H_5NH_2 + Br_2(aq) \rightarrow$

ANS. (i)

$$\underset{\text{Aniline}}{C_6H_5NH_2} + CHCl_3 + 3\text{alc. KOH} \xrightarrow[\text{reaction}]{\text{Carbylamine}} 3H_2O + 3KCl + \underset{\text{Phenyl isocyanide}}{C_6H_5-NC}$$

(ii)

$$\underset{\text{Benzenediazonium chloride}}{C_6H_5N_2Cl} + H_3PO_2 + H_2O \rightarrow \underset{\text{Benzene}}{C_6H_6} + N_2 + H_3PO_3 + HCl$$

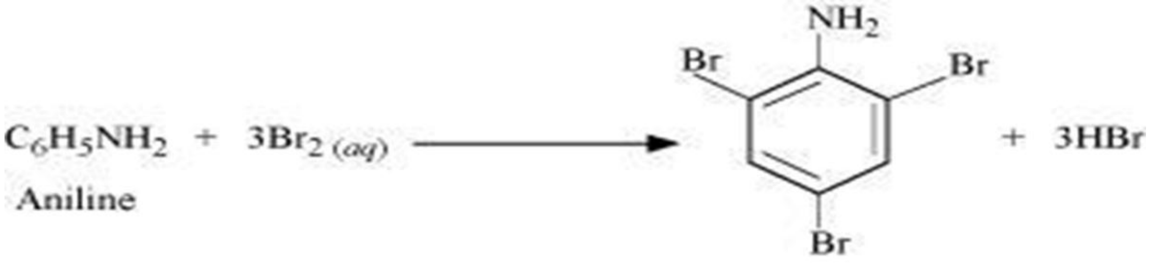
(iii)

$$\underset{\text{Aniline}}{C_6H_5NH_2} + \text{conc.}H_2SO_4 \rightarrow \underset{\text{Anilinium hydrogen sulphate}}{C_6H_5\overset{+}{N}H_3H S\overset{-}{O}_4}$$

(iv)

$$\underset{\text{Benzenediazonium chloride}}{C_6H_5N_2Cl} + \underset{\text{Ethanol}}{C_2H_5OH} \rightarrow \underset{\text{Benzene}}{C_6H_6} + \underset{\text{Ethanal}}{CH_3CHO} + N_2 + HCl$$

(v)



2,4,6 – Tribromoaniline

Assignments

Level 1

1. Write IUPAC Name of $C_6H_5N(CH_3)_3Br$?
2. Which reaction is used for preparation of pure aliphatic & aromatic primary amine?
3. Name one reagent used to distinguish between primary, secondary & tertiary amines?
4. What is the directive influence of amino group in arylamines?
5. Why are benzene diazonium salts soluble in water?
6. Which is more basic: CH_3NH_2 & $(CH_3)_3N$?
7. Which is more basic, aniline or ammonia?
8. Write the IUPAC name of $C_6H_5NHCH_3$?
9. Mention two uses of sulphanilic acid?

Level 2

1. Write the use of quaternary ammonium salts?
2. What product is formed when aniline is first diazotized and then treated with Phenol in alkaline medium?
3. How is phenyl hydrazine prepared from aniline?
4. What is the IUPAC name of a tertiary amine containing one methyl, one ethyl and one n-propyl group?
5. Explain why silver chloride is soluble in aqueous solution of methylamine?
6. Write the IUPAC name of $C_6H_5N^+(CH_3)_3Br^-$?
7. Primary amines have higher boiling points than tertiary amines why?
8. Why is it necessary to maintain the temperature between 273 K & 278 K during diazotization?
9. Arrange the following in order of decreasing basic strength: Ethyl amine, Ammonia, Triethylamine ?
10. Why aniline is acetylated first to prepare mono bromo derivative?

LEVEL 3

1. Arrange the following in decreasing order of their basic strength.

$C_6H_5NH_2$, $C_2H_5NH_2$, $(C_2H_5)_2NH$, NH_3

2. Write chemical equation for the conversion

CH_3-CH_2-Cl into CH_3–CH_2-CH_2-NH_2

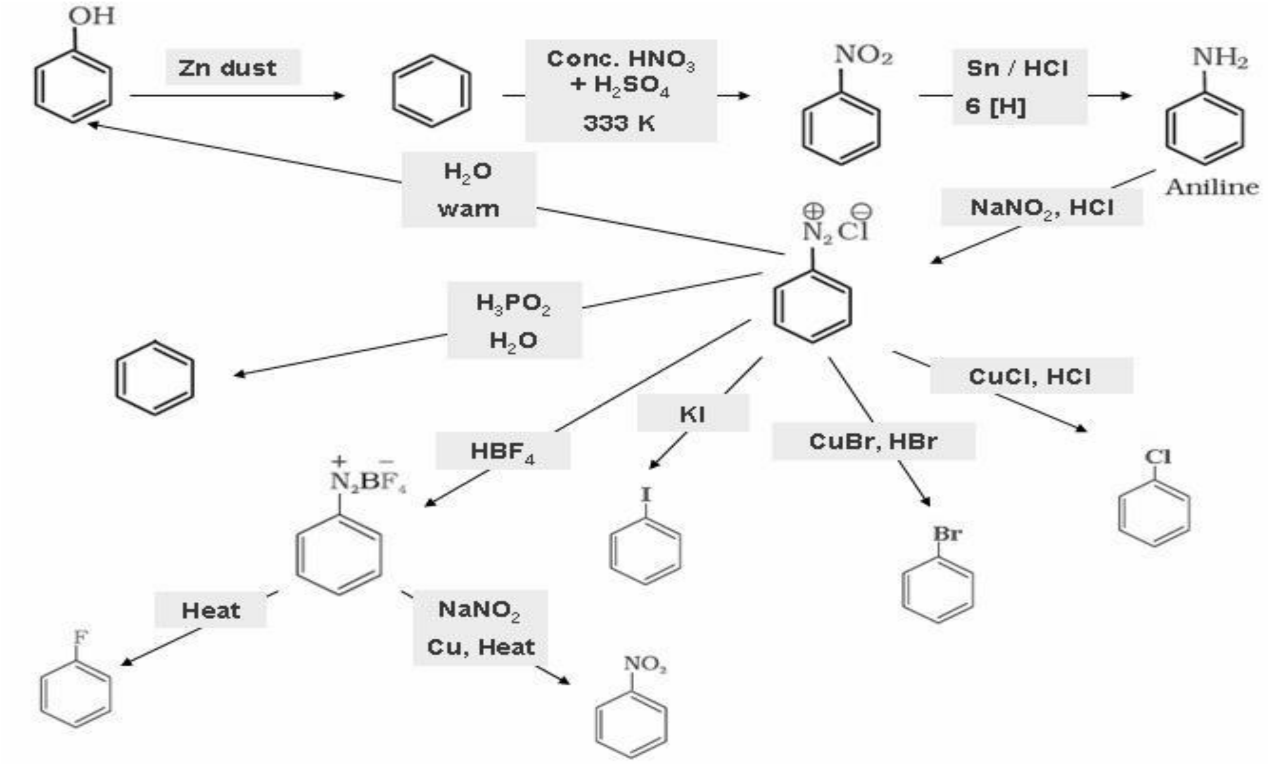
3. Write the equation involved in Carbylamines reactions?

4. How will you distinguish the following pairs?

(i) Methanamine and N-methyl methanamine

(ii) Aniline and ethylamine

5. Write chemical reactions involved in following name reactions.
(i) Hoffmann Bromoamide reaction.
(ii) Diazotisation reaction.



COMMON ERRORS

Basic character of amines in aqueous and in gaseous state, p_{ka} and p_{kb} values

1 MARK QUESTIONS

Q1. Arrange the following in decreasing order of their basic strength:
$C_6H_5NH_2$, $C_2H_5NH_2$, $(C_2H_5)_2NH$, NH_3

Q2. Arrange the following in decreasing order of the pK_b values:
$C_2H_5NH_2$, $C_6H_5NHCH_3$, $(C_2H_5)_2NH$ and $C_6H_5NH_2$

Q3. pK_b of aniline is more than that of methylamine. Why?

Q4. Ethylamine is soluble in water whereas aniline is not. Give reason.

Q5. Methylamine in water reacts with ferric chloride to precipitate hydrated ferric oxide. Why?

Q6. Although amino group is *o*– and *p*– directing in aromatic electrophilic substitution reactions, aniline on nitration gives a substantial amount of *m*-nitroaniline. Give reason.

Q7. Aniline does not undergo Friedel-Crafts reaction. Why?

Q8. Diazonium salts of aromatic amines are more stable than those of aliphatic amines. Why?

Q9. Gabriel phthalimide synthesis is preferred for synthesising primary amines. Give reason

Q10. Why cannot aromatic primary amines be prepared by Gabriel phthalimide synthesis?

Q11. Why do primary amines have higher boiling point than tertiary amines?
Q12. Why are aliphatic amines stronger bases than aromatic amines?
Q13. Direct nitration of aniline is not carried out. Give reason.
Q14. The presence of base is needed in the ammonolysis of alkyl halides. Why?

2 MARKS QUESTIONS

Q1. Write structures and IUPAC names of
(i) the amide which gives propanamine by Hoffmann bromamide reaction.
(ii) the amine produced by the Hoffmann degradation of benzamide.
Q2. Give one chemical test to distinguish between the following pairs of compounds.
(i) Methylamine and dimethylamine (ii) Ethylamine and aniline
Q3. Write short notes on the following:
(i) Carbylamine reaction (ii) Diazotisation
Q4. Explain the following with the help of an example.
(i) Hofmann's bromamide reaction (ii) Coupling reaction
Q5. Explain the following with the help of an example.
(i) Ammonolysis (ii) Gabriel phthalimide synthesis
Q6. How can you convert an amide into an amine having one carbon less than the starting compound? Name the reaction.
Q7. Give a chemical test to distinguish between:
(a) $C_6H_5NH_2$ & CH_3NH_2
(b) CH_3NHCH_3 & $(CH_3)_3N$
Q8. Give the IUPAC names of:
(a) $(CH_3)_2CHNH_2$
(b) $(CH_3CH_2)_2NCH_3$
Q9. Write the structures of:
(a) 3-Bromobenzenamine
(b) 3-Chlorobutanamide

3 MARKS QUESTIONS

Q1. How will you convert
(i) Benzene into aniline (ii) Benzene into N, N-dimethylaniline
(iii) Aniline to Sulphanilic acid

Q2. An aromatic compound 'A' on treatment with aqueous ammonia and heating forms compound 'B' which on heating with Br_2 and KOH forms a compound 'C' of molecular formula C_6H_7N. Write the structures and IUPAC names of compounds A, B and C.

Q3. How will you carry out the following conversions (Write Chemical equations and reaction conditions):
(a) Aniline to Phenol
(b)Acetamide to Ethylamine
(c) Aniline to *p*-nitroaniline

Chapter - 14

Biomolecules

Gist Of The Chapter

1. Carbohydrates- These are optically active polyhydroxy aldehydes or ketones due to presence of chiral `C' or the compounds which produce these on hydrolysis except dihydroxy acetone which is not optically active.

2. Classification-

(i) Monosaccharides – Those carbohydrates which cannot get hydrolysed e.g. glucose, fructose, galactose etc.

(ii) Oligosaccharides- Those carbohydrates which give two or more monosaccharide's on hydrolysis e.g. sucrose on hydrolysis gives glucose and fructose. Raffinose on hydrolysis gives glucose, fructose and galactose.

(iii) Polysaccharides- Those carbohydrates which on hydrolysis give large number of monosaccharide's. e.g. starch, cellulose, glycogen.

3. Sugar-

(i)Reducing Sugars- Those which reduce Fehling's or Tollen's reagent. They have free aldehydic groups, eg , glucose, galactose

(ii)Non Reducing Sugars- Those which do not reduce Fehling's or Tollen's reagent. They do not have free functional group, e.g. sucrose

4. Glucose- It is a monosaccharide's with molecular formula $C_6H_{12}O_6$

5. Preparation

(i)From Sucrose

$C_{12}H_{22}O_{11} + H_2O$ -------> $C_6H_{12}O_6 + C_6H_{12}O_6$ (Only from sucrose)

(ii)From Starch

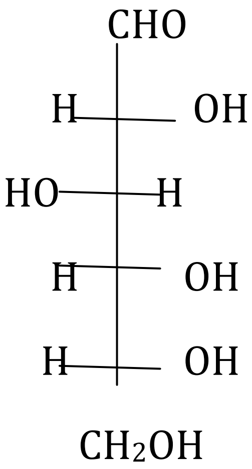
$(C_6H_{10}O_5)_n + nH_2O$ -------> $C_{12}H_{22}0_{11} + H_20$ ------> $2C_6H_{12}O_6$

6.Structure

(i)Fischer structure –

CHO — $(CHOH)_4$ — CH_2OH

(+) Glucose has `D' configuration as shown



`D' means —OH group on first chiral `C' from the bottom is on right hand and + means it is dextro rotatory, i.e. it rotates plane polarized light towards right.

(ii) Cyclic Structure OF Glucose: the straight chain is unable to explain the following reactions.

(a) It does not give the 2, 4-DNP test, Schiff's Test and does not form the hydrogensulphide product with $NaHSO_3$.

(b) The pentaacetate of glucose does not react with NH_2OH, indicating the absence of free aldehydic group.

(iii) Glucose exist in 2 different crystalline forms α and β forms. These are called anomers. They differ in optical rotation, they also differ in melting point.

Anomers are isomers which have a different configuration across C-1 (first chiral 'C' atom).

7. Glycosidic Linkage: The linkage between two monosaccharide units through oxygen is called the glycosidic linkage.

8. Proteins: These are macro molecules made up of amino acids joined via a peptide link (-(-CO-NH-)- is the peptide linkage). These are required for growth and development of the body.

9. Amino Acids: These contain an amino (-NH_2) and an acidic (-COOH) group and are therefore amphoteric in nature. In solution they exist in the form of zwitter ion.

10. Classification

Fibrous Protein	**Globular Protein**
(i) Polypeptide chains run parallel or anti-parallel and held together by hydrogen and disulphide bonds.	(i) Chains of Polypeptide coil around to give a spherical shape.
(ii) Generally insoluble in water. e.g. Keratin, collagen, myosin, fibroin.	(ii) Usually soluble in water. e.g., insulin, thyroglobin, albumin, haemoglobin and fibrinogen gets converted into fibrous protein fibroin on clotting of blood.

11. Structure and Shape of Protein

Primary Structure	**Secondary Structure**	**Tertiary Structure**	**Quaternary Structure**
The specific sequence of amino acids in the polypeptide chain. Change in amino acids sequence	It is the shape in which the long polypeptide chain can exist. It is of two types : α- helix and β- pleated. These structures arise due	Represents overall folding of the polypeptide chain. It gives rise to the fibrous or globular molecular shapes.	Protein can be composed of two or more polypeptide chains called sub units. The spatial arrangement of

changes the protein. They have covalent bonds.	to regular folding of the backbone of the polypeptide chain due to H-bonding between the C=o and –NH- groups of the peptide bond.	Forces stabilizing the 2^{o} and 3^{o} structures are hydrogen bonds, disulphide linkages, van der waal's and electrostatic forces of attraction.	these sub units with respect to each other quaternary structure of the protein.

12. Denaturation of Protein: The protein in native state, when subjected to a physical change like temperature, pH etc undergoes uncoiling and looses it's biological activity. The 2^{o} and 3^{o} structures are destroyed, only 1^{o} structure is retained.

Renaturation of Protein:

Some proteins regain their biological activity by reversible process it is called Renaturation of Proteins. In such a cases, when temperature in pH of a denatured proteins is brought back to conditions in which the native protein is stable, secondary and tertiary structures of proteins are restored to which leads to recovery of biological activity.

13. Enzymes: These are biocatalyst which catalyse biochemical reactions and generally are globular proteins e.g., invertase, zymase, phenylalaninehydroxylase, urease etc.

14. Vitamins: They are organic compounds required in the diet in small amounts to perform specific biological functions for maintenance of optimum growth and health of the organism. They are classified as follows

(i) Fat Soluble Vitamins: Vitamin A, D, E and K. They are stored in liver and adipose tissues.

(ii) Water Soluble Vitamins: B complex vitamins and vitamin C. They need to supplied regularly in diet as they are excreted in urine and cannot be stored (except vitamin B_{12}) in our body.

Their deficiency causes diseases.

Biotin (Vit H) is however neither fat nor water soluble. It's deficiency leads to loss of hair.

15. Nucleic Acids: These are biomolecules which are long chain polymers of nucleotides. They are:

(i) Deoxyribonucleic acid (DNA)

(ii) Ribonucleic acid (RNA)

They are responsible for protein synthesis and transfer of genetic characteristics to offspring's.

16. Composition of Nucleic Acid:

They are made up of pentose sugar (β-D-2-deoxyribose in DNA and β-D-ribose in RNA), phosphoric acid and nitrogen containing heterocyclic compound (base).

DNA- Bases present are Adenine (A), Thymine (T), Guanine (G) and Cytosine(C).

RNA- contains Adenine (A), Guanine (G), Cytosine(C) and Uracil (U).

17. Nucleoside: The unit formed by the attachment of a base to 1'-position of sugar (Base + Sugar).

18. Nucleotide: Nucleoside and phosphoric acid at 5’-position. Nucleotides are bonded by phosphodiester linkages between 5’ and 3’ carbon atoms of pentose sugar (Base+ Sugar+ Phosphoric Acid).

19. DNA : has a double helical structure with AT and GC linked together through 2 and 3 hydrogen bonds respectively. It is responsible for transfer of genetic characteristics.

20. RNA: is of three types- messenger RNA (m-RNA), ribosomal RNA (r-RNA) and transfer RNA (t-RNA). RNA helps in protein synthesis.

21. Biological Functions of Nuclei Acid: DNA is chemical basis of hereditary and have the coded message for proteins to be synthesized in the cell. RNA carry out the protein synthesis in the cell.

Biomolecules

VSA Type Questions – (1 Mark)

Q1 – Which functional groups are present in monosaccharides?

Ans - —OH and —CHO or —OH and >CO

Q2 – Name an aldopentone, aldohexone and ketohexone.

Ans – Ribose,glucose and fructose respectively.

Q3 – What is animal starch?

Ans – Glycogen.

Q4 – Which types of bonds are present in a protein molecule?

Ans – Peptide bonds, hydrogen bonds, sulphide bonds, ionic bonds etc.

Q5 – Which α-helix or β-helix is more stable?

Ans – α-helix is right handed and is more stable due to intermolecular H bonding between first and fourth amino acid.

Q6 – The sequence of bases in one strand of DNA is TACGGACA. What is the sequence of bases of complementary strand of DNA.

Ans – ATGCCTGT.

Q7 – Name the vitamin whose deficiency causes rickets?

Ans – Vitamin D.

Q8 – Name the purine bases present in DNA.

Ans – Adenine and guanine.

Q9 – Give an example of Vitamin which is

(a)Water soluble (b) Fat soluble

Ans – (a) Vitamin C (b)Vitamin D.

Q10 – Name a protein which is insoluble in water.

Ans – Keratin.

SAI Type Questions

Q1 – Name polysaccharides that make up starch and what is the difference between them.

Ans – Amylose which is linear polymer of α-glucose and amylopectin which is branched polymer of α-glucose. Amylose is water soluble whereas amylopectin is water insoluble.

Q2 – What are anomers?

Ans – Monosaccharide which differ only in the orientation of the —OH group at C-1.e.g, α-glucose and β-glucose.

Q3 – Where does the water present in the egg go after boiling the egg?

Ans – On boiling during denaturation process water gets adsorbed/absorbed in the denatured proteins.

Q4 – Write two main functions of carbohydrates in plants.

Ans – (i) Structural material (ii) Reserved food material.

Q5 – What do you understand by glycosidic linkage?

Ans – During condensation of two monosaccharides, a water molecule given out and two monosaccharides get linked together by an oxide or ethereal linkage (—O—) called as glycosidic linkage.

Q6 – What are essential and non essential amino acid? Give two examples of each type.

Ans – Essential amino acids are those which are not produced in our body.e.g., valine, leucine.

Non-essential amino acids are those which are produced by our body. e.g. glycine and alanine.

Q7 – How do you explain the amphoteric behavior of amino acids?

Ans – Amino acids have both acidic as well as basic group and they react both with acids as well as bases, therefore they are amphoteric in nature.

Q8 – What is the difference between a nucleoside and a nucleotide?

Ans - Nucleoside = sugar + base

Nucleotide = sugar + base + phosphoric acid

Q9 – Define (a) Enzymes (b)Antibody

Ans – (a) Enzymes – they are biological catalyst which catalyse biochemical reactions. e.g.,

$C_{12}H_{22}0_{11} + H_20$ ----------> $C_6H_{12}0_6 + C_6H_{12}0_6$

sucrose glucose fructose

This reaction is catalysed by the enzyme investase.

(b)Antibody – they are the proteins which destroy antigens that cause infections. e.g. vaccination for typhoid produces antibodies in our body to prevent typhoid.

Q10 – What is invert sugar?

Ans – An equimolar aqueous solution of glucose and fructose is called invert sugar.

SA II Type Questions –

Q1 – Give three differences between DNA and RNA.

Ans –

DNA	RNA
1. It has deoxyribose as sugar.	1. it contains ribose as sugar.
2. It contains thymine along with adenine, cytosine and guanine as bases.	2.it contains uracil in place of thymine with other bases.
3. It is responsible for maintaining heredity traits from generation to generation.	3. it is responsible for protein synthesis.

Q2 – Difference between globular protein and fibrous protein.

Ans –

Globular Protein	Fibrous Protein
1. they form α-helix structure. 2. they are water soluble. 3. they involve H bonding.	1. they have β-pleated structure. 2. they are water insoluble. 3. they have strong intermolecular forces of attraction.

Q3 – Give reactions with support cyclic structure of glucose.

Ans – (a)Glucose does not give 2,4-DNP test, Schiff`s test and sodium hydrogen suphide test.

(b)The pentaacetate of glucose does not react with NH_2OH indicating absence of free —CHO group.

(c)Glucose exists in two crystalline form α and β.

Q4 – Define with example

(a)Isoelectric point (b)Mutarotation (c)Transcription

Ans –

(a) Isoelctric point – the pH at which there is no net migration of any ion towards electrode. e.g, amino acids have isoelectric point at pH = 5.5-6.3

(b)Mutarotation - it is spontaneous change in optical rotation when an optically active substance is dissolved in water. e.g, α-glucose when dissolved in water changes its optical rotation from 111^o to $52.5^{o.}$

(c)Transcription – it is process by which m—RNA is generated from DNA. e.g, if DNA has base sequence ATACA then m—RNA has base sequence TATCGT.

Q5 – What happens when glucose reacts with

(a)HI (b) HNO_3 (c)Br_2 water

Ans –

(a) $C_6H_{12}0_6$ + HI ------> n-hexane C_6H_{14}
(b) $C_6H_{12}0_6$ + HNO_3 -------> saccharic acid
(c) $C_6H_{12}0_6$ +Br_2 water --------> gluconic acid

Q6 – Differentiate primary, secondary and tertiary structure of protein.

Ans – -In primary structure specific sequence of amino acid are present joined by covalent bonds.

-secondary structure is responsible for the shape of a protein. α-helix and β-pleated in which polypeptide chains have peptide bonds.

-tertiary structure represents overall folding of polypeptide chain and give rise to the fibrous or globular molecular shape.

Q7. Discuss the specificity and mechanism of enzyme action.

Ans. In case of enzymatic reaction the enzyme is so built that it binds to the substrate in a specific manner. Enzymatic reaction involves following steps (Lock and Key Model)-

Step (i): Binding of substrate(S) to enzyme (E) to form complex

E + S → [ES]* (Enzyme substrate complex)

Step (ii): Product formation in complex

[ES]* → EP (Enzyme product complex)

Step (iii): Dissociation of enzyme product complex, leaving enzyme unchanged

EP → E + P

The specificity of enzyme is due to presence of some specific regions called active site on their surface.

Q8. Mention structural differences between amylopectin and cellulose.

Ans.

Amylopectin	Cellulose
1. It is linear polymer of α-glucose. 2. It consists of branched chains of α-glucose.	1. It is linear polymer of β-glucose. 2. In cellulose, the chains are arranged to form bundles and held together by hydrogen bond between glucose and adjacent strands.

Q9. What deficiency diseases are caused due to lack of vitamins $B_{1,}$ B6 and K in human diet?

Ans.

Vitamins	Deficiency Disease
B_1	Beri beri (loss of appetite)
B_6	Convulsions
K	Increased blood clotting time

Q10. Glucose or Sucrose are soluble in water but cyclohexane and benzene are insoluble in water. Explain.

Ans. Glucose contains five-OH groups and Sucrose contains eight-OH groups, because of this they form intermolecular hydrogen bonding, so they are soluble in water. But benzene and cyclohexane does not contain –OH groups, hence does not form intermolecular hydrogen bonding, so they are not soluble in water.

HOTS Questions

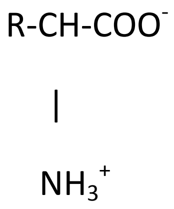
VSA (1 Mark)

Q1. How many atoms are present in the ring of pyranose structure of glucose?

Ans. 5 Carbon atoms and one Oxygen atom.

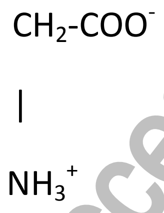
Q2. Write the formula of Zwitter ion for Glycine.

Ans.



$$\begin{array}{l}R\text{-}CH\text{-}COO^- \\ \quad | \\ \quad NH_3^+\end{array}$$

General Formula



$$\begin{array}{l}CH_2\text{-}COO^- \\ | \\ NH_3^+\end{array}$$

Zwitter ion of glycine

Q3. Which proteins possess α-Helix structure?

Ans. Keratin and myosin possess α-Helix structure.

Q4. What is the native state of protein?

Ans. The energetically most stable shape of the protein at normal pH and temperature is called native state.

Q5. Fresh tomatoes are a better source of Vitamin C that which have been stored for some time. Explain.

Ans. Vitamin C is destroyed on prolonged exposure to air due to its oxidation.

Q6. Why are carbohydrates generally active?

Ans. It is due to the presence of Chiral Carbon atoms in their molecules.

Q7. What type of linkages hold together monomers in DNA?

Ans. Monomers in DNA are linked by phosphate linkages.

Q8. Why is cellulose not digested in human body?

Ans. It is due to the fact that human beings do not have enzymeto digest cellulose.

Q9. Name the enzyme that is used to dissolve blood clots?

Ans. Streptokinase.

Q10. Name two diseases caused due to deficiency of enzymes.

Ans. Albinism and phenylketonuria.

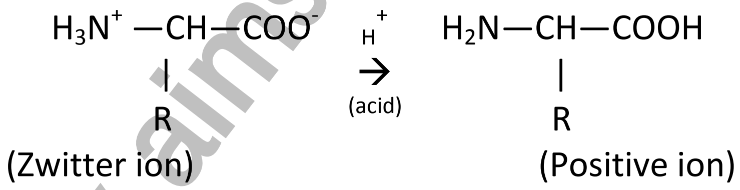
SA Type I (2 Marks)

Q1. Give reasons for the following-

(i) On electrolysis in acidic solution amino acids migrate towards cathode, while in alkaline solution these migrate towards anode.

(ii) The monoamino monocarboxylic acids have two pK_a values.

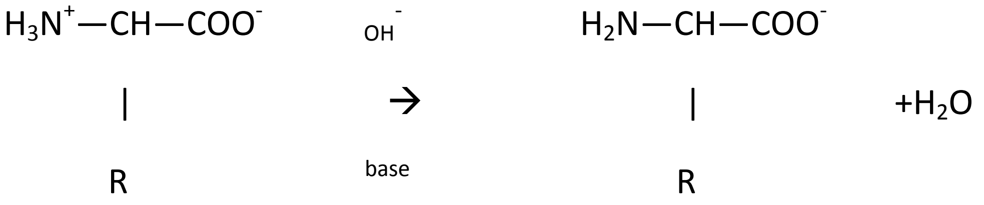
Ans. (i) In acidic solution, the carboxylate anion accept a proton and gets converted into carboxylic group resulting in the formation of positive ion.



$$H_3N^+-\underset{\underset{R}{|}}{CH}-COO^- \xrightarrow[\text{(acid)}]{H^+} H_2N-\underset{\underset{R}{|}}{CH}-COOH$$

(Zwitter ion) (Positive ion)

In presence of a base the NH_3^+ ion changes to $—NH_2$ group by losing a proton and this gives a negative ion.

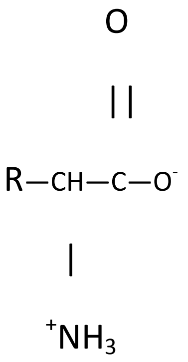


$$H_3N^+-\underset{\underset{R}{|}}{CH}-COO^- \xrightarrow[\text{base}]{OH^-} H_2N-\underset{\underset{R}{|}}{CH}-COO^- + H_2O$$

(Zwitter ion) (Negative ion)

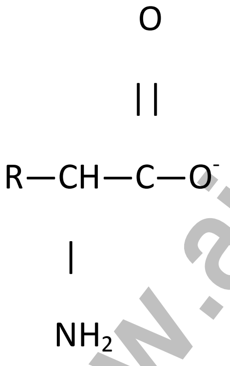
This means that in acidic medium, the amino acid migrates towards the cathode while in alkaline solution it migrates towards anode on electrolysis.

(ii) In aqueous solution, monoamino monocarboxylic amino acid behaves like salt at isoelectric point. At a pH lower than isoelectric point (i.e. in acidic medium) it shows one pK_a value which corresponds to structure



$$R-\underset{\underset{^+NH_3}{|}}{CH}-\overset{\overset{O}{||}}{C}-O^-$$

and at a pH higher than isoelectric point, it shows a pK_a value which corresponds to another,



$$R-\underset{\underset{NH_2}{|}}{CH}-\overset{\overset{O}{||}}{C}-O^-$$

Q2. Which forces are responsible for the stability of α-helix? Why is it named as 3.6_{13} helix?

Ans. Hydorgen bonds between – N-H and —C=O groups of peptide bonds give stability to the structure.

It is known as 3.6_{13} helix, since each turn of helix has approximately 3.6 amino acid residue and a 13 member ring is formed by hydrogen bonding.

Q3. Write about the following protein synthesis-

(i) Name the location where the protein synthesis occurs?

Ans. Protein synthesis occurs at the ribosome in cytoplasm.

(ii) How do 64 codones code for only 20 amino acids?

Ans. The 64 codones for 20 amino acids; more than one codon can code for same amino acids, e.g., CUU and CUU both can code leucine. Proline is encoded by CCU, CCA, CCG, and CCC.

Q4. Describe the mechanism of replication of DNA.

Ans. Replication of DNA:- The process by which a DNA molecule produces two identical copies of itself is called replication of DNA. In the DNA double helix the sequence of bases in one chain is in complementary to the sequence in the other chain, therefore one controls the other. During all division the two strands of the DNA double helix partly unwind and each serves as the template for the synthesis of a new DNA molecule. DNA replication follows the base pairing rules by which A pairs with T and G pairs with C. Therefore, each daughter molecule is an exact replication of the parent molecule. DNA replication is semi conservative i.e. only half of the parental DNA is conserved and only one strand is synthesized. DNA replication takes place only in 5’→3’ direction.

Q5. Answer the following queries about proteins-

(i) How are proteins related to amino acids?

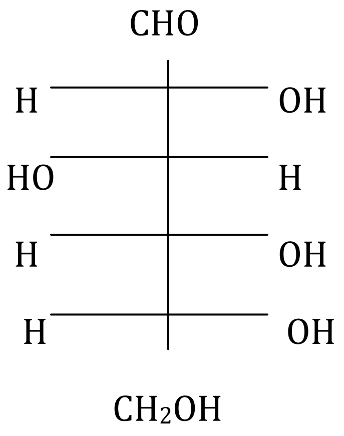
Ans. Proteins consist of large number of amino acids linked to each other by peptide linkage, having 3- dimensional structure. Thus, proteins are biopolymers of amino acids.

(ii) When is protein said to be denatured?

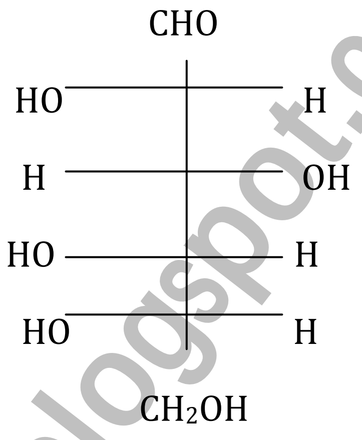
Ans. When natural proteins are subjected to the action of heat, acids or alkalies, they are coagulated or precipitated. The protein in this state is said to be denatured. During denaturation process the water soluble form of globular protein change to water insoluble fibrous protein.

SA (II) 3 Marks

Q6. Draw simple Fischer projections of D and L- glucose. Are these enantiomers?



D-Glucose



L-Glucose

Yes these two Fischer projections are called enantiomers.

Q7. A tripeptide on complete hydrolysis gives glycine, alanine and phenylalanine using three letter symbols write down the possible sequence of tripeptide.

Ans. Each amino acid may be present at the N-terminal as well as C-terminal.

(i) Gly-Ala-Gly

(ii) Gly-Phe-Ala

(iii) Ala-Gly-Phe

(iv) Ala- Phe-Gly

(v) Phe-Ala-Gly

(vi) Phe-Gly-Ala

Q8. Glycine exists as a Zwitter ion but 0-and p-amino benzoic acids do not. Explain.

Ans. The lone pair of N-atom in O- and p-aminobenzoic acid is involved in resonance. The lone pair of N-atom in transferred towards benzene ring. This decreases the acidic character of $-NH_2$ group. Therefore these groups do not transfer and accept H^+ ions, respectively.

Q9. Write short notes on-

(i) Co-enzymes

(ii) Prosthetic groups

Ans. (i) Co-enzymes:- These are usually derived from vitamins such as thaimine, riboflavin, niacin etc. They are loosely held to the protein and can be easily separated by dialysis.

(ii) Prosthetic groups:- They are also derived from vitamins such as biotin but are tightly held to the protein molecule by covalent bonds. They can be separated only by careful hydrolysis.

Q10. The melting points and solubility in water of amino acids are generally higher than that of the corresponding halo acids. Explain.

Ans. The amino acids exists as zwitter ion ($H_3N—CHR—COO^{-}$). They have salt like structure. There are strong dipole-dipole and electrostatic attractions. Therefore, amino acids have high melting points. Amino acids strongly interact with water molecules and are soluble in it. The halo-acids do not have salt like structure and have low melting points. Halo-acids do not interact as strongly with water molecules as do amino acids. Therefore, solubility of amino acids in water is more than those of halo-acids.

Unit-15

POLYMERS

GIST

1. Polymer:

It is a very large molecule having molecular mass 10^3 - 10^7 g mol^{-1}. They are formed by joining together repeating structural units.

2. Classification of Polymers:

(a) Based On Source:

(i) Natural: Found in plants and animals, e.g. Proteins, cellulose, natural rubber, silk, wool.

(ii) Synthetic: Man-made e.g. Nylon, polyester, neoprene, Bakelite, Teflon, PVC, polystyrene.

(b) Based On Structure:

(i) Linear Polymers: this consist of long and straight chain repeating units e.g. Polythene (HDPE), PVC, nylon, polyester.

(ii) Branched Polymers: This contain linear chains having some branches e.g. amylopectin, glycogen etc.

(iii) Cross Linked Polymers: Strong covalent bonds are present between various linear polymer chains. e.g. Bakelite, urea- formaldehyde polymer, melamine, formaldehyde polymer etc.

(c) Based On Mode Of Polymerization:

(i) Addition Polymers: These are formed by the repeated addition of monomer molecules possessing multiple bonds, e.g., polythene, polypropene, polystyrene, PMMA (polymethyl methacrylate)

(ii) Condensation Polymers: These are formed by the repeated condensation reaction of different bifunctional or trifunctional monomers, with the elimination of small molecules like water, HCl, NH_3, alcohol etc. e.g. Bakelite, nylon, polyester, urea- formaldehyde resin.

(d) Based On Molecular Forces:

(i) Elastomers: Forces of interaction between polymer chains is weakest, e.g. natural rubber, neoprene, vulcanized rubber.

(ii) Fibers: Strong hydrogen bonds are present between the polymer chains. They have high tensile strength e.g., nylon, polyester, silk, wool, orlon, rayon etc.

(iii) Thermoplastics: They are linear/slightly branched chains molecules capable of repeated softening on heating and hardening on cooling e.g., polythene, PVC, polystrene, polypropene.

(iv) Thermosetting Plastics: They are cross-linked or heavily branched molecules, which on heating undergo extensive cross-linkages and become infusible, e.g. Bakelite, urea formaldehyde resin.

(e) Based On Growth of Polymerization: Depending upon the mechanism of Polymerization, polymers are classified as

(i) Addition Polymers or Chain Growth Polymers:

They follow mostly free radical mechanism.

(ii) Condensation Polymers or Step Growth Polymers

because they are formed in gradual steps.

Polymer	Monomer	Uses
(i) Polythene	Ethene	Insulation of wires, manufacture of dustbins etc.
(ii) Polytetra Fluroethene(Teflon)	Tetrafluoroethene	Oil seal and Gasket and non Stick kitchen wares
(iii) Polyarcylonitrile	Acrylonitrile	Substitute for wool
(iv) Terylene or Decron	Glycol + Terephthalic Acid	Ropes, safety belts, tyre -cord , sails of boats, saree and dress material
(v) Nylon-6,6	Hexamethylenediamine + Adipic acid	Stocking, socks, ropes, Parachutes, fabrics, bristles of tooth brush
(vi) Nylon-6	Caprolactum	Tyre-cords, Ropes, fabrics
(vii) Novolac	Phenol + Formaldehyde	Used for binding glue, lamin wooden planks
(viii) Phenol Formaldehyde resin	Formaldehyde + Phenol	Combs, records, switches boards
(ix) Melamine polymers	Melamine + Formaldehyde	Manufacture of unbreakable crockery
(x) Buna-S Copolymer	1,3-Butadiene + Styrene	Auto tyres floor tiles, foot- components
(xi) Natural rubber	2-methyl-1,3-butadiene	Used for tyres
(xii) Neoprene	2-chloro-1,3-butadiene	Conveyor belts, gasket , hoses
(xiii) Buna-N	1,3-butadiene + acrylonitrile	Resistance to action of petrol. Make oil seals, tank linings etc.
(xiv) (PHBV) p hydroxybutyrate co- β- hydroxyl valerate (biodegradable)	3-hydroxybutanoic acid + 3-hydroxypantanoic acid	Packaging orthopaedic devices
(xv) Nylon-2-nylon-6	Glycine + aminocaproic acid	It is biodegradable step growth Polymer
(xvi)Poly(glycolicacid	Glycolic acid + lactic acid	Sutures, i.e. for stitching wo

Poly(lactic acid) (dexton) (biodegradable)		after operation. Biodegradables

VSA (1 marks)

1. Name a natural elastomer.

Ans. Natural rubber.

2. Write name of a synthetic polymer which is an ester.

Ans. Nylon 6 or Nylon 6,6.

3. Name of monomer of Nylon 6.

Ans. Aminocaproic acid

4. Write the monomer units of Bakelite.

Ans. Phenol and formaldehyde.

5. Define a copolymer.

Ans. The polymers made by addition polymerisation from two different monomers are termed as **copolymers**, *e.g.*, Buna-S, Buna-N, etc.

6. Write one use of PVC.

Ans.: In manufacture of rain coats& vinyl flooring.

7. Define Polymer.

Ans.: Polymer is defined as very large molecules having molecular mass (10^3-10^7u). These are also referred to as **macromolecules,**

8. Give an example of thermoplastics.

Ans: Thermoplastics are polythene, polystyrene, polyvinyls, etc.

9. To which class of polymers does Nylon-66 belong?

Ans: ***Polyamides***

10. Name the type of monomers in terylene?

Ans: Ethylene glycol and terephthalic acid.

SA-1 (2 marks)

1. Arrange the following polymers in increasing order of their intermolecular forces.

(i) Nylon 6,6, Buna-S, Polythene.

(ii) Nylon 6, Neoprene, Polyvinyl chloride.

Ans. (i) Buna-S < Polythene<Nylon 6, 6

(ii)Neoprene < Polyvinyl chloride < Nylon 6.

2. Classify the following as addition and condensation polymers: Terylene, Bakelite, Polyvinyl chloride, Polythene.
Ans. (i) addition polymers: Polyvinyl chloride, Polythene.

(ii) condensation polymers: Terylene , Bakelite.

3. What is a biodegradable polymer ? Give an example of a biodegradable aliphatic polyester.
Ans. Polymers which decomposes over a period of time due to environmental degradation by bacteria, etc. are called biodegradable polymers. e. g. PHBV

4. How can you differentiate between addition and condensation polymerization

Ans.: In addition polymerization the molecules of the same monomer or different monomers add together on a large scale to form a polymer. The monomers used are unsaturated compounds, *e.g.*, alkenes, alkadienes and their derivatives.

Condensation polymerisation generally involves a repetitive condensation reaction between two di-functional monomers. These polycondensation reactions may result in the loss of some simple molecules as water, alcohol, etc., and lead to the formation of high molecular mass condensation polymers. *e.g.* , Nylon 6,6.
5. What is meant by PTFE? Give its popular name.

Ans.Polytetrafluoroethylene.it is called Teflon.

6. Write chemical name of (Ziegler-Natta catalyst).

Ans.: Triethylaluminium and titanium tetrachloride

7. Write down the two differences between thermoplastic and thermosetting plastic and examples.

Ans.: Thermoplastic are the linear or slightly branched long chain molecules capable of repeatedly softening on heating and hardening on cooling. These polymers possess intermolecular forces of attraction intermediate between elastomers and fibers. Some common thermoplastics are polythene, polystyrene, polyvinyls, etc.

Thermosetting plastic polymers are cross linked or heavily branched molecules, which on heating undergo extensive cross linking in moulds and again become infusible. These cannot be reused. Some common examples are Bakelite, urea-formaldehyde resins, etc.

8.Differentiate Novolac and Bakelite on the basis of structure.

Ans: A linear product of ***Phenol - formaldehyde polymer*** is n**ovolac,** used in paints. Novolac on heating with formaldehyde undergoes cross linking to form an infusible solid mass called **bakelite**. It is used for making combs, phonograph records, electrical switches and handles of various utensils.

9. Distinguish between the terms homopolymer and copolymer and give an example of each.
Ans: the addition polymers formed by the polymerisation of a single monomeric species are known as **homopolymers**, *e.g.*, polythene.
The polymers made by addition polymerisation from two different monomers are termed as **copolymers**, *e.g.*, Buna-S, Buna-N, etc.

10. How will you differentiate between LDP and HDP?

Ans: ***Low density polythene*****:** It is obtained by the polymerization of ethene under high pressure of 1000 to 2000 atmospheres at a temperature of 350 K to 570 K in the presence of traces of dioxygen or a peroxide initiator (catalyst).

Low density polythene is chemically inert and tough but flexible and a poor conductor of electricity.e.g., squeeze bottles, toys and flexible pipes.

High density polythene: It is formed when addition polymerisation of ethene takes place in a hydrocarbon solvent in the presence of a catalyst Ziegler-Natta catalyst at a temperature of 333 K to 343 K and under a pressure of 6-7 atmospheres. HDP consists of linear molecules and has a high density due to close packing. It is more tougher and harder. It is used for manufacturing buckets, dustbins, bottles, pipes, etc.

SA-II (3 marks)

1. Write the names of monomers of the following polymers:
   (i) Nylon 6,6 (ii) Neoprene(iii) Buna –N

Ans. (i) hexamethylenediammine and adipic acid.

(ii) Chloroprene.

(iii)1, 3 – butadiene and acrylonitrile.

3. How are polymers classified on the basis of structure?
Ans. On the basis of structure, the polymers are classified as below:
(i) Linear polymers such as polythene, polyvinyl chloride, HDP etc.
(ii) Branched chain polymers such as low density polythene, LDP, etc.
(iii) Cross linked polymers such as Bakelite, melamine, etc.

4. Write the monomers of the following polymers:
   (i) Buna-N (ii) Teflon(iii) Neoprene.

Ans.(i) 1, 3 – butadiene and acrylonitrile (ii) ***tetrafluoroethene (iii)*** chloroprene.

6. Write use of each orlon and Nylon-6.
Ans: use of orlon is clothing as a substitute for wool& for Nylon-6. use of Nylon-6 is as fibrics

8. Explain elastomeric polymers & Fibres
Ans: These are rubber – like solids with elastic properties. In these elastomeric polymers, the polymer chains are held together by the weakest intermolecular forces. These weak binding forces permit the polymer to be stretched. A few 'crosslinks' are introduced in between the chains, which help the polymer to retract to its original position after the force is released as in vulcanised rubber. The examples are buna-S, buna-N, neoprene, etc. Fibres are

the thread forming solids which possess high tensile strength and high modulus. These characteristics can be attributed to the strong intermolecular forces like hydrogen bonding. These strong forces also lead to close packing of chains and thus impart crystalline nature. The examples are polyamides (nylon 6, 6), polyesters (terylene), etc.

9 . What is the function of sulphur in vulcanisation of rubber?
Ans: Sulphur introduces sulphur cross linkages between the chains. So it becomes more tensile strength, elasticity and resistance to abrasion etc.

10. Write **Commercially Importance of following Polymers**
(1) Polypropene (2) Polystyrene (3) Glyptal
Ans: (1) Manufacture of ropes, toys, pipes, fibres, etc.
(2)As insulator, wrapping material, manufacture of toys, radio and television cabinets.
(3) Manufacture of paints and lacquers.

HOTS QUESTIONS

VSA (1mark)

1. What is the main constituent of bubble gum?
Ans - Styrene - butadiene copolymer (SBR).
2. What is a plasticizer?
Ans; The substances which are added to increase the softness of hard polymers.

3. Draw the structures of the monomer of PAN.

Ans: $CH_2=CH-CN$

4. Give the name of polymer which is used for making non- stick utensils.
Ans: Teflon($CF_2=CF_2$)

5.What is the % of sulphur using during in vulcanization of rubber ?
Ans: 3% to 5%

SA-I(2 marks)

1.Give the common and the IUPAC name of the monomer of natural rubber.

Ans: cis-Isoprene & 2-methyl-1,3-butadiene

2.Discuss the two main purpose of vulcanization of rubber.

Ans: (i)It makes the rubber hard.

(ii)It is more elastic.

(iii)It has more wear and tear resistance.

3.Explain the term ***Thermosetting polymers*** and give one example.

Ans: ***Thermosetting polymers:*** These polymers are cross linked or heavily branched molecules, which on heating undergo extensive cross linking in moulds and again become infusible. These cannot be reused. Some common examples are Bakelite, urea-formaldelyde resins, etc.

4. Why should one always use purest monomer in free radical polymerisation?

Ans: Impurities of other substances if present may inhibit or hinder the chain propagation.

5. How is dacron obtained from ethylene glycol and terephthalic acid?

Ans: It is the condensation product of ethylene glycol and terephthalic acid Carried out at 420 to 460K in the presence of catalyst mixture of zinc acetate and antimony trioxide.

SA-II(3 marks)

1. What does the following polymers stand for ?

(i)PVC (ii) DOP (iii) PAN

Ans: (1) Polyvinylchloride

(2)Dioctylphthalate

(3) Polyacrylonitrile

2. Why is Bakelite a thermosetting polymer?

Ans: It is a cross-linked polymer. On heating it sets permanently into a solid. It cannot be remoulded by heating again.

3. A regular copolymer of ethylene and vinyl chloride contains alternate monomers of each type. What is the weight percent of ethylene in this copolymer?

Ans: the weight percent of ethylene in this copolymer

[28/(28+62.5)] X 100

30.93%

4.$C_6H_{10}=NOH \xrightarrow{\text{Acid}} A \xrightarrow{\text{polymerisation}} B$ Give the products A& B.

A= Aminocaproic acid

B=nylon-6

5.(i) Give an example of a synthetic rubber.

(ii) Mention main advantage of synthetic rubber.

(iii)Arrange the polymers in the increasing order of tensile strength,

Nylon-6, Buna-S,Polythene.

Ans: (i) synthetic rubber is Buna-S

(ii) It is used for making oil seals, tank linings.

(iii) Buna-S<Polythene< Nylon-6

Unit-16 CHEMISTRY IN EVERYDAY LIFE

POINTS TO BE REMEMBERED

1. **DRUGS – Drugs are chemical of low molecular masses, which interact with macromolecular targets and produce a biological response.**
2. **CHEMOTHERAPY- The use of chemicals for therapeutic effect is called chemotherapy.**
3. **CLASSIFICATION OF DRUGS –**

(a) *ON THE BASIS OF PHARMACOLOGICAL EFFECT*-drugs for a particular type of problem e.g. as analgesics-----for pain relieving.

(b) *ON THE BASIS OF DRUG ACTION*-Action of drug on a particular biochemical process.

(c) *ON THE BASIS OF CHEMICAL ACTION*-Drugs having similar structure .eg- sulpha drugs.

(d) *ON THE BASIS OF MOLECULAR TARGETS*- Drugs interacting with biomolecules as lipids, proteins.

4. **ENZYMES AS DRUG TARGETS**

(i) *CATALYTIC ACTION OF ENZYMES*-

(a) Enzymes have active sites which hold the substrate molecule .it can be attracted by reacting molecules.

(b) Substrate is bonded to active sites through hydrogen bonds, ionic bonds, Vander Waal or dipole –dipole interactions.

(ii) *DRUG- ENZYME INTERACTIONS*-

(a)Drug complete with natural substrate for their attachments on the active sites of enzymes .They are called competitive inhibitors.

(b)Some drugs binds to a different site of the enzyme called allosteric sites which changes the shape of active sites.

5. **ANTAGONISTS- The drugs that bind to the receptor site and inhibit its natural function.**
6. **AGONISTS-Drugs mimic the natural messenger by switching on the receptor.**
7. **ANTACIDS-These are compounds which neutralize excess acid of stomach.eg-Aluminium hydroxide, Magnesium hydroxide.**
8. **ANTI HISTAMINES-The drugs which interfere with the natural action of histamines and prevent the allergic reaction. eg- rantidine, tegamet, avil.**
9. **TRANQULIZERS-The class of chemical compounds used for the treatment of stress, mild or even severe mental diseases. Eg- luminal, seconal, equanil, idardil, iproniagid.**
10. **ANALGESICS-They reduce pain without causing impairment of consciousness, mental confusion or some other disturbance of the nervous system.**

Eg - aspirin, seridon, phenacetin.

11. **<u>ANTIMICROBIALS</u>-They tend to prevent/destroy or inhibit the pathogenic action of microbes as bacteria ,virus ,fungi etc. They are classified as**

(i)*<u>ANTIBIOTICS</u>*-Those are the chemicals substances which are produced by micro-organisms and use to kill the pathogenic micro-organism.

Eg- Pencillin , ofloxacin .

***<u>NARROW SPECTRUM ANTI-BIOTICS</u>*-These are effective mainly against gram positive or gram negative bacteria. Eg- Penicillin , streptomycin.**

***<u>BROAD SPECTRUM ANTI-BIOTICS</u>*-They kill or inhibit a wide range of micro-organisms.**

eg- chloramphenicol , tetracycline .

(ii)*<u>ANTISEPTICS OR DISINFECTANT</u>*-These are which either kill/inhibit the growth of micro-organisms. Antiseptics are applied to the living tissues such as wounds, cuts, ulcers etc. eg- furacine, chloroxylenol & terpinol (Dettol) .Disinfectant are applied to inanimate objects such as floors , drainage , system.

Eg- 0.2% solution of phenol is an antiseptic while 1% solution is disinfectant.

12. **<u>ANTIFERTILITY DRUGS</u>- These is the chemical substances used to control the pregnancy. They are also called oral contraceptives or birth control pills.**

Eg-Mifepristone, norethindrone.

13. **<u>ARTIFICIAL SWEETNING AGENTS</u>-These are the chemical compounds which give sweetening effect to the food without adding calorie.**

They are good for diabatic people e.g.- aspartame, saccharin, alitame , sucrolose.

14. **<u>FOOD PRESERVATIVES</u>- They prevents spoilage of food to microbial growth.eg-salt, sugar, and sodium benzoate.**

15. **<u>CLEANSING AGENTS</u>-**

(i) *<u>SOAPS</u>*- They is sodium or potassium salts of long chain fatty acids. They are obtained by the saponification reaction, when fatty acids are heated with aqueous sodium hydroxide.

They do not work well in hard water.

(iii) *<u>TOILETS SOAP</u>*-This is prepared by using better grade of fatty acids and excess of alkali needs to be removed. colour & perfumes are added to make them attractive.

(iv) *<u>MEDICATED SOAPS</u>*- Substances of medicinal value are added.eg- Bithional, Dettol.

16. **<u>SYNTHETIC DETERGENTS</u>-They are cleaning agents having properties of soaps, but actually contain no soap .They can used in both soft and hard water .They are-**

(i)*<u>ANIONIC DETERGENTS</u>*-They are sodium salts of sulphonated long chain alcohols or hydrocarbons.eg-sodium lauryl sulphonate. They are effective in acidic solution.

$CH_3\ (CH_2)\ CH_2OH \rightarrow CH_3\ (CH_2)_{10}CH_2OSO_3H$
(laurylalchol)
$\rightarrow CH_3\ (CH_2)_{10}CH_2SO_3^-Na^+$
(Sodium lauryl sulphonate)

(ii)*CATIONIC DETERGENTS*- They are quaternary ammonium salts of amines with acetates , chlorides, or bromides.They are expensive used to limited extent.eg-cetyltrimethylammoniumbromide

(iii)*NON-IONIC DETERGENTS*- They does not contain any ions. Some liquid dishwashing detergents which are of non-ionic type.

17. BIODEGREDABLE DETERGENTS- The detergents which are linear and can be attacked by micro-organisms are biodegradable.

Eg -sodium 4-(1-dodecyl) benzene \ sulphonate.

18. NON-BIODEGREDABLE DETERGENTS- The detergents which are branched and cannot be decomposed by micro-organisms are called non-biodegdradable.eg-sodium 4-(1,3,5,7 tetramethyloctl)-benzene sulphonate .It creates water pollution.

VERY SHORT ANSWER TYPE QUESTION
(1 marks)

Q-1 Define the term chemotherapy?

Ans-1 Treatment of diseases using chemicals is called chemotherapy.

Q-2 why do we require artificial sweetening agents?

Ans-2 To reduce calorie intake.

Q-3 what are main constituent of Dettol?

Ans-3 Choloroxylenol & Terpinol.

Q-4 what type drug phenacitin?

Ans-4 It is antipyretics.

Q-5 Name the drug that are used to control allergy?

Ans-5. Antihistamines, Citrizine, Avil.

Q-6Why is the use of aspartame limited to cold food and drinks?

Ans-6 It is unstable at cooking temperature and decompose.

Q-7What is tranquilizers? Give an example?

Ans-7 They are the drug which are used to reduce the stress, mild and severe mental disease.

Q-8 what type of drug chloramphenicol?

Ans-8 It is broad spectrum antibiotic.

Q-9 Why is bithional is added to the toilet soap?

Ans-9 It acts as antiseptic.

Q-10 what are food preservatives?

Ans-10 The substances that prevent spoilage of food due to microbial growth. eg- sodium benzonate.

SHORT ANSWER TYPE QUESTION
(2 marks)

Q-1 Mention one important use of the following-

(i) Equanil (ii)Sucrolose

Ans-1 (i) Equanil- It is a tranquilizer.

(ii) Sucrolose-It is an artificial sweetener.

Q-2 Define the following and give one example-

(i)Antipyretics (ii) Antibiotics

Ans-2 (i) Antipyretics- Those drugs which reduce the temperature of body are called Antipyretics. Eg - Paracetamol

(ii) Antibiotics-The drugs which prevent the growth of other micro-organisms. e.g. - Penicillin.

Q-3 Name the medicines used for the treatment of the following-

(i) Tuberculosis (ii) Typhoid

Ans. Tuberculosis- Streptomycin

Typhoid- Choloroamphenicol

Q-4 what are tincture of iodine?

Ans-4 2-3% iodine solution of alcohol water is called tincture of Iodine. It is a powerful antiseptics and is applied on wounds.

Q- 5 What is artificial sweetening agent? Give two examples?

Ans-5 The substances which give sweetening to food but don't add calorie to our body .

Eg- Saccharin, alitame.

Q-6 How is synthetic detergents better than soaps?

Ans- 6 (i) Detergents can be used in hard water but soaps cannot be used.

(ii) Detergents have a stronger cleansing action than soaps.

Q-7 what are sulpha drugs? Give two examples?

Ans-7 a group of drugs which are derivatives of sulphanilamide and are used in place of antibiotics is called sulpha drugs. Eg- sulphadizine, sulphanilamide.

Q-8 what forces are involved in holding the active sites of the enzymes?

Ans-8 The forces are involved in holding the active sites of the enzymes are hydrogen bonding , ionic bonding , dipole-dipole attractions or Vander waals force of attractions.

Q-9 Describe the following giving an example in each case- (i) Edible colours

(ii) Antifertility drugs

(i) Edible colours- They are used for dying food.
Eg- saffron is used to colour rice.

(ii) Antifertility drugs- Those drugs which control the birth of the child are called antifertility drugs.

Q-10 Give two examples of organic compounds used as antiseptics?

Ans-10 Phenol (0.2%), iodoform

SHORT ANSWER TYPE QUESTION (3 marks)

Q-1 what are Biodegredable and non-biodegdredable detergents? Give one example of each.

Ans-1 Detergents having straight hydrocarbon chain and are easily decomposed by micro-organisms are called Biodegredable detergents.The detergents having branched hydrocarbon chain and are not easily decomposed by micro-organisms are called Non-Biodegredable detergents.

Q-2 what are barbiturates? To which class of drugs do they belong? Give two examples.

Ans-2 Derivatives of barbituric acid are called barbiturates. They are tranquilizers. They also act as hypnotics. eg- luminal, seconal.

Q-3 what is the use of –

(i) Benadryl (ii) sodium benzoate (iii) Progesterone

Ans-3 (i) Antihistamines

(ii) Preservatives

(iii) Antifertility drug

Q-4 Identify the type of drug-

(i) Ofloxacin (ii) Aspirin (iii) Cimetidine

Ans- 4 (i) Antibiotic (ii) Analgesics & Antipyretics

(iii) Antihistamines & antacid

Q-5 Describe the following with suitable example-

(i) Disinfectant (ii) Analgesics

(iii) Broad spectrum antibiotics

(i) Disinfectant- chemicals used to kill the micro-organisms can applied on non-living articles.

(ii) Analgesics- They are the drugs which are used to relieve pain . eg – Aspirin , Ibuprofen.

(iii) Broad spectrum antibiotics- They kill the wide range of gram positive and gram negative bacteria.

Eg- Chloramphenicol , ofloxacin.