केन्द्रीय विद्यालय संगठन

KENDRIYA VIDYALAYA SANGATHAN

STUDY MATERIAL

2016-17

CHEMISTRY

CLASS XII

PREFACE

Kendriya Vidyalaya Sangathan is a pioneer organization which caters to the all round development of the students. Time to time various strategies have been adopted to adorn the students with academic excellence.

This support material is one such effort by Kendriya Vidyalaya Sangathan, an empirical endeavour to help students learn more effectively and efficiently. It is designed to give proper platform to students for better practice and understanding of the chapters. This can suitably be used during revision. Ample opportunity has been provided to students through master cards and question banks to expose them to the CBSE pattern. It is also suggested to students to keep in consideration the time-management aspect as well.

I extend my heartiest gratitude to the Kendriya Vidyalaya Sangathan authorities for providing the support material to the students prepared by various Regions. The same has been reviewed by the Regional Subject Committee of Patna Region who have worked arduously to bring out the best for the students. I also convey my regards to the staff of Regional Office, Patna for their genuine cooperation.

In the end, I earnestly hope that this material will not only improve the academic result of the students but also inculcate learning habit in them.

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SOLID STATE

KEY CONCEPTS

As we know that matter exists in different physical states under different conditions of temperature and pressure. For example solid state, liquid, gases , plasma and BEC etc.

Introduction:

1. The state of matter whose m.p. is above room temperature is found in solid state. Their constituent particles are held strongly.
2. Types of solid(Based on arrangement of particles) : 1 : Crystalline 2 :Amorphous
3. Crystalline solids have regular arrangement of constituent particles throughout, melting point is sharp, anisotropic in nature and give clear cut cleavage.
4. Amorphous solids have irregular arrangement of constituent particles, short range order, no sharp melting point, isotropic in nature. They do not exhibit cleavage property.
5. Amorphous silica is used in photovoltaic cells (Device for converting light into electricity, solar panels etc.).
6. Space lattice is the regular 3D arrangement of constituent particles in the crystalline solid.
7. The 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 — No. of atoms per unit cell
   i. Simple cubic unit cell — 8 x1/8 =1
   ii. FCC (Face centered cubic) — 8 x 1/8 + 6 x1/2=4
   iii. BCC (Body centered cubic) — 8 x 1/8 + 1 x1=2
10. Coordination number of spheres in ccp (fcc or hcp) = 12; C.N. in bcc = 8.
11. Hexagonal close packing and cubic close packing have only 74% of the available space occupied.
12. Packing efficiency =volume occupied by spheres (Particles)/volume of unit cell x 100
13. For simple cubic unit cell the packing efficiency=$1x4/3 \times \pi r^3/8 \times r^3 \times 100$ =52.4 %
14. The packing efficiency in **fcc** =$4 \times 4/3 \times \pi r^3/16 \times 2^{1/2} r^3 \times 100$ =74 %
15. The packing efficiency in **bcc** =$2 \times 4/3 \times \pi r^3/64 \times 3^{3/2} r^3 \times 100$ =68 %
16. The packing efficiency in **hcp =74%**
17. Packing efficiency in bcc arrangement is 68% and simple cubic unit cell is 52.4%
18. Unoccupied spaces in solids are called interstitial voids or interstitial sites.
19. Two important interstitial voids are (I). Tetrahedral void and (II). Octahedral void.
20. Radius ratio is the ratio of radius of Cation to the radius of anion.
    a. For tetrahedral arrangement(Cordination Number=4), radius ratio=0.225-0.414
       For octahedral arrangement(Cordination Number=6), radius ratio=0.414-0.732
21. No. of tetrahedral void=2 x N (N=No. of particles)
22. No. of octahedral void=N
23. Formula of a compound depends upon arrangement of constituent particles.
24. Density of unit cell

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

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

25. The relationship between edge length and radius of atom and interatomic or interionic distance for different types of unit is different as given below
    a. Simple cubic unit cell a=2R
    b. f c c a=4R/$\sqrt{2}$
    c. b c c a=4R/$\sqrt{3}$ (where R = Radius of sphere)
26. Imperfection is the irregularity in the arrangement of constituent particles.
27. Point defect or Atomic defect: It is the deviation from ideal arrangement of constituent atoms.
28. Vacancy defect lowers the density of crystal lattice.
29. Interstitial defect increases the density of crystal.
30. Point defects in the ionic crystal may be classified as:
    a. Stoichiometric defect (Ratio of cation and anion is same).
    b. Non Stoichiometric defect (Ratio of cation and anion gets disturbed).
    c. Impurity defects (due to presence of some impurity ions at the lattice sites)
31. Schottky defect lowers the density of crystal. It arises due to missing of equal no. of cations and anions from lattice sites e.g. NaCl.
32. Frenkel defect is the combination of vacancy and interstitial defects. Cations leave their actual lattice sites and come to occupy the interstitial spaces. Density remains the same eg. AgCl, AgBr, ZnS.
33. Non stoichiometric defect
    a. Metal excess defect due to anion vacancy.
    b. Metal excess defect due to presence of interstitial cation.
    c. Metal deficiency due to absence of cation.

SHORT ANSWER QUESTIONS

Q1. What do you mean by paramagnetic substance?
Q2. Which substance exhibit schottky and Frenkel both defects.
Q3. Name a salt which is added to AgCl so as to produce cation vacancies.
Q4. Why Frenkel defects not found in pure Alkali metal halide?
Q5. What is the use of amorphous silica?
Q6. Analysis shows that a metal oxide has the empirical formula $M_{0.98}O_{1.00}$. Calculate the percentage of M^{2+} and M^{3+} ions in the crystal.
Q9. What is F centre?
Q10. What makes Alkali metal halides coloured when heated in alkali metal vapours?

Very Short Answers(1 mark) :

1. How does amorphous silica differ from quartz?
2. Which point defect lowers the density of a crystal?
3. Why is glass called supper cooled liquids?
4. Some of the very old glass objects appear slightly milky instead of being transparent why?
5. What is anisotropy?
6. What is the coordination number of atoms
   a) in fcc structure b) in bcc structure ?

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

a) fcc b) bcc c) simple cubic ?

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

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

Ans. It is 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. Define the following terms with suitable examples
    - Ferromagnetism
    - Paramagnetism
    - Ferrimagnetism
    - 12-16 and 13-15 compounds
5. In terms of band theory what is the difference
    - Between conductor and an insulator
    - Between a conductor and a 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 removed 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 corners 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=0.144nm)?**

Ans. r=0.144nm

a=2 x √2r

=2 x 1.414 x 0.144nm

=0.407nm

4. **Classify each of the following as either a p-type or n-type semi-conductor.**

a) Ge doped with In

b) Si doped with P

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

(b) Since P is a group 15 element and Si is 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.

6. **$CdCl_2$ will introduce impurity defect if added to AgCl crystal. Explain.**

Ans.For every Cd^{++} ion dopped to the AgCl crystal, one cation vacancy is created.

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. Lithium chloride on heating with lithium vapour turns pink. Explain
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 wt= 107.9u).
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.

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 =289x10^{-10} cm, M=52g mol^{-1}, d=7.2g cm^{-3}

$$Z = \frac{d \times a^3 \times Na}{M} = \frac{7.2(g\ cm^{-3)} \times [289 \times 10^{-10}\ cm]^3 \times 6.022 \times 10^{23}(atom\ mol^{-1})}{52\ g\ mol^{-1}}$$

2. An element A crystallizes in FCC structure; 200 g of this element has 4.12 x 10^{24} atoms. If the density of A is 7.2g cm^{-3}, calculate the edge length of unit cell.
3. Niobium crystallizes in bcc structure. If its density is 8.55 cm^{-3}, calculate atomic radius of [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 50u has edge length 290pm. Calculate its density the element has bcc structure (N_A = 6.02 x 10^{23} atoms $mol^{-1)}$.
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 is 2.165g cm^{-3}. NaCl crystallizes in fcc lattice.
9. Find the type of cubic lattice having edge length of 400pm, atomic wt. = 60u and density =6.25g/cc.

HOTS Short Answer:

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 cells are there in 100 cm^3 of Aluminium.
2. Zinc oxide is white but it turns yellow on heating. Explain.

Long Answer(3 Marks):

1. Metal A has face centered cubic lattice. Edge length of lattice cell is $2A^0$. The density of metal is 2.4g $cm^{-3.}$ 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 its density?
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 8.92g/cc.
5. Niobium crystallizes in bcc structure with density 8.55g/cc, Calculate atomic radius using atomic mass i.e. 93u.

HOTS Long Answer:

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

Hint: d=Z X M /a3 X NA

a^3=4X99 / 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 dropped 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.

3. The edge length of the unit cell of metal having molecular weight 75g/mol is A^0 which crystallizes into cubic lattice. If the density is $2g/cm^3$ then find the radius of metal atom ($N_A = 6.022 \times 10^{23}$)
4. The density of KBr is 2.75 gm cm^{-3} . The length of edge of the unit cell is 654 pm. Predict the type of cubic lattice..
   $N_A=6.023 \times 10^{23}$; at mass of K=39: Br. = 80
   Hint- Calculate value of z= 4 so it has fcc lattice
5. CsCl has bcc arrangement and its unit cell edge lenth is 400 pm . calculate the interionic distance of CsCl. Ans. 34604 pm
6. What is the distance between Na^+ and Cl^- in a NaCl crystal if its density is 2.165 gcm^{-3} NaCl crystalline in the fcc lattice. Ans.281pm
7. Copper crystallises with fcc unit cell. If the radius of copper atom is 127.8 pm. Calculate the density of copper metal. At. Mass of Cu=63.55u $N_A= 6.02 \times 10^{23}$ Ans. $a=2\sqrt{2}\ .r$, $a^3=4.723 \times 10^{-23}$, d=8.95/ 5.74 g cm^{-3}
8. Name the substance which shows Schottky and Frenkel defects both.

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SOLUTION

KEY CONCEPTS

Solution is the homogeneous mixture of two or more substances in which the components are uniformly distributed into each other. 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. Ternary solution consists of three components

Solubility - Maximum amount of solute that can be dissolved in 100g of solvent at particular temp. 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 present in 100grm solution.

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

   Percentage by volume is expressed as = $\frac{Volume\ of\ solute(V_B)}{volume\ of\ solution(V_A+V_B)} \times 100$(Liquid- liquid solution)

2. **Mole fraction** it is the ratio of no. of moles of one of the components 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 as volume of solution increases with temperature.

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

No effect of change of temperature on molality as it is mass to mass ratio.

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

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

Vapour 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 mole fraction in the solution at particular temperature.

   $p_A=P^0_A.X_A$, $p_B=P^0_B.X_B$

   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 –

$P_A = P^0_A X_A$, $P_B = P^0_B.X_B$

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

This is only possible if A-B interaction is same as A-A and B-B interaction nearly ideal solution are –

1. Benzene and Toluene
2. Chlorobenzene and Bromobenzene

Very dilute solutions exhibit ideal behavior to greater extent.

Non-ideal solution –

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

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

$P_A > P^0_A$, $P_B > P^0_B$. X_B

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

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

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:

$$\frac{(P^o_A - P_A)}{P^o_A} = X_B$$

Determination of molar mass of solute

$$M_B = \frac{W_B \times M_A \times P^o_A}{W_A \times (P^o_A - P_A)}$$

Elevation in Boiling Point

$$\Delta T_B = K_b . m$$

Where $\Delta T_B = T'_B - T^o_B$

K_b = molal boiling elevation constant or Ebullioscopic costant

m = molality

$$M_B = \frac{K_b \times 1000 \times W_B}{\Delta T_B \times W_A}$$

Depression in Freezing Point:

$$\Delta T_f = k_f . m$$

Where $\Delta T_f = T_f - T'_f$; m = molality

K_f = molal freezing depression constant or cryoscopic cosntant

unit = $K.kgmol^{-1}$

Osmotic Pressure

When two solutions of different concentrations are separated by semipermeable membrane, there is spontaneous flow of solvent from dilute solution to concentrated solution. This phenomenon is Osmosis. The minimum external pressure applied on concentrated solution to stop the flow of solvent is known as Osmotic pressure. It is denoted by **π** and is expressed as

$$\pi V = nRT$$

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

$$\pi = CRT$$

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

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

→**Isotonic solutions** have same osmotic pressure.

→Solutions having comparatively higher osmotic pressure are **Hypertonic Solutions** and those having comparatively lower osmotic pressure are called **hypotonic solutions**.

→Blood fluid possess osmotic pressure equal to that of 0.91% (w/v) solutions of sodium chloride.

→**Abnormal molecular mass**: Molar mass of solute in solution either less or more than the normal molar mass is called abnormal molar mass. Abnormality in the molar mass arises either due to association or dissociation of the solute particles in the solute particles in the solution. Such abnormality in the calculation of molecular mass is overcome by Van't Hoff factor.

→**Van't Hoff factor(i)** = Observed Colligative property = Normal molecular mass

Normal Colligative properties Observed molecular mass

→**Degree of association(α)** = $\frac{i-1}{1/n - 1}$

→**Degree of dissociation(α)** = (i-1) / (n-1)

Important Questions

Q1- What do you mean by Henry's Law? The Henry's Law constant for oxygen dissolved in water is 4.34×10^4atm at 25° 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° C.

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

$P_A \alpha X_A$; K_H = Henry's Law constant

$P_A = K_H \times X_A$

$K_H = 4.34\times10^4$ atm

$pO_2 = 0.2$ atm

$Xo_2 = pO_2 / K_H = 0.2 / 4.34\times10^4 = 4.6\times10^{-6}$

If we assume 1L solution = 1L water

n water = 1000/18 = 55.5

$XO_2 = nO_2 /(nO_2 + n\ H_2O) \sim = nO_2 / nH_2O$

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

$M = 2.55 \times 10^{-4}$ M

Q.2. What is Van't Hoff factor?

Ans.

Van't Hoff factor(i) = Observed Colligative property / Normal Colligative properties or Normal molecular mass / Observed molecular mass or No.of obs particles / No. of actual particles

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

Ans 5 and 3

Q.4. Why the molecular mass becomes abnormal?

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

Q.5. Define molarity?

Q.6. How molarity is related with percentage and density of solution ?

Ans. M = Mass%xdensity x10 /molar mass

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. $\alpha = i - 1 / 1/n - \mathbf{1}$

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

Ans. It lowers f.p of water

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

Ans. Solutions have lower vapour pressure than pure liquid(solvent).

HOTS

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

Ans. 1M solution

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.

Ans. Azeotropes are constant boiling liquid mixture. Solution showing negative deviation from ideal behaviour.

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 = Mass percent x d x 10 /98

$M_1 V_1 = M_2V_2$

14.5ml

Value based questions:

1. We have many types of water purifiers Zero-B is based on disinfecting properties of iodine. UV purifier is based on killing of bacteria by UV light. These R.O. Purifiers are being used
   (a) What is the full form of R.O. Purifier?
   (b) What is the function of Porous membrane ?
   (c) Which method of purification is more economical for countries using sea water, flash distillation or reverse osmosis for getting portable water. Why?
2. Water is used as coolant in vehicles. In cars, ethylene glycol is used as coolant. In cold countries, water gets frozen so it cannot act as coolant. Ethylene glycol is added to water so that its freezing point is lower and it does not freeze. At hill station snow fall takes place. Clearing the snow from the road is essential for smooth running of traffic-
   (a) What is the role of ethylene glycol when added to water?
   (b) Why does sprinkling of salt help in clearing snow covered roads in hilly areas? Explain the phenomenon involved in the process.
   (c) How is life of people affected by snow fall?

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 L=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 g.

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

Q.3. What do you mean by colligative properties? Which colligative property is preferred to determine the molar mass of biomolecule & polymer and why?

Q.4. Define reverse osmosis. Write its one use.

Q.5. Why does an azeotropic mixture distill 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.8. Why is it advised to add ethylene glycol to water in a car radiator in hill station?

Hint: Anti- freeze.

Q 9. (a). Define the following terms.

3. Mole fraction
4. Ideal solution

(b)15 g of an unknown molecular material is dissolved in 450 g of water. The resulting solution freezes at -0.34 ^{0}c . What is the molar mass of material? K_f for water= 1.86 K Kg mol^{-1} .

Ans. 182.35 g/mol

Q 10.(a) Explain the following :

1. Henry's law about dissolution of a gas in a liquid.
2. Boling point elevation constant for a solvent

(b) A solution of glycerol ($C_3H_8O_3$) in water was prepared by dissolving some glycerol in in 500 g of water. The solution has a boiling point of 100.42 ^{0}C . What mass of glycerol was dissolved to make this solution?

K_b for water = 0.512 k Kg mol^{-1}

(hint: $\Delta T_b = \frac{K_B \times W_B \times 1000}{M_B \times W_A}$

Ans. 37.73 g

Q 11. 2 g of benzoic acid (C_6H_5COOH) dissolved in 25 g of benzene shows a depression in freezing point equal to 1.62 K .K_f for benzene is 4.9 K Kg mol^{-1}. What is the percentage association of acid if it forms a dimer in solution. Ans. 99.2%

Q12. Osmotic pressure of a 0.0103 molar solution of an electrolyte is found to be 0.70 atm at 27^0C. Calculate Van't Hoff factor.(R=0.082 L atom mol^{-1} K^{-1}) Ans. 2.76

UNIT-3

ELECTROCHEMISTRY

Concepts:

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. Batteries and fuel cells are very useful forms of galvanic cells

In Electrolytic cell electrical energy is used to carry out a non-spontaneous redox reaction.

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

The standard potential of the cells are related to standard Gibbs energy as

$\Delta_r G^0 = -n F E^0_{cell}$

The standard potential of the cells is related to equilibrium constant as

$\Delta_r G = -RT\ln K = -2.303RT\log K$

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

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

The conductivity, K of an electrolytic solution depends on the concentration of the electrolyte, nature of solvent and temperature.

Molar Conductivity, λ_m, is defined by λ_{sp} /C where C is the concentration in mol L^{-1}

λ_m or $\Lambda_M = \frac{k \times 1000}{M}$

the unit of molar conductivity is Ω^{-1} cm^2 mol^{-1}. Conductivity(Specific conductance) decreases but molar conductivity increases with decrease in concentration. It increases slowly with decrease in concentration for strong electrolyte . there is sharp increase in molar conductivity of weak electrolyte on decreasing concentration or increasing dilution.

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

$$\Lambda_m^\circ = \nu_+ \lambda^0_+ + \nu_- \lambda^0_-$$

Faraday's laws of Electrolysis

I. The amount of chemical reaction which occurs at any electrode during electrolysis by a current is proportional to the quantity of electricity passed through the electrolyte.
II. The amount of different substances liberated by the same quantity of electricity passing through the electrolytic solution is proportional to their chemical equivalent weights.

Cells and Batteries:

Cells are of two types: (a) Primary Cell (b) Secondary cell

There are mainly two types of batteries.

(a)Primary

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 CARRYING 1 MARK

1. Name the factor on which emf of a cell depends:-

Ans. 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.

2. What are the units of molar conductivity?
(cm^2 ohm^{-1} mol^{-1} or Scm^2mol^{-1})

3. What is the EMF of the cell when the cell reaction attains equilibrium?

Ans. Zero

4. What is the electrolyte used in a dry cell?

Ans. A paste of NH_4Cl, MnO_2 and C

8. How is cell constant calculated from conductance values?

Ans. Cell constant= specific conductance/ observed conductance.

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

Ans. Ions

10. Define electrochemical series.

Ans. 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. 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

Ans. Cell reaction is as follows.

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

n = 2

T=298K

$E_{cell} = (E^0Cu^{2+}/Cu - E^0Zn^{2+}/Zn) + 0.0591V \log \frac{[Zn^{2+}(aq)]}{[Cu2+(aq)]}$

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

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

$= 1.10V+2 \times 0.02955$

$= 1.10V + 0.0591$

$= 1.1591V$

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

3. Define corrosion. Write chemical formula of rust.
   Corrosion is a process of deterioration of metal as a result of its reaction with air and water, surrounding it. It is due to formation of sulphides, oxides, carbonates, hydroxides, etc.

   Formula of rust- $Fe_2O_3.xH_2O$

4. How are standard electrode potentials measured?
5. What is cell constant? How it is determined?
6. Why it is necessary to platinize the electrodes of a conductivity cell before it is used for conductance measurement?
7. Why mercury cell gives the constant voltage.
8. What is fuel cell? write reaction involved in H_2-O_2 fuel cell.

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

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

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

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.

Ans. From the cell representation

Ag/Ag^{+} electrode is cathode and Cu/Cu^{2+} electrode is anode .

Reaction at anode **$Cu(s) \rightarrow Cu^{2+}(aq) + 2e^-$**

Reaction at cathode **$2Ag^{+}(aq) + 2e \rightarrow 2Ag(s)$**

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

$= E^0_{Ag+/Ag} - E^0_{Cu2+/Cu}$

$= +.80\ V - (+0.34V)$

$= +0.80V - 0.34V$

$= 0.46V$

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

Ans.(i) No (ii) Yes

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

Since standard reduction potential of Zn^{2+}(E^0Zn^{2+}/Zn = -0.76V) is less than the standard reduction potentialof Cu^{2+} (E^0Cu^{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. Define electrode potential. Why absolute value of reduction potential of electrode cannot be determined?
6. Write the equation showing the effect of concentration on the electrode potential.
7. Derive the relationship between Gibb's free energy change and the cell potential.
8. How Nernst equation can be applied in the calculation of equilibrium constant of any cell reaction?
9. 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?
5. Describe normal hydrogen electrode and its applications.
6. Conductivity of 0.00241 M acetic acid is 7.896×10^{-5} s cm^{-1}. Calculate its molar conductivity if Λ_m^o for acetic acid is 390.5 s cm^2 mol^{-1}. What is its dissociation constant ?
7. Three electrolytic cells A,B,C containing solutions of $ZnSO_4$, $AgNO_3$ and $CuSO_4$ respectively are connected in series. A steady current of 1.5 amperes passed through them until 1.45g of silver deposited at the cathode of cell B. How long did the current flow? What mass of copper and zinc were deposited?

HOT QUESTIONS

1 Mark questions:-

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 of greater problem in winter when salts are spread on roads to melt ice and snow. Why?

Ans: Salts provide electrolytic medium which accelerates electrochemical process.

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 copper displaces Ag from $AgNO_3$ 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.

2 mark questions:-

1. Why is Li best reducing agent where as Fluorine is best oxidizing agent ?

2. Equilibrium constant is related to E^0_{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 ? 2

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 200cc of the solution or Sol B. 1 mol KCl dissolved in 500cc of the solution.

3/ 5 mark questions:-

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

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

3. ‘ Corrosion is an electrochemical phenomenan’, explain.

4. Calculate the pH of following cell: Pt, H_2/ H_2SO_4, if its electrode potential is0.03V.

5 . 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.

6. 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.

7. 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 $E^0_{Zn^{2+}/Zn} = -0.76V$

8. 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?

09 Electrolysis of the solution of MnSO4 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?

Electrochemistry

Q 1.What do you mean by kohlrauch's law? From the following molar conductivities at infinite dilution

Λ^0_m $Ba(OH)_2$ =457.6 Ω^{-1} cm^2 mol^{-1}

Λ^0_m $Ba Cl_2$ = 240.6 Ω^{-1} cm^2 mol^{-1}

Λ^0_m NH_4Cl= 129.8 Ω^{-1} cm^2 mol^{-1}

Calculate Λ^0_m for NH_4OH

Ans. 238.3 $\Omega^{-1}cm^2$ mol^{-1}

Q2. Calculate the equilibrium constant for the reaction at 298 K.

$Zn + Cd^{2+} \rightarrow Zn^{2+} + Cd$

If E^0 Cd^{++}/Cd =-.403 v

E^0 Zn^{++}/Zn= -0.763 v

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Ans.1.52 x 10^{-12}

Q3. Predict the products of electrolysis of the following

(a) a dil. Solution of H_2SO_4 with Pt. electrode

(b). An aqueous solution of $AgNO_3$ with silver electrode

(c) An aq. Solution of $CuSO_4$ using platinum electrode.

(d) An aq. Solution of $CuSO_4$ using copper electrode

Q4. Write the electrode reaction of

(a) Dry Cell (b) Lead storage cell (c) Mercury cell (d)Nickel cadmium cell (e) Fuel Cell

UNIT-4

CHEMICAL KINETICS

CONCEPT

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.

$$\textbf{Avg rate } \Delta x/\Delta t = -\Delta[R]/\Delta t = +\Delta[P]/\Delta t$$

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

$$\textbf{Instantaneous rate } dx/dt = -\, d[R]/dt = d[P]/dt$$

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 which may or may not be equal to stoichiometric coefficient experimentally.

For a reaction

$aA+bB \rightarrow cC+dD$

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

Where powers P and Q are determined experimentally

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

ORDER OF REACTION- The sum of powers to which the concentrations terms are raised in a rate law expression is called order of reactions. For above case order = P+Q: orders of rkn is determined experimentally

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. OR

Minimum energy required to initiate the chemical reaction.

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

Arhenius Equation-

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

K-rate constant

A-Arrhenius energy

E_a-Activation energy

R- Rate constant

T-Temperature

Log K = Log A- Ea / (2.303RT)

Energy of activation can be evaluated as

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

1 MARK QUESTION

1. The gas phase decomposition of acetaldehyde

$$CH_3CHO \rightarrow CH_4 + CO$$

Follows the rate law of 3/2 order.What is the unit of its rate constant?

Ans. sec^{-1}

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

$$H_2O_2 + 3I^- + 2H^+ \rightarrow 2H_2O + I_3^-$$

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

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 = $k [X]^2$

$= k [3X]^2$

$= 9k [X]^2$

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. Why rate of reaction does not remain constant throughout?

Ans: The reaction rate depends on concentration of the reactants.

7. Define specific reaction rate or rate constant.
Ans: The rate of reaction when the concentration of the reacting species is unity.

8. Write the expression for half-life period of zero and first order reaction?
Ans: For zero order $t_{½} = R_0 / 2K$
For first order $t_{½} = 0.693 / K$

2 MARKS QUESTION

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

Ans. $K_2/K_1 = 4$,

T1= 293K T2 = 313K

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

$\text{Log } [K_2/K_1] = Ea[T_2-T_1]/19.15$

Thus on calculating and substituting values we get….

$Ea = 52.86 \text{ kJ mol}^{-1}$

2. If the decomposition of nitrogen penta 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 = $K [N_2O_5]$

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

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

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

ii) What concentration of N_2O_5 would give a rate of 2.45×10^{-5} mol $L^{-1}s^{-1}$

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

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

$$= 0.82 \text{ M}$$

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

Ans.	ORDER	MOLECULARITY
(1)	It is the sum of the powers of concentration terms in the rate law expression.	It is the number of reacting speci-es undergoing simultaneous Collision in a reaction.
(2)	It is determined experimentally	it is a theoretical concept
(3)	It need not to be a whole number	It is whole no. only
(4)	Order of reaction can be zero,fractional.	It can't be zero or fractional

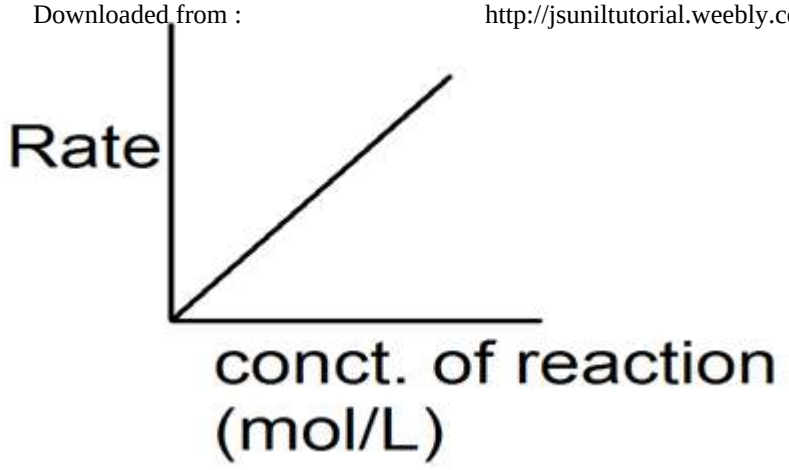
4) Define Threshold energy and activation energy. How they are related?

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 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]

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

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

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’ or ‘specific reaction rate’.

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

10. What is half life period? Derive an 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 per s. How much time will it take to reduce the concentration of the reactant to 1/10 of its initial value.

Ans:-

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

$$t = \frac{2.303}{K} \log \frac{[R_0]}{[R_o] \times 0.1}$$

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

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

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:-

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

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

Ea = 52.89KJ/mol

3. A first order reaction takes 69.3 min for 50% completion. Set up on equation for determining the time needed for 80% completion.

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

$= 0.693/69.3 min$

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

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

$T = 2.303/10^{-2} \log 5$

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. $2NO + O_2 \rightarrow 2NO_2$

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

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

$$\frac{-1}{2}\frac{d[NH_3]}{dt} = \frac{d[N_2]}{dt} + \frac{1}{3}\frac{d[H_2]}{dt}$$

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

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

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

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

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

 = $3.75X10^{-4}$ $molL^{-1}sec^{-1}$

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

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

Rate of production of N_2 = $2.5X10^{-4}$ $molL^{-1}sec^{-1}$

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. During nuclear explosion , one of the products is ^{90}Sr with half life of 28.1 years. If 1 μg of ^{90}Sr was absorbed in the bones of newly born baby instead of calcium, it will remain in the bones upto 60 years if not lost metabolically.

(i) What precautions should be taken while carrying out nuclear explosion?

(ii) Calculate the value of rate constant k.

QUESTIONS CARRYING 5 MARKS

1. 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
2. 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?

1. The half-life period of two samples are 0.1 and 0.4 seconds. Their initial Concentrations are 200 and 50 mol L 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

$CH_3OCH_3 \rightarrow CH_4(g) + H_2(g) + CO(g)$

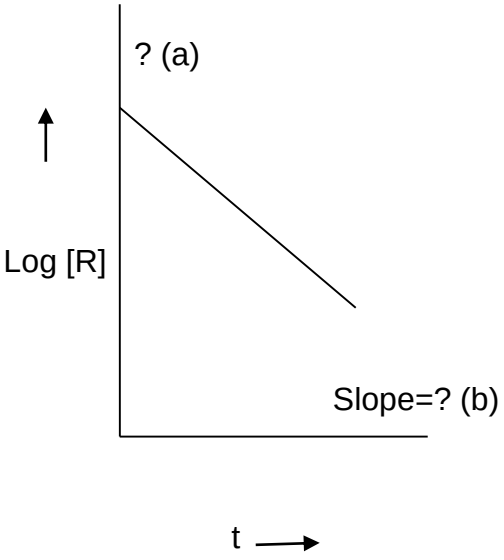
The reaction is carried out at a constant volume of the container at 500^0 C and has $t_{1/2}$ =14.5min.

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.

Q 7. See the graph and answer the following question

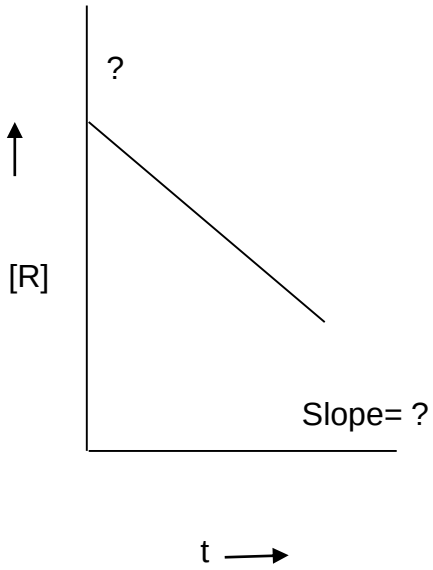
1). What is the order of rk^n?

2) what is the value of a and b?

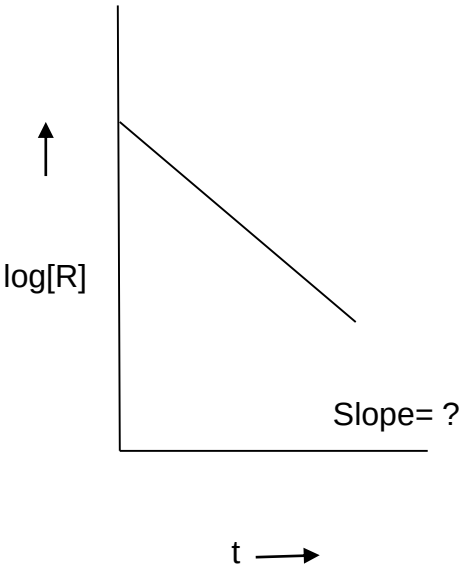


Q 8. 1) what is the order of rk^n?

2) what is the value of slope and intercept?



q 9.1). what is the value of slope?



The branch of the Chemistry wich deals with the study of surface phenomena is called 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 adsorbate and adsorbent, adsorption is of two types*:

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

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

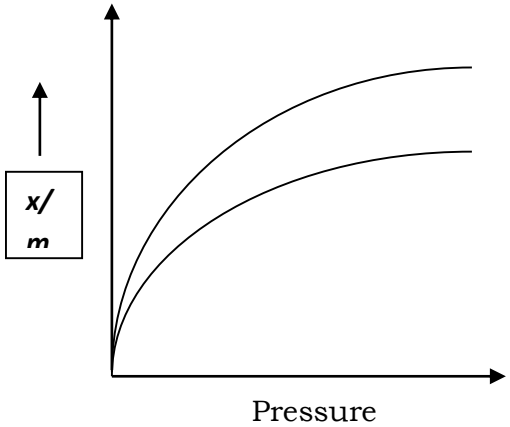
5. ***Adsorption isotherm***:-*The variation in the amount of gas adsorbed by the adsorbent with pressure at constant temperature can be expressed by means of a curve termed as adsorption isotherm.*

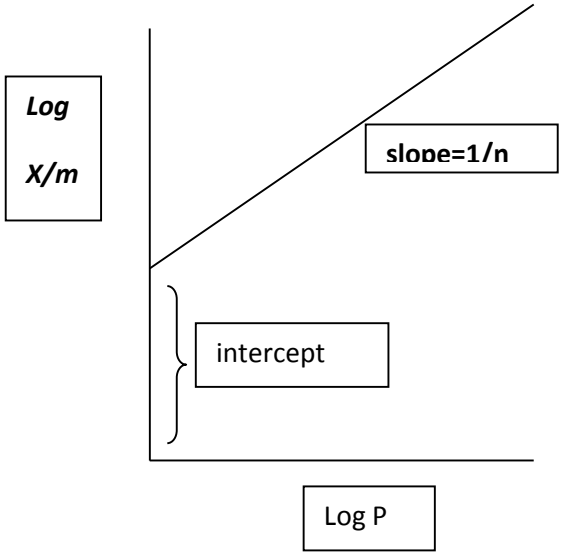
6. ***Application of adsorption***:-

(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 .Factors affecting adsorption:-

(i)**Surface area**: - *Adsorption increases with increases of surface area of adsorbent.*

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

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

(iv)**Pressure: -** *Pressure increases, adsorption increases.*

9. CATALYSIS:- *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. PROMOTERS AND POISONS

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= catalytic promoter*

11. ***Homogenous catalyst*** *– when reactants and catalyst are in same phase.*

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

12. ***Heterogeneous catalyst*** – *The catalytic process in which the reactants and catalyst are in different phase.*

e.g. $SO_2 + O2 \xrightarrow{Pt} 2SO3\ (g)$

13. ***Adsorption theory of Heterogeneous catalysis*** – *It explains the mechanism of heterogeneous catalyst.*

The mechanism involves 5 steps:-

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. IMPORTANT FEATURES OF SOLID CATALYST

Activity - *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. $CO + 3H_2 \xrightarrow{Ni} CH_4 + H2O$

2. $CO + H_2 \xrightarrow{Cu} HCHO$

15. SHAPE SELECTIVE CATALYSIS

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

e.g. Zeolites are good shape selective catalyst. ZSM-5 is used in petrochemicals industry.

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 and size of dispersed phase is from 1nm-1000 nm.

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) Lyophlic 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 of colloidal range when mixed in suitable dispersion medium form macromolecular colloids. Usually polymers belong to this category.

e.g. starch, cellulose 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. eg. Soap solution

(3) Kraft temperature- Temp. 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. $FeCl_3 + 3H_2O \rightarrow Fe(OH)_3\,(sol) + 3HCl$

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

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

1. Charge on colloidal particles – Colloidal particles which carry on electric charge and nature of charge is same on all particles.
2. Electrophoresis - Movement of Colloidal particles towards opposite electrode in presence of external electric field.

3. Coagulation – The process of setting of colloidal particles is called coagulation of the sol.
4. Hardy Sehulze 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.

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

5. Emulsion – Liquid – liquid colloidal system is known as Emulsion.

There are two types of Emulsion.

a) O/W type - Oil dispersed in water. Eg: milk, vanishing cream.
b) W/O type – Water dispersed in oil. Eg: Butter & Cream.

6. 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 miceller 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 for catalyst in 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 hydrophilic.	a) Behave as colloidal size particles at higher conc. b) They have both lyophobic character & Lyophilic

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.
$x/m \propto p^{1/n}$ Here $1/n = 1$

ii) At high pressure range, the extent of adsorption of a gas (x/m) is independent of the applied pressure i.e.
$x/m \propto p^{1/n}$ Here $1/n = 0$

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

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

$\log(x/m) = \log k + 1/n \log p$

Effect of temperature 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.

Alcohols $\xrightarrow[Dehydration]{ZSM-5}$ Gasolene(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 Schulze 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.

5. Explain the following –

(i) Alum is used to purify water.

(ii) Ferric chloride is preferred over potassium chloride to stop bleeding in case of cut.

(iii) Enthalpy change is always negative for adsorption?

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. From ore metal can be obtained economically.
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 magnetic 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. 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.

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

$$ZnCO_3 \longrightarrow ZnO + CO_2$$

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.

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

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

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

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)(Haematite Fe_2O_3)

↓

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 in 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:-

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

20. Vapour phase refining is used for extraction of Nickel (MOND PROCESS) and Zirconium &Titanium (VAN ARKEL PROCESS).

Mond's process : $Ni + 4CO \xrightarrow{\Delta} [Ni(CO)_4] \xrightarrow{\Delta} Ni + 4CO$

VAN ARKEL PROCESS: $Zr + 2I_2 \xrightarrow{\Delta} ZrI_4 \xrightarrow{\Delta} Zr + 2I_2$

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) + $SiO2_{(}$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.

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 $Ni(CO)_4 \rightarrow Ni + 4\,CO$

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 principle 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 principle 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.

A.4- Refer points no 10 &11.

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:-

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

$2Cr_2O_3 \rightarrow 4Cr + 3O_2 \quad \Delta_f G^0 = = + 540$ 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) $2FeS + 3O_2 \rightarrow 2FeO + 2SO_2$, (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- Name the principal ore of aluminium and describe how Al is extracted from its ore.

Q.3- Describe the principles of extraction of Zinc from zinc blende ?

A.3- 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.

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

***

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 outer 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.:- $3HNO_2 \longrightarrow H_2O + 2NO + HNO_3$

  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 members of this group do not form pπ –pπ because there 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 availibility of d-orbitals whereas other elements can.

Trends In Properties:-

Thermal Stability(decresing order) - $NH_3>PH_3>AsH_3>SbH_3>BiH_3$

Bond(E-H) Dissociation Enthalpy(decreasing order)- $NH_3>PH_3>AsH_3>SbH_3>BiH_3$

Reducing character(decreasing order) - $BiH_3 > SbH_3>AsH_3> PH_3 > NH_3$

Basic character(decreasing order)- $NH_3>PH_3>AsH_3>SbH_3>BiH_3$

Acidic character(decreasing order)- $N_2O_3>P_2O_3>As_2O_3>Sb_2O_3>Bi_2O_3$

Boiling points(decreasing order)- $BiH_3>SbH_3>NH_3>AsH_3>PH_3$

Acidic Character(decreasing order)- $N_2O_5>N_2O_4> N_2O_3$

Dinitrogen:-

Preparation

- Commercial preparation – By the liquification& 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
  $N_2 + 3H_2 = 2NH_3$
  $\Delta H^0 = -46.1 kJ/mol$
  Acc.to Lechatelier's principle the favourable conditions for the manufacture of NH_3 are:-
  Optimum temperature : 700 K
  High pressure : 200 atm

Catalytst: 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 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.

$CuSO_4 + 4NH_3 \rightarrow [Cu(NH_3)_4]SO_4$

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
Dinitrogenpentaoxide	N_2O_5	+5	Acidic

NITRIC ACID

Industrial preparation: Ostwald'sprocees – it is based upon catalytic oxidation of ammonia by atmospheric oxygen . The main steps are

$$4NH_3 + 5O_2 \xrightarrow[\Delta]{Rh-Pt\ guage} 4NO + 6H_2O$$

$$2NO + O_2 \Rightarrow 2NO_2$$

$$3NO_2 + H_2O \Rightarrow 2HNO_3 + NO$$

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 protective film of oxide on the surface.

(iii) It oxidises non metals like I_2 to HNO_3, C to CO_2 , S to H_2SO_4

(iv) Brown ring test is used to detect (Nitrate)NO_3^-.

PHOSPHOROUS:-

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

White phosphorous is more reactive than red phosphorous because white P exists as discrete P_4 molecules and red P possess several P_4 molecules linked together.

PHOSPHINE

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

Inert atmosphere of CO_2 [$P_4+3NaOH+3H_2O \rightarrow PH_3+3NaH_2PO_2$]

Other methods: $Ca_3P_2 + 6H_2O \rightarrow 3Ca(OH)_2 + 2PH_3$

$Ca_3P_2 + 6HCl \rightarrow 3CaCl_2 + 2PH_3$

Phosphorous halides

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

Trihalides have pyramidal shape and pentahalides have trigonalbipyramidal structure**.**

OXOACIDS OF PHOSPHOROUS

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

  $4H_3PO_3 \rightarrow 3H_3PO_4+PH_3$

- Acids which contains P-H bond have strong reducing properties.EX:-H_3PO_2
- Hydrogen atom which are attached with oxygen in P-OH bond are ionisable and account for the basicity.

GROUP-16 ELEMENTS (CHALCOGENS)

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

General electronic configuration: ns^2np^4

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 telurium are metalloids.Po is a radioactive metal.
- Oxygen is a diatomic gas while S,Se&Te are octa atomic solid S_8,Se_8&Te_8 molecules which has puckered ' ring' structure**.**

CHEMICAL PROPERTIES

- Common oxidation state:- -2,+2,+4 &+6.
- Due to inert pair 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 OF SULPHUR

DI HALIDES:sp^3hybridisation but angular structure,SCl_2

TETRA HALIDES:SP^3hybridisation-see-saw geometry,SF_4

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

DIOXYGEN

$2Fe^{3+}+SO_2+2H_2O \rightarrow 2Fe^{2+} + SO_4^{2-} + 4H^+$

$5SO_2+2MnO_4^- +2H_2O \rightarrow 5SO_4^{2-} +4H^+ +2Mn^{2+}$

SO_2 molecule is angular.

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:**metallicoxides.Aqueous solutions are alkalis. Neutralize acids to form salts.Ex:Na_2O,K_2o,etc.
- **Amphoteric oxides:-**some metallic oxides exhibit a dual behavior. Neutralize bothacids& bases to form salts.
  Ex:-Al_2O_3,SbO_2,SnO,etc**……..**

Neutral non metal oxide → CO, N_2O, NO

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 oxidisesleadsulphide 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

$4FeS_2 + 110_2 \rightarrow 2Fe_2O_3+8SO_2$

(Iron pyrites)

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

(Zinc blende)

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 gas).

SULPHURIC ACID

PREPARATION

It is manufactured by contact process which involves following reactions.

$S+O_2 \rightarrow SO_2$

$$2SO_2+O_2 \xrightarrow{V_2O_5} 2SO_3$$

$SO_3+H_2SO_4 \rightarrow H_2S_2O_7$(Oleum)

$H_2S_2O_7 + H_2O \rightarrow 2H_2SO_4$

PROPERTIES

1. **H_2SO_4 is a di-basic acid which ionizes as -**

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

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

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

$$C_{12}H_{22}O_{11} \xrightarrow{H_2SO_4} 12C + 11H_2O$$

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

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 colour 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

Bond dissociation Enthalpy(Increasing order): $I_2 < F_2 < Br_2 < Cl_2$

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.

$$2\underset{cold\,\&\,dil}{NaOH} + Cl_2 \rightarrow NaCl + NaOCl + H_2O$$
$$6\underset{hot\,\&\,conc}{NaOH} + 3Cl_2 \rightarrow 5NaCl + NaClO_3 + 3H_2O$$

ii. With dry slaked lime it gives bleaching powder.

$Ca(OH)_2 + Cl_2 \rightarrow Ca(OCl)Cl + H_2O$

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 (SEE TABLE 7.10& FIG.7.8)

Interhalogen compounds

They 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: 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 (1175kJmol^{-1}) was almost identical with that of xenon (1170kJmol^{-1}).

PROPERTIES

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

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

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

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

$XeF_2+PF_5 \rightarrow [XeF]^+[PF_6]^-$

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

SOLVED QUESTIONS

1 MARK QUESTIONS

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

   -AMMONIA FORMS INTERMOLECULAR H-BOND.

2. Why BiH_3 the strongest reducing agent amongst all the hydrides of group 15 elements ?

3. Why does PCl_3 fume in moisture ?

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

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

4. What Happens when $H_3PO_3$is Heated ?

   It disproportionate to give orthophosphoric acid and Phosphine .

   $4H_3PO_3 \rightarrow 3H_3PO_4 + PH_3$

5. 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 atomis bigger than that of O atom . Hence H_2S can dissociate to give H^+ Ions in aqueous solution .

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

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

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

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

8. 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.

9. Draw the structure of peroxosulphuricacid .

10. 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.

Ans- (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.

Phosphine 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 (Ph9.2), Iodide is liberated which can be titrated against a standard solution of sodium thiosulphate . This is a quantitative method for estimating O_3gas.

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

PCl5 has a trigonalbipyramidal structure and the three equatorial P-Cl bonds are equivalent, while the two axial bonds are different and longer than equatorial bonds.

7. NO2 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_2O_4 molecule with even number of electrons.

8. Write the balanced chemical equation for the reaction of Cl2 with hot and concentrated NaOH .Is this reaction a dispropotionationreaction? 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 forms chemical compounds.

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 IClmoe reactive than I_2?

Ans-(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)$AgCl_{(s)}$ +NH3 (aq)→

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

(ii)$Ca_2P_2+6H_2O\rightarrow 3Ca(OH)_2+2PH_3$

(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 XeF_6

$XeF_6+H_2O\rightarrow XeOF_4+2HF$

Structure-square pyramidal. See Fig7.9

(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.

Ans-(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, exhibitparamagnetism.

(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.

$XNO_3 + H_2SO_4 \rightarrow XHSO_4 + HNO_3$

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)HOCl, $HClO_2$, $HClO_3$, $HClO_4$ (Acidic strength)

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

(iii)NH_3, PH_3, AsH_3, SbH_3 (HEH bond angle)

(iv)HF, HCl, HBr, HI (Acidic strength)

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

Ans-

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

(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 is N_2 not particularly reactive?

10) Ammonia acts as 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(H_3PO_2) behave 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)Peroxomonosulphuric 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) →

iv) $NH_3 + NaOCl$→

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

3) Give reasons:

a) Nitric oxide becomes brown when released in air.

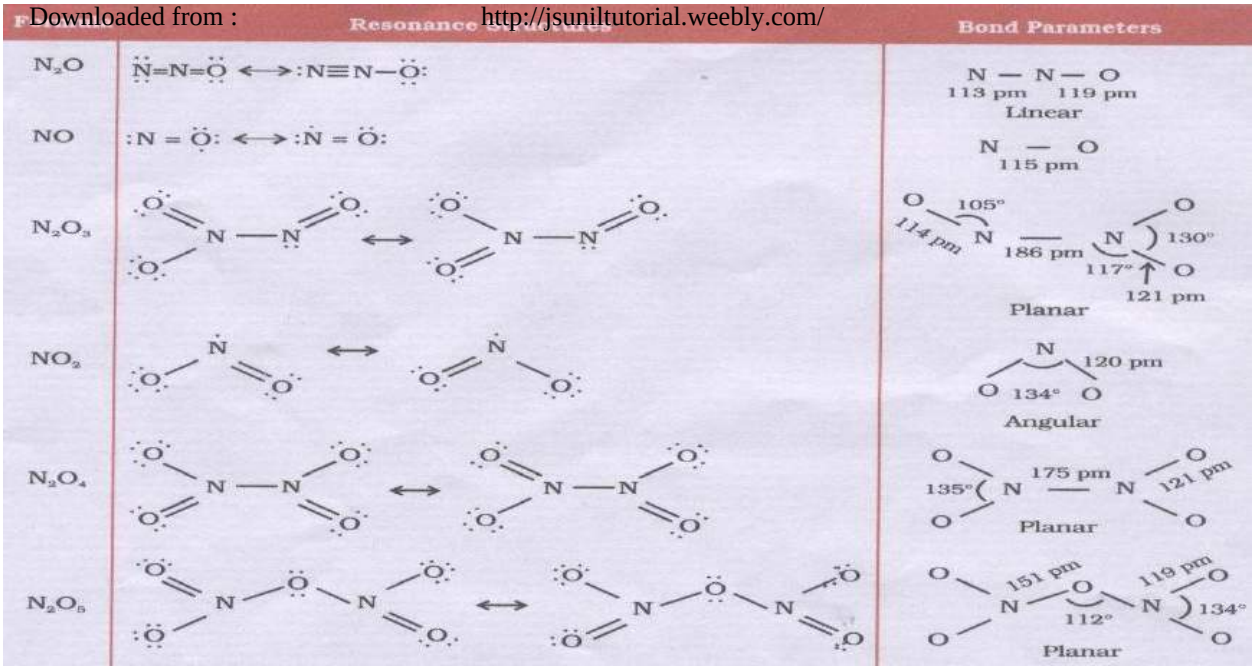
b) PCl5 is ionic in nature in the solid state.

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

5) Addition of Cl_2 to Kl solution gives if brown colour but excess at if turns it colourless. Explain.

Identify hybridization state of central atom and use concept of VSEPR theory .also its shape (geometry) and draw the structure.

PCl_3	sp^3	bp=3	lp=1	Pyramidal
PCl_5	sp^3d	bp=5	lp=0	Trigonalbipyramid
BrF_3	sp^3d	bp=3	lp=2	T- Shape
XeF_2	sp^3d	bp=2	lp=3	Linear
XeF_4	sp^3d^2	bp=4	lp=2	Sq Plane
$XeOF_4$	sp^3d^2	bp=5	lp=1	Sq Pyramid
XeO_3	sp^3	bp=3	lp=1	Pyramidal
XeF_6	sp^3d^3	bp=6	lp=1	Distorted Octahedral
SF_4	sp^3d	bp=4	lp=1	Sea Saw



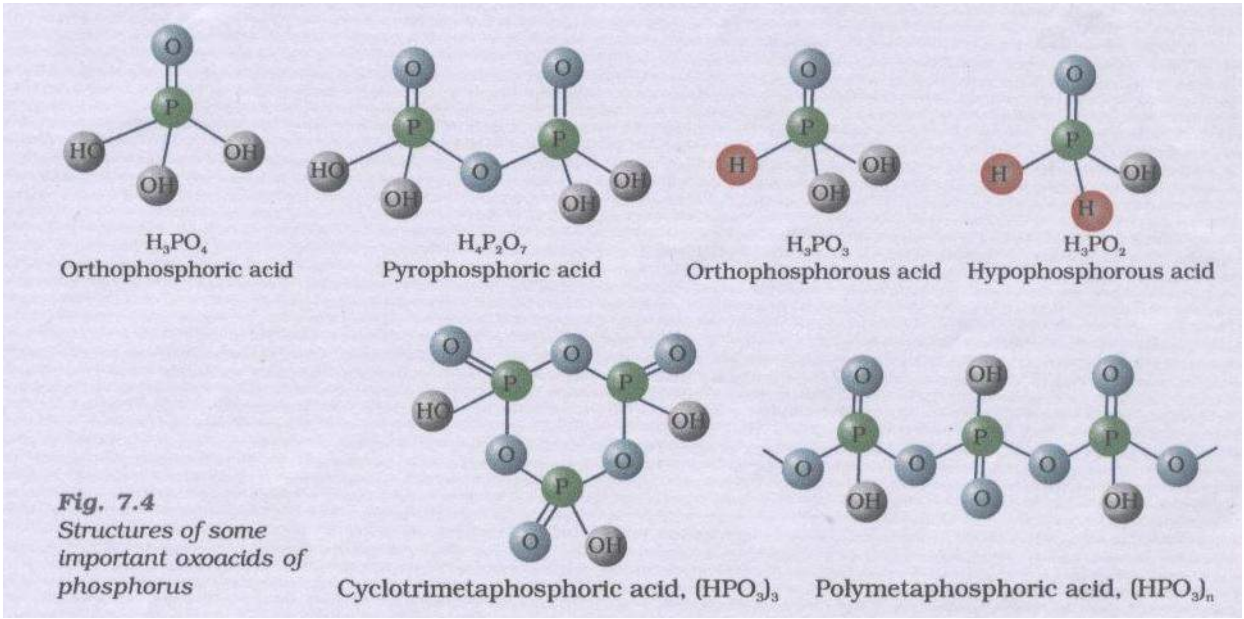
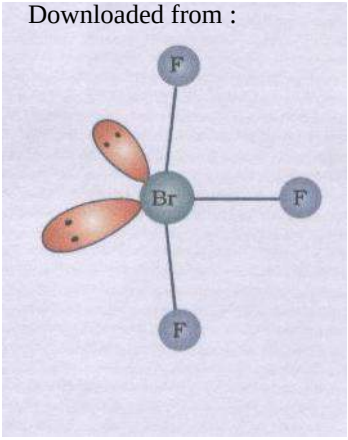
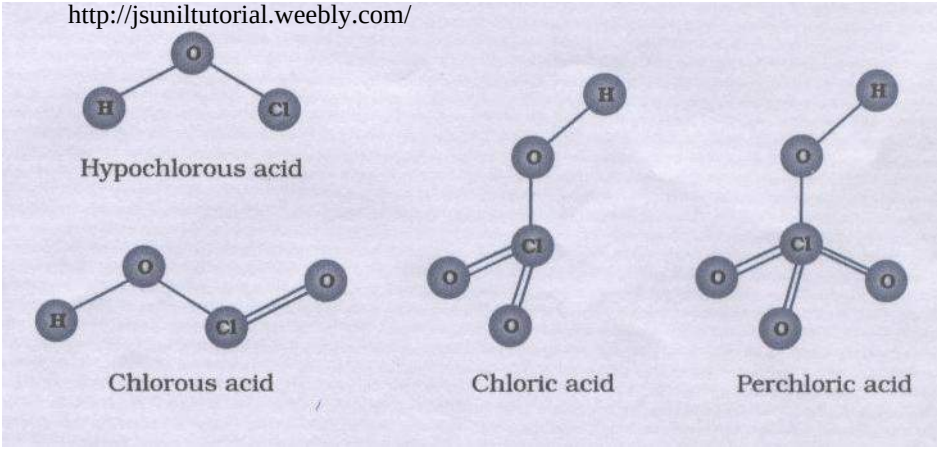


Fig. 7.4 *Structures of some important oxoacids of phosphorus*





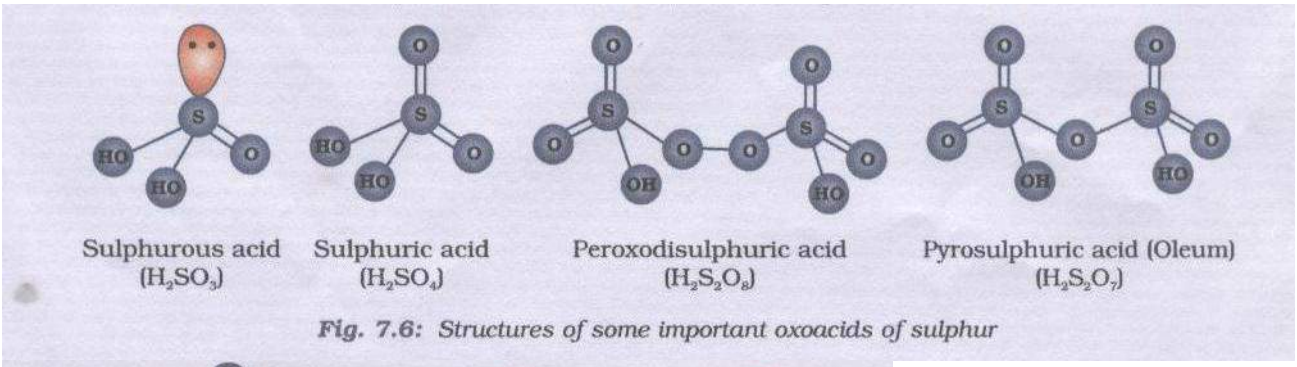
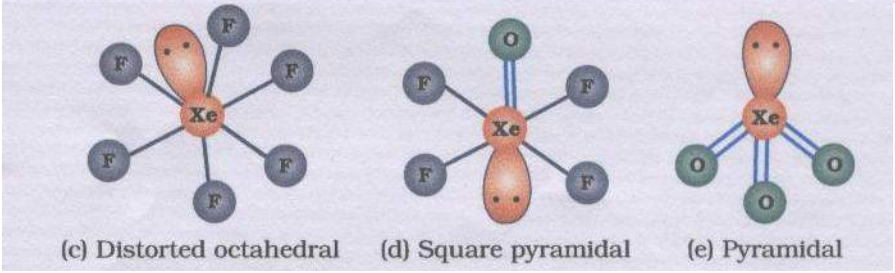
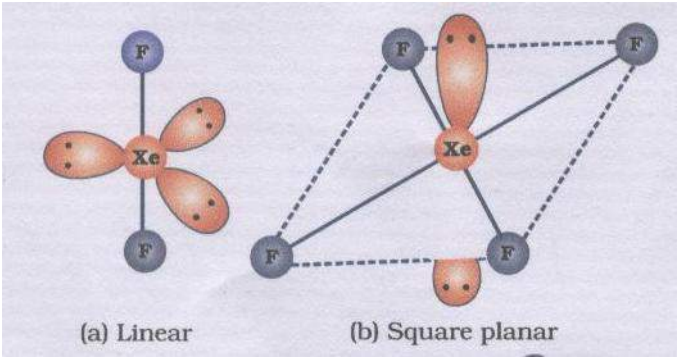


Fig. 7.6: Structures of some important oxoacids of sulphur





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

POINTS TO BE REMEMBERED:

The elements of periodic table belonging to group 3 to 12 are known as d-Block elements.
The general electronic configuration of these elements is $(n-1)d^{1-10}\ ns^{1-2}$
d- Block elements are collectively known as Transition Elements because properties of these elements vary in between s-Block and p-Block elements.
A transition element should have partially filled (n-1) d orbital.
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.
All these elements are metals. They are less electropositive than s-block elements & more electropositive than p-block elements.
The atomic radii decreases from group 3 to 6 (i.e. Sc to Cr) because of increase in effective nuclear charge gradually.
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.
Group 11 &12 elements i.e. Cu & Zn have bigger size due to strong shielding of completely filled (n-1)d orbital.
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.
The highest oxidation state of an element is equal to number of unpaired electrons present in (n-1)d &ns orbital.
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.
Most of transition elements are paramagnetic due to presence of unpaired electrons in (n-1) d orbital.
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.
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.
Most of transition elements form complex compounds due to (i) small size (ii) high charge (iii) presence of vacant d-orbital of suitable energy.
Transition elements have lower value of Reduction Potential due to high ionization potential, high heat of sublimation & low enthalpy of hydration.
Transition elements form interstitial compounds because size of interstitial voids is similar to size of non- metals C, N, O, H.
Transition elements form alloys due to similar ionic radii.
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:--

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

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

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

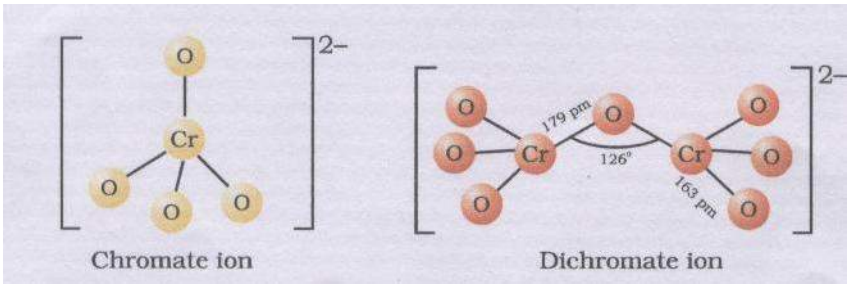
The chromates and dichromates are interconvertible in aqueous solution depending upon Ph of the solution.

A) In Acidic medium(PH<7)

$$2CrO_4^{2-} + 2H^+ \rightarrow Cr_2O_7^{2-} + H_2O$$

B) In basic medium (PH >7)

C) $2CrO_7^{2-} + 2OH^- \rightarrow Cr_2O_4^{2-} + H_2O$



POTASSIUM PERMANGNATE:--

Preparation: --

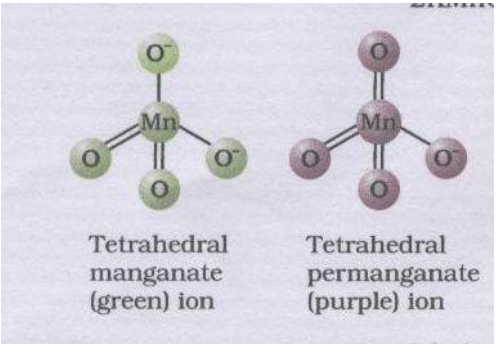
It takes place in two steps:-

(i) Conversion of pyrolusite ore into potassium mangnate
(ii) Conversion of potassium mangnate to potassium permanganate
Following reactions take place:-

$$2\ MnO_2 + 4\ KOH + O_2 \longrightarrow 2\ K_2MnO_4 + 2H_2O$$

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

Structures of manganate and permanganate ions



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 side the electronic configuration of $Fe^{2+}$is [Ar] $3d^6$, i.e. Loss of one electron requires low energy.

Q.7-What is meant by disproportionation? Give two examples.

A.7-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.8- Which metal in the first series of transition metals exhibits +1 oxidation state most frequently and why?

A.8- 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.9- What are inner transition elements?

A.9- 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.10- The paramagnetic character in 3d-transition series elements increases upto Mn and then decreases. Explain why?

A.10- 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.11- Comment on the statement that elements of the first transition series possess many properties different from those of heavier transition metal

A.11-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.12-What are transition elements? Which d-block elements are not regarded as transition elements and why?

A.12- 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.13-What are interstitial compounds? Why are such compounds well known for transition metal?

A.13- 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.14-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.14-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] $3d^1 4s^2$; Sc^{3+}=[Ar] ; it has no unpaired electron so diamagnetic

Cr=[Ar] $3d^5 4s^1$; 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, 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:-

$2\ Cr0_4^{2-}$ (yellow) $+2\ H^+ \rightarrow Cr_2O_7^{2-}$ (orange) $+ H_2O$

$Cr_2O_7^{2-}$ (orange) $+2\ OH^- \rightarrow 2\ Cr0_4^{2-}$ (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 Actinides**

Properties	Lanthanoids	Actinides
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 actinides 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) $MnO_4^- + O H^- + I^- \rightarrow$ ----------+----------+----------

A.10-(i) $MnO_4^- + 8H^+ + 5 Fe^{2+} \rightarrow Mn^{2+} - + 5 Fe^{3+} + 4H_2O$

(ii) $2 MnO_4^- + 5 C_2O_4^{2-} + 16 H^+ \rightarrow 2 Mn^{2+} - + 10 CO_2 + 8H_2O$

(iii) $2 MnO_4^- + H_2O + I^- \rightarrow 2MnO_2 + 2OH^- + IO_3^-$

(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 $[Sc(H_20)_6]$ 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 ∏ -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) Cu^{+} undergoes disproportionation reaction in aq. Medium, where it forms Cu^{2+}. Water is a good complexing agent and forms complex with Cu^{2+} .

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

(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

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 valenceis equal to the coordination number ares fixed for a metal in a complex.
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 carnalite,$KCl.MgCl_2.6H_2O$,Mohr's salt, $FeSO_4.(NH_4)_2SO_4.6H_2O$,potashalum, $KAl(SO_4)_2.12H_2O$,etc. Dissociate into simple ions completely when dissolved inwater. 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)Coordinationentity: 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**:Ligates through two donor atoms. Ex-$C_2O_4^{2-}$(ox); $H_2NCH_2CH_2NH_2$(en)
c) **Polydentate**: which ligates through two or more donor atoms present in a single ligand. Ex-$(EDTA)^{4-}$
d) **Chelating ligands**: Di-orpolydentate ligands that uses two or more donor atoms to bind to a single metal ion to formring-like complexes.(Ox); (edta)
e) **Ambidentateligand**: 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 towhich 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 $3Cl^-$ in $[Co(NH_3)_6]Cl_3$
vii) **Coordination Polyhedron**:The spatial arrangementof 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-$[Co(NH_3)_4 Cl_2]^+$

5. NAMING OF MONONUCLEAR COORDINATION COMPOUNDS

***** For rules refer to the Page No. 242 , Article 9.3.2 in NCERT Text Book and solve all the solved & unsolved examples.

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-NH_2 CH_2NH_2	(1,2-Ethane diamine)	0
NH_2^-	Amido	-1	POSITIVELIGANDS		
NH^{2-}	Imido	-2	NH_2-$NH3^+$	Hydrazinium	+1
ONO^-	Nitrito-O	-1	NO^+	Nitrosonium	+1
NO_2^-	Nitrito-N	-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			

7.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 instructures of coordination compounds.It is further subdivided into the following types-

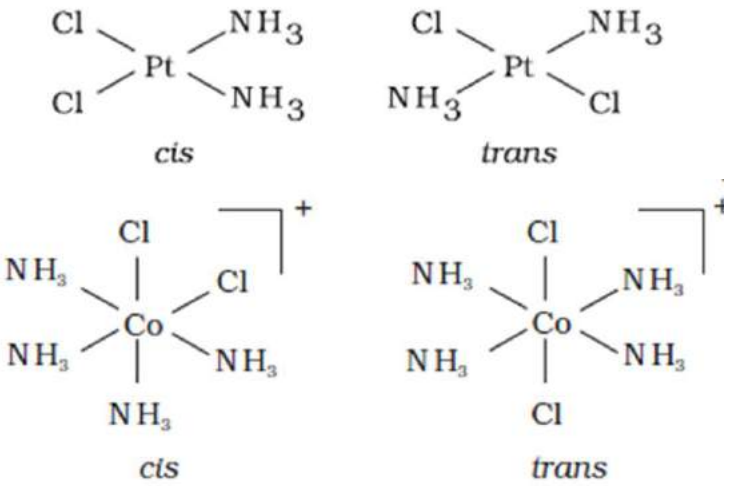
1)**Ionisation isomerism:** This form of isomerism arises when the counterionin a complex salt is itself a potential ligand and can displace a ligand which can then become the counterion.An example is provided by the ionization isomers $[Co(NH_3)_5SO_4]Br$ and $[Co(NH_3)_5Br]SO_4$.
2)**Hydrate or solvate 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 themetal ion or merely present as free solvent molecules in the crystal lattice. An exampleis provided by the aquacomplex $[Cr(H_2O)_6]Cl_3$ (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. Asimple 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: Stereoisomers have the same chemical formula and chemical bonds but they have different spatial arrangement.They areof two kinds

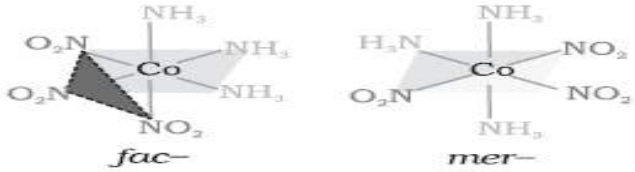
A. Geometrical isomerism

B.Optical isomerism

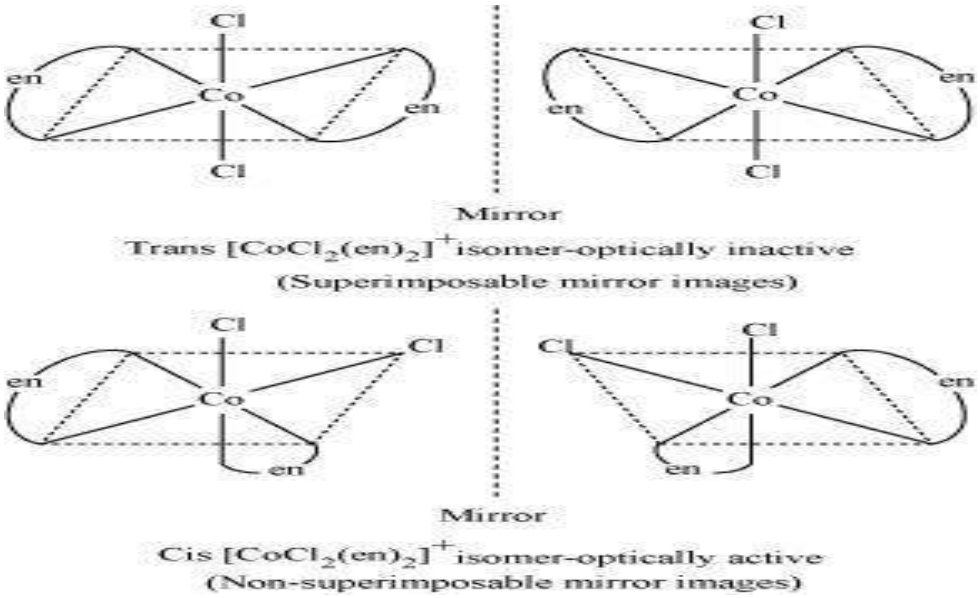
GEOMETRICAL ISOMERISM- This type of isomerism arises in heteroleptic complexes due to different possible geometric arrangements of the ligands. Important examples of this behaviour are found with coordination numbers 4and 6. In a squareplanar complex of formula $[MX_2L_2]$
(X and L are unidentate), the two ligands X may be arranged adjacent to each other in a cis isomer, or opposite to each other in a trans isomer [MABXL]-WhereA,B,X,L are unidentate Two cis-and one trans-isomers are possible.



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.



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



TYPES OF HYBRIDISATION

Coordination number	Type of hybridisation	Acquired geometry
4	sp^3	Tetrahedral
4	dsp^2	Squareplanar
5	sp^3d	Trigonal bipyramidal
6	sp^3d^2	Octahedral
6	d^2sp^3	Octahedral

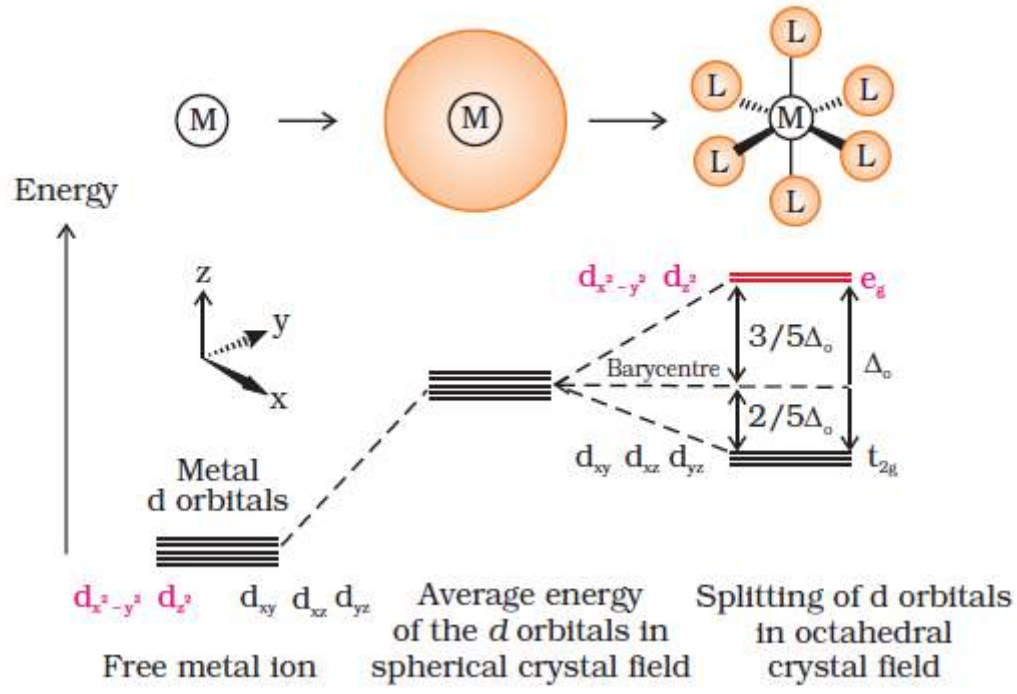
8.CRYSTAL FIELD THEORY:

1. The metal-ligand bond is ionic arising purely from electrostatic interactions between the metal ion and theligand.
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 Δ_o<P, the fourth electron enters oneof the e_g orbitals giving the

configuration $t^3_{2g}\, e^1_g$. Ligands for which Δ_o <P are known as weak field

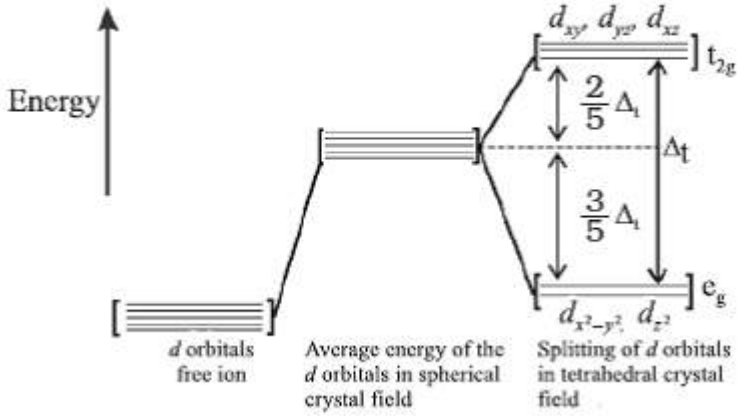
ligands and form high spin complexes.

(ii) IfΔo>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

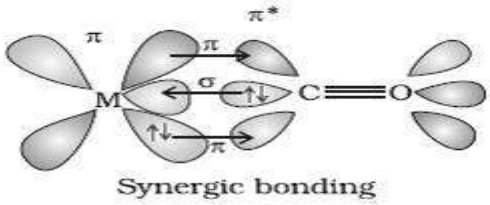
1. The four surrounding ligands approach the central metal atom/ion along the planes between the axes.
2. The t_{2g} orbitals are raised in energy (2/5) $_t$.
3. The two e_g orbitals are lowered in energy (3/5) $_t$
4. The splitting is smaller as compared to octahedral field splitting, Δ_t=(4/9) $_0$.

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 carbonmonoxide. The metal to ligand bonding creates a synergic effect which strengthens the bond between CO and the metal.



Synergic bonding

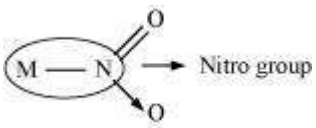
SOLVED QUESTIONS

1 MARK QUESTIONS

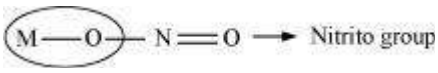
1. What are ambidentate ligands? Give two examples foreach.

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)
ANS. $[Zn(OH)_4]^{2-}$

Q3.Using IUPAC norms write the formula for the following: Hexaamminecobalt(III) sulphate
ANS. $[Co(NH_3)_6]_2(SO_4)_3$

Q4.Using IUPAC norms write the formula for following: Pentaamminenitrito-O-cobalt(III)
ANS. $[Co(ONO)(NH_3)_5]^{2+}$

Q5.Using IUPAC norms write the systematic name of the following :$[Co(NH_3)_6]Cl_3$

ANS. Hexaamminecobalt(III)chloride

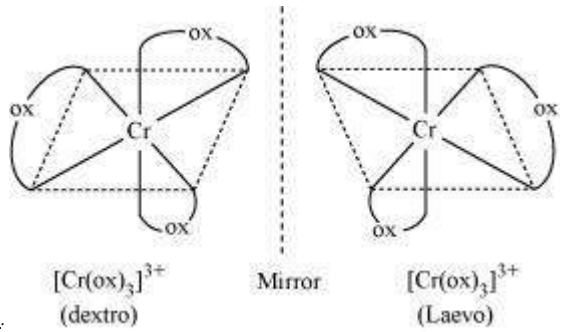
Q6.Using IUPAC norms write the systematic name of the following: $[Pt(NH_3)_2Cl(NH_2CH_3)]Cl$

ANS. Diamminechlorido(methylamine)platinum(II)chloride

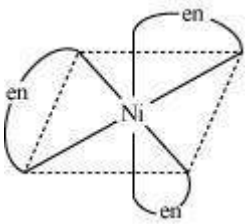
Q7.Using IUPAC norms write the systematic name of the following:$[Co(en)_3]^{3+}$

ANS. Tris(ethane-1, 2-diammine)cobalt(III)ion

Q8.Draw the structures of optical isomers of: $[Cr(C_2O_4)_3]^{3-}$

ANS. 

Q9.What is meant bythechelate effect? Givean example.
ANS. 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.



2/3 MARK QUESTIONS

Q1.What is spectrochemical series? Explain the difference betweena weak field ligand and a strong field ligand.

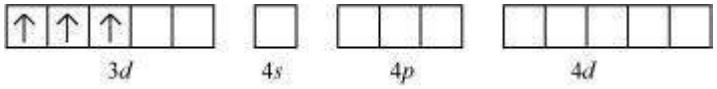
ANS. A spectrochemical series is the arrangement of common ligands in the increasing order of their crystal-field splitting energy (CFSE) values.

$I^- < Br^- < S^{2-} < SCN^- < Cl^- < N^{3-} < F^- < OH^- < C_2O_4^{2-} \sim H_2O < NCS^- \sim H^- < CN^- < NH_3 < en \sim SO_3^{2-} < NO_2^- < phen < CO$

Q2.$[Cr(NH_3)_6]^{3+}$ is paramagnetic while $[Ni(CN)_4]^{2-}$ is diamagnetic. Explain why?

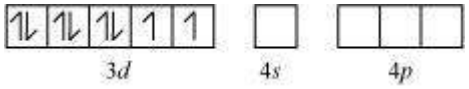
ANS. Cr is in the +3 oxidation state i.e., d^3 configuration. Also, NH_3 is a weak field ligand that does not cause the pairing of the electrons in the 3d orbital.

Cr^{3+} :

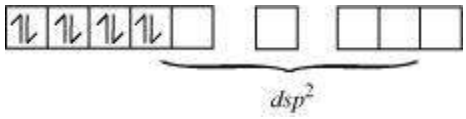


Therefore,it undergoes d^2sp^3 hybridization and the electrons in the3d orbitals remain unpaired.
Hence, it is paramagnetic in nature.
In$[Ni(CN)_4]^{2-}$,Ni exists in the+2 oxidation state i.e., d^8 configuration.

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.

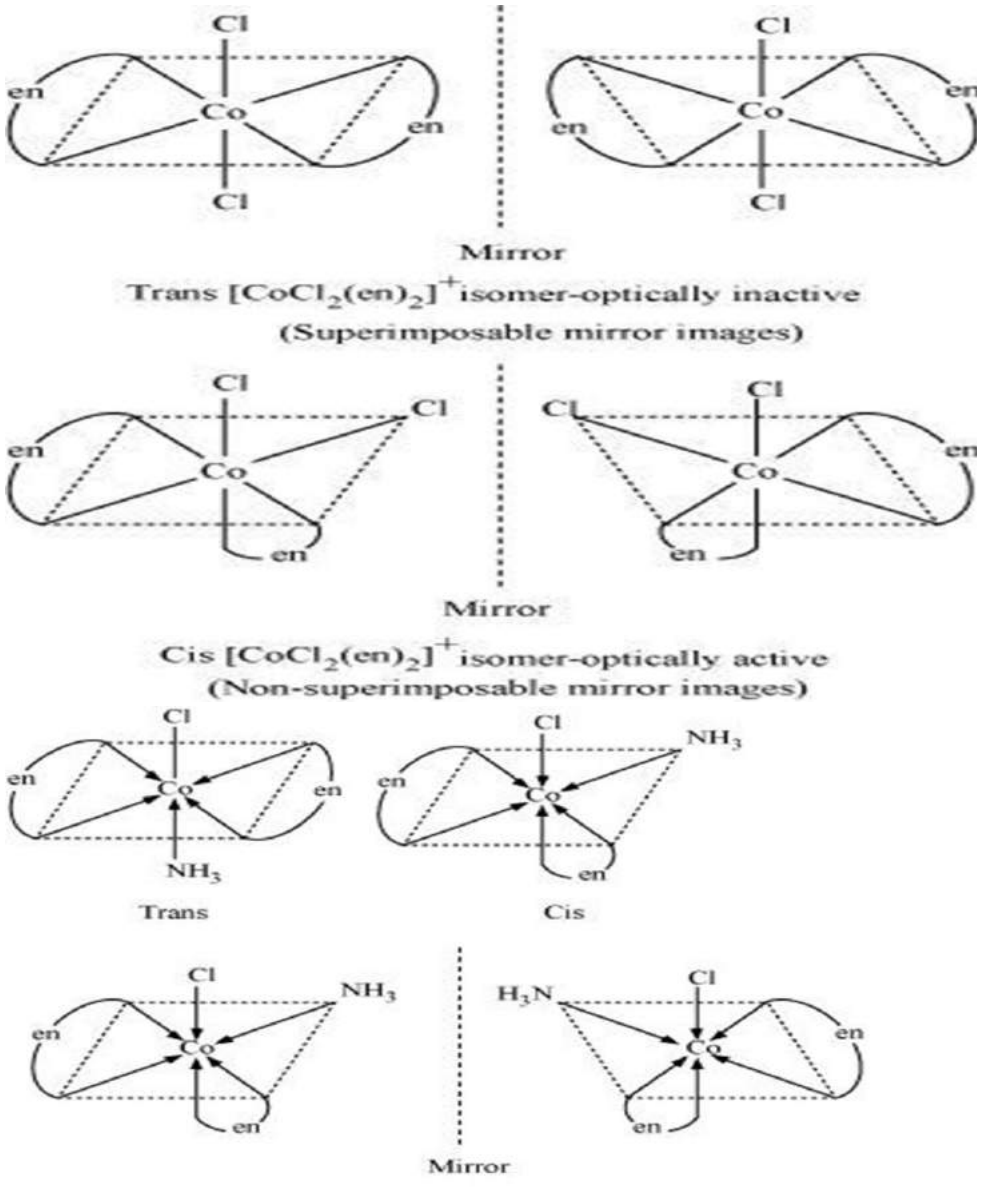
Ans.-In $[Ni(H_2O)_6]^{2+}$, $\ddot{H_2O}$ is a weak field ligand. Therefore, there are unpaired electrons in Ni^{2+}.In this complex, the d electrons from the lower energy level can be excited to the higher energy level i.e., the possibility of d−d transition is present. Hence, $Ni(H_2O)_6]^{2+}$is 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)$[Co(NH_3)_2Cl_2(en)]^+$

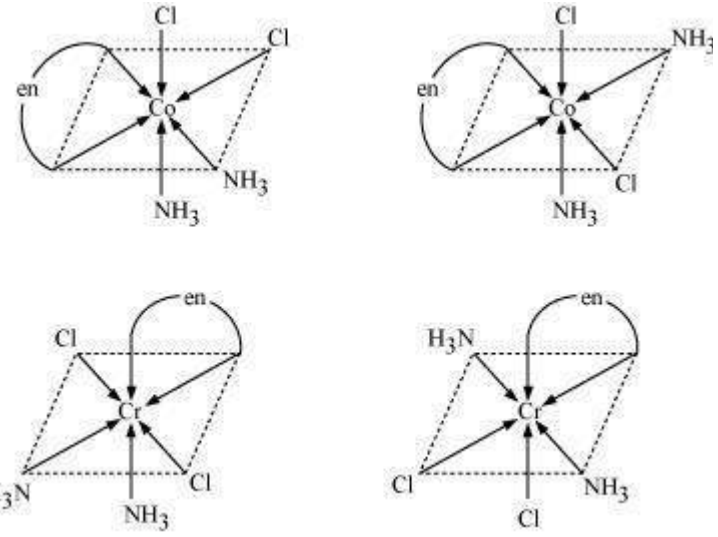
ANS.(i)$[CoCl_2(en)_2]^+$



In total, three isomers are possible.

Trans-isomers are optically inactive.

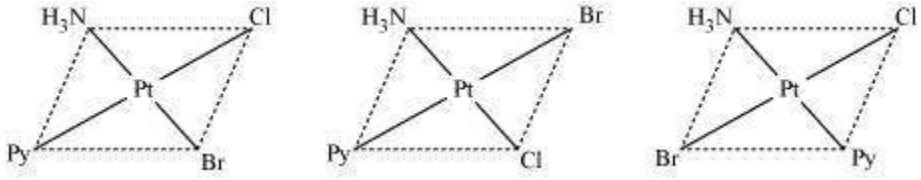
Cis-isomers are optically active.



(iii)$[Co(NH_3)_2Cl_2(en)]^+$

Q3.Writeallthegeometricalisomersof [Pt(NH₃)(Br)(Cl)(py)] andhowmany of thesewill exhibitopticalisomers?

ANS.[Pt(NH₃)(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 involve d in a state of equilibrium. Stability can be expressed quantitatively in terms of stability constant or formation constant.

$$M + 3L \longleftrightarrow ML_3$$

$$\text{Stability constant, } \beta = \frac{[ML_3]}{[M]\,[L]^3}$$

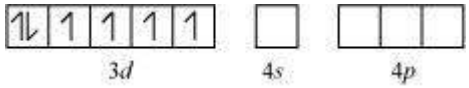
For this reaction, the greater the value of the stability constant, the greater is the proportion of ML_3 in the solution.

5MARKSQUESTIONS

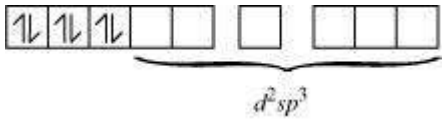
Q1.(a)Discuss the nature of bonding in the following coordination entities on the basis of valence bond theory:

(i)$[Fe(CN)_6]^{4-}$(ii)$[FeF_6]^{3-}$ (iii)$[Co(C_2O_4)3]^{3-}$(iv)$[CoF_6]^{3-}$

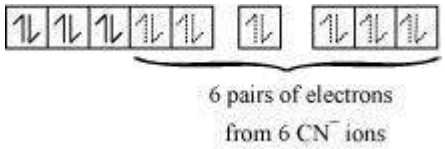
ANS.(i)$[Fe(CN)_6]^{4-}$In the above coordination complex, iron exists in the +II oxidation state.Fe^{2+} : Electronic configuration is$3d^6$ Orbitals of Fe^{2+} ion:



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^3 orbitals. Then,

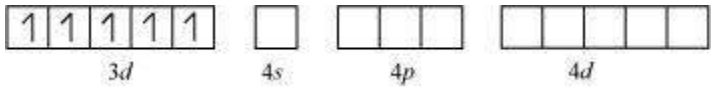


Hence,thegeometryof thecomplexisoctahedralandthe complexis diamagnetic (asthereare nounpairedelectrons).

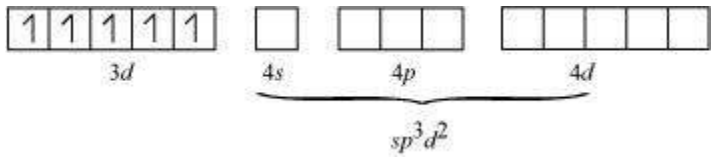
(ii)$[FeF_6]^{3-}$

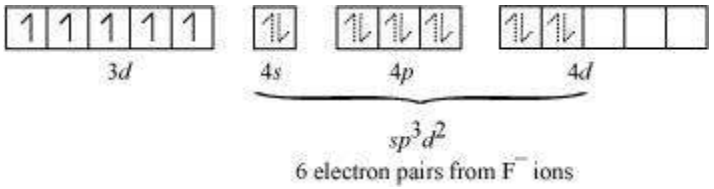
Inthiscomplex, theoxidationstateofFeis+3.

OrbitalsofFe^{+3}ion:



There are $6F^-$ ions. Thus, it will undergo d^2sp^3 or sp^3d^2 hybridization. As $F^-$is aweak 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:

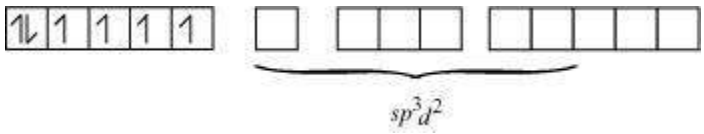




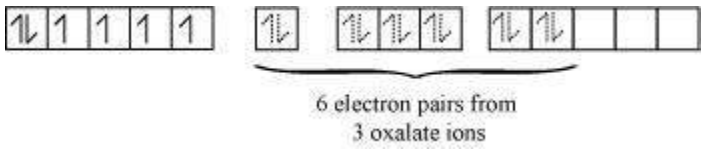
Hence, the geometry of the complex is found to be octahedral.

(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+}:



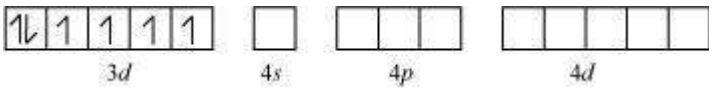
The 6 electron pairs from the 3oxalate ions (oxalate anion is a bidentate ligand) occupy these sp^3d^2 orbitals.



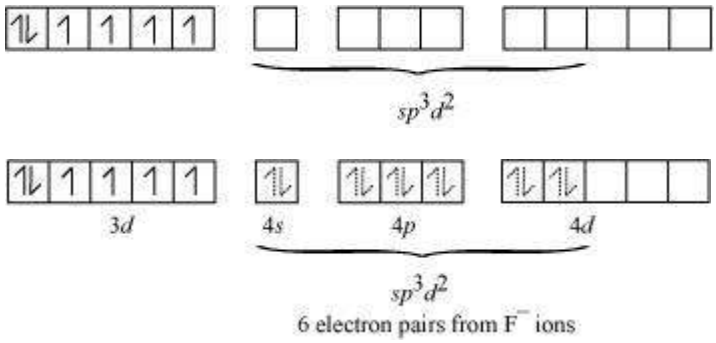
Hence, the geometry of the complex is found to be octahedral.

(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 theIUPAC name foreach of the following complexes and indicate the oxidation state, electronic configuration and coordination number. Also give stereochemistry and magnetic moment of the complex:

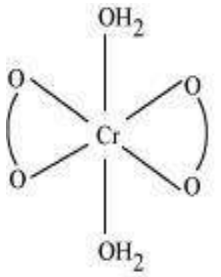
(i)$K[Cr(H_2O)_2(C_2O_4)_2].3H_2O(ii)[Co(NH_3)_5Cl]Cl_2$

ANS.(i) Potassium diaquadioxalatochromate (III)trihydrate.

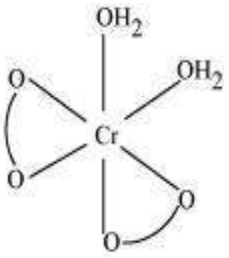
Oxidation state of chromium =3 Electronic configuration:$3d^3:t_{2g}^3$

Coordination number=6 Shape: octahedral

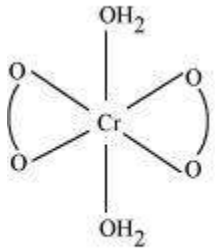
Stereochemistry:

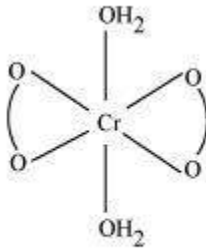


Trans

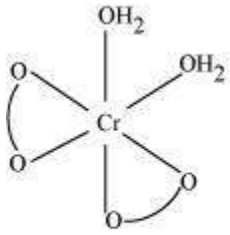


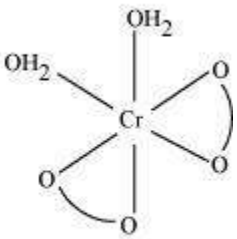
Cis





Trans is optically inactive





Cis is optically active

Magnetic moment, $\mu = \sqrt{n(n+2)}$

$= \sqrt{3(3+2)}$

$= \sqrt{15}$

~4BM

(II) $[Co(NH_3)_5Cl]Cl_2$

IUPAC name: Pentaamminechloridocobalt(III)chloride

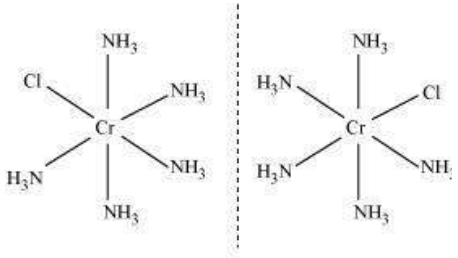
Oxidation state of Co=+3

Coordination number=6

Shape: octahedral.

Electronic configuration:d^6:t_{2g}^6.

Stereochemistry:



2 isomers

Magnetic Moment=0

LEVEL1

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 toa ferric salt solution?

LEVEL2

5.A coordination compound has aformula ($CoCl_3.4NH_3$).It does not liberate NH_3 but 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 $[Co(NH_3)_5Br]SO_4Br$. 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 coppersulphate 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 $Cr(NH)_4Cl_2Br$ has been isolated in two forms, A and B.The form A reacts with $AgNO_3$ solution to give a white precipitate readily solublein 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.H_4^+ion does not form any complex.

iii.$(SCN)^{-1}$ ion is involved in linkage isomerism in co-ordination compounds.

14.A metal ion Mn^+ having d^4 valence electronic configuration combines with three didentate ligands to form complexes. Assuming Δ_o>P draw the diagram showing d orbital splitting during this complex formation. Write the electronic configuration of the valence electrons of the metal Mn^+ ion in terms of t_{2g} and e_g.What type of the hybridization will Mn^+ 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 .

HALOALKANES and HALOARENES

1- Important mechanism

(i) Nucleophilic substitution
(ii) Electrophilic substitution
(iii) Elimination reaction
(iv) Carbylamine reaction
(v) Reimer Tiemann reaction
(vi) Wurtz reaction
(vii) Wurtzfittig reaction

Nucleophillic substitution it involves the replacement 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

$$R - X + OH^- \rightarrow R - OH + X^-$$

$$R - X + O\text{-}C_2H_5 \rightarrow R\text{-}O\text{-}C_2H_5 + X^-$$

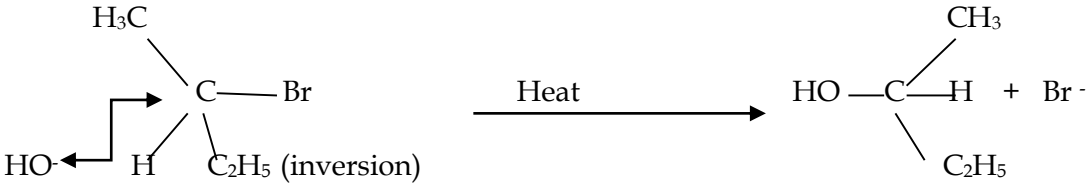
In general

$$R - X + :B^- \rightarrow R - B + X^-$$

$$:B^- \rightarrow OH^-, RO^-, CN^-, RCOO^-, NO_3^-, SH^-, RS^-$$

Bimolecular Nuclephilic substitution SN^2

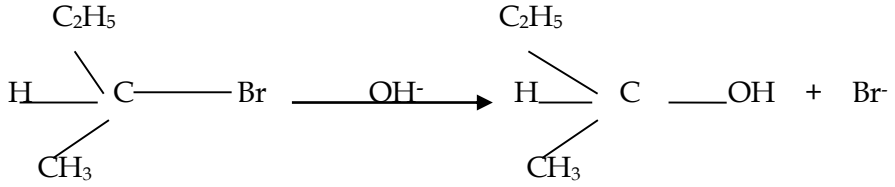
(i) It takes place in one step.
(ii) Most of the SN^2 reactions are of second order but some time when Nucleophillic reagent is present in excess quantity the reaction is of I_{ts} order but still proceeds by SN^2
(iii) It is bimolecular
(iv) It leads to inversion of configuration and attack of Nucleophile occurs from direction opposite to the leaving group.



SN^1 Reactions →

It takes place in two steps.
(i) It is of Istorder.

(ii) Unimolecular
(iii) It leads racemisation i:e inversion as well as retention

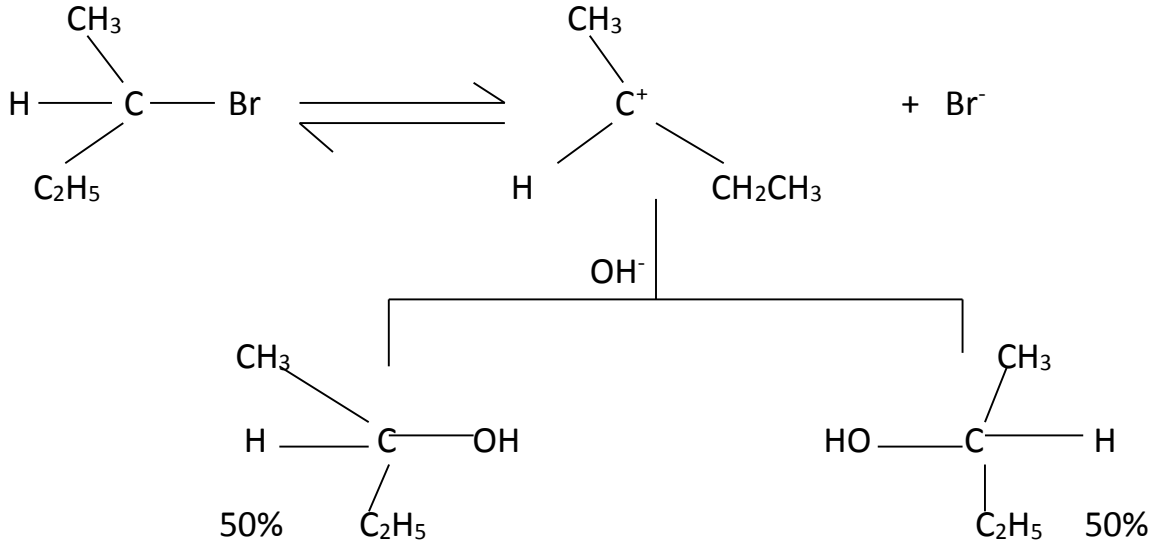


Retention of configuration

The preservation of spatial arrangement of bonds at an asymmetric centre during the chemical reaction.

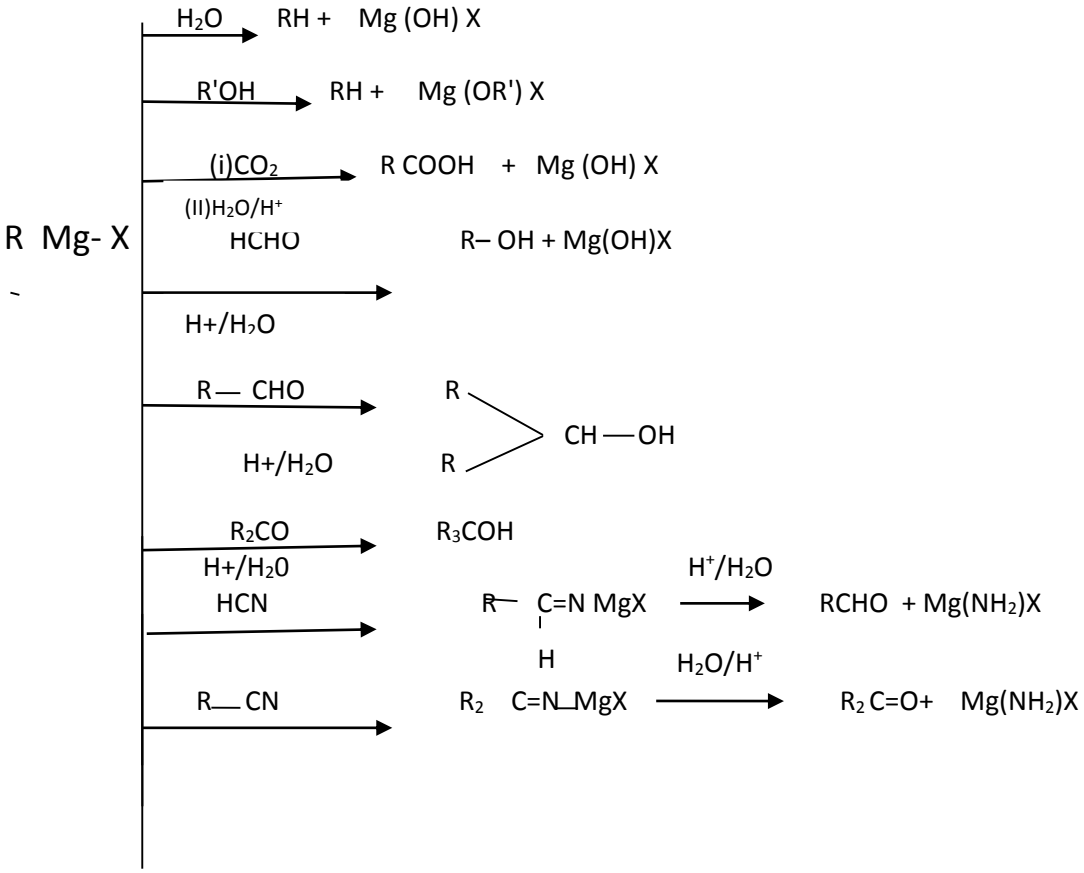
Stereochemistry of SN^1 reaction

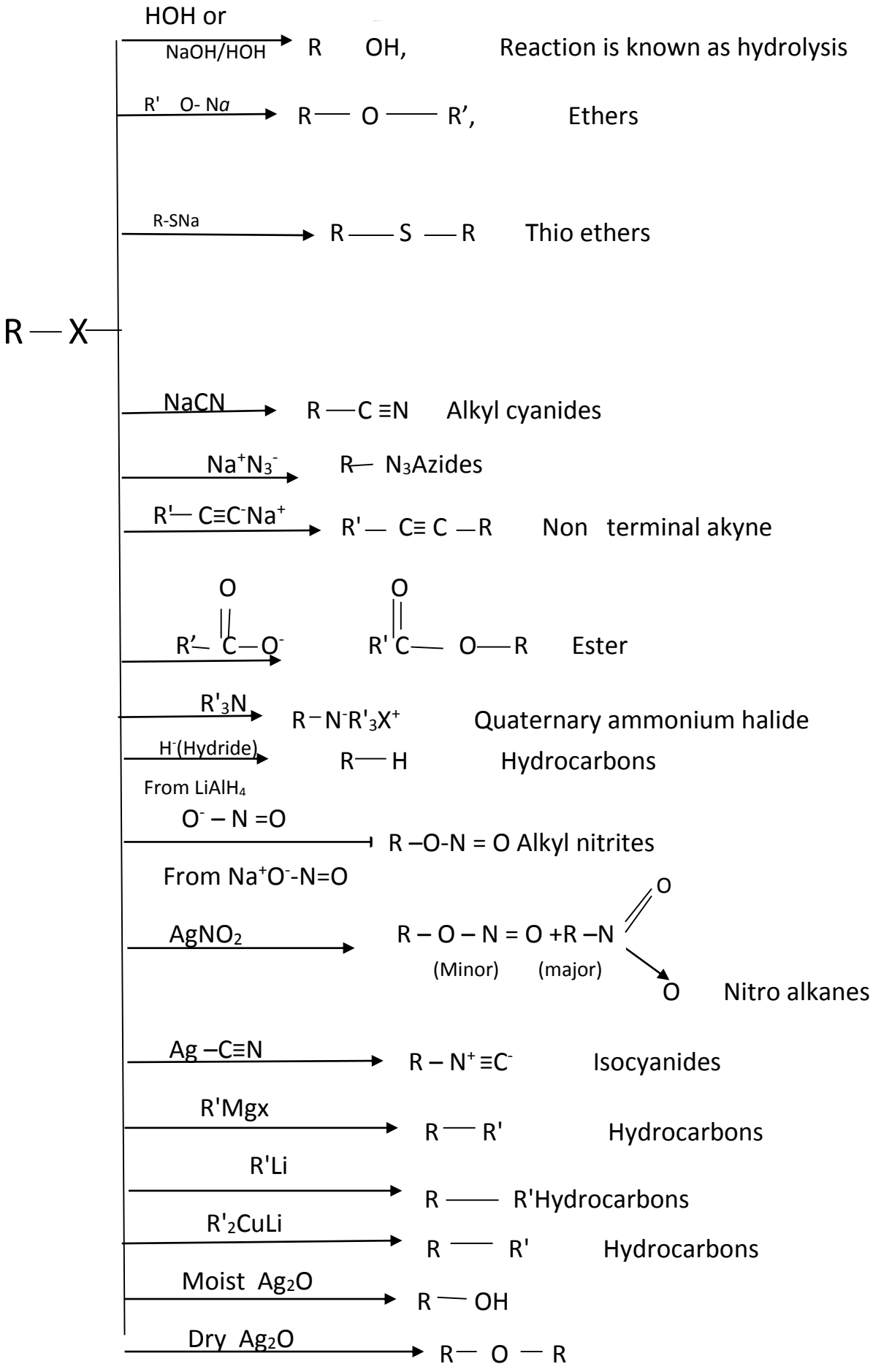
If an alkyl halide is optically active then the product is racemic mixture, Here the attack of Nucleophile takes place from the both side (50:50 mix of the two enantiomers).

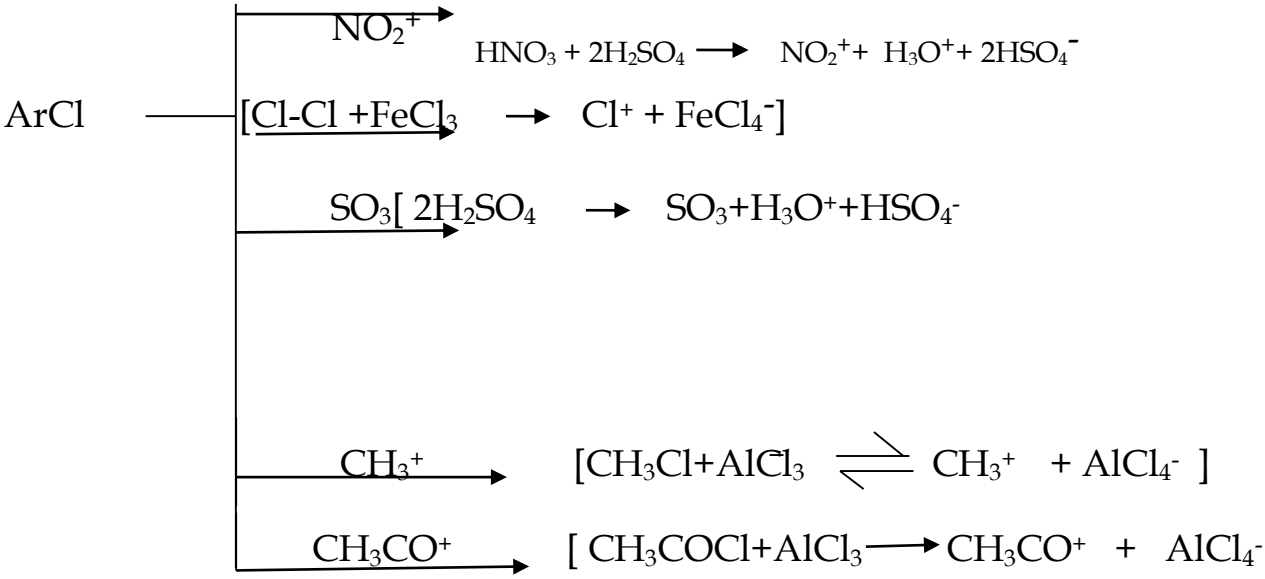


Chemistry of Grignard reagent

RMgX







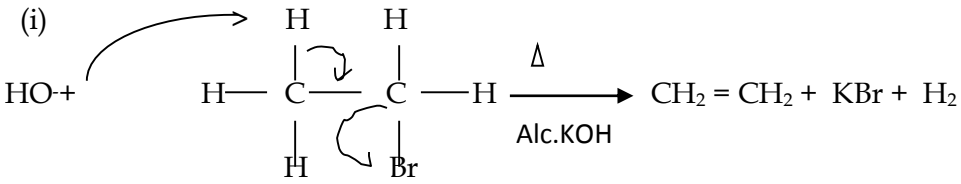
Elimination reaction

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

Saytzaff's Rule



$CH_3 - CH_2 - CH(Br) - CH_3 \rightarrow CH_3 - CH = CH - CH_3$ More highly substituted Alkene

81%

Some important name reaction

1. **Haloform reaction**

$CH_3CH_2OH + 4I_2 + 6\ NaOH \rightarrow CHI_3 + HCOONa + 5NaI + 5H_2O$

$CH_3CH(OH)CH_3 + 4I_2 + 6\ NaOH \rightarrow CHI_3 + CH_3COONa + 5NaI + 5H_2O$

$CH_3COC_6H_5 + 3I_2 + 4NaOH \rightarrow CHI_3 + C_6H_5COONa + 3NaI + 3H_2O$

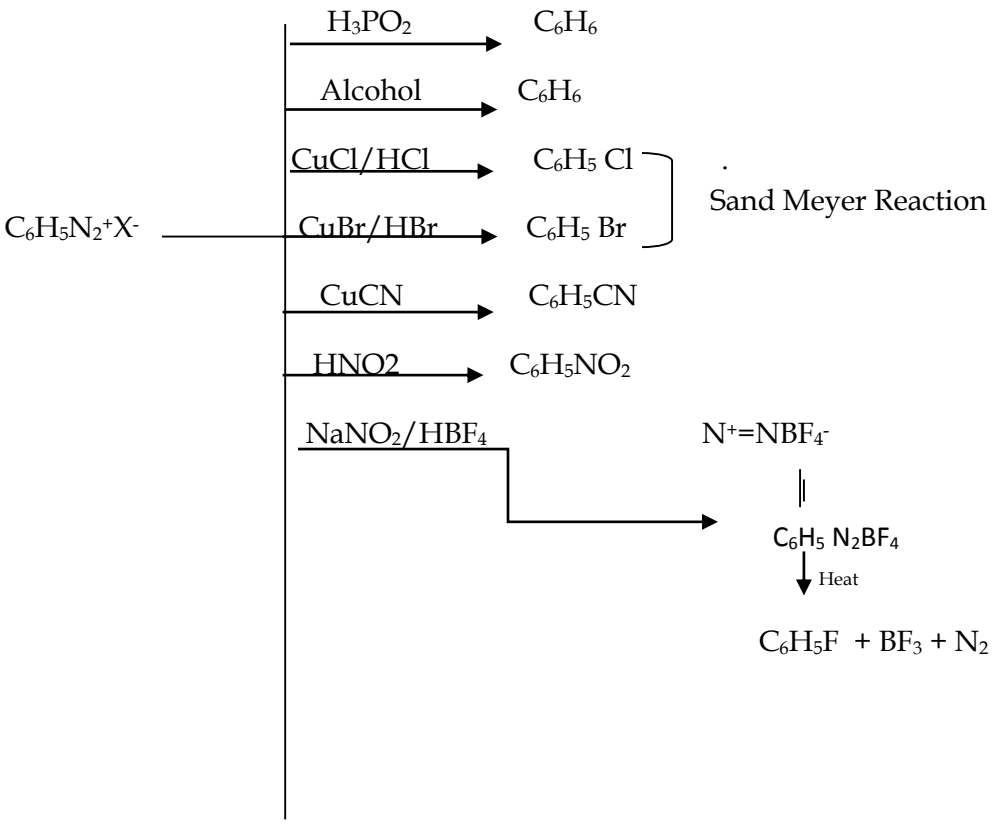
2. Wurtz reaction

$R - X + 2Na + Rx \xrightarrow{ether} R - R + 2\,NaX$

WurtzFITTIG REACTION

$C_6H_5Br + 2Na + Br\,C_2H_5 \xrightarrow{ether} C_6H_5\,C_2H_5 + 2\,NaBr$

Diazonium Salt



CONCEPTUAL QUESTIONS

Q1. Why haloalkanes are more reactive than haloarenes?

Ans. In haloarenes, there is partial double bond character b/w carbon and halogen due to + resonance effect which makes it less reactive.

(ii) In halo benzene, carbon being sp^2 hybridisedwhich is smaller in size than sp^3 present in haloalkanes . So C-Cl bond in aryl halides is shorter and stronger.

Q2. Why do haloalkenesunder gonucleophillic substitution whereas haloarenes under go electophillic substitution .

Ans. Due to more electronegative nature of halide atom in haloalkanescarbon 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.

Q.4. 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.

Q5. Why Grignard reagent should be prepared under an hydrous conditions.?

Ans. Grignard reagent react with H_2O to form alkanes , therefore they are prepared under anhydrous condition.

Q6. 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.

Q7. 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.

Q8. Although chlorine is an electron- withdrawing group, yet it is ortho and para directing inelectrophillic aromatic substitution reactions.Why

Ans.Chlorobenzene is resonance hybrid such that there is –ve charge at ortho and para positions, electrophillic substitution reaction will take place at orthoand para position due to +R effect. +R effect is dominating over – I effect. .

Q9. 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.

$$R\text{-}X + KOH \longrightarrow R\text{-}OH + KX$$

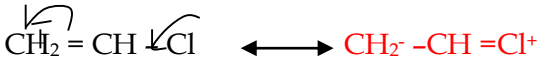
Where as in alcoholic KOH

$$C_2H_5OH + KOH \longrightarrow C_2H_5O^- + K^+$$

$$CH_3CH_2\text{-}Cl + \text{alcoholic KOH} \longrightarrow CH_2 = CH_2 + C_2H_5OH$$

Q10. 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.



Q11. Arrange the following compounds according to reactivity towards nucleophillic substitution reaction with reagents mentioned :-

(i) 4- nitro chloro benzene, 2,4- di nitro chlorobemzene, 2,4,6- trinitrochlorobenzene with CH_3ONa

Ans- 2,4,6- trinitrochlorobenzene> 2,4 -dinitrochlorobemzene> 4- nitrochlorobenzene

Q12. 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) $(CH_3)_3C$-Cl or CH_3Cl (SN^2)

CH_3Cl will react faster than 3^0 halide

Q13. 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) Isopropyl chloride <1-chloropropane <1-Chlorobutane

(As Branching increases , boiling point decreases)

Q 14. Predict the reactivity in SN^1

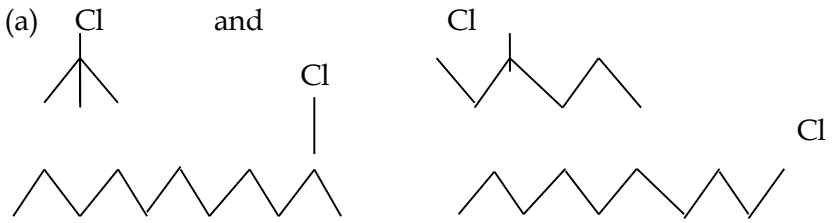
(a) $C_6H_5CH_2Br$, $C_6H_5CH(C_6H_5)Br$, $C_6H_5CH(CH_3)Br$, $C_6H_5C(CH_3)(C_6H_5)Br$

Ans. $3^0 > 2^0 > 1^0$ (SN_1)

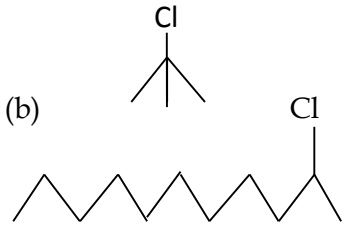
$C_6H_5C(CH_3)(C_6H_5)Br > C_6H_5CH(C_6H_5)Br > C_6H_5CH(CH_3)Br > C_6H_5CH_2Br$

(3^0) (2^0) (2^0) (1^0)

Q15. Which compound undergoes SN^1 reaction fast ?

(a) 

(a) Ans. Cl

(b) 

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 exihibitenantiomerism ?

Q.5. Write down the structure of the following compounds.

(a) 1- chloro-4-ethyl cyclohexane

(b) 1,4-Dibromobut-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 SN^2 reactionwith –OH?

Q.7. A hydrocarbon C_5H_{10} does not react with chlorine in dark but it gives a single monobromo compound in brightsunlight.identify the compound.

Q.8. Out of $C_6H_5CH_2Cl$ & $C_6H_5CH_2Cl$ $_6H_5$ which is more easily hydrolysed with aq. KOH &why ?

Q.9. 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.2. Rearranging the following in order of increasing case of dehydro halogenations

$CH_3CH_2CH_2Cl$, $CH_3CHClCH_3$, $CH_3 - CHClC(CH_3)_3$

Q.3. Give the uses of (a) CCl_4 (b) iodoform

Q.4. 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.5. Which will have a higher boiling point 1-chloropentane or 2-chloro-2-methylbutane?

Q.6.How will you bring the following conversion?

(a) Propene to Propyne

(b) Toluene to Benzyl Alcohol

(c) Aniline to Phenylisocyanide

Q.7.What happens 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.8.Complete the following reaction;

(a)$Cl_2CH\text{-}CH\text{-}Cl_2 + Zn \xrightarrow{\Delta}$

(b)$(CH_3)_2\text{-}CH\text{-}\underset{\displaystyle Cl}{\underset{|}{CH}}\text{-}CH_2\text{-}CH_3 \xrightarrow[C_2H_5ONa]{\text{Ethanol}}$

(c)$C_6H_5ONa + C_2H_5Cl \longrightarrow$

IUPAC Name

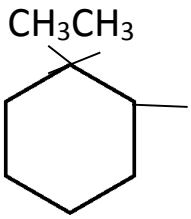
$CH_3– O – CH_2 – CH_2 – CH_3$ —— 1- Methoxypropane

$C_6H_5OCH_3$ Methoxy benzene

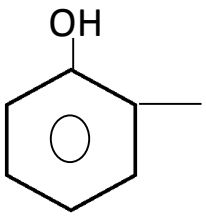
[Anisole]

$C_6H_5O(CH_2)_6 – CH_3$ 1- Phenoxyheptanes

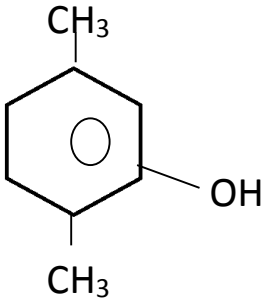
$CH_3 – O – \underset{\displaystyle CH_3}{\underset{|}{CH}} – CH_3$ 2- Methoxy propane



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
$CH_3 - \underset{\displaystyle OH}{\underset{\vert}{CH}} - CH_3$	Propan-2-ol
$CH_3 - CH_2 - CH_2 - CH_2 - OH$	Butan-1-ol
$CH_3 - \underset{\displaystyle OH}{\underset{\vert}{CH}} - CH_2 - CH_3$	Butan-2-ol
$CH_3 - \underset{\displaystyle OH}{\underset{\vert}{CH}} - CH_2 - CH_3$	2-Methylpropan-1-ol
$CH_3 - \underset{\displaystyle CH_3}{\underset{\vert}{\overset{\displaystyle CH_3}{\overset{\vert}{C}}}} - OH$	2-Methylpropan-2-ol
$\underset{\displaystyle OH}{\underset{\vert}{CH_2}} - \underset{\displaystyle OH}{\underset{\vert}{CH}} - \underset{\displaystyle OH}{\underset{\vert}{CH_2}}$	Propane -1, 2, 3-triol

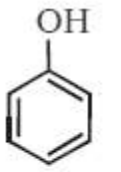
(i) $CH_3 - \underset{\displaystyle CH_3}{\underset{\vert}{CH}} - \underset{\displaystyle OH}{\underset{\vert}{CH}} - \underset{\displaystyle CH_3}{\underset{\vert}{\overset{\displaystyle CH_3}{\overset{\vert}{C}}}} - CH_3$

2,2,4-Trimethylpentan-3-ol

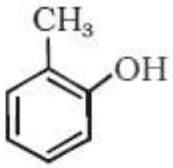
(ii) $H_3C - \underset{\displaystyle OH}{\underset{\vert}{CH}} - CH_2 - \underset{\displaystyle OH}{\underset{\vert}{CH}} - \underset{\displaystyle C_2H_5}{\underset{\vert}{CH}} - CH_2 - CH_3$

5-Ethylheptane-2,4-diol

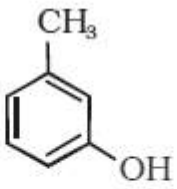
IUPAC names of phenols



Phenol

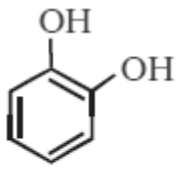


2-Methylphenol

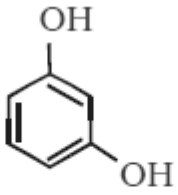


3-Methylphenol

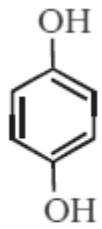
4-Methylphenol



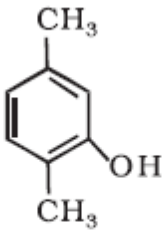
Benzene-1,2-diol



Benzene-1,3-diol

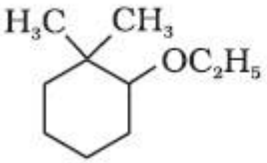


Benzene-1,4-diol



2,5-Dimethylphenol

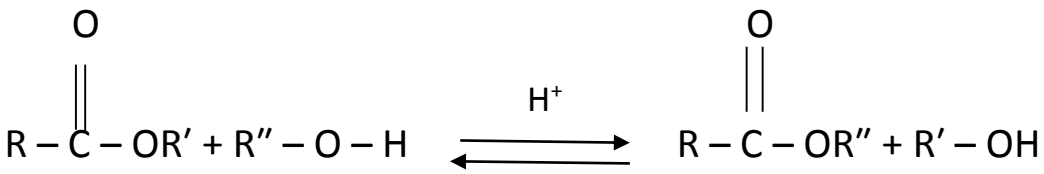
IUPAC names of some ethers

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
$CH_3O-\underset{\displaystyle CH_3}{\underset{\vert}{CH}}-CH_3$	2-Methoxypropane
$C_6H_5-O-CH_2-CH_2-\underset{\displaystyle CH_3}{\underset{\vert}{CH}}-CH_3$	3- Methylbutoxybenzene
$CH_3-O-CH_2-CH_2-OCH_3$	1,2-Dimethoxyethane
	2-Ethoxy- -1,1-dimethylcyclohexane

Name reaction

(1)Trans esterification
(2) Williamson synthesis
(3) Kolbe reaction
(4)Friedel craft

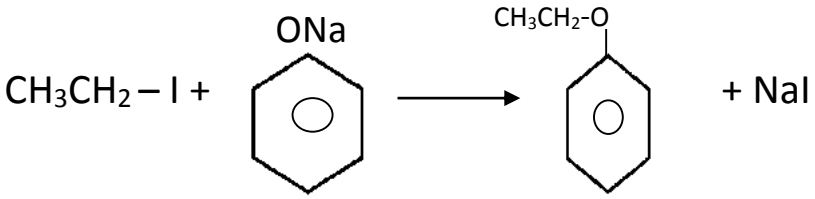
Trans esterification :



Williamson synthesis:- Reaction with alkyl halide with sodium alkoxide or sod. Phenoxide called Williamson synthesis.

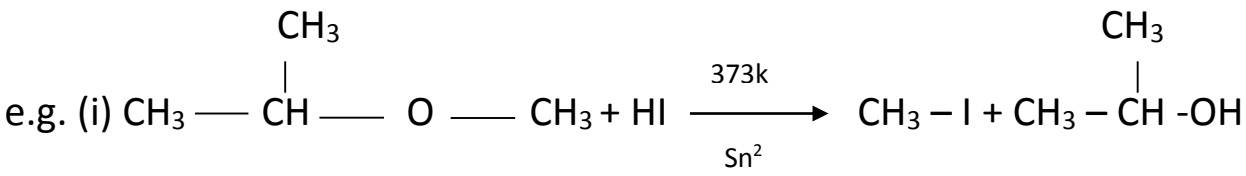
$R – X + R^1 – O – Na \longrightarrow R – O - R' + NaX$

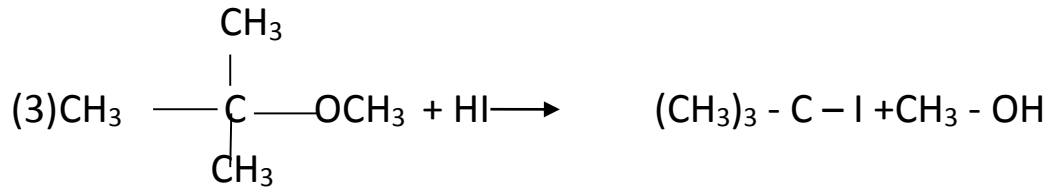
$H_3I + CH_3CH_2ONa \longrightarrow CH_3O.CH_2 – CH_3 + NaI$



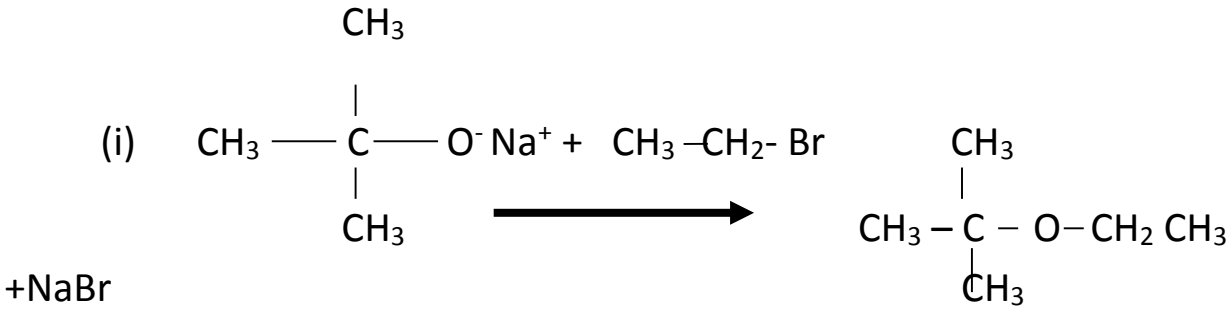
Both simple and mixed ether can be produced.

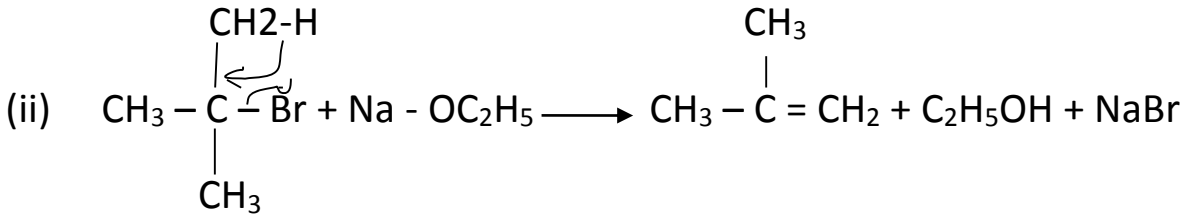
Depending upon structure and cleavage of unsymmetrical ethers by halogen acid may occur either by SN^2 or SN^1 mechanism.

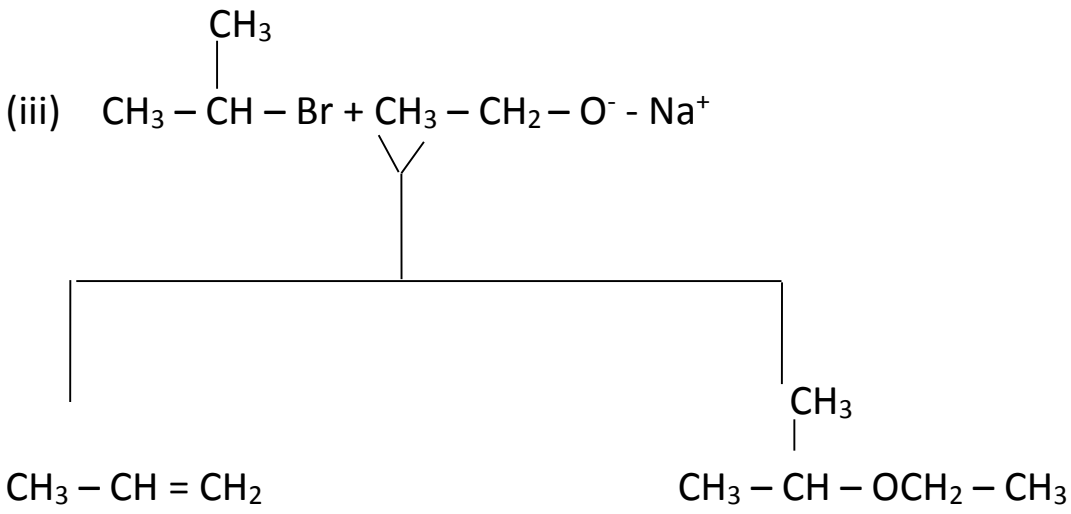




LIMITATIONS OF WILLIAMSON SYNTHESIS

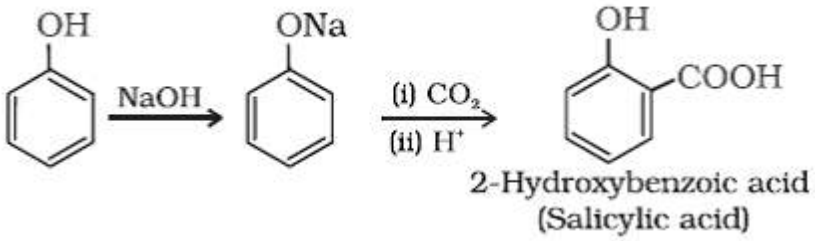




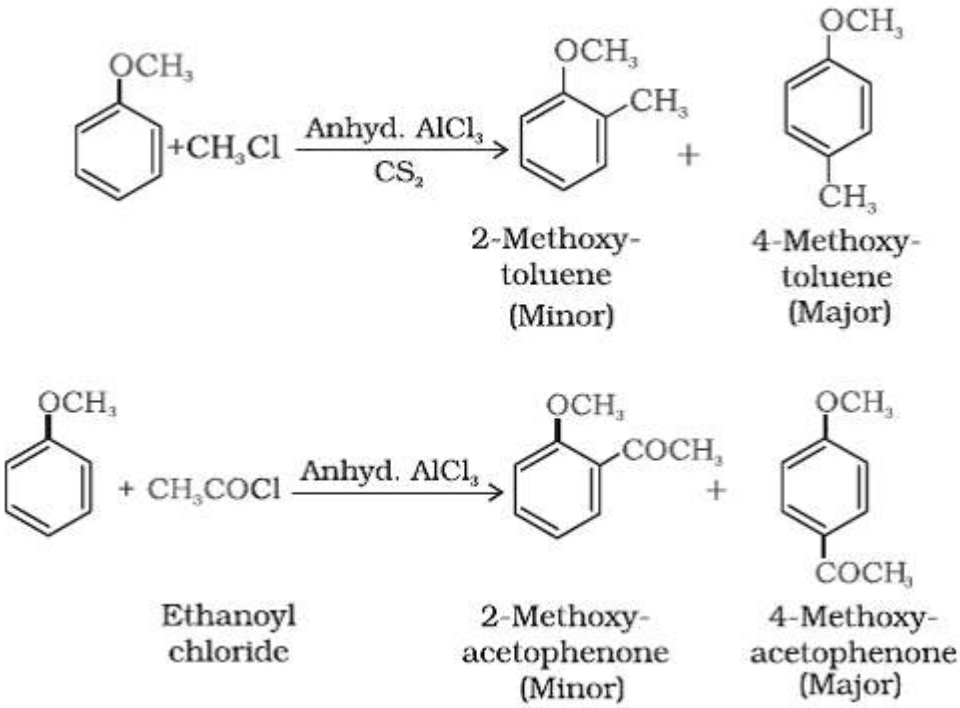


79% 21%

Kolbe reaction



Friedelcraft reaction



DISTINCTION BETWEEN PAIR OF COMPOUNDS

When 1^0,2^0, and 3^0 alcohol treated with lucas reagent [conc. 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 compounds 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) $CH_3 – COCH_3$

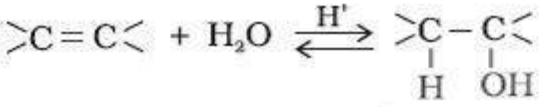
(V) $C_6H_5 – COCH_3$

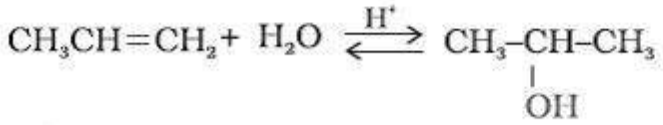
(VI) $CH_3 – CH(OH) – CH_2 – CH_2 – CH_3$

(VII) $CH_3 – C(=O) – CH_2 – CH_2 – CH_3$

Important mechanism

Hydration of alkenes



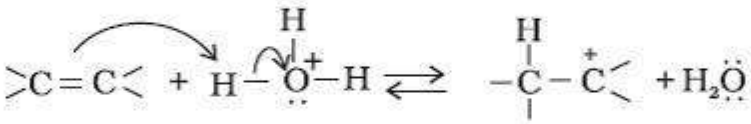


Mechanism

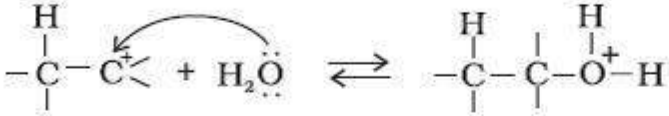
The mechanism of the reaction involves the following three steps:

Step 1: Protonation of alkene to form carbocation by electrophilic attack of H_3O^+.

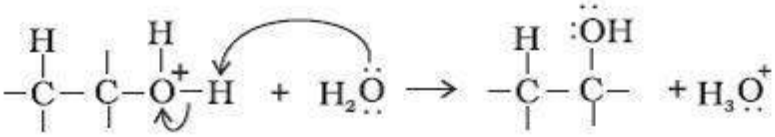
$H_2O + H^+ \rightarrow H_3O^+$



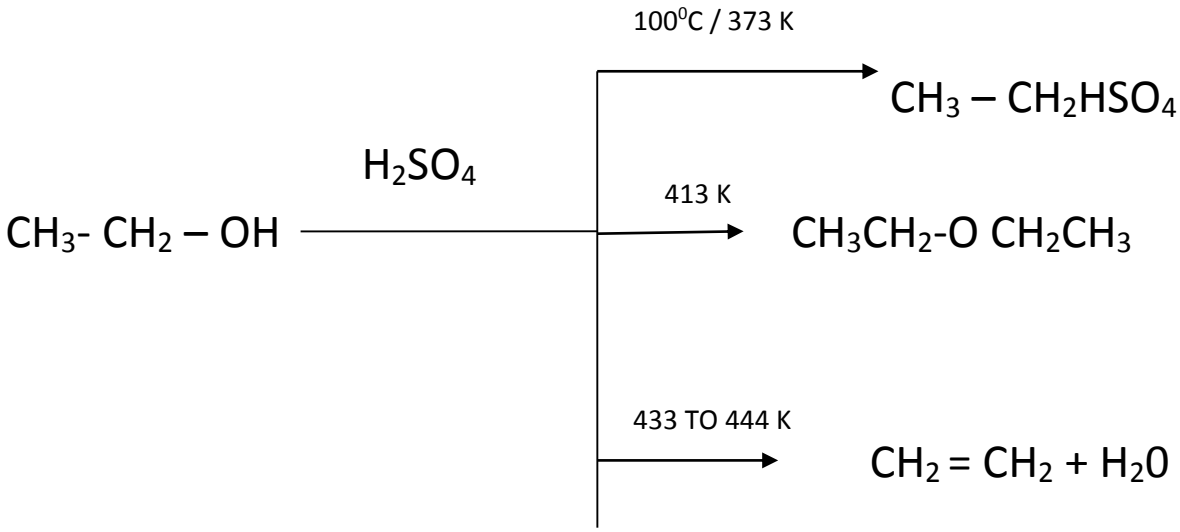
Step 2: Nucleophilic attack of water on carbocation.



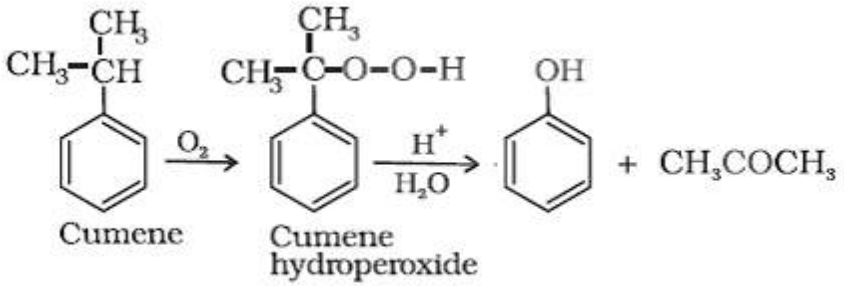
Step 3: Deprotonation to form an alcohol.



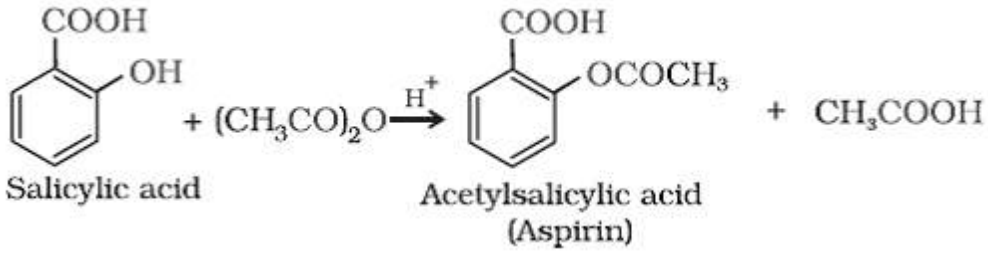
Important reaction



(2) Preparation of phenol from Cumene

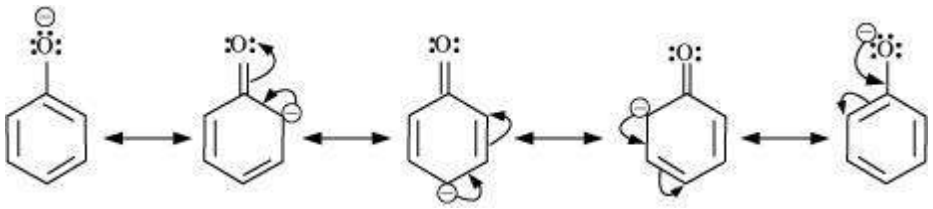


(3) Preparation of aspirin and salol



Explain phenol is acidic?

Phenoxide ion is resonance stabilised



:-If electron withdrawing group are attached into the benzene ring it enchances acidic character and vice versa.

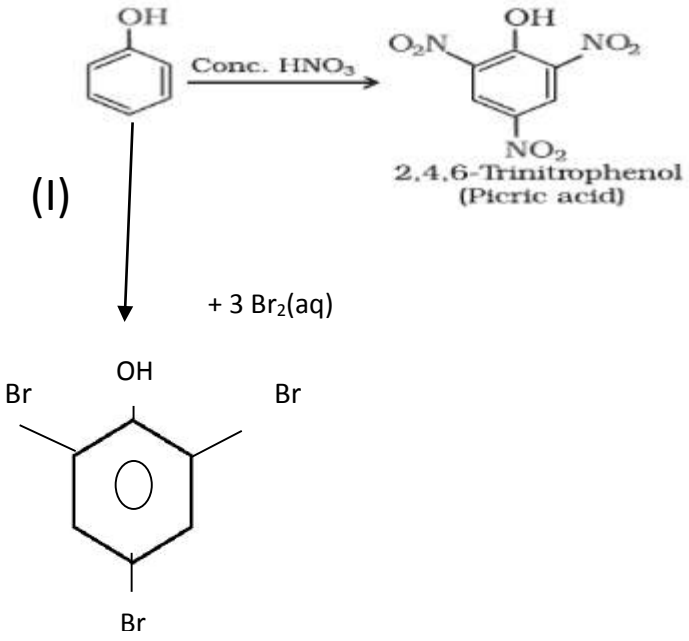
2,4,6-trinitrophenol> 2,4-dinitrophenol> 4-nitrophenol > phenol

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



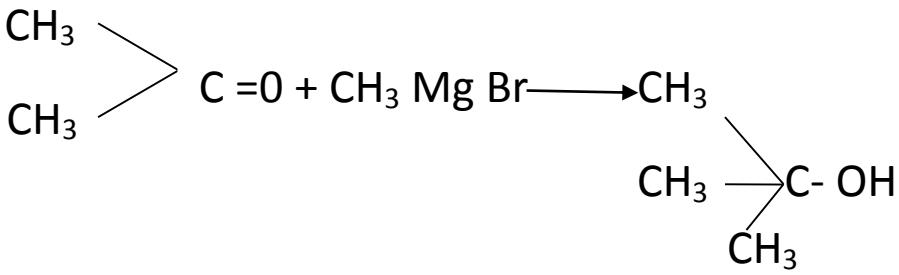
2,4,6-Tribromo phenol (white ppt)

(I)Phenol gives violet colour with $Fecl_3$solution .

PREPARATION OF $1^0,2^0,3^0$ ALCOHOLS

$$HCHO + R\,Mg\,x \xrightarrow{\text{Followed by hydrolysis}} R\text{-}CH_2OH \quad 1^0\text{alc}$$

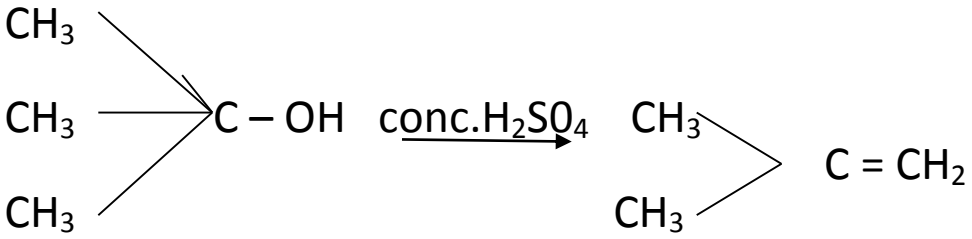
$$CH_3CHO + R\,Mg\,x \xrightarrow{\text{Followed by hydrolysis}} R\text{-}CH(CH_3)OH$$



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 – methoxyphenol ?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.

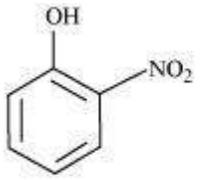
Q2. Alcohols are comparatively more soluble in water than hydrocarbons of comparable molecular masses. Explain this fact.

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.

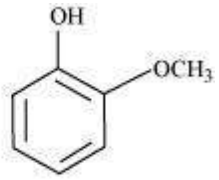
Q3 . While separating a mixture of ortho and para nitrophenols by steam distillation, name the isomer which will be steam volatile. Give reason.

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 orthonitrophenol more acidic than orthomethoxyphenol?



o – Nitrophenol



o – Methoxyphenol

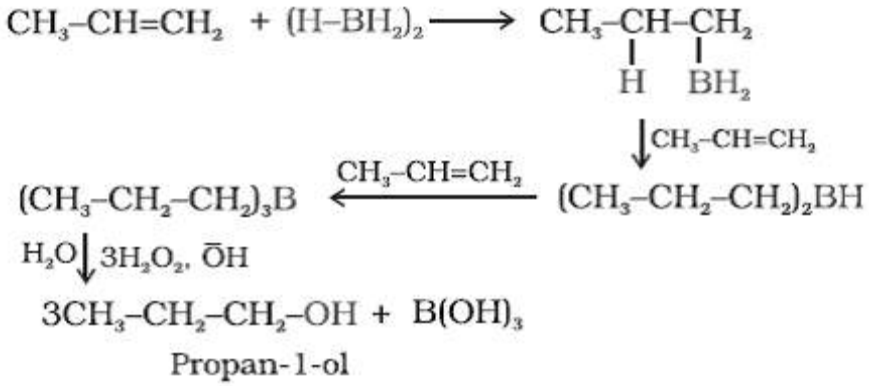
ANS. The nitro-group is an electron-withdrawing group. Thepresence of this group in the ortho position decreases the electron density in the O-H bond . As a result, it is easier to lose a proton. Also,the o-nitrophenoxide ion formed after the loss of protonis stabilized by resonance. Hence,ortho-nitrophenol is 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. Therefor ortho-nitrophenol is more acidic than ortho- methoxyphenol.

5. 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 SN^2 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.

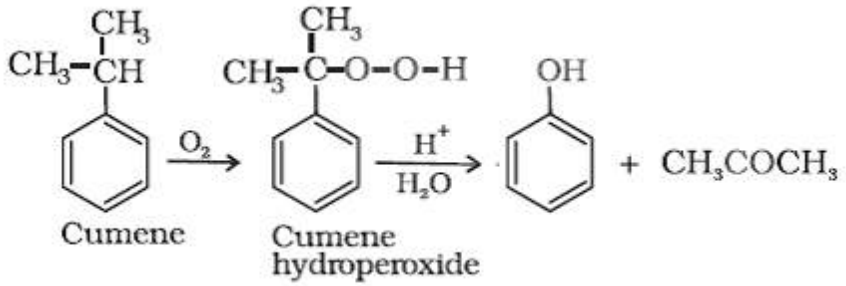
Q6. What is meant by hydroboration-oxidation reaction? Illustrate it with an example .

ANS.Diborane $(BH_3)_2$ reacts with alkenes to give trialkylboranes as addition product. This is oxidised to alcohol by hydrogen peroxide in the presence of aqueous sodium hydroxide.

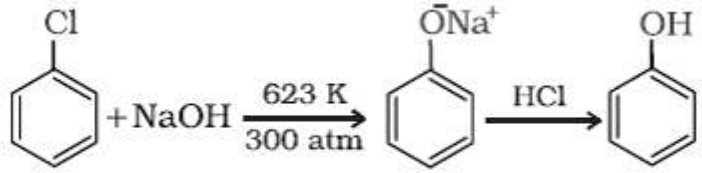


Q7. Give the equations of reactions for the preparation of phenol from cumene.

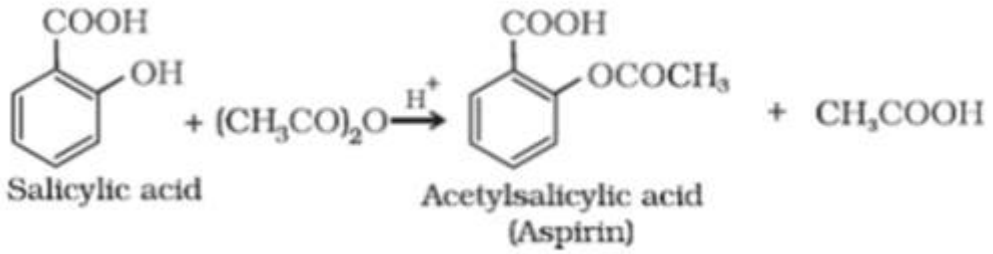
Ans.



Q8. 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.



Q9. How is aspirin (Acetylsalicylic acid) prepared from salicylic acid?Ans. Acetylation of salicylic acid produces aspirin.



Q10. 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 $1^0 > 2^0 > 3^0$.

Q11. 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.

Q12. Give IUPAC name of $CH_3OCH_2OCH_3$

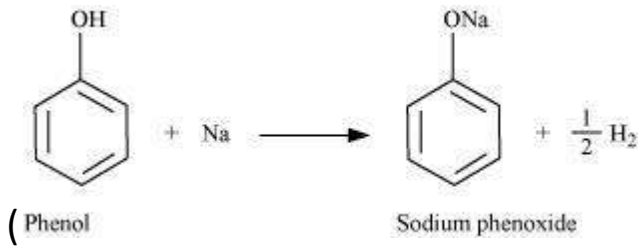
ANS. Dimethoxymethane

Q13. Diethyl ether does not react with sodium. Explain.

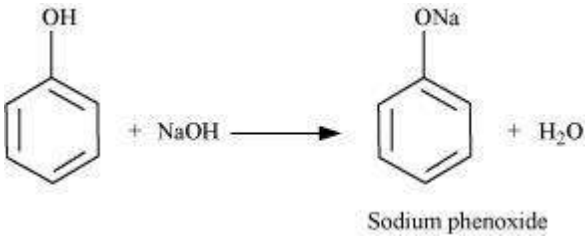
ANS. Diethyl ether does not contain any active hydrogen.

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.

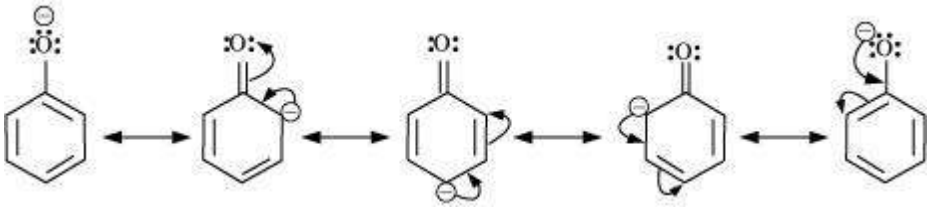


(ii) Phenol reacts with sodium hydroxide to give sodium phenoxide and water as by-products



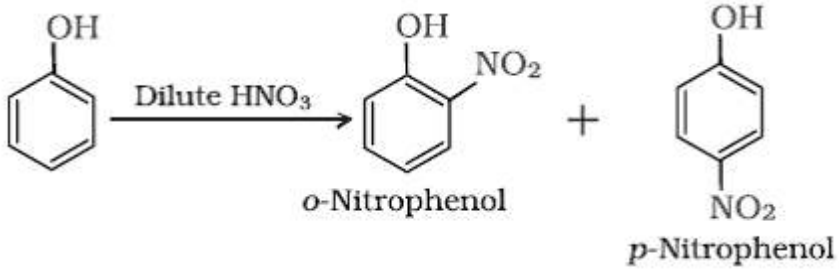
Sodium phenoxide

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 ?

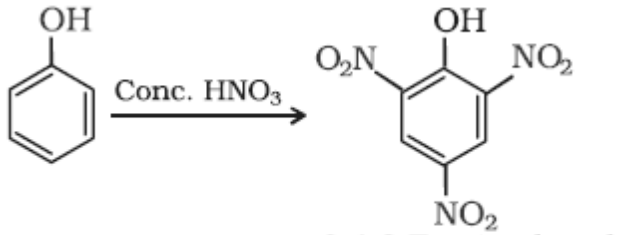
ANS. (i) With dilute nitric acid at low temperature (298 K), phenol yields a mixture of ortho



o-Nitrophenol

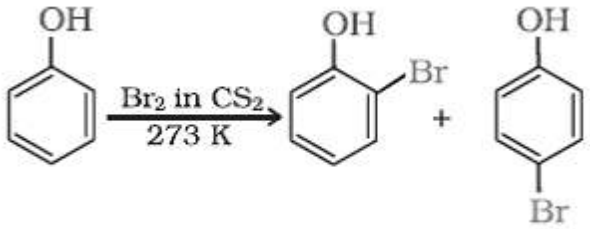
p-Nitrophenol

and para nitrophenols. (ii) With concentrated nitric acid, phenol is converted to 2,4,6-trinitrophenol. The product is commonly known as picric acid.



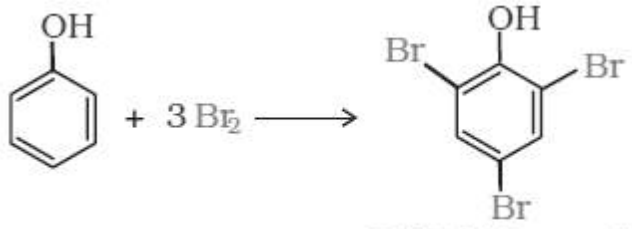
2,4,6-Trinitrophenol
(Picric acid)

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.



Minor Major

(iii) 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 likealcohols.

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.

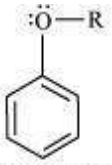
Q9. Account for the following:
i) Phenols has a smaller dipole moment than methanol

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.

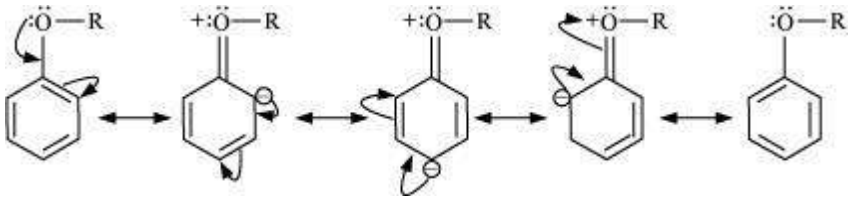
(b). The lone pair on oxygen of –OH in phenol is being shared with benzene ring through resonance. Thus, lone pair is not fully present on oxygen and hence phenols do not undergo protonation reactions.

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.



Aryl alkyl ether

ANS. (i)
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.



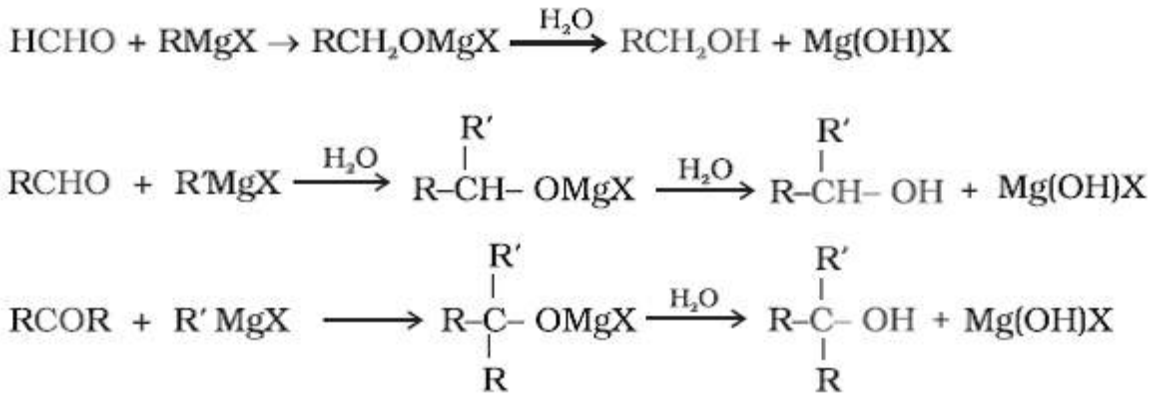
Thus, benzene is activated towards electrophilic substitution by the alkoxy group.

(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 .

3 MARKS QUESTIONS

Q1. How are primary, secondary and tertiary alcohols prepared from Grignard Reagents?

ANS.



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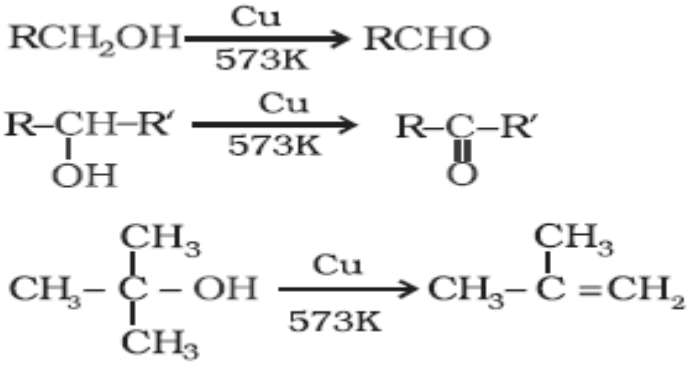
The reaction produces a primary alcohol with methanal, a secondary alcohol with other aldehydes and tertiary alcohol with ketones.

Q2. Give the equations of oxidation of primary, secondary and tertiary alcohols by Cu at 573 K.

ANS.



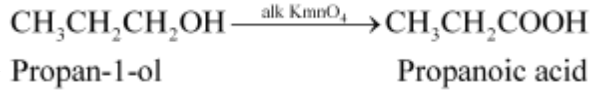
Q3. Give equations of the following reactions:

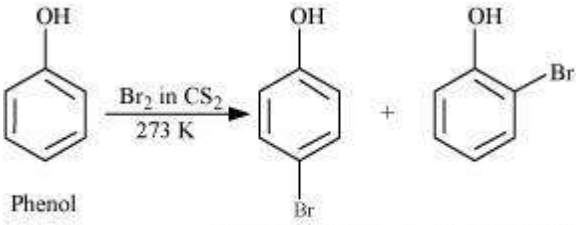
(i) Oxidation of propan-1-ol with alkaline $KMnO_4$ solution.

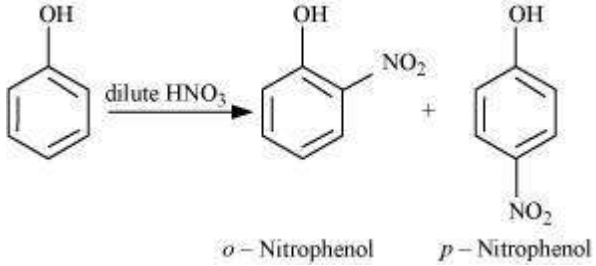
(ii) Bromine in CS_2 with phenol.

(iii) Dilute HNO_3 with phenol.

ANS.(i)







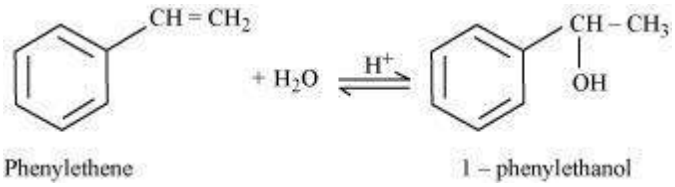
Q4. Show how will you synthesize:

(i) 1-phenylethanol from a suitable alkene.

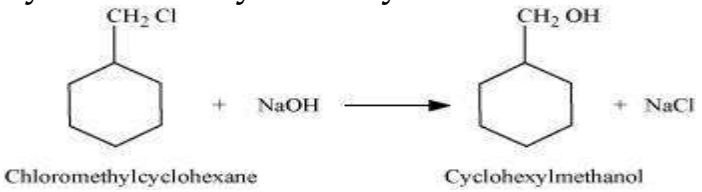
(ii) (ii) cyclohexylmethanol using an alkyl halide by an SN_2 reaction.

(iii) (iii) pentan-1-ol using a suitable alkyl halide?

ANS. (i) By acid-catalyzed hydration of ethylbenzene (styrene), 1-phenylethanol can be synthesized.



(ii) When chloromethylcyclohexane is treated with sodium hydroxide, cyclohexylmethanol is obtained.



(iv) When 1-chloropentane is treated with NaOH, pentan-1-ol is produced.

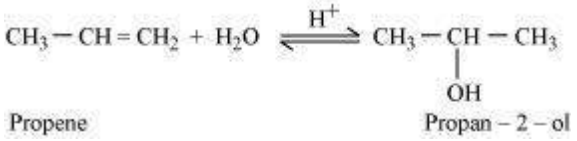
Q5. How are the following conversions carried out?

(i)Propene → Propan-2-ol

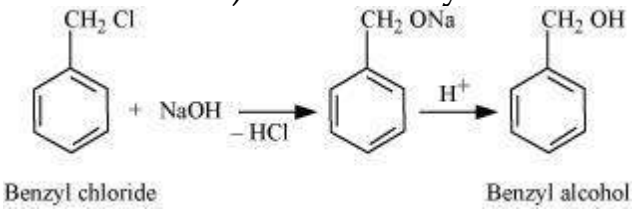
(ii) Benzyl chloride → Benzyl alcohol

(iii) Ethyl magnesium chloride → Propan-1-ol.

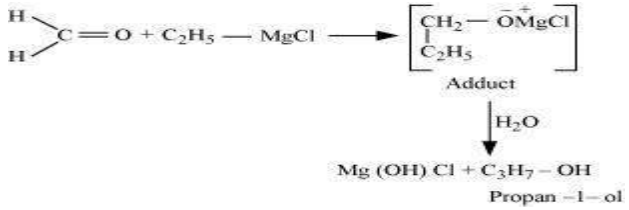
ANS.(i)If propene is allowed to react with water in the presence of an acid as a catalyst, then propan-2-ol is obtained.



(ii) If benzyl chloride is treated with NaOH (followed by acidification) then benzyl alcohol is produced.



(iii)When ethyl magnesium chioride is treated with methanol, 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.

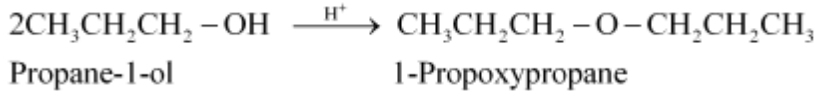
ANS. (i) Acidified potassium permanganate

(ii) Pyridiniumchlorochromate (PCC)

(iii) Bromine water

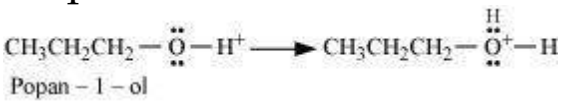
Q7. How is 1-propoxypropane synthesised from propan-1-ol? Write mechanism of this reaction.

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.

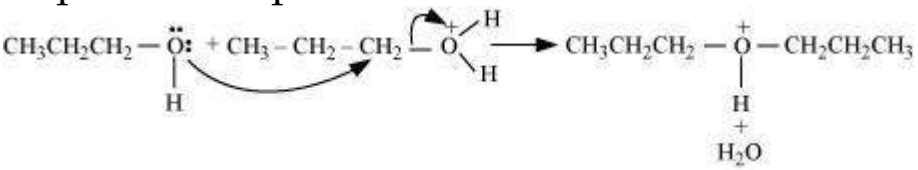


The mechanism of this reaction involves the following three steps:

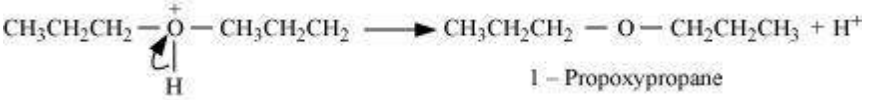
Step 1: Protonation



Step 2: Nucleophilic attack



Step 3: Deprotonation



Q8. Write the equation of the reaction of hydrogen iodide with:

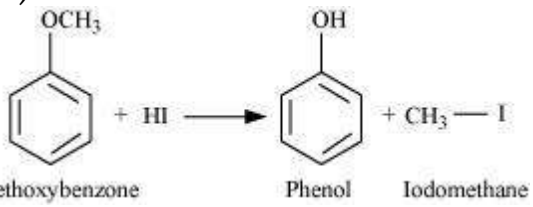
(i) 1-propoxypropane (ii) Methoxybenzene and (iii) Benzyl ethyl ether

ANS. (i)

$$C_2H_5CH_2-O-CH_2C_2H_5 + HI \xrightarrow{373K} CH_3CH_2CH_2-OH + CH_3CH_2CH_2-I$$

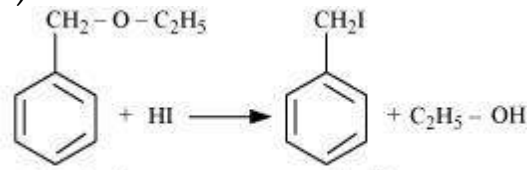
1-Propoxypropane Propan-1-ol 1 – Iodopropane

(ii)



Methoxybenzone Phenol Iodomethane

(iii)



Benzyl ethyl ether Benzyl iodide Ethanol

5 MARKS QUESTIONS

Q1. Write equations of the following reactions:

(i) Friedel-Crafts reaction−alkylation of anisole.

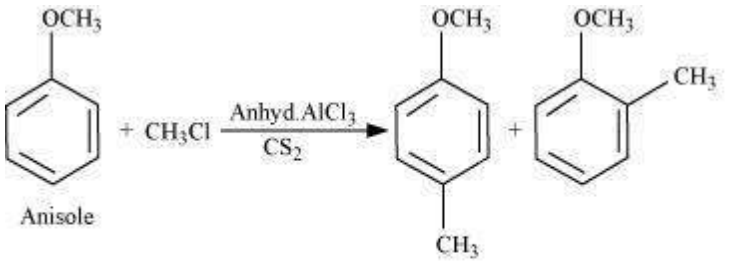
(ii) Nitration of anisole.

(iii) Bromination of anisole in ethanoic acid medium.

(iv) Friedel-Craft's acetylation of anisole.

(v)Reaction of phenol with Zn dust.

ANS.(i)

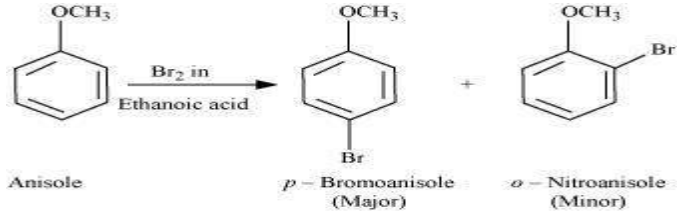


Anisole 4 – Methoxytoluene (Major) 2 – Methoxytoluene (Minor)

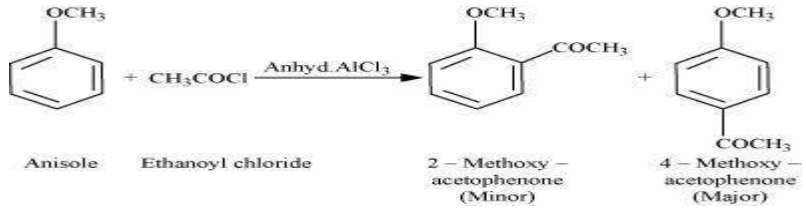
(ii)

Anisole 2 – Nitroanisole (Minor) 4 – Nitroanisole (Major)

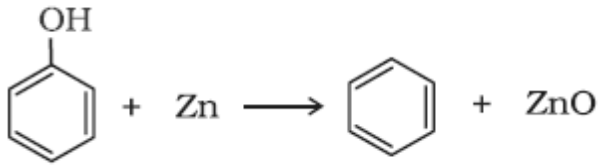
(iii)



(iv)



(v)



3 MARKS QUESTIONS

Q 1.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 cleared by X^- ions to form halobenzenes. But in alcohols a pure C — O bond is maintained and can be cleared by X^- ions.

Q 2. Explain why o-nitrophenol is more acidic than o-methoxy phenol?
Ans . Due to — R and — I effect of — NO_2 group, e– density on ‗O' if O — H bond decreases and loss of H+ is easy.– I effect In contrast, 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)
Q3. Of benzene and phenol, which is more easily nitrated and why?
Ans.Nitration is an electrophilic substitution. The –OH group in phenol increases the electron density at ortho and para position as follows Since phenol has higher electron density due to electron releasing nature of -OH group , compared to benzene , therefore nitration is easy in phenol than benzene.

Q4. 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.

Q 6. How do 1°, 2° and 3° alcohols differ in terms of their oxidation reaction and dehydrogenation ?

Ans. (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 alken

Q7. (i)How is diethyl ether prepared from ethyl alcohol?

Ans. Ethyl alcohol is first treated with sodium to form sodium ethoxide
$C_2H_5OH + Na\ C_2H_5O^- Na^+ + H_2$ Sodium ethoxide is then treated with ethyl halide to form di ethyl ether. SN^2
$C_2H_5O\ Na + - C_2H_5X \rightarrow C_2H_5O\ C_2H_5 + NaX$ (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) 2 CH_3Cl (b) $CH_3Cl + C_2H_5OH$ (c) $C_2H_5Cl + C_2H_5OH$

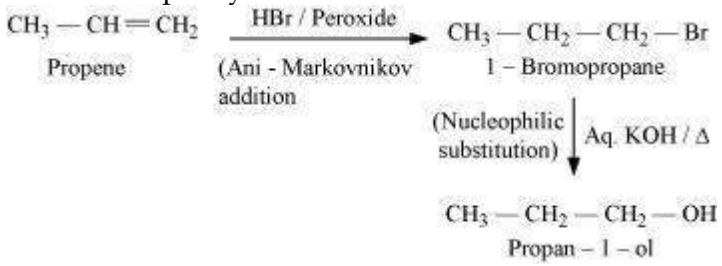
Q8. Why are reactions of alcohol/phenol and with acid chloride in the presence of pyridine?

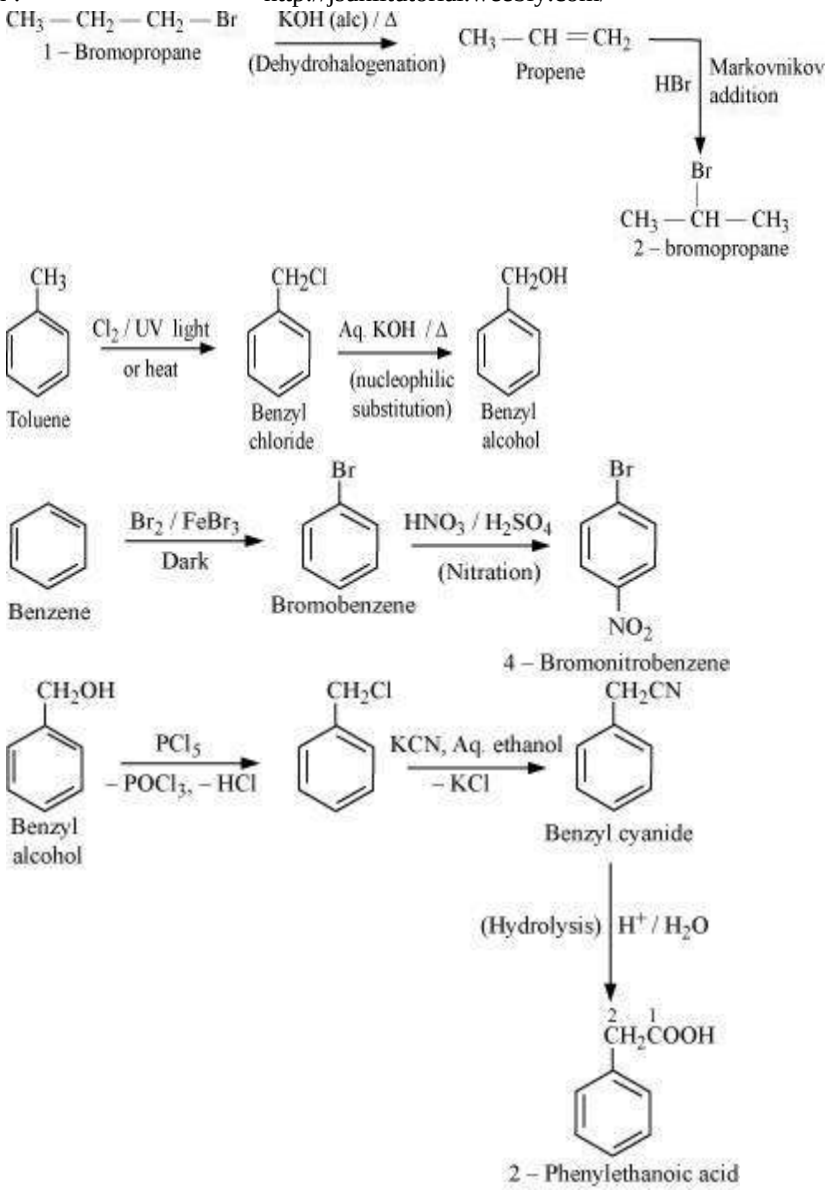
Ans. Because esterification reaction is reversible and presence of base (pyridine) neutralisesHCl produced during reaction thus promoting forward reaction.

LONG ANSWER TYPE QUESTIONS

Q1) How the following conversions can be carried out?

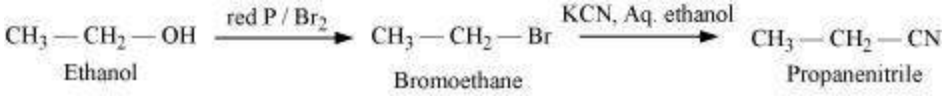
(i) Propene to propan-1-ol
(ii) 1-Bromopropane to 2-bromopropane
(iii) Toluene to benzyl alcohol
(iv) Benzene to 4-bromonitrobenzene
(v) Benzyl alcohol to 2-phenylethanoic acid

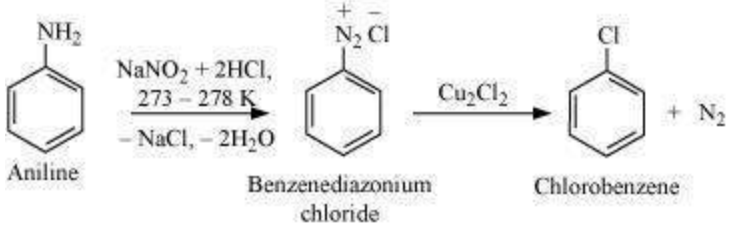


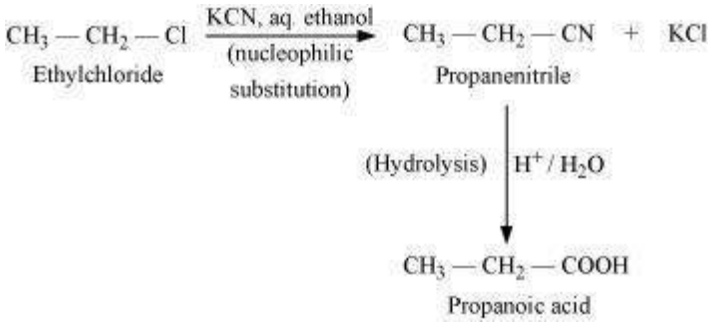


Q2) How the following conversions can be carried out?

(i) Ethanol to propanenitrile
(ii) Aniline to chlorobenzene
(iii) 2-Chlorobutane to 3, 4-dimethylhexane
(iv) 2-Methyl-1-propene to 2-chloro-2-methylpropane
(v) Ethyl chloride to propanoic acid

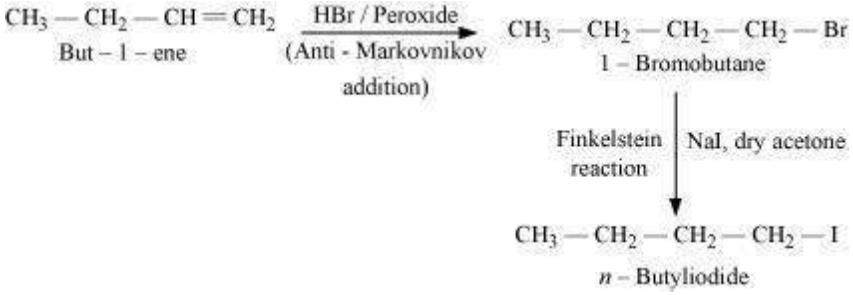


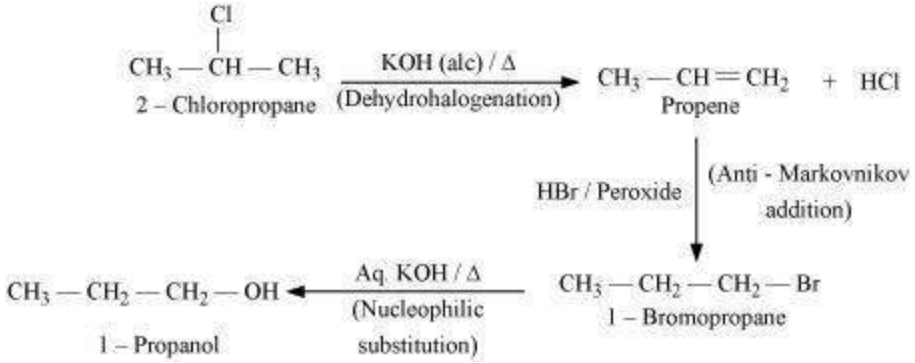


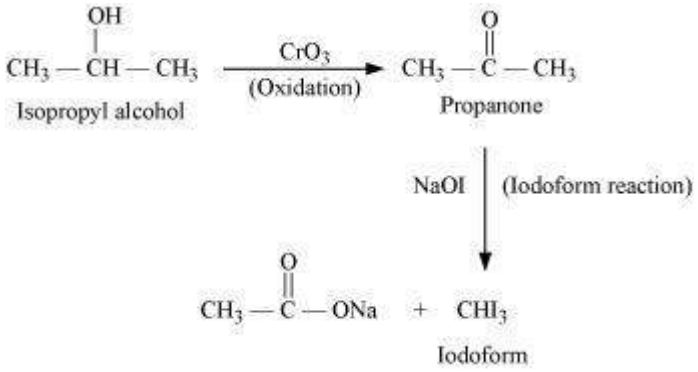


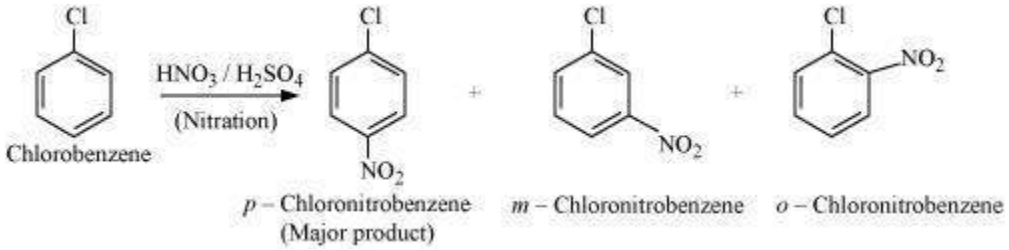
Q3) How the following conversions can be carried out?

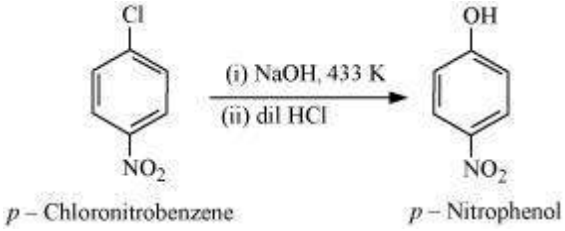
(i) But-1-ene to n-butyliodide
(ii)2-Chloropropane to 1-propanol
(iii) Isopropyl alcohol to iodoform
(iv) Chlorobenzene to p-nitrophenol
(v) 2-Bromopropane to 1-bromopropane



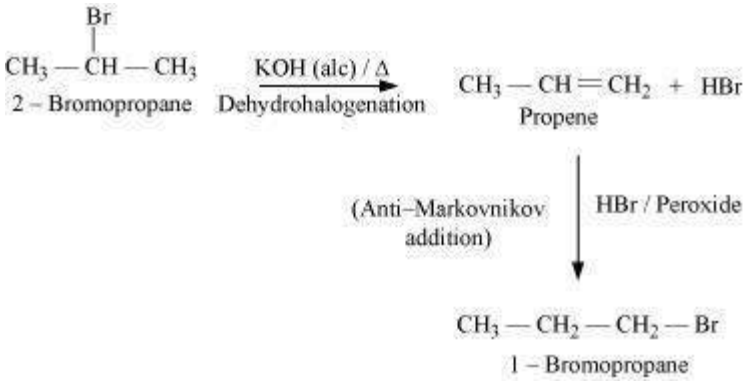








p – Chloronitrobenzene *p* – Nitrophenol



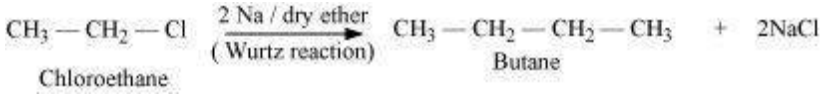
Q4) How the following conversions can be carried out?

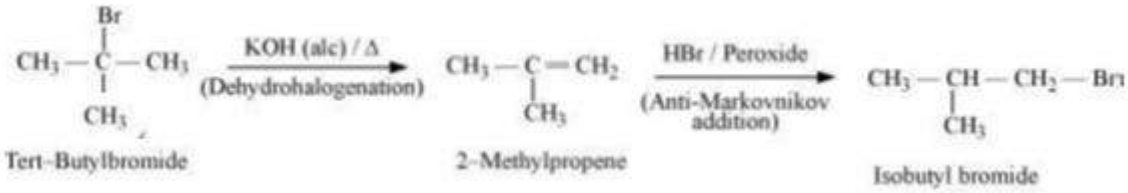
(i) Chloro ethane to butane

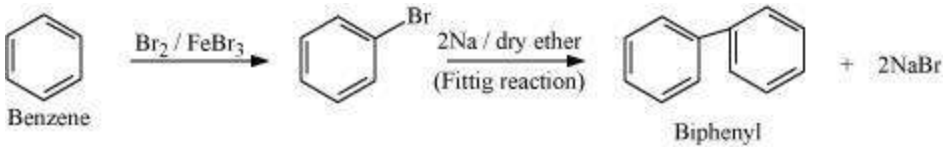
(ii)Benzene to diphenyl

(iii) tert-Butyl bromide to isobutyl bromide

(iv) Aniline to phenylisocyanide







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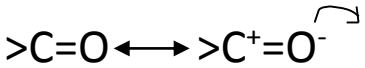
Unit-11

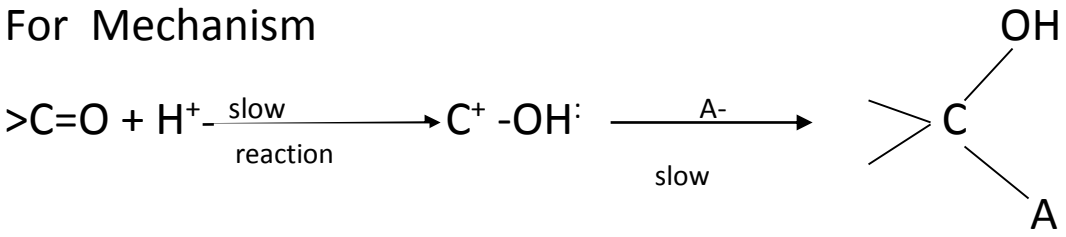
ALDEHYDES, KETONES AND CARBOXYLIC ACIDS

Addition to C=O bonds

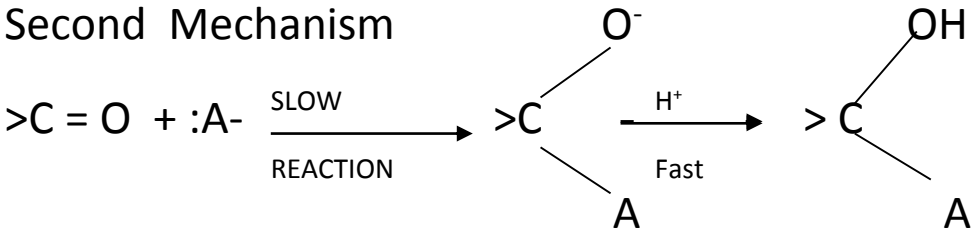
The structure of the carbonyl group in aldehydes and Ketones is not adequately represented by >C=O, nor by the alternative $>C^{+}\text{-}O^{-}$. The real structure or resonance hybrid lies somewhere between the following structure:



For Mechanism



Second Mechanism



Reactivity of aldehyde and Ketones is as

$HCHO>RCHO>RCOR>RCOOR>RCONH_2$.

POINTS TO REMEMBER

:-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 aluminiumchloride / 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

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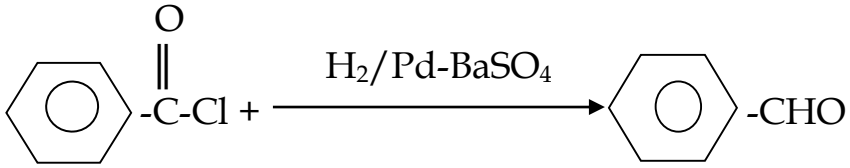
1.**ROSENMUND REDUCTION**:

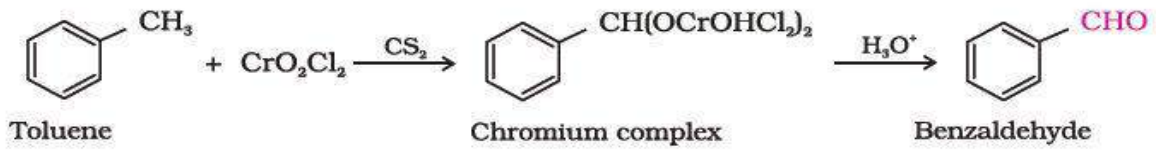


Benzoyl chloride Benzaldehyde

2. STEPHEN REACTION

$$RCN + SnCl_2 + HCl \longrightarrow RCH{=}NH \xrightarrow{H_3O^+} RCHO$$

ETARD REACTION:



This reaction is called Etard reaction.

CLEMMENSEN REDUCTION

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

WOLFF- KISHNER REDUCTION

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

ALDOL CONDENSATION

Aldehydes and ketones having at least one α-hydrogen condense in the presence of dilute alkali as catalyst to form β-hydroxyalddilehydes (aldol) or β-hydroxy ketones (ketol).

$$\underset{\text{ethanal}}{2CH_3\text{-}CHO} \xrightleftharpoons{NaOH} \underset{\substack{\\ OH\ (Aldol)}}{CH_3\text{-}\overset{\displaystyle OH}{\overset{|}{C}}H\text{-}CH_2\text{-}CHO} \xrightarrow[-H_2O]{Heat} \underset{But\text{-}2\text{-}enal}{CH_3\text{-}CH{=}CH\text{-}CHO}$$

$$\xrightarrow{Ba(OH)_2} \overset{CH_3}{\overset{|}{\ }} \qquad \xrightarrow{Heat} \overset{CH_3}{\overset{|}{\ }}$$

$2CH_3\text{-}CO\text{-}CH_3 \rightleftharpoons CH_3\text{-}C(OH)(CH_2\text{-}CO\text{-}CH_3)$ (Ketal) $\xrightarrow{-H_2O}$ $CH_3\text{-}C{=}CH\text{-}CO\text{-}CH_3$

Propanone — 4-Metylpent-3-en2-one

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.

$CH_3CHO + CH_3\text{-}CH_2\text{-}CHO \xrightarrow[2\ \triangle]{1NaOH}$ $CH_3CH{=}CH\text{-}CHO$ + $CH_3CH_2CH{=}C(CH_3)\text{-}CHO$

But-2-en-1-al — 2-Methylpent-2-enal

$CH_3\text{-}CH{=}C(CH_3)\text{-}CHO$ + $CH_3CH_2\text{-}CH{=}CHCHO$

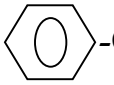
2 -Methylbut-2-enal — Pent-2-enal

CANNIZZARO 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.

$H\text{-}CHO + H\text{-}CHO + Conc.KOH \longrightarrow CH_3OH + HCOOK$

Formaldehyde — Methanol — Potassium Formate



$\text{-}CHO + NaOH\ (conc.) \longrightarrow C_6H_5CH_2OH + C_6H_5COONa$

Benzaldehyde — Benzyl Alcohol — Sodium benzoate

CARBOXYLIC ACID

1. HELL-VOLHARD-ZELINSKY REACTION (HVZ)

1. $RCH_2\text{-}COOH \xrightarrow[(ii)\ H_2O]{(i)\ X_2/\ \text{Red phosphorus}} R\text{-}CH(X)\text{-}COOH$

X=Cl,Br

α –halocarboxylic acids

2. **ESTERIFICATION**

$$\underset{\text{Carboxylic acid}}{RCOOH} + \underset{\text{alcohol}}{R'OH} \overset{H^+}{\rightleftharpoons} \underset{\text{Ester}}{RCOOR'} + H_2O$$

3. **DECARBOXYLATION**:

$$RCOONa \xrightarrow{NaOH \text{ and } CaO \,/\, \Delta} R\text{-}H + Na_2CO_3$$

PAIR DISTINCTION

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)Pentan-2-one and Pentan-3-one

(h) 2^0 Alcohol and 3^0alcohol

(i)1^o,2^o,3^o amine

(j)Benzoic acid and benzene

(k)Phenol and benzoic acid

(l)Aniline and ethyl amine

(m)Aniline and nitrobenzene

(n)Benzaldehyde and acetophenone

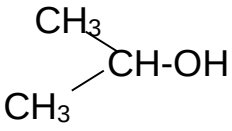
(o)Methanol and benzaldehyde

(p)Chloro benzene and benzyl chloride

ANSWERS

(a)	Phenol	Alcohol
	It gives $FeCl_3$ test. (violet colour)	It doesn't give this test.
(b)	Benzaldehyde	Propanal
	It gives tollen's reagent test.	It also give tollen's reagent test.
	It doesn't give fehling's solution test.	It gives fehling's 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

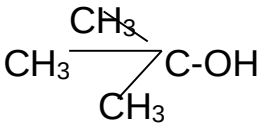
(h) 2^o alcohol



$HCl+ZnCl_2$

It takes 5 minutes

3^o alcohol



$HCl + ZnCl_2$

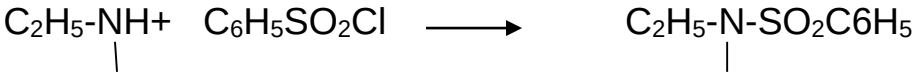
turbidity immmediatly

(i) 1^0 amine by Hinsbergtest :Hinsberg reagent

$C_2H_5NH_2$+ $C_6H_5SO_2Cl$ ⟶ $C_6H_5NH\text{-}SO_2\text{-}C_6H_5$

(benzenesulphonyl chloride) soluble in alkali

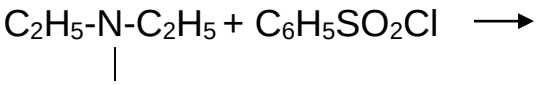
2 amine



$C_2H_5\text{-}NH\text{-}C_6H_5SO_2Cl$ ⟶ $C_2H_5\text{-}N(C_2H_5)\text{-}SO_2C6H_5$

Insoluble in KOH

3^o amine



$C_2H_5\text{-}N(C_2H_5)\text{-}C_2H_5 + C_6H_5SO_2Cl$ ⟶ X (No reaction)

(J) Benzoic acid

add $NaHCO_3$

Effervescence obtained(CO_2)

Benzene

no effervescence obtained

(k) Phenol

It gives violet colour with $FeCl_3$ test

Benzoic acid

It doesn't give violet colour with $FeCl_3$

No effervescene with aq $NaHCO_3$

Effervescence of CO_2

(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 — Acetophenone

It gives tollen's test — It doesn't

It doesn't give iodoform test — It gives iodoform test

(o) Methanal — Benzaldehyde

It gives fehling solution test — It doesn't

(p) Chlorobenzene — Benzyl choride

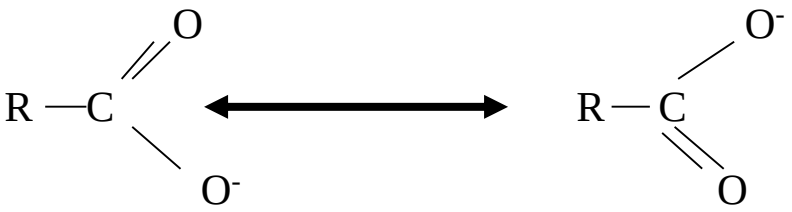
Does not give test with aq.KOH — gives test (white precipitate of AgCl) with $AgNO_3$

CONCEPTUAL QUESTIONS

Q1) Although phenoxide ion has more no. of resonating structures than carboxylate ion , even though carboxylic 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.



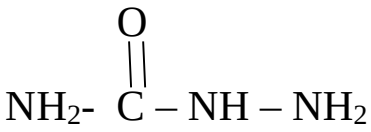
Q.2 Why Corboxylic acid have higher boiling point than alcohols as alcohol forms strongest inter molecular hydrogen bonding?

Ans.As Corboxylic acid forms a dimer due to which their surface area increses and forms strong intermolecular H-bonding

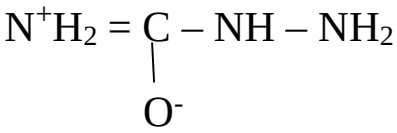
- It having more boiling point than alcohols.

Q.3 There are two-NH_2 group in semicarbazide .However only one is involved in formation of semicarbazones. Why?

Ans.



Due to resonance one NH_2 group undergoes or involved in resonance and hence can't participate in the formation of semicarbazone.



Long 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 carboxytic 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 groups in Ketones due to their e-releasing character decrease the +ve charge on C-atom and thus reduce its reactivity.

(b) Steric hindrance:- Due to steric hindrance in ketones they are less reactive.

Q.6 Why PCC cannot oxidise 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.

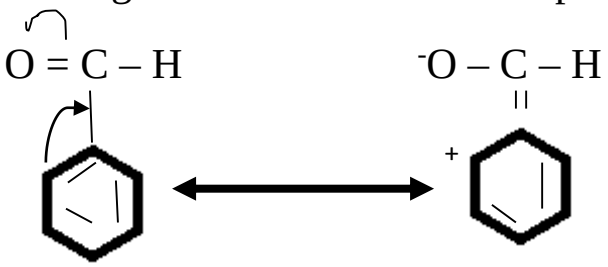
Ans. Because Butanol has strong intermolacular H-bonding while butanal has weak dipole-dipole interaction.

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 propanal? Explain.

Ans. C-atom of Carbonyl group of benzaldehyde is less electrophilic than C-atom of Carbonyl group in propanal.

Polarity of Carbonyl group in benzaldehyde is reduced due to resonance making it less reactive in nucleophillic addition reactions.



Q.11 Why does methanal not give aldol condensation while ethanal gives?

Ans.This is because only those compounds which have α-hydrogen atoms can undergo aldol reaction. Ethanal possesses α-hydrogen and undergoes aldol condensation. Methanal has no alpha hydrogen atoms hence does not undergo aldol condensation.

Q.12 Why does methanal undergo Cannizzaro's reaction?

Ans. Because it does not possess 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-hydroxybenzaldehyde is a liquid at room temperature while p- hydroxybenzaldehyde is a high melting solid.

Ans. Due to intramolecular H-bonding in O-hydroxybenzaldehyde exists as discrete molecule whereas due to intermolecular H-bonding p-hydroxybenzaldehyde 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-hydroxybenzaldehyde 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 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-trimethylcyclo-hexanone does not. Why?

Ans.In 2,2,6-trimethylcyclohexanone there is steric hindrance of 3 methyl groups, It does not form cynohydrin in good yield.

Q.18 Why is carboxyl group in benzoic acid meta directing?

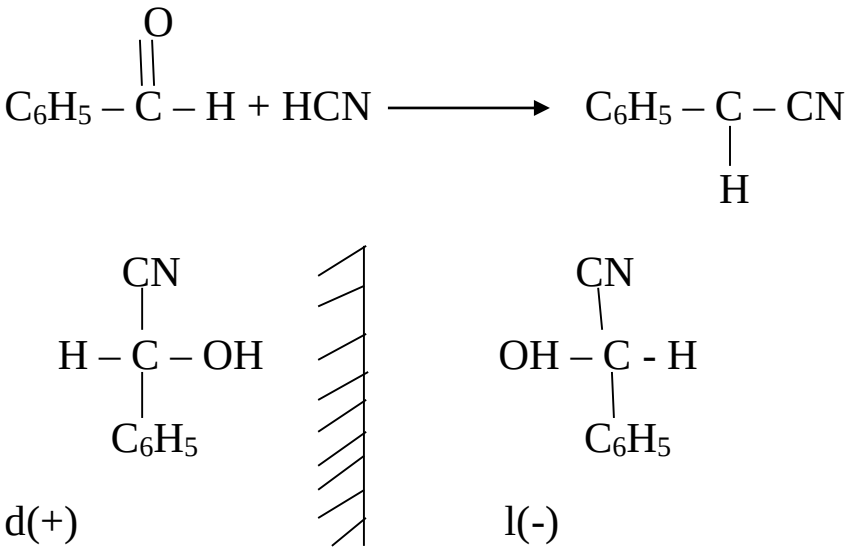
Ans. In benzoic acid the Carboxyl group is meta directing because it is electron-withdrawing

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?

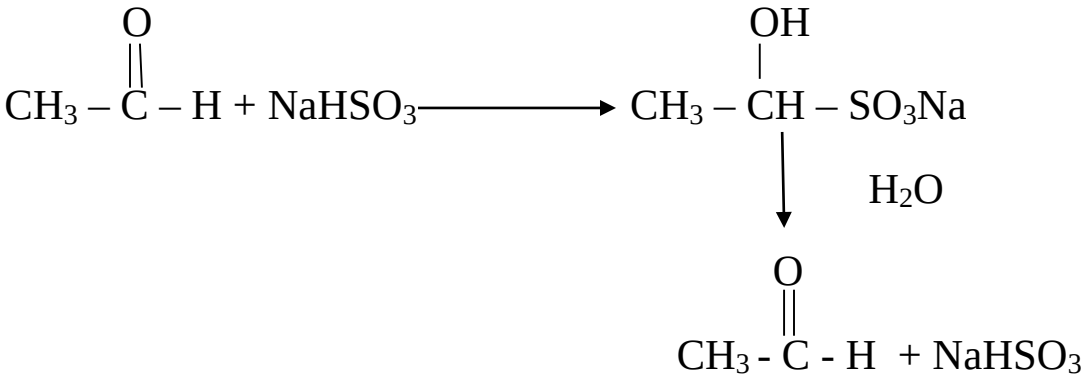
Ans.It is because we get two optical isomers which have same physical properties and cannot be separated by Fractional distillation.



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.



(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 alcohol to get aldehyde carried out under controlled conditions?

Ans.It is because aldehyde gets further oxidised to acid, oxidation of alcohol to aldehyde needs to be controlled.

Q.24 Why is the oxidation of toluene to benzaldehyde with CrO_3 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 H-bonding whereas alcohols are associated with intermoleculer H-bonding .

Q.27 Why do aldehydes behave like polar compounds?

Ans. Due to presence of  group which is polar

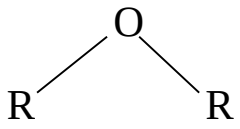
Q.28 Most aromatic acids are solids while acetic acid and others of this series are liquids. Explain why?

Ans. Aromatic acids have higher molecular weight,

More van-der waals force of attracrtion as compared to aliphalic acidsThey are solids.

Q.29 Ethers possess a dipole moment even if the alkyl radicals in the molecule are identical. Why?

Ans. It is because ethers are bent molecles, dipole do not get cancelled.



Q.30 Why does acyl chorides have lower boling 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. In presence of sunlight they react with oxygen to form peroxides which may cause explosion.

Q.32 Why not formaldehyde be prepared by Rosenmund's reduction?

Ans. Because the formyl chloride is unstable at room temperature.

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)

+

$CH_3CH_2CH_2CH_2OH$

(C)

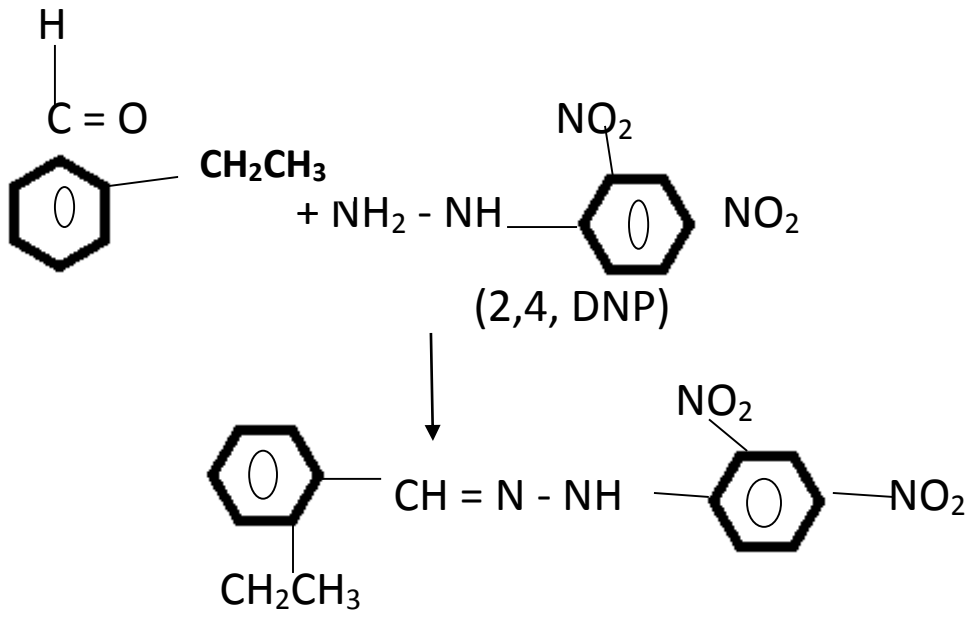
$CH_3CH_2CH_2\ CH_2OH \xrightarrow{K_2Cr_2O_7} CH_3\ CH_2CH_2COOH$

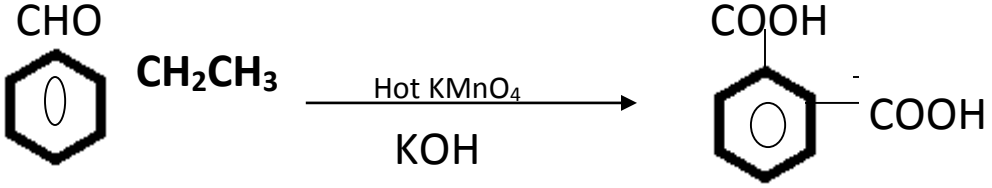
(c) (B)

$CH_3CH_2CH_2\ CH_2OH \xrightarrow[H_2SO_4]{Conc.} CH_3CH_2CH = CH_2$ (but – 1-ene)

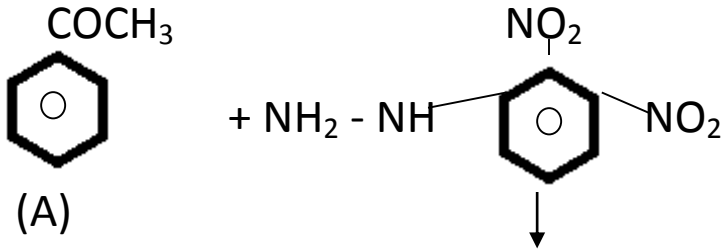
Q2 -: An organic compound with the molecular formula $C_9H_{10}O$ forms 2,4 DNP derivative reduces tollens reagent and undergoes cannizaro reaction . on vigorous oxidation ,it gives 1,2 benzenecarboxylic acid . identify the compound .

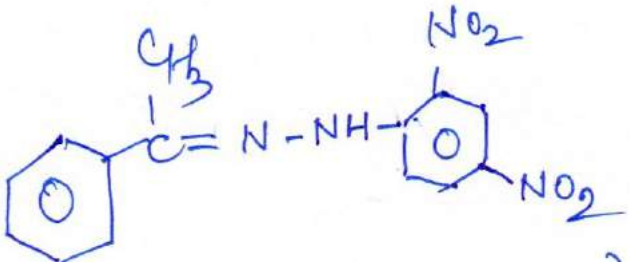
Ans:-





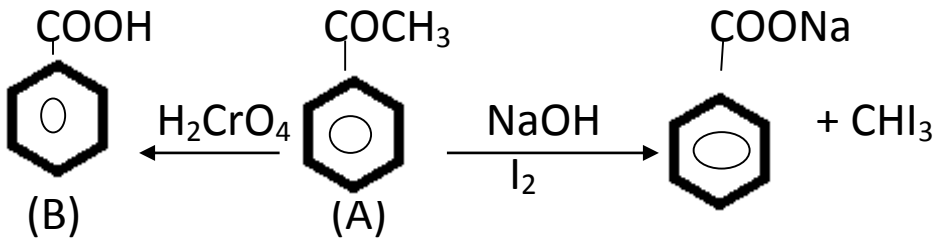
Q3. An organic compound (A) with molecular formula C_8H_8O forms an orange-red precipitate with 2,4 DNP reagent and gives yellow precipitate on heating with iodine in the presence of sodium hydroxide. It neither reduces tollen's or fehling's reagent , nor does it decolourise bromine water or baeyer's 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:- $2HCHO \xrightarrow[KOH]{Conc.} HCOOK + CH_3OH$

(A) (C) (B)

$CH_3OH \xrightarrow[573\ K]{Cu} HCHO$

(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 alkalene medium on warming gives a yellow precipitate 'C'. Identify the component A,B,C

Ans:- $CH_3COCH_3 + C_6H_5NH - NH_2 \longrightarrow CH_3C(CH_3)=N - HN - C_6H_5$

O (A) (B)

$CH_3\overset{\overset{O}{\|}}{C} - CH_3 + 3I_2 + NaOH \longrightarrow CHI_3$

(A) (Iodoform)

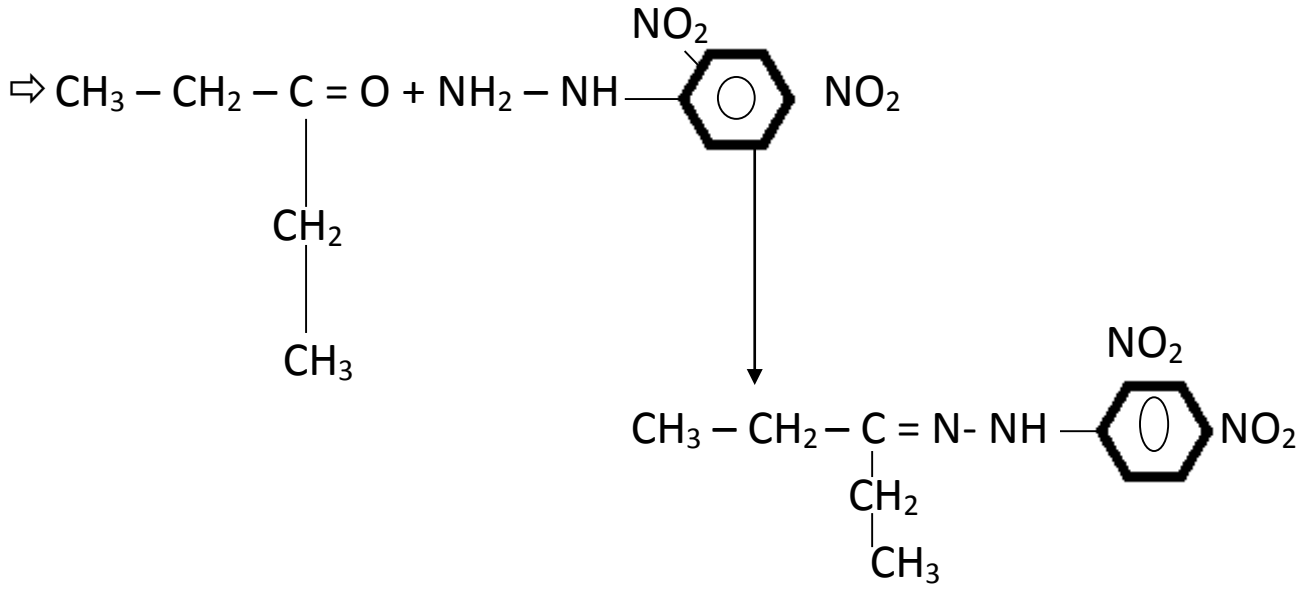
(c)

Q6 .A compound'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 carboboxylic acid'B' with molecular formula

$C_3H_60_2$when treated with alkalines $KMnO_4$ under vigrous condition . sodium salt of 'B' gave hydrocarbon 'C' on kolbeeletrolysis reduction . Identify A,B,C and D.

Ans:- $CH_3 - CH_2 - \underset{\underset{O}{\|}}{C} - CH_2 - CH_3 \xrightarrow[KOH]{KMnO_4} CH_3CH_2COOH$

(A) (B)



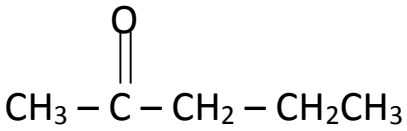
⇨ $2CH_3CH_2COONa \xrightarrow{electrolysis} CH_3CH_2CH_2CH_3 + 2CO_2$

Sodium propanoate (c)

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.

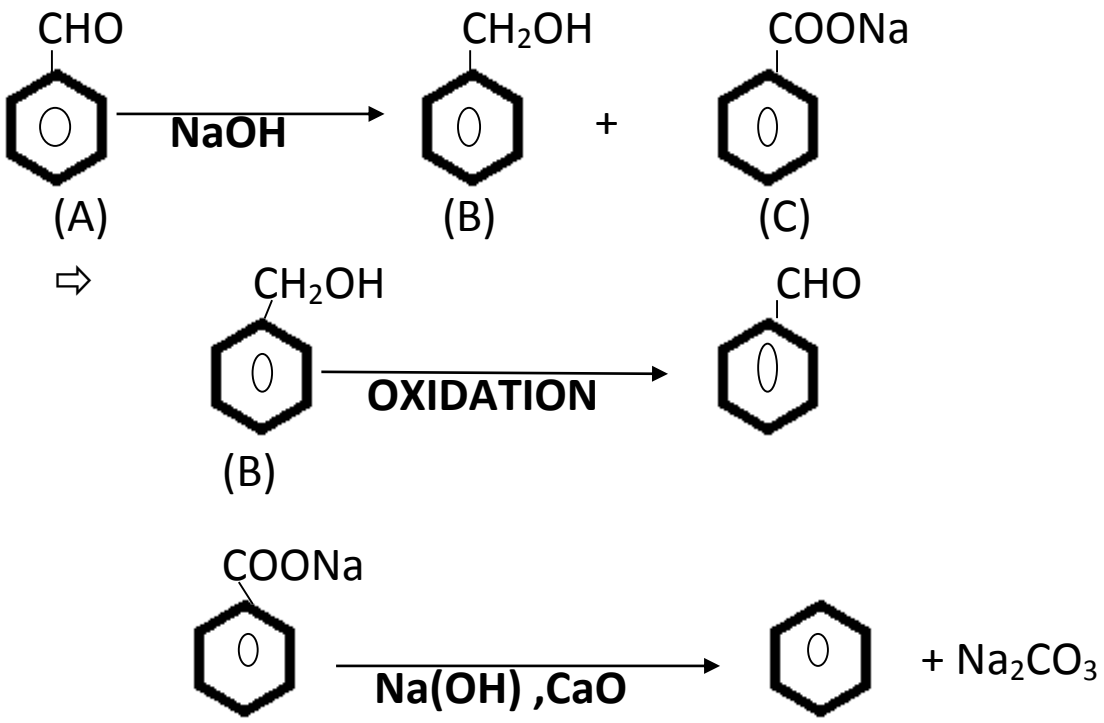
Ans-: it does not reduce fehling's solution but forms bisulpphite compound so it is a ketone therefore it gives positive iodoform test therefore it is methyl ketone .

The possible structure are-:



Q8. An 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

Ans.



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 withalkoholic KOH forms an alkene 'D' (C_3H_6). Deduce A,B,C,D.

Ans:- $CH_3 - \underset{\underset{O}{\|}}{C} - CH_3 \xrightarrow{LiAlH_4} CH_3\underset{\underset{OH}{|}}{CH} - CH_3$

(A) (B)

$CH_3\text{-}\underset{\underset{OH}{|}}{CH} - CH_3 + HBr \longrightarrow CH_3\underset{\underset{Br}{|}}{CH} - CH_3$

(B) (C)

$CH_3\text{-}\underset{\underset{Br}{|}}{CH} - CH_3 \xrightarrow{alc\ KOH} CH_3 - CH = CH_2 + KBr$

Br (D)

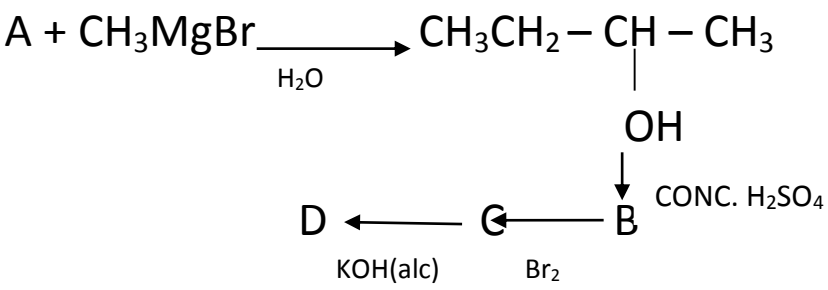
Q10. Eherial solution of an organic compound 'A' when heated with magnesium gave 'B' on treatment with ethanal followed by acid hydrolysis gave 2-propanol .Identify the compound 'A' . What is 'B' known as?

Ans:- $CH_3\ Br + Mg \xrightarrow{Dry\ ether} CH_3MgBr$

(a) (b)

$CH_3CHO + CH_3MgBr$ $CH_3 - \underset{\underset{OH}{|}}{CH} - CH_3 + Mg(OH)Br$

Q11. Identify A,B,C,D



ANS.

A = CH_3CH_2CHO

B = $CH_3CH = CH – CH_3$

C = $CH_3 – CH(Br) – CH(Br) – CH_3$

D = $CH_3 –CH =CH –CH_3$

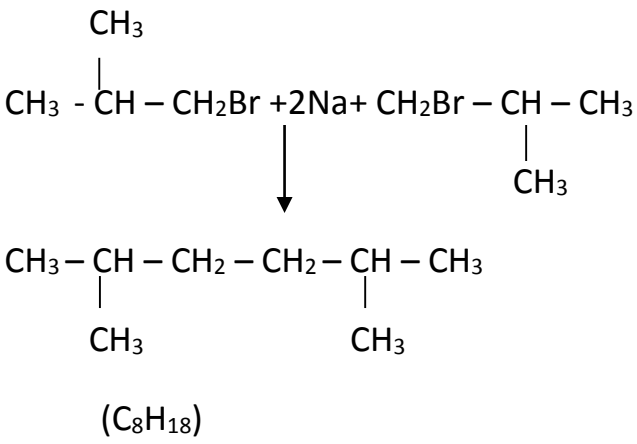
Q12. Primary alkyl halide C_4H_9Br (A) reacted with alcoholic KOH to give compound (B) is reacted with HBr to give (C) which is an isomer of (A). When (A) is reacted with sodium metal it gives compound (D) C_8H_{18} that was different from the compound formed when n-butyl bromide is reacted with sodium . Give the formula of (A) and write equations.

Ans:- $CH_3 – CH(CH_2Br) – CH_3$ (A) **+ alc. KOH** → $CH_3 – C(CH_3) = CH_2$ (B)

$CH_3 - C(CH_3) = CH_2 + HBr \longrightarrow CH_3 – C(Br) – CH_3$

(B) (c)

C is the isomer of A

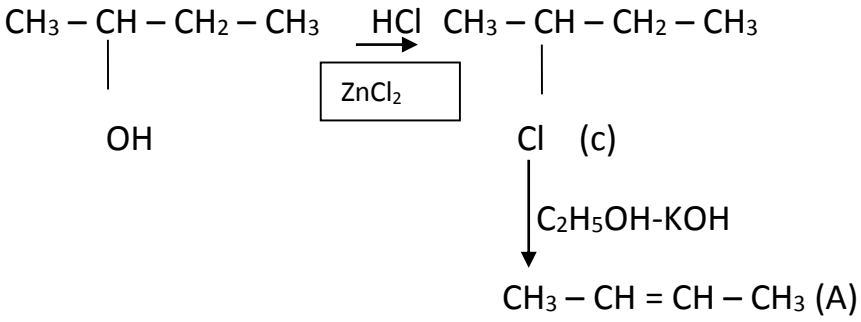


(C_8H_{18})

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 methoxide gives back A.Identify A,B,C.

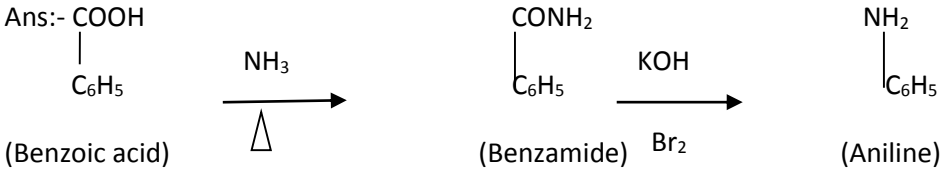
Ans:- $CH_3CH = CH - CH_3 + H_20 \xrightarrow{H_2SO_4}$ (B)

(A) $CH_3 - CH(OH) - CH_2 - CH_3$



Q14.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 .Identify A,B,C .



Q15 . 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 and gives a positive Iodoform test. Identify A and B .

Ans:- $CH_3 - \underset{\underset{NH_2\ (B)}{|}}{CH} - CH_2 - CH_3 + HNO_2 \longrightarrow CH_3 - \underset{\underset{OH\ \ (D)}{|}}{CH} - CH_2 - CH_3 + N_2$

$$CH_3 - \underset{\underset{NH_2}{|}}{\overset{\overset{CH_3}{|}}{C}} - CH_3 + HNO_2 \longrightarrow CH_3 - \underset{\underset{OH\ (c)}{|}}{\overset{\overset{CH_3}{|}}{C}} - CH_3 + N_2$$

$$CH_3 - \underset{\underset{OH}{|}}{\overset{\overset{CH_2CH_3}{|}}{C}} - CH_3 \xrightarrow[Anhy\ Zncl_2 \triangle]{CONC.\ HCl} CH_3 - \underset{\underset{Cl}{|}}{\overset{\overset{C_2H_5}{|}}{C}} - CH_3 \quad (3^0)$$

©

But 'D' respond to lucas reagent in 5 minutes.

$$.. \quad CH_3 - \underset{\underset{OH\ (D)}{|}}{CH} - CH_2 - CH_3 + HCl \xrightarrow{\triangle} C\,H_3 - \underset{\underset{Cl}{|}}{CH} - CH_2 - CH_3$$

$\triangle$

$CH_3 – CH(OH) – CH_2 – CH_3 + I_2 + NaOH \longrightarrow CHI_3 + CH_3 – CH_2COONa$

Q16. An organic compound 'A' having molecular formula $C_2H_5O_2N$ reacts with HNO_2 and gives $C_2H_4O_3N_2$. On reduction 'A' gives a compound 'B' with molecular formula C_2H_7N.'C' on treatment with HNO_2 gives 'C' which givespositiveidoform test . Identify A,B,C.

Ans:- $CH_3CH_2NO_2 + HNO_2 \longrightarrow CH_3 – \underset{\underset{N\text{-}OH}{\|}}{CH} – NO_2$

(A) (B)

$CH_3 – CH_2NO_2 + Sn/HCl \longrightarrow CH_3\ CH_2NH_2$

$\downarrow HNO_2$

CH_3CH_2OH

(C) $I_2/NaOH \downarrow$

CHI_3 (IODOFORM)

Q17. 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 alcohalic caustic potash give the offensive smelling C .Identify A,B,C

Ans:- $C_2H_5CN + 2H_2 \longrightarrow CH_3CH_2CH_2NH_2 \xrightarrow{HNO_2} CH_3CH_2CH_2OH$

(A) (B)

$CH_3CH_2CH_2NH_2 + CHCl_3 + 3KOH \longrightarrow CH_3CH_2CH_2NC$

(B) (C)

Q18 .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 colur complex C . Identify A,B,C

Ans .M $CH_3I + KCN \longrightarrow CH_3 - CN \longrightarrow CH_3CH_2NH_2$ (B)

$CH_3CH_2NH_2$ (B) $\xrightarrow{CuCl_2}$ $[Cu(CH_3CH_2NH_2)_4]Cl_2$

Bluecomplex

Q19. 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:- $CH_2 = CH - Cl + AgCN \longrightarrow CH_2 = CH - CN + CH_2 = CH - NC$

(A) (MINOR) (MAJOR)

$CH_2 = CH - C \equiv N \xrightarrow[H_2]{} CH_3 - CH_2 - CH_2 - NH_2$

B

Q20. 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 ethanolN_2 gas. Identify X,Y,

Ans:- $CH_3CH_2CONH_2 + Br_2 + 4\ KOH \longrightarrow CH_3CH_2NH_2$

(X) (Y)

$\xrightarrow{HNO_2}$

$CH_3CH_2OH + N_2(g)$

Q21. 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:- $CH_3CH_2CH_2NO_2 \longrightarrow CH_3CH_2CH_2NH_2$ (B)

$NaNO_2/HCL$ ↓

$CH_3CH_2CH_2OH$ (C)

Na ↓

$CH_3CH_2CH_2ONa$

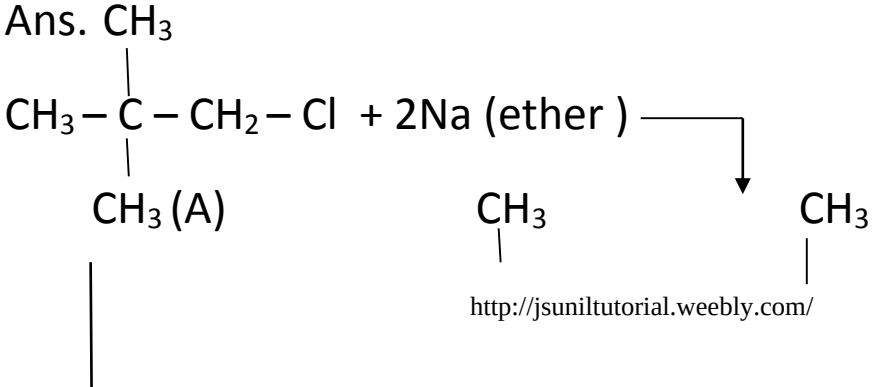
Sodium propoxide

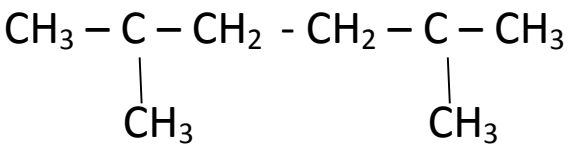
$CH_3\ CH_2CH_2OH \xrightarrow{CrO_3} CH_3CH_2CHO$

(C)

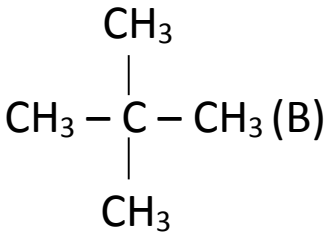
Q22. A Chloro compound 'A' on reduction with Zn – Cu and alcohol gives the hydro carbon (B) with five carbon atom.When'A' is dissolved in ether and treated with sodium 2,2,5,5 tetramethylhexhane is formed structure of A and B?

Ans.





Zn- CU



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. $C_6H_5NO_2 \xrightarrow{Fe/HCl} A \xrightarrow{NaNO_2} B \xrightarrow{C_6H_5OH} C$

Q4. $CH_3CH_2Br \xrightarrow[CuCN]{KCN} A \xrightarrow[H_2O/H^+]{LiAlH_4} B \xrightarrow[NH_3]{HNO_2} C$

Q5. $C_6H_5N^+{}_2Cl^- \longrightarrow A \longrightarrow B \longrightarrow C$

Q6. $CH_3CH_2I \xrightarrow{NaCN} A \xrightarrow[\text{Partial hydrolysis}]{OH^-} \xrightarrow{Br_2+NaOH} C$

Q7. $C_6H_5NH_2 + (CH_3C0_2)_2O \longrightarrow A$

Q8. $C_6H_5N_2^+Cl^- \xrightarrow[HBF_4]{NaNO_2/Cu,\ \Delta} A$

Q9. $A \xrightarrow[Br_2]{NaOH} B \xrightarrow[\text{Dil } HNO_3]{HNO_2} C \xrightarrow[NaNO_2 + HCl]{Red\ P/I_2} D\ (CH_3I)$

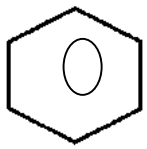
Q10. A $\xrightarrow{\triangle}$ B $\xrightarrow{Br_2}$ C $\longrightarrow$ $C_6H_5N_2^+Cl^-$

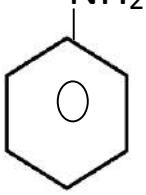
Q11. A $\xrightarrow[KOH]{}$ B $\xrightarrow[HNO_2]{}$ C $\xrightarrow[CH3I]{}$ $C_2H_5NH_2$

Q12. A $\xrightarrow{AgCN}$ B $\xrightarrow[H^+/H_2O]{Sn/HCl}$ C $\xrightarrow[LiAlH_4]{}$ CH_3 –CH2- N H– CH_3

Q13. CH_3CN $\longrightarrow$ A $\longrightarrow$ B

Q14. R_2CO $\xrightarrow{NH_2}$ A $\xrightarrow{LI/H_2}$ B

Q15.  $\xrightarrow{CN}$ A $\xrightarrow{LiAlH_4}$ B

Q16.  $\xrightarrow[O^0C]{NaNO_2/HCl}$ A $\xrightarrow[CuCl]{}$ B

1 MARK QUESTIONS

Q1 Suggest a reason for the large difference in the boiling points of butanol and butanal, although they have same solubility in water

. A. 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.

Q 2.What type of aldehydes undergo Cannizzaro reaction ?

A.Aromatic and aliphatic aldehydes which do not contain α- hydrogens.

Q 3. Out of acetophenone and benzophenone, which gives iodoformtest ? Write the reaction involved. (The compound should have CH_3CO-group to show the iodoform test.)

A. Acetophenone ($C_6H_5COCH_3$) contains the grouping (CH_3CO attached to carbon) and hence given iodoform test while benzophenone does not contain this group and hence does not give iodoform test.

$C_6H_5COCH_3 + 3\ I_2 + 4\ NaOH \longrightarrow CHI_3 + C_6H_5COONa + 3\ NaI + 3\ H_2O$

AcetophenaneIodoform

$$C_6H_5COC_6H_5 \xrightarrow{I_2/NaOH} \text{No reaction}$$

Q4. Give Fehling solution test for identification of aldehyde gp (only equations). Name thealdehyde which does not give Fehling's soln. test.

A. $R - CHO - 2\ Cu^{2+} + 5\ OH^- \longrightarrow RCOO^- + Cu_2O + 3\ H_2O$

Benzaldehyde does not give Fehling soln. test. (Aromatic aldehydes do not give this test.)

Q5. What makes acetic acid a stronger acid than phenol ?

A. Greater resonance stabilization of acetate ion over phenoxide ion.

Q.6 Why HCOOH does not give HVZ (Hell VolhardZelinsky) reaction but CH_3COOH does?

A. CH_3COOH contains α- hydrogens and hence give HVZ reaction but HCOOH does not contain α-hydrogen and hence does not give HVZ reaction

Q7. 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.

A. The formation of esters from a carboxylic acid and an alcohol in the presence of acidcatalyst in a reversible reaction.

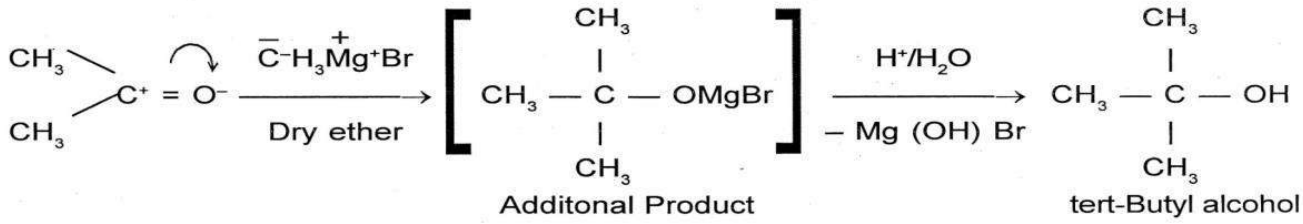
$$\underset{\text{Carboxylic acid}}{RCOOH} + \underset{\text{alcohol}}{R'OH} \overset{H_2SO_4}{\rightleftharpoons} \underset{\text{Ester}}{RCOOR'} + H_2O$$

To shift the equilibrium in the forward direction, the water or ester formed should be removed as fast as it is formed

Q 8.**Arrange the following compounds in increasing order of their acid strength. Benzoic acid, 4-Nitrobenzoic acid, 3, 4-dinitrobenzoic acid, 4-methoxy benzoic acid.**

A. 4-methoxybenzoic acid < benzoic acid < 4-nitrobenzoic acid <4, dinitrobenzoic acid.

Q9. **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.**

CH_3CHO, CH_3CH_2OH, CH_3OCH_3, $CH_3CH_2CH_3$.

A. The molecular masses of all these compounds are comparable :

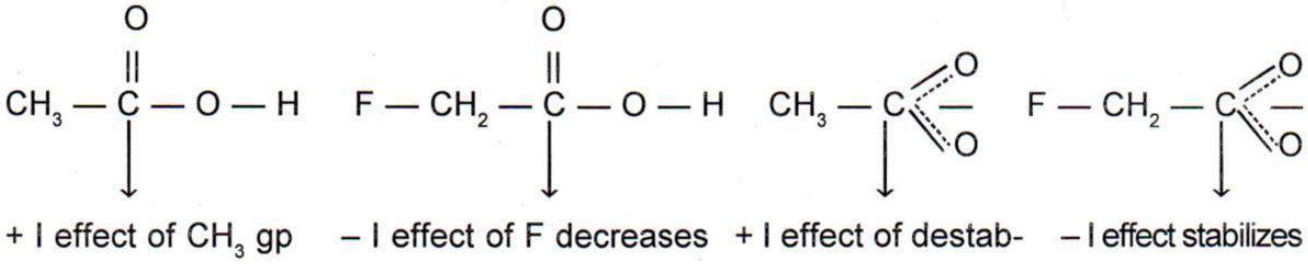
CH_3CHO (44), CH_3CH_2OH (46), CH_3COCH_3 (46), $CH_3CH_2CH_3$ (44).

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?

$F_3C — C_6H_4 — COO H$, $CH_3 — C_6H_4 — COOH$

A. CF_3 has a strong(– I) effect. CH_3 has a weak (+ I) effect.
It stabilises the carboxylate ion by dispersing the – ve charge. Itstabilises the carboxylate ion by intensifying the – ve charge.

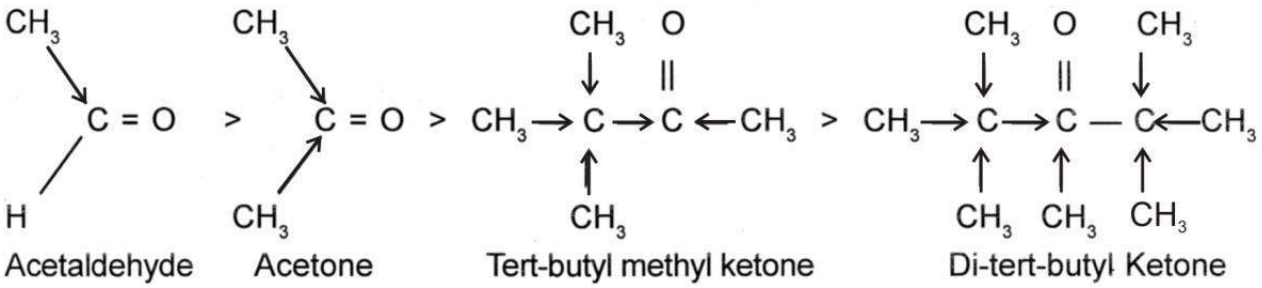
Therefore due to greater stability of $F_3C — C_6H_4 — COO^-$ (p) ion over $CH_3 — C_6H_4COO^-$ (p) ion, $F_3C — C_6H_4 — COOH$ is a much stronger acid than $CH_3 — C_6H_4 — COOH$.

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-hydroxybenzaldehyde 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.p. and b.p. than that of o-hydroxybenzaldehyde. As a result, o-hydroxybenzaldehyde is a liquid at room temperaturewhile p-hydroxybenzaldehyde 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 ketonereactivity 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 inketones 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) $CH_3CH_2CHBrCOOH$,$CH_3CHBrCH_2COOH$, $(CH_3)_2CHCOOH$, $CH_3CH_2CH_2COOH$ acid strength

-$(CH_3)_2CHCOOH < CH_3CH_2CH_2COOH < CH_3CHBrCH_2COOH < CH_3CH_2CHBrCOOH$

-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 –CH3 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.

***

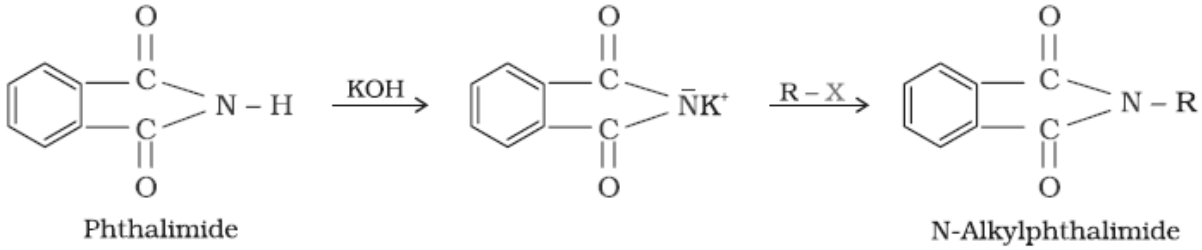
UNIT 13:
AMINES

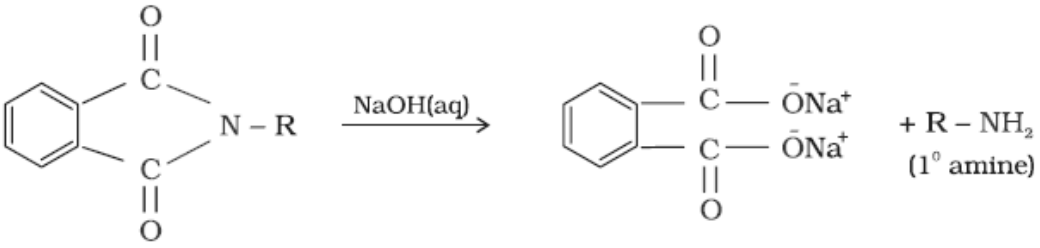
IUPAC NOMENCLATURE

For practice refer Page No. 383 and Exercise Question Page No. 400 of NCERT Text Book.

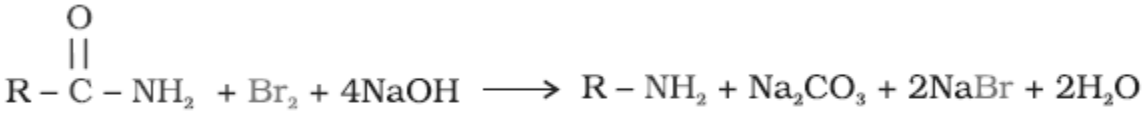
NAMEREACTIONS

1.Gabrielphthalimidesynthesis





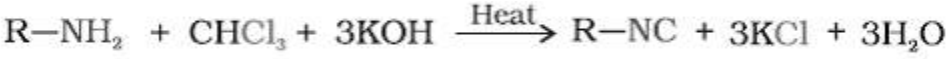
2.Hoffmann bromamide degradation reaction



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

Alkanamide Alkyl amine

3.Carbylamine reaction (Isocyanide Test for Primary Amine)



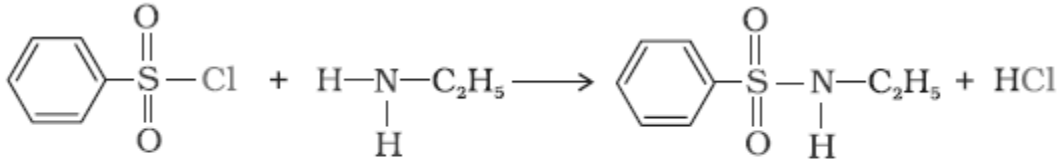
$$R-NH_2 + CHCl_3 + 3KOH \xrightarrow{Heat} R-NC + 3KCl + 3H_2O$$

4.HinsbergTest: (to distinguish 1º,2º and 3º amines)

Benzenesulphonylchloride ($C_6H_5SO_2Cl$), which is also known as Hinsberg's reagent, reacts with primary and secondary amines to form sulphonamides.

(a) The reaction of benzenesulphonylchloride with primary amine yields

N-ethylbenzenesulphonylamide.

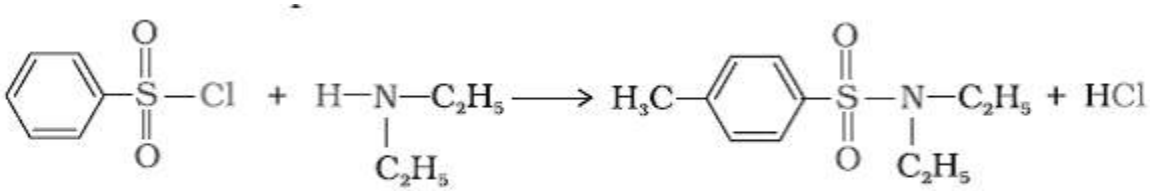


N-Ethylbenzenesulphonamide
(soluble in alkali)

The hydrogen attached to nitrogen in sulphonamide is strongly acidic due to the presence of strong electron with drawing sulphonyl group. Hence, it is soluble in alkali.

(b) In the reaction with secondary amine, N,N-diethylbenzenesulphonamide is

formed.



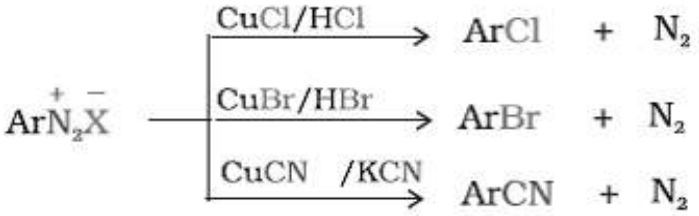
N,N-Diethylbenzenesulphonamide

Since N,N-diethylbenzenesulphonamide doesnot contain any hydrogen atom attached to nitrogen atom, it is not acidic and hence insoluble in alkali.

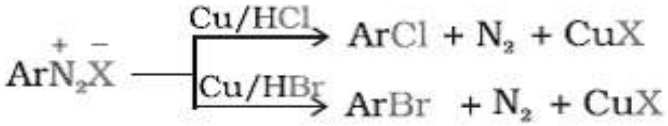
(c) Tertiary amines donot react with benzenesulphonylchloride.

5.Sandmeyer Reaction

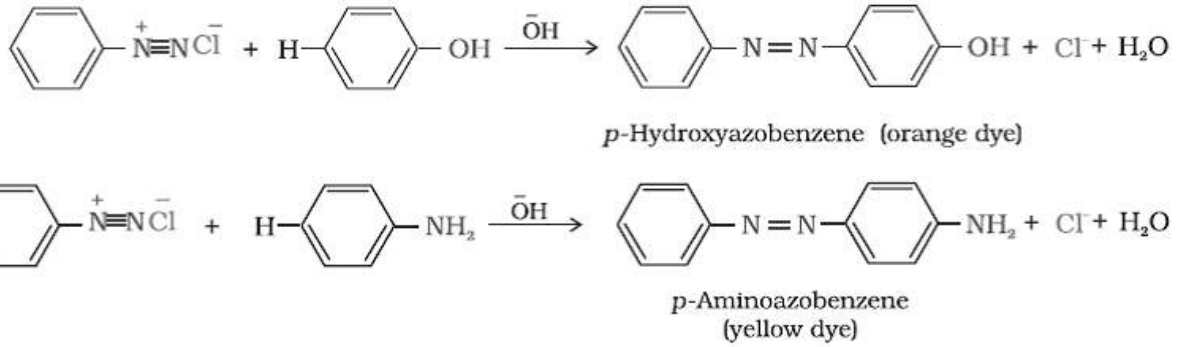
The Cl–,Br–and CN–nucleophiles can easily be introduced in the benzene ring of diazonium salts in the presence of Cu(I) ion.



6.Gatterman Reaction



7.Coupling reactions



DISTINCTION BETWEEN PAIRS OF COMPOUNDS

Give one chemical test to distinguish between the following pairs of compounds.

(i) Methylamine and dimethylamine
(ii) Secondary and tertiaryamines
(iii) Ethylamine and aniline
(iv) Aniline and benzylamine
(v) Aniline and N-methylaniline.

ANS. (i) Methyl amine and dimethylamine can be distinguished by the carbylamines test. Carbylaminetest: Aliphatic can 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 carbyl amine test, but dimethylamine doesnot.

$$CH_3-NH_2 + CHCl_3 + 3KOH \xrightarrow{\Delta} CH_3-NC + 3KCl + 3H_2$$

Methylamine (1^0) Methyl isocyanide (foul smell)

$$(CH_3)_2NH + CHCl_3 + 3KOH \xrightarrow{\Delta} \text{No reaction}$$

(ii)Secondary and tertiary amines can be distinguished by allowing them to react with Hinsberg's reagent (benzenesulphonylchloride, $C_6H_5SO_2Cl$). 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, donot 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 o f N_2 gas) under similar conditions.

(iv) Aniline and benzylamine can be distinguished by the reactions with the help of nitrous acid, which is prepared in situ from a mineral acid and sodium nitrite.

Benzyl amine reacts with nitrous acid to form unstable diazonium salt, which in turn gives alcohol with the evolution of nitrogen gas.

On the other hand, aniline reacts with HNO_2 at a low temperature to form stable diazonium

salt. Thus,nitrogen gas is not evolved.
(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 isocyanidesorcarbylamines. Aniline,being an aromatic primary amine, gives positive carbylamines test. However,N-methylaniline,being a secondary amine doesnot.

REASONINGQUESTIONS

Q1. Accountfor the following:

(i) pKb of anilineis more than that of methylamine.

(ii)Ethyl amine is soluble in wate rwhereas aniline is not.

(iii) Methyl amine in water reacts with ferric chloride to precipitate hydrated ferric oxide.

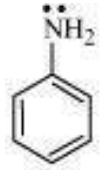
(iv) Although amino group is o–and p–directing in aromatic electrophilic substitution reactions, aniline on nitration gives a substantial amount of m-nitroaniline.

(v) Aniline does not undergo Friedel-Crafts reaction.

(v) Diazonium salts of aromatic amines are more stable than those of aliphatic amines.

(vi) Gabriel phthalimide synthesis is preferred for synthesising primary amines.

NS. (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, theelectrons on the N-atom areless availabletodonate.

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 aresult, aniline is less basic than methylamine. Thus, pK_b of aniline is more than that of methylamine.
(ii) Ethylamine is soluble in water where as aniline is not:
Ethylamine when added to water forms intermolecular H−bonds with water. Hence, it
Is soluble in water.
Butaniline 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:
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.

$$2Fe^{3+} + 6OH^- \longrightarrow \underset{\text{Hydrated ferric oxide}}{Fe_2O_3 \cdot 3H_2O}$$

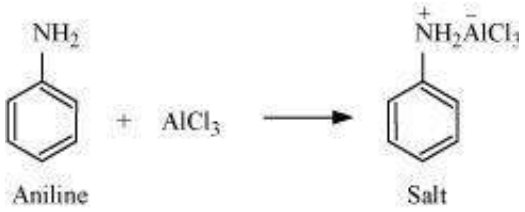
(iv) Although amino group is o,p− directing in aromatic electrophilic substitution reactions, aniline on nitration gives a substantial amount of m-nitroaniline:

Nitration is carried out in an acidic medium. In an acidic medium, aniline is protonated to give anilinium ion (which is meta-directing).

For this reason,aniline on nitration gives a substantial amount of m-nitroaniline.

(v)Aniline does not undergoFriedel-Crafts reaction:

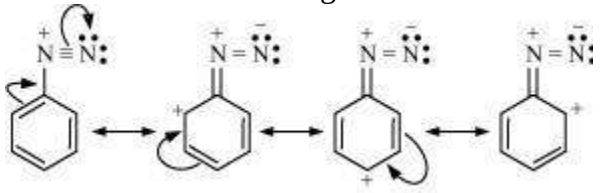
AFriedel-Crafts reaction is carried out in the presence of $AlCl_3$. But $AlCl_3$ is acidic in nature, while aniline is a strong base.Thus, aniline reacts with $AlCl_3$ to form a salt (as shown in the following equation).



Due to the positive charge on the N-atom, electrophilic substitution in the benzene ring is deactivated. Hence, aniline does not undergo the Friedel-Crafts reaction.

(vi) Diazonium salts of aromatic amines are more stable than those of aliphatic amines:

The diazonium ion undergoes resonance as shown below:



This resonance accounts for the stability of the diazonium ion.Hence, diazonium salts of aromatic amines are more stable than those of aliphatic amines.

(vii) Gabriel phthalimide synthesis is preferred for synthesis in primary amines:

Gabrielphthalimidesynthesisresultsintheformationof1°amineonly.2°or3°amines arenotformed in the synthesis.Thus, a pure1°amine can be obtained. Therefore,

Gabriel phthalimide synthesis is preferred forsynthesizingprimaryamines.

Q2.Why cannot aromatic primary amines 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 alkylhalides by the anion formed bythe phthalimide. Butarylhalides donot undergo nucleophilic substitution with the anion formed by the phthalimide.

Hence, aromatic primary amines cannot be prepared bythis process.

Q3.Give plausible 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?

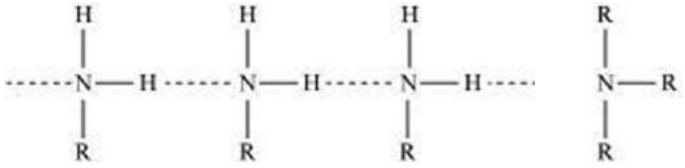
ANS. (i) Amines undergo protonation to give amide ion.

$$R-NH_2 \longrightarrow \underset{\text{Amide ion}}{R-\bar{N}H} + H^+$$

Similarly, alcohol loses a proton to give alkoxide ion.

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.

(iv) 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.

1 MARK QUESTIONS SOLVED QUESTIONS

Q1.Give the IUPAC name of the compound and classify into primary, secondary or tertiary amines.

$(CH_3)_2CHNH_2$ 1-Methylethanamine(1^0amine)

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.

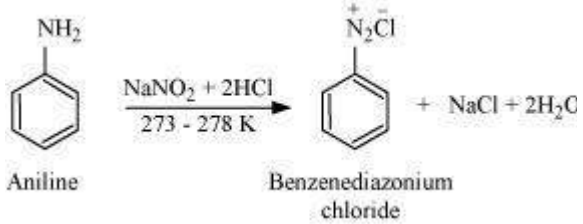
$(CH_3)_3CNH_2$ 2-Methylpropan-2-amine(1^0amine)

Q5.Give the IUPAC name of the compound and classify into primary, secondary or tertiary amines.

$C_6H_5NHCH_3$ N−MethylbenzamineorN-methylaniline(2^0 amine)

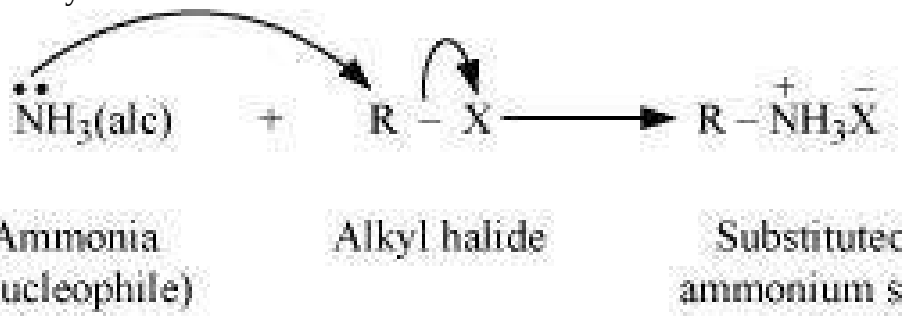
Q6.Write short notes on diazotization.

Aromatic primary amines react with nitrous acid (prepared in situ from $NaNO_2$ and a mineral acid such as HCl) at low temperatures (273-278K) 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 benzenediazoniumchloride, with NaCl and H_2O as by-products.

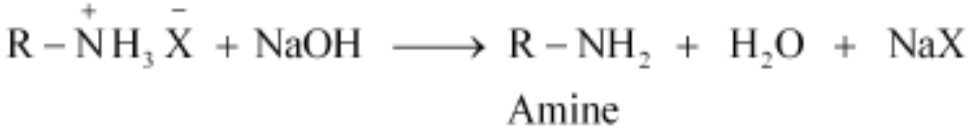


Q7.Write short notes on ammonolysis.

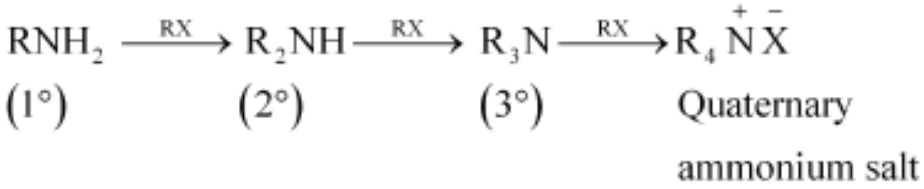
When an alkyl or benzyl halide is allowed to react with an ethanolic solution of ammonia, it undergoes nucleophilic substitution reaction in which the halogen atom is replaced by an amino (−NH_2) group. This process of cleavage of the carbon-halogen bond is known as ammonolysis.



When this substituted ammonium salt is treated with a strong base such as sodium hydroxide, amine is obtained.



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



Q8.Write short note 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 (suchas 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 (2Marks)

Q1.Write chemical equations for the following reactions: (i)

Reaction of ethanolic NH_3 with C_2H_5Cl.

(ii) Ammonolysis of benzylchloride and reaction of amines of formed with

two moles of CH_3Cl

ANS.

(i) $C_2H_5–Cl \xrightarrow[-HCl]{NH_3} C_2H_5–NH_2 \xrightarrow[-HCl]{C_2H_5-Cl} C_2H_5–\underset{H}{N}–C_2H_5 \xrightarrow[-HCl]{C_2H_5-Cl} C_2H_5–\underset{C_2H_5}{\underset{|}{N}}–C_2H_5$

Chloroethane Ethanamine N-Ethylethanamine N,N-Diethylethanamine

(ii) $C_6H_5–CH_2–Cl \xrightarrow{NH_3} C_6H_5–CH_2NH_2 \xrightarrow{2CH_3Cl} C_6H_5–CH_2–\underset{CH_3}{\underset{|}{N}}–CH_3$

Benzylchloride Benzylamine N,N-Dimethylphenylmethanamine

Q2.Write chemicalequations forthe followingconversions: (i)CH_3

$–CH_2–Cl$ into $CH_3–CH_2–CH_2–NH_2$

(ii)$C_6H_5–CH_5–Cl$ into$C_6H_5–CH_2–CH_2–NH_2$

(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

(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 andIUPAC names of

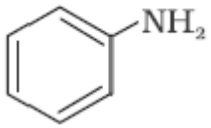
(i) The amide which gives propanamine by Hoffmann bromamide reaction.

(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:

$CH_3–CH_2–CH_2–\underset{\underset{O}{\|}}{C}–NH_2$ (Butanamide)

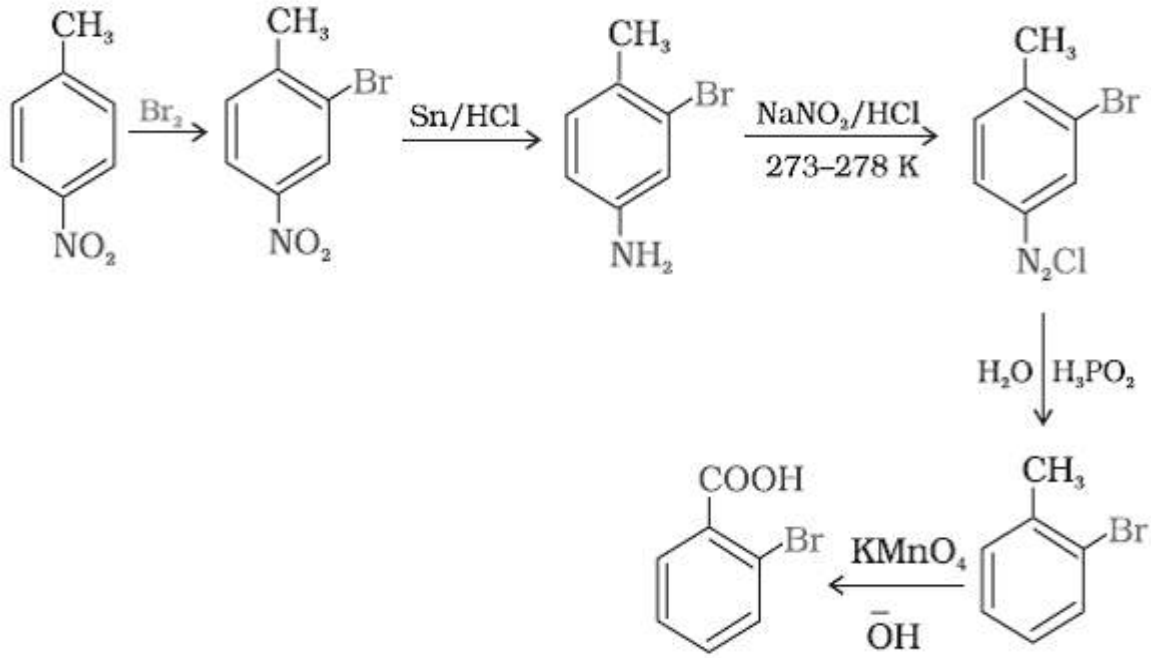
(ii)Benzamide is an aromatic amide containing seven carbon atoms. Hence, the amine formed From benzamide is aromatic primary amine containing six carbon atoms.



(Aniline or benzenamine)

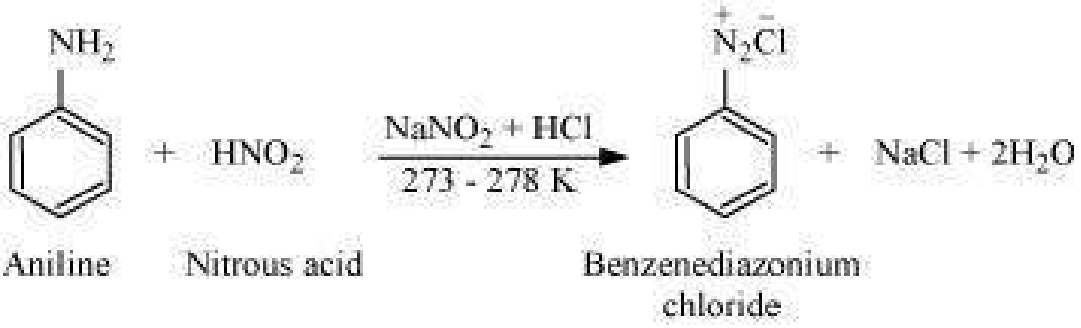
Q4.How will you convert 4-nitrotoluene to 2-bromobenzoic acid?

ANS.

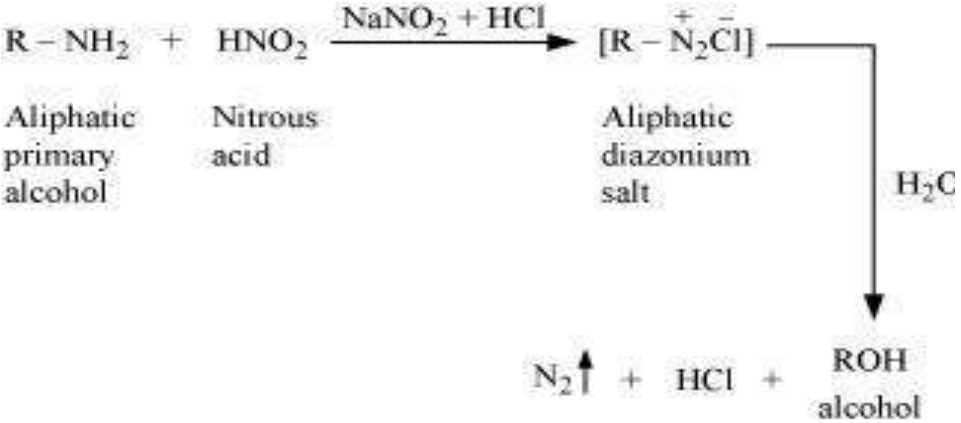


Q5.Write the reactions of (i) aromatic and (ii) aliphatic primary amines with nitrous acid.

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.

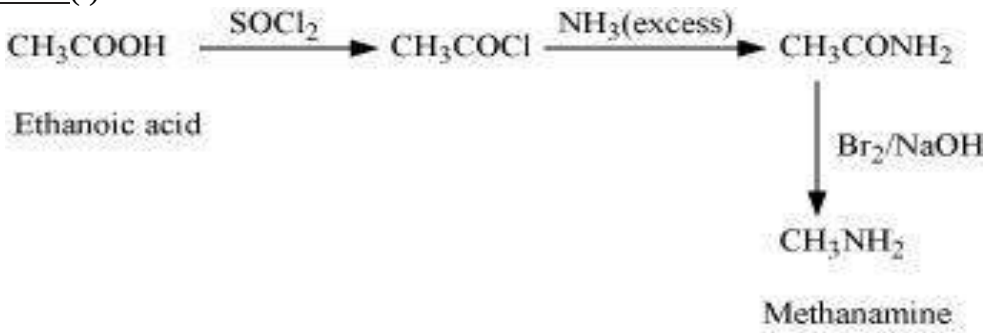


Q6.How will you convert:

(i) Ethanoic acid in to methanamine

(ii) Hexanenitrile into1-aminopentane

ANS.(i)



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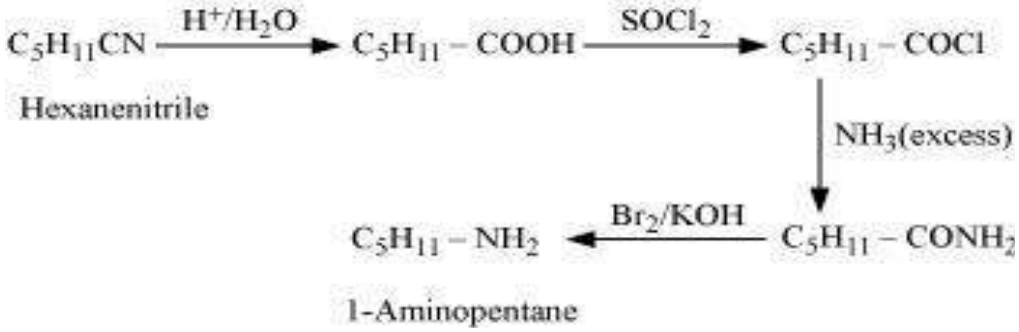
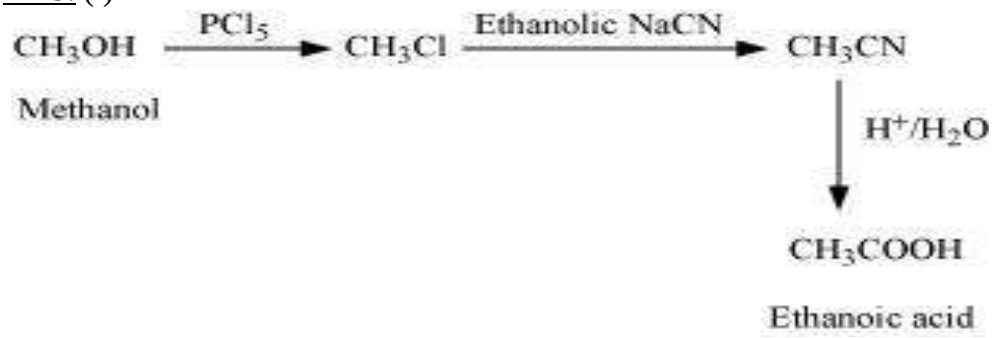


Q7.How willyou convert:

(i)Methanol to ethanoic acid

(ii)Ethanamine into methanamine

ANS. (i)



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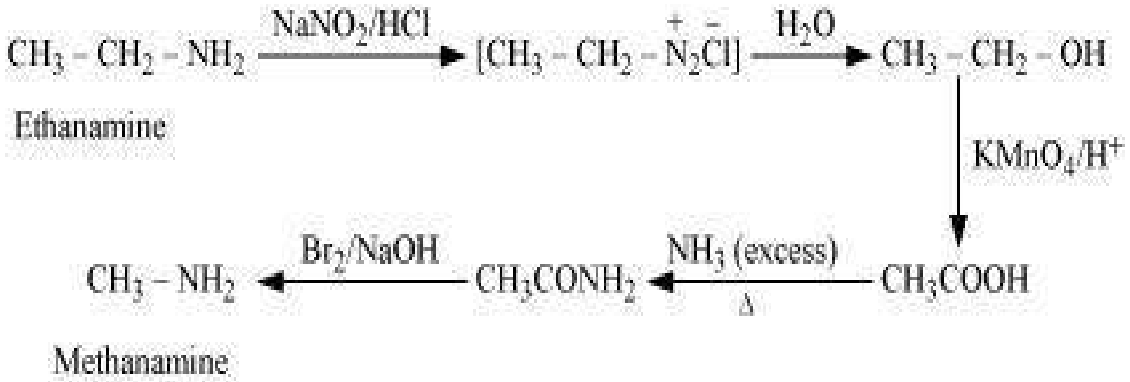
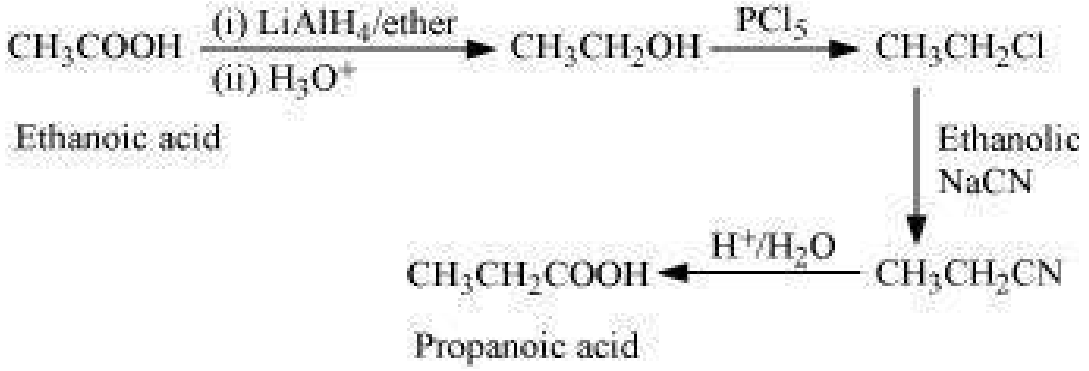


Q8.How will you convert

(i)Ethanoic acid into propanoic acid

(ii)Methanamine into ethanamine

ANS. (i)



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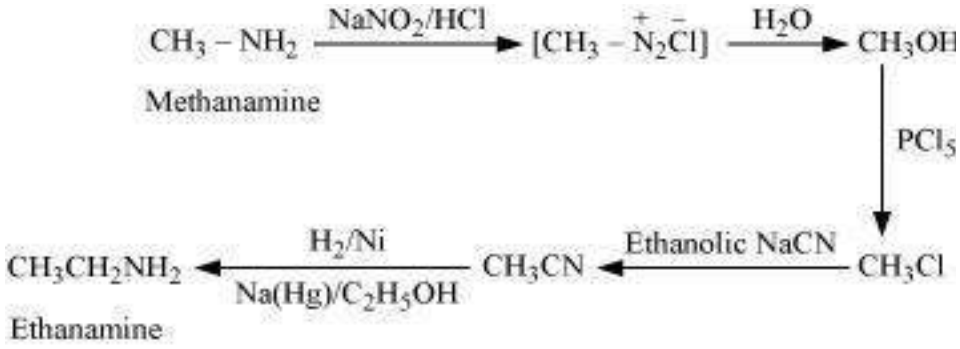
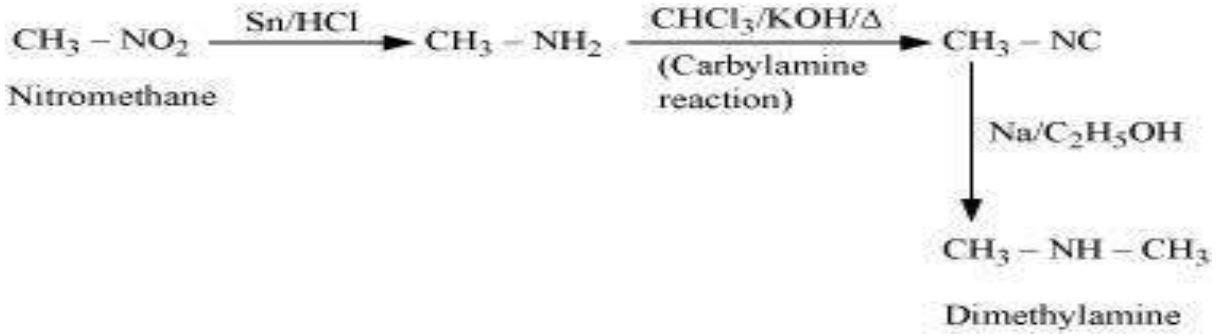


Q9.How will you convert

(i) Nitromethane into dimethylamine

(ii) Propanoic acid into ethanoic acid?

(i)



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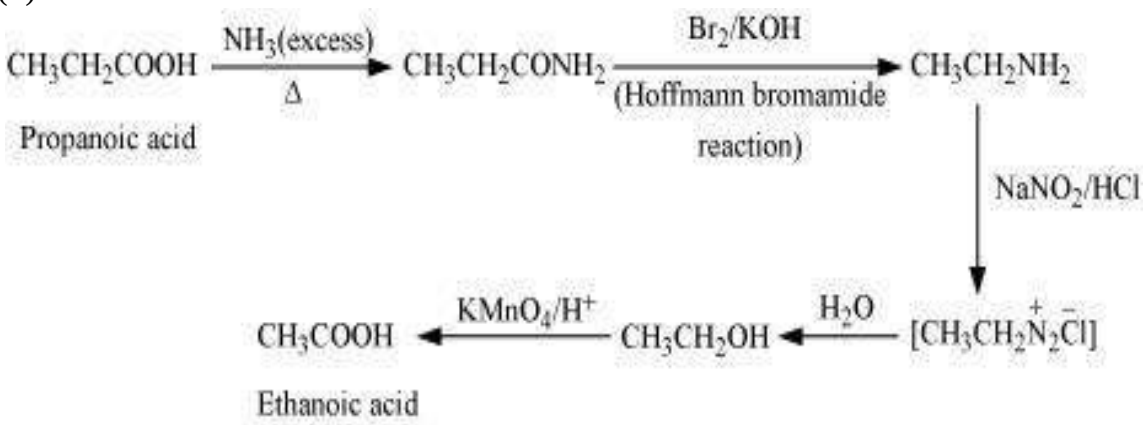
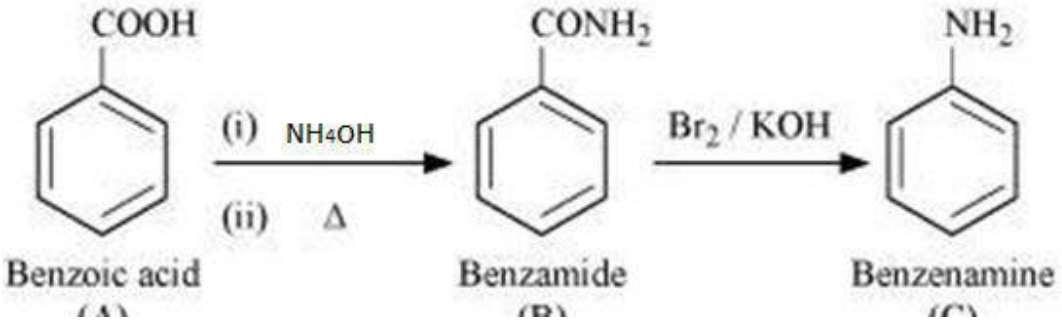


Q10. An aromatic compound ‗A' on treatment with aqueous ammonia and heating forms compound‗B'which on heating with Br_2 and KOH forms a compound ‗C' of molecular formula C_6H_7N. Write the structures and IUPAC names of compounds A, B and C.

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-nitroanilineandp-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 compoundsis:
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 $(C_2H_5)_2NH$.

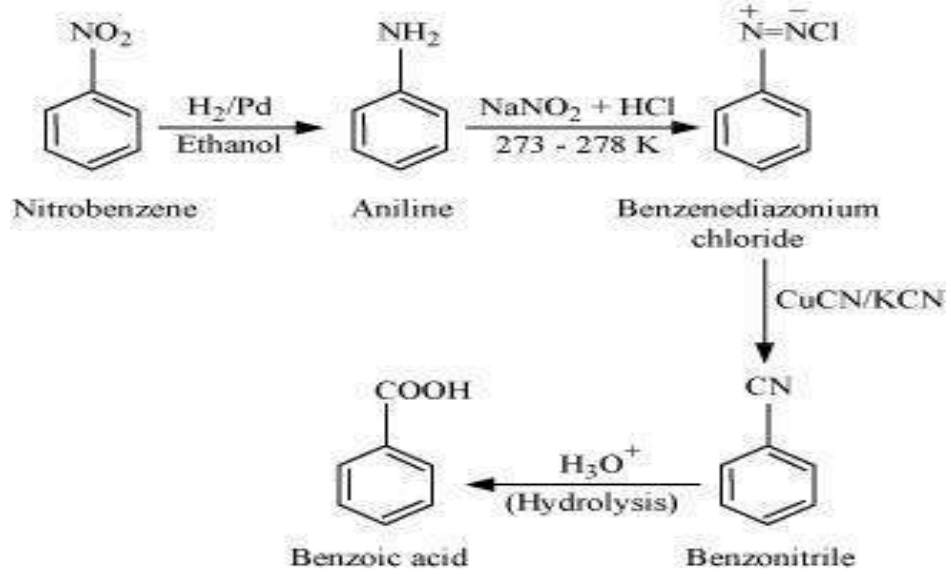
Q3.Accomplish the following conversions:

(i) Nitrobenzene to benzoicacid

(ii) (ii) Benzene to m-bromophenol

(iii) (iii) Benzoicacid toaniline

ANS.(i)



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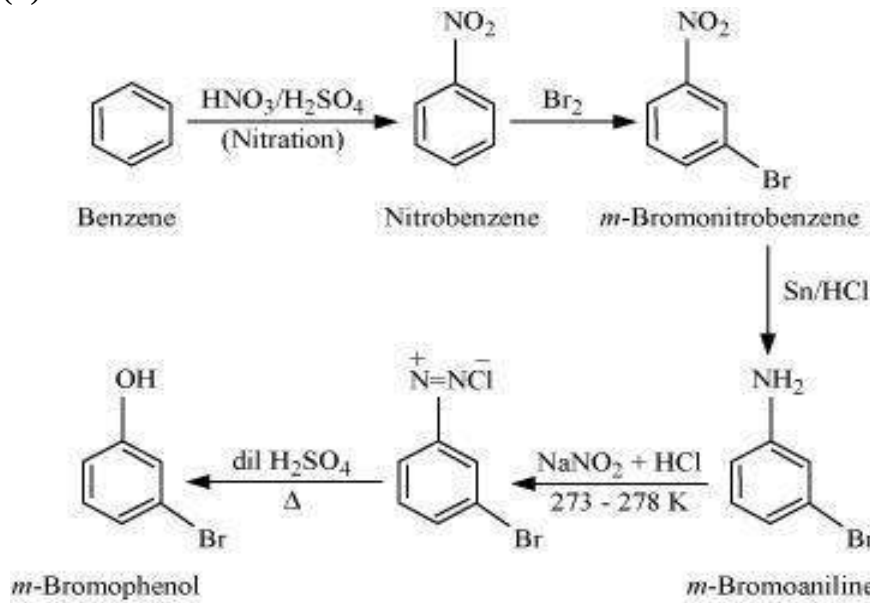

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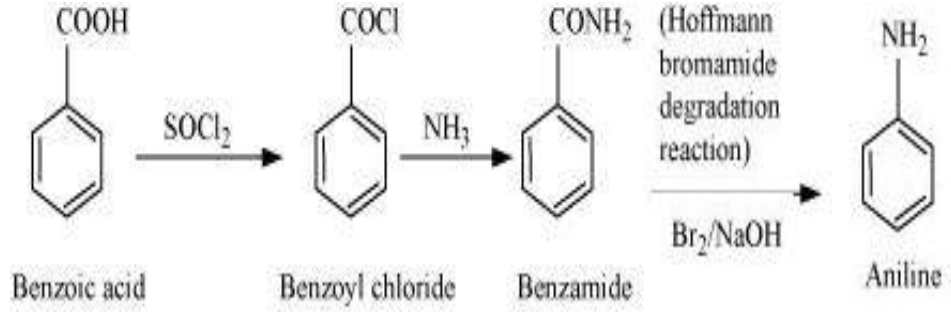
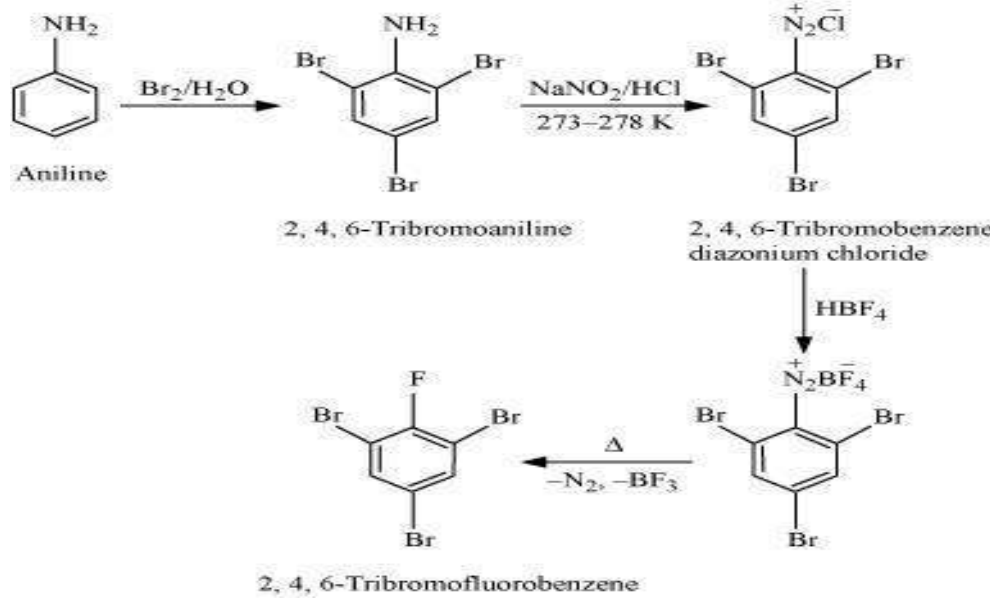


Q4.Accomplish the following conversions:

i) Aniline to 2,4,6-tribromofluorobenzene
ii) Benzyl chloride to 2-phenylethanamine
iii) Chlorobenzene to p-chloroaniline

ANS. (i)



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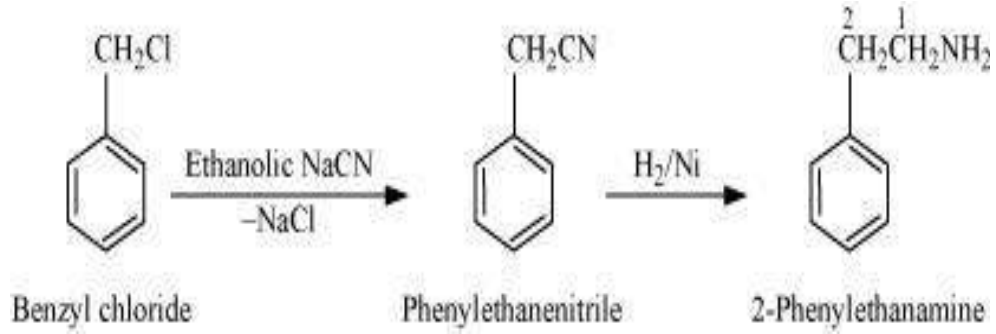

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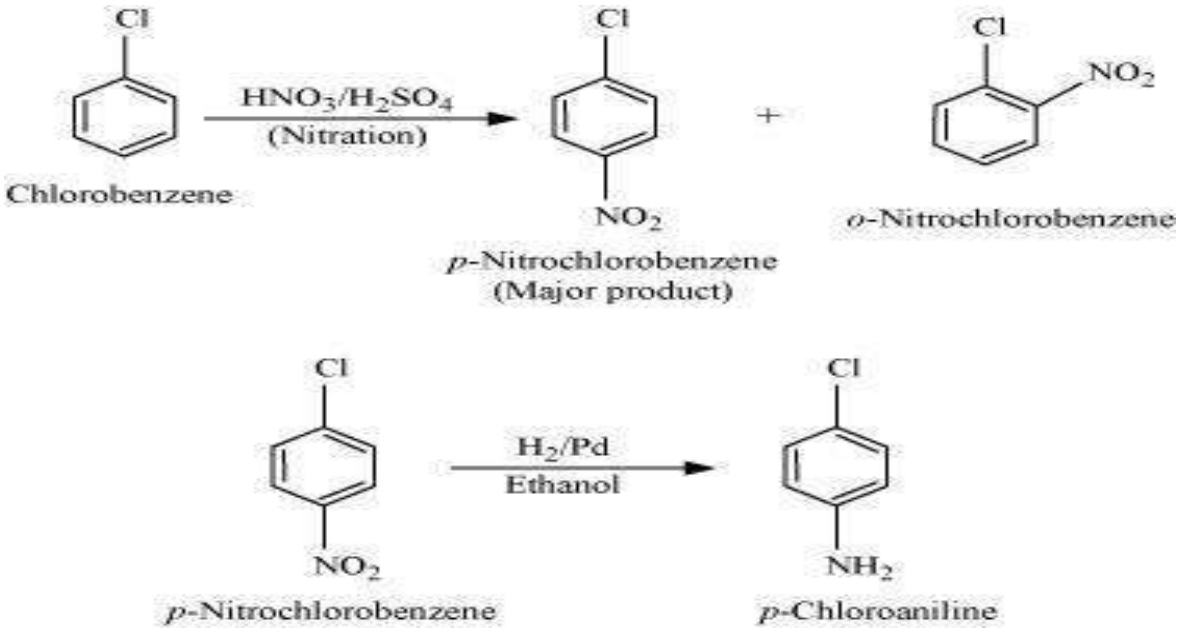
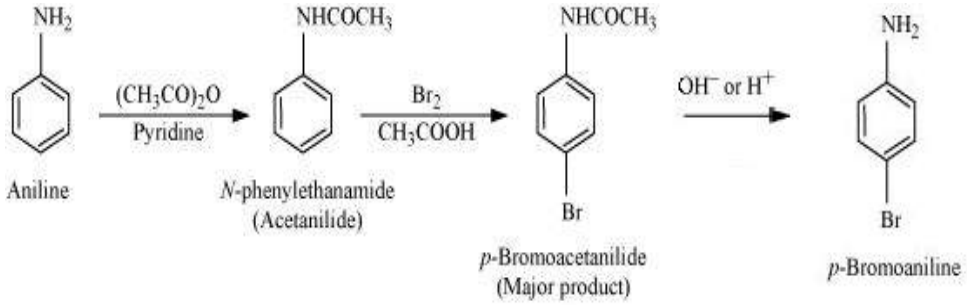


Q5.Accomplish the following conversions:
(i) Aniline to p-bromoaniline
(ii) Benzamide to toluene
(iii) Aniline to benzyl alcohol.

ANS. (i)



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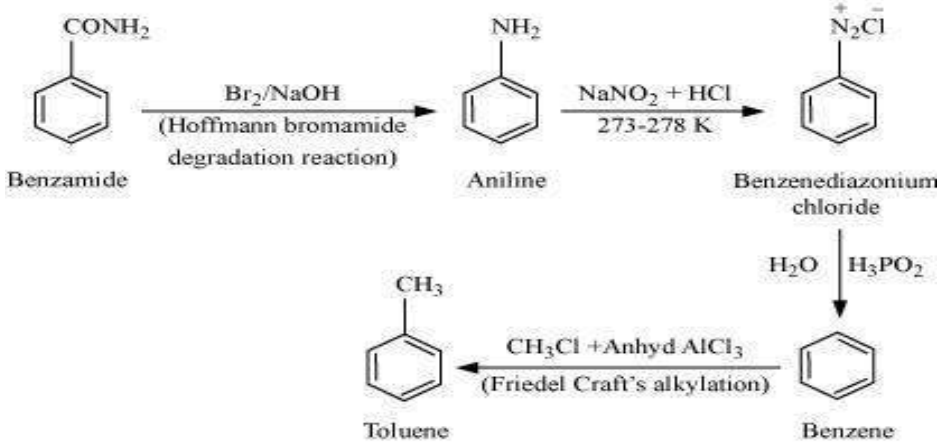

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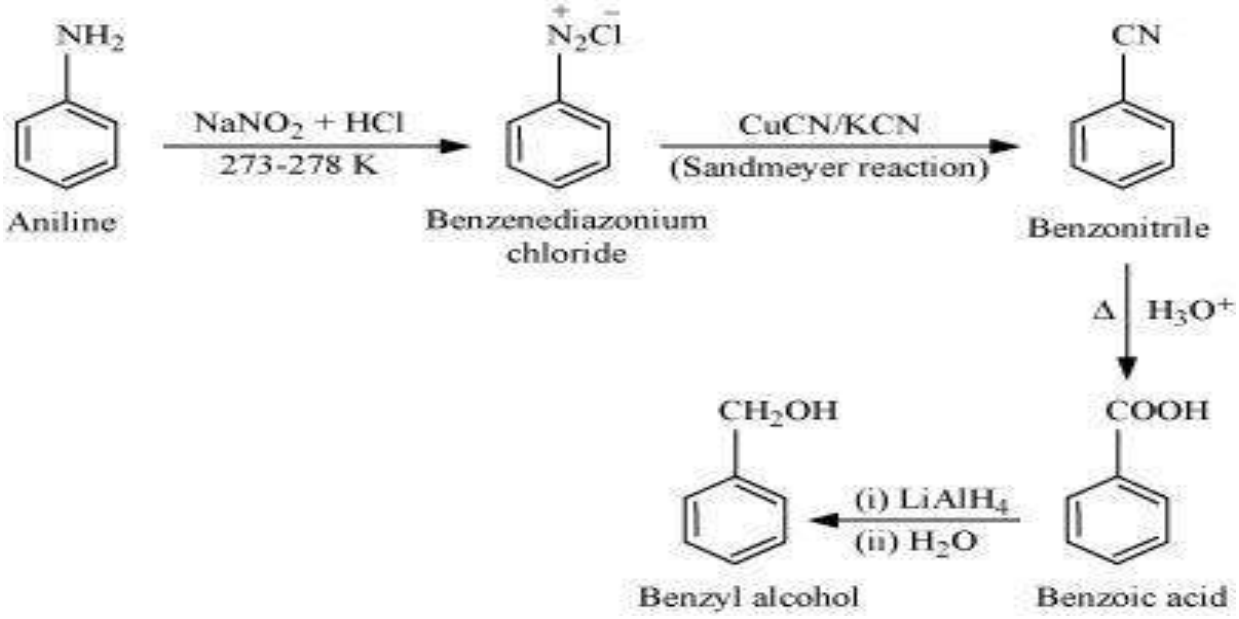


5 MARKS QUESTIONS

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)

$CH_3CH_2Br \xrightarrow{KCN} A \xrightarrow{LiAlH_4} B \xrightarrow[0^0C]{HNO_2} C$

(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)

$CH_3CH_2I \xrightarrow{NaCN}$ CH_3CH_2CN Propanenitrile (A) $\xrightarrow[\text{Partial hydrolysis}]{OH^-}$ $CH_3CH_2-\overset{O}{\overset{\|}{C}}-NH_2$ Ethanamide (B)

$\xrightarrow{NaOH + Br_2}$ $CH_3CH_2NH_2$ Ethanamine (C)

(ii)

$C_6H_5N_2Cl \xrightarrow{CuCN}$ C_6H_5CN Cyanobenzene (A) $\xrightarrow{H_2O/H^+}$ C_6H_5COOH Benzoic acid (B)

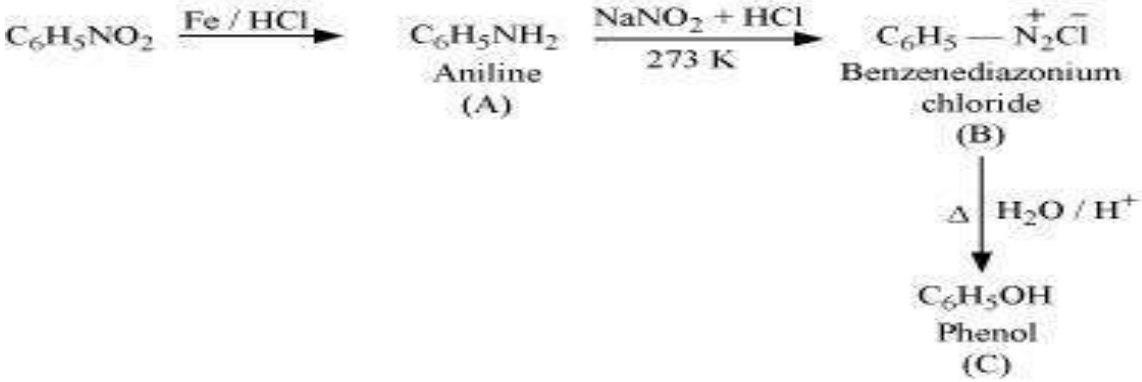
$\xrightarrow[\Delta]{NH_3}$ $C_6H_5CONH_2$ Benzamide (C)

(iii)

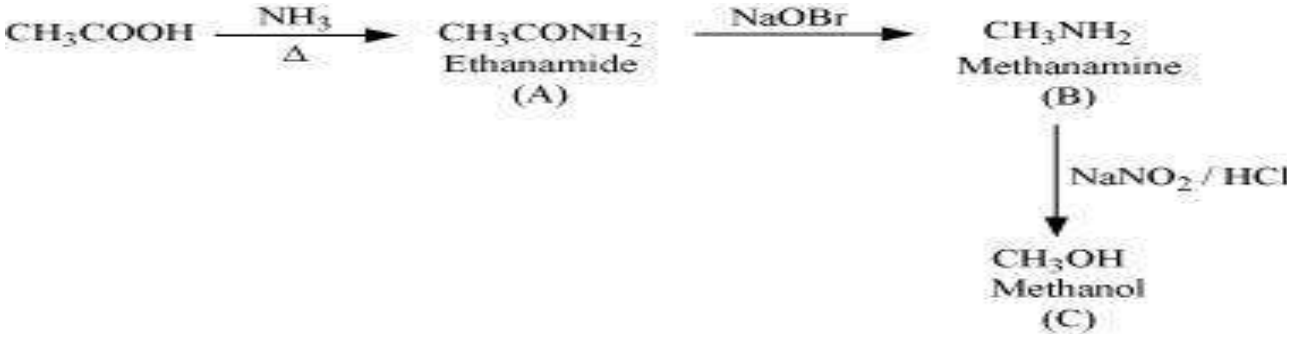
$CH_3CH_2Br \xrightarrow{KCN}$ CH_3CH_2CN Cyanoethane (A) $\xrightarrow{LiAlH_4}$ $CH_3CH_2CH_2NH_2$ Propan – 1 – amine (B)

$\xrightarrow[0\,^oC]{HNO_2}$ $CH_3CH_2CH_2OH$ Propan – 1 – ol (C)

(iv)



(v)



Q2.Completethefollowingreactions:

(i) $C_6H_5NH_2 + CHCl_3 + alc.KOH \rightarrow$

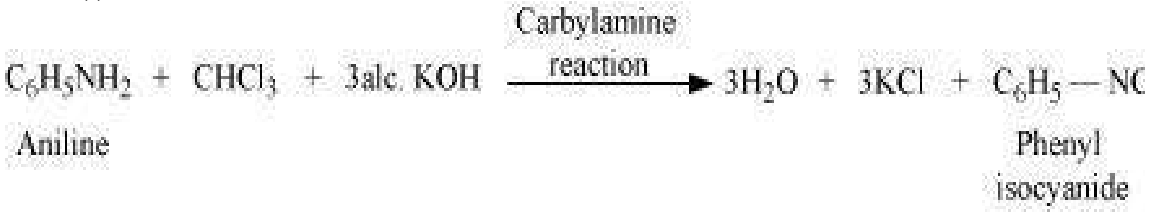
(ii) $C_6H_5N_2Cl + H_3PO_2 + H_2O \rightarrow$

(iii) $C_6H_5NH_2 + H_2SO_4(conc.) \rightarrow$

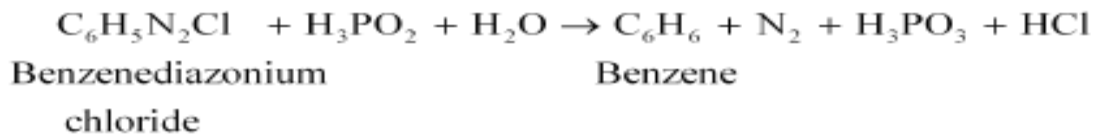
(iv) $C_6H_5N_2Cl + C_2H_5OH \rightarrow$

(v) $C_6H_5NH_2 + Br_2(aq) \rightarrow$

ANS. (i)



(ii)



(iii)

$$C_6H_5NH_2 + \text{conc.}H_2SO_4 \rightarrow C_6H_5\overset{+}{N}H_3H\overset{-}{S}O_4$$

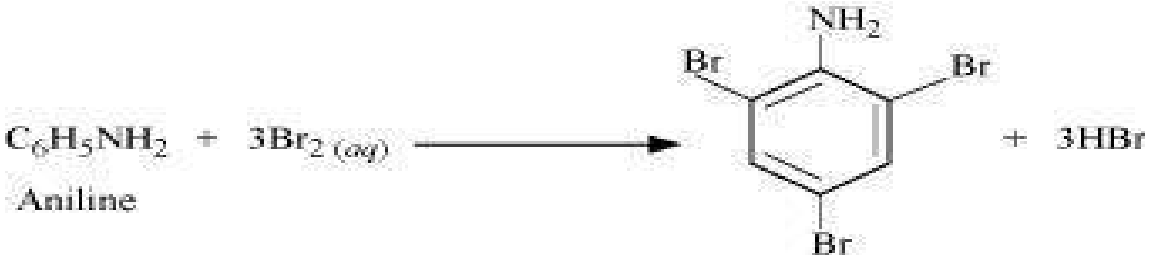
Aniline — Anilinium hydrogen sulphate

(iv)

$$C_6H_5N_2Cl + C_2H_5OH \rightarrow C_6H_6 + CH_3CHO + N_2 + HCl$$

Benzenediazonium chloride — Ethanol — Benzene — Ethanal

(v)



2,4,6 – Tribromoaniline

Assignments

Level1

1. Write IUPAC Name of $C_6H_5N(CH_3)_3Br$?
2. Which reaction is used for preparation of pure aliphatic & aralkyl primaryamine ?
3. Name one reagent used for the separation of primary, secondary & tertiaryamine?
4. What amine salts areused for determing their molecular masses?
5. What is the directive influence of amino group in arylamines?
6. Why are benzene diazonium salt ssoluble in water?
7. Which is more basic: CH_3NH_2 & $(CH_3)_3N$?
8. Which is more acidic, aniline or ammonia?
9. Write the IUPAC name of $C_6H_5NHCH_3$?
10. Mention two uses of sulphanilic acid?

Level 2

1. What for are quaternary ammonium salts widely used?
2. What product is formed when aniline is first diazotized and then treated with Phenol in alkaline medium?

3. How is phenylhydrazine prepared from aniline?
4. What is the IUPAC name of a tertiaryamine 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 then 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: Ethylamine, Ammonia, Triethylamine?
10. Why aniline is acetylated first to prepare monobromo 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-ClintoCH$_3$ –CH_2-CH_3-NH_2

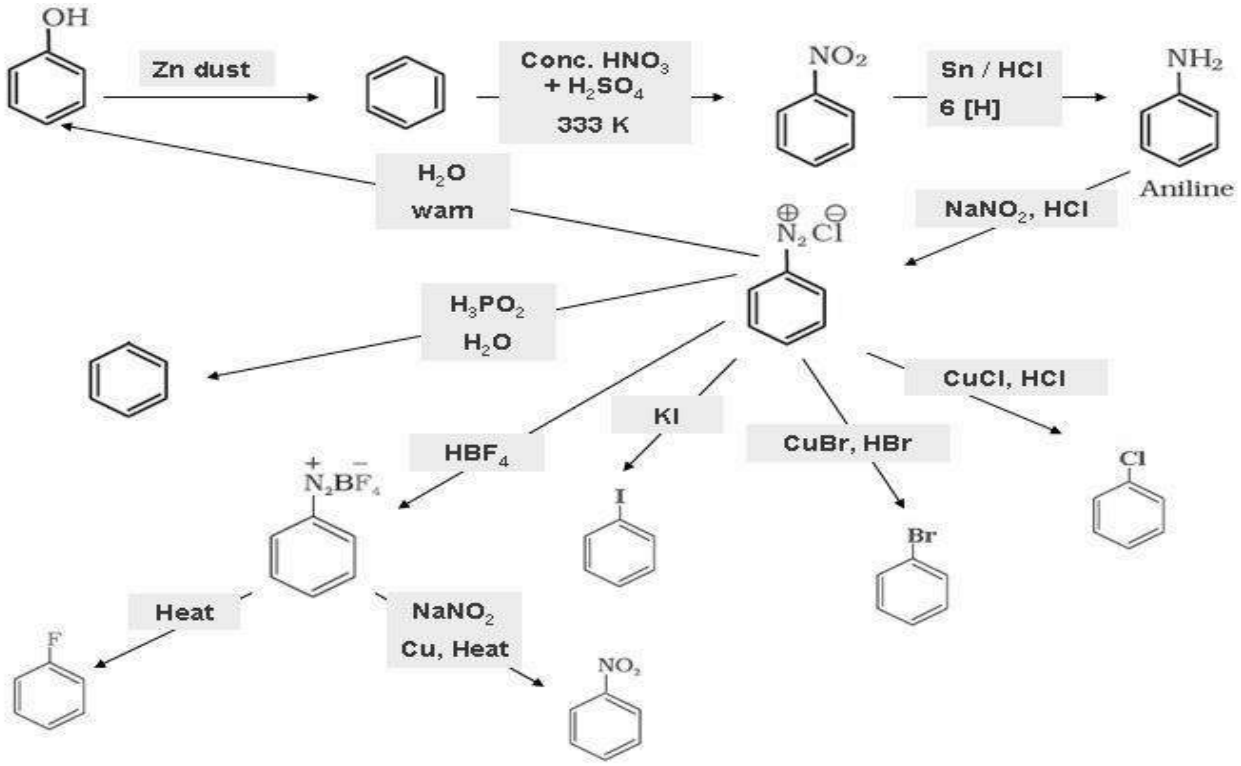
3.Write the equation involved in Carbylamines reactions?

4. How will you distinguish the following pairs?

(i) Methanamine and N-methylmethaneamine

(ii)Aniline and ethylamine

5.Write chemical reactions involved in following name reactions.
(i) Hoffmann Bromoamid ereaction.
(ii)Diazotisation reaction.



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 p*Kb*values:
$C_2H_5NH_2$, $C_6H_5NHCH_3$, $(C_2H_5)_2NH$ and $C_6H_5NH_2$

Q3. p*Kb*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 heatingforms 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

Bio molecule

1.Carbohydrates- These are polyhydroxy aldehydes or ketones or the compounds which produce these on hydrolysis.

2. Classification-

(i) Monosaccharides – Those carbohydrates which cannot be hydrolysed into further simpler carbohydrates. e.g. glucose ,fructose, galactose etc.

(ii)Disaccharides: Those carbohydrates which produces two monosaccharides on hydrolysis. Eg; Sucrose, maltose and lactose

(iii) Oligosaccharides- Those carbohydrates which give two to ten monosaccharides on hydrolysis .

(iv) Polysaccharides- Those carbohydrates which on hydrolysis give large number of monosaccharides hydrolysis.eg starch, cellulose, glycogen.

3. Sugar- Carbohydrates which are sweet in taste

(i)Reducing Sugars- Those which reduce Fehling's or Tollen's reagent due to availability of free aldehydic groups, eg , glucose, fructose , galactose

(ii)Non Reducing Sugars- Those which do not reduce Fehling's or Tollen's reagent. They do not have free aldehydic group ,e.g., sucrose

4. Glucose- It is a monosaccharides 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)

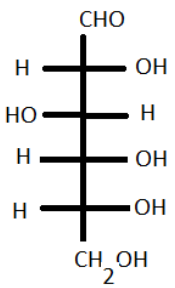
(ii)From Starch

$(C_6H_{10}O_5)_n + nH_2O$ -------> $C_{12}H_{22}0_{11} + H_20$ ------> $2C_6H_{12}O_6$

6.Structure

(i)Fischer structure –

(+) 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 rotator, i.e, it rotates plane polarized light towards right.

Objections against Open chain structure of Glucose

The open chain structure was 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 pentacetate 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.

After which a close chain(cyclic) structure of glucose was proposed by Haworth.

*** Anomers are isomers which have a different configuration at C-1**

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 by amide linkage (-(-CONH-)- is here called as 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(a dipolar 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(Ref. page No-416 NCERT book)

Primary Structure	**Secondary Structure**	**Tertiary Structure**	**Quaternary Structure**
The specific sequence of amino acids in the polypeptide chain. Change in amino acids sequence changes the protein completly. They have covalent bonds.	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 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.	Represents overall folding of the polypeptide chain. It gives rise to the fibrous or globular molecular shapes. Forces stabilizing the 2^o and 3^o structures are hydrogen bonds, disulphide linkages, van der waal's and electrostatic forces of	Protein can be composed of two or more polypeptide chains called sub units. The spatial arrangement of these sub units with respect to each other is quaternary structure of the protein.

		attraction.	

12.Native State of Protein: The parental state or the natural state in which the protein is found.

13. Denaturaion of Protein: Destruction of the native state of protein is denaturation. It can be brought by physical and chemical methods. The 2^o and 3^o structures are destroyed, only 1^o structure is retained.

Enzymes: These are biocatalyst and generally globular proteins e.g., invertase,zymase,phenyl, alaninehydroxylase, urease etc.

Main Characteristics of Enzyme:

1.It speed up the biological reaction upto million times.

2.It is highly specific and work on lock and key theory.

3.It is highly sensitive to pH and temperature.

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 group 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.(Ref table in page no-418of NCERT book)

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 of two types:

(i) Deoxyribonucleic acid (DNA)

(ii) Ribonucleic acid (RNA)

They are responsible for protein synthesis and transfer of genetic characteristics to offsprings.

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 a 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).

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.

22.DNA fingerprinting: A sequence of bases on DNA is unique for a person and can not be altered by any known treatment. It is therefore very much useful in identification of criminals, paternity of individuals.

Questions – (1 Mark)

Q1 – Which functional groups are present in monosaccharides?

Ans - —OH and —CHO or —OH and >CO

Q2 – Name an aldopentose, aldohexose and ketohexose.

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 one of α-helix and β-helix is more stable and why?

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 – Classify the bases present in DNA.

Ans – Purine derivatives:Adenine and guanine.

Pyrimidine derivatives: Cytocine and Thymine

Q9 – Give an example of

(a)water soluble (b)fat soluble is

Ans – (a)Vitamin C (b)Vitamin D.

Q10. Differentiate Nucleotides and nucleoside.

Nucleotides: Pentose sugar + N- containing base+ Phosphate

Nucleosides: Pentose sugar + N- containing base only

Q11 – Name a protein which is insoluble in water.

Ans – Veratin.

SAI Type Questions

Q1 – Name the constituents of starch and what is the difference between them.

Ans – Amylose: A linear polymer of α-glucose, water soluble

Amylopectin: Branched polymer of α-glucose. water insoluble.

Q2 Differentiate DNA and RNA

DNA	RNA
1.Bases:A, T, C, G	1.Bases A, U, C, G
2.Double helix	2.Single helix
3.Replication	3.Protein Synthesis
4. 2-deoxyRibose	4.Ribose Sugar

Q2 – What are anomers?

Ans – Monosaccharides which differs in configuration 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 and required to be supplied from outside 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 carboxylic acid as well as basic amino group, therefore they are amphoteric in nature.

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 invertases.

(b)Antibody – they are chemical substances which destroy antigens that cause infections. e.g., vaccination for typhoid produces antibodies in our body to prevent typhoid.

SA II Type Questions –

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)Isoelectric 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

$E + S \rightarrow [ES]$ (Enzyme substrate complex)

Step (ii): Product formation in complex

$[ES] \rightarrow EP$ (Enzyme product complex)

Step (iii): Dissociation of enzyme product complex, leaving enzyme unchanged

$EP \rightarrow E + P$

The specificity of enzyme is due to presence of some specific regions called active site on their surface.

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.

$R\text{-}CH\text{-}COO^-$	$CH_2\text{-}COO^-$
$\vert$	$\vert$
NH_3^+	NH_3^+
General Formula	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 phenyl keto urea.

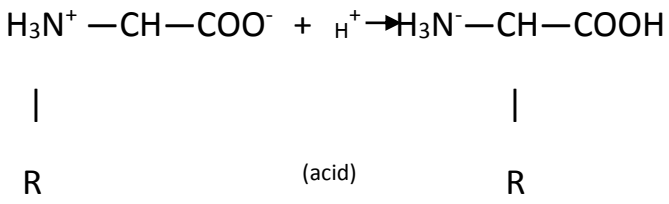
SA Type I (2 Marks)

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.

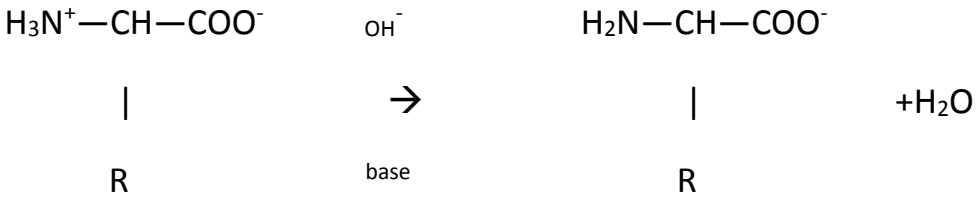
(ii) The monoamino monocarboxylic acids have two pK_a values.

Ans. (i) In acidic solution, the carboxylate anion accept a proton and gets converted into carboxylic group resulting in the formation of positive ion.



(Zwitter ion) (Positive ion)

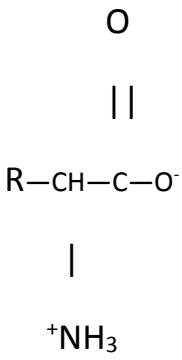
In presence of a base the N^+H_3 ion changes to $—NH_2$ group by losing a proton and this gives a negative ion.



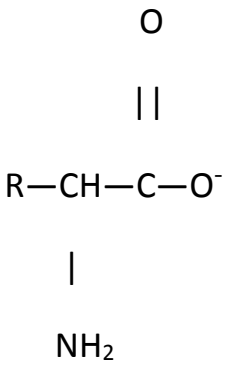
(Zwitter ion) (Negative ion)

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 behave 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



and at a pH higher than isoelectric point, it shows a pK_a value which corresponds to another,



Q2. Which forces are responsible for the stability of α-helix? Why is it named as 3.6_{13} helix?

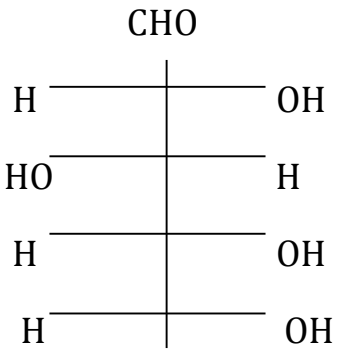
Ans. Hydorgen bonds between – N-H and —C=O groups of peptide bonds give stability to the structure.

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.

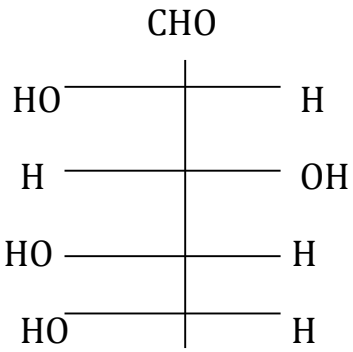
SA(II)

3 Marks

Q6. Draw simple Fishcher projections of D and L- glucose. Are these enantiomers?



D-Glucose



L-Glucose

Yes these two fischer projections are called enatiomers.

Value based Question

1.Vitamines are required in small amounts in our diet but their deficiency causes many diseases. Most of the vitamins can not be synthesised in our body, so these are essential for our good health.

A. Name a vitamin whose deficiency causes pernicious anemia. Which metal atom is present in it?

B . Deficiency of which vitamins cause rickets (bone deformation) in children and is needed for adsorption of calcium by body? Give its chemical name.

POLYMERS

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, polyster, 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 metha crylate)

(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,polyster,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.polyster, 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 heavy 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) Polyethene	Ethene	Insulation of wires, toys, 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, laminated wooden planks
(viii) Phenol Formaldehyde resin	Formaldehyde + Phenol	Combs, switches boards etc
(ix) Melamine polymers	Melamine + Formaldehyde	Manufacture of unbrea kable crockery
(x) Buna-S	1,3-Butadiene + Styrene	Auto tyres, floor,

Copolymer		foot-wear components
(xi) Natural rubber	2-methyl-1,3-butadiene	Used for tyres
(xii) Neoprene	2-chloro-1,3-butadiene	Conveyor belts, gasket , hoses
(xiii) Buma-N	1,3-butadiene + acrylonitrile	Resistance to action of petrol. Make oil seals, tank linings etc.
(xiv) (PHBV) poly-β hydroxybutyrateco-β- hydroxyl valerate (biodegradable)	3-hydroxybutanoic acid + 3-hydroxypantanoic acid	Packaging orthopedic devices
(xv) Nylon-2-nylon-6	Glycine + aminocaproic acid	It is biodegradable step growth Polymer

Note : For formation of polymer from monomer see pages 425 to 435 of NCERT book

VSA (1 marks)

1.Name a natural elastomer.

Ans . Natural rubber.

2. Name of monomer of Nylon 6.

Ans. Caprolactam

3. Write the monomer units of Bakelite.

Ans. Phenol and formaldehyde.

4. 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.

5. Write one use of PVC.

Ans: In manufacture of rain coats & vinyl flooring.

6. Define Polymer.

Ans: Polymer is defined as very large molecules having molecular mass (10^3-10^7u). These are also referred to as **macromolecules,**

7. Give an example of thermoplastics.

Ans: Thermoplastics are polythene, polystyrene, polyvinyl chloride etc.

8. Name the monomers of terylene?

Ans: Ethylene glycol and teryphthalic 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 disintegrate by themselves over a period of time due to environmental degradation by bacteria,etc.are called biodegradable polymers. e.g. PHBV

4.What is meant by PTFE ?Give its popular name.

Ans.Polytetrafluoroethylene.it is called Teflon.

5.Write chemical name of (Ziegler-Natta catalyst).

Ans: Triethylaluminium and titanium tetrachloride

6.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 fibres. 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-formaldelyde resins, etc.

7. 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.

8. How will you differentiate between LDP and HDP?

Ans: ***Low density polythene*****:** It is obtained by the polymerisation 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) hexamethylenediamine and adipic acid.

(ii) chloroprene.

(iii) 1, 3 – butadiene and acrylonitrile.

2. 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.

3. What is the function of sulphur in vulcanisation of rubber?
Ans: Sulphur introduces sulphur bridges.So it is become more tensile strength,elasticity and resistance to abrasion etc.

4. Write **Commercially Importants 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.Give the name of polymer which is used for making non- stick utensils.
Ans: Teflon($CF_2=CF_2$)

4.What is the % of sulphur using during in vulcanization of rubber ?
Ans: 3% to 5%

SA-I(2 marks)

1.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.
2.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.

3. 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.

4.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) PAN

Ans: (i) Polyvinylchloride

(ii) Polyacrylonitrile

2. Why is Bakelite a thermosetting polymer?

Ans: It is a cross-linked polymer. On heating it sets permanently into a solid.It can not be remoulded by heating again.

3.(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

Value Based Question:

Synthetic polymers find their application in almost all spheres of life because of their resistance to wear and tear, chemicals and temperature. But there is one major problem associated with them is their resistance to biodegradability over a period of time. It has created a serious problem of waste management . If over use of plastic continues , soon the entire civilization might got buried under it.

(a)Is it advisable to continue with the overuse of plastic due to their immense usefulness in daily life? Explain

(b)Enlist some values from above passage.

Ans(a)Though it is impossible to discontinue with the synthetic polymer, but their overuse can be minimized. We should opt for those polymers which are biodegradable. If we do not control this things at the right time the life become miserable for us. To minimize the use of plastic is meant for the betterment of mankind and nature.

(b)Concern the mankind awareness towards hazards of overuse of plastic. Health, consciousness and good citizenship are some of the values evident from the above passage.

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 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 EN ZYMES*-

(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 interfare with the natural action of histamines and prevent the allergic reaction. eg- rantidine,tegarnet, avil.**
9. **TRANQULIZERS-The class of chemical compounds used for the treatment of stress,mild or even severe mental diseases. Eg-idardil, iproniagid, luminal, second equaqnil .**
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. **ANTIMICROBIALS-They tend to prevent/destroy or inhibit the pathogenic action of microbes as bacteria ,virus ,fungi etc .They are classified as**

(i)*ANTIBIOTICS*-Those are the chemicals substances which are produced by micro-organisms.

Eg- Pencillin , ofloxacin .

***NARROW SPECTRUM ANTI-BIOTICS*-These are effective mainly against gram positive or gram negative bacteria. Eg- Penicillin , streptomycin.**

***BROAD SPECTRUM ANTI-BIOTICS*-They kill or inhibit a wide range of micro-organisms.**

eg- chloramphenicol , tetracydine .

(ii)*ANTISEPTICS OR DISINFECTANT*-These are which either kill/inhibit the growth of micro-organisms

Antiseptics are applied to the living tissuses 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 an disinfectant.

12. **ANTIFERTILITY DRUGS- These is the chemical substances used to control the pregnancy. They are also called oral contraceptives or birth control pills.**

Eg-Mifepristone, norethindrone.

13. **ARTIFICIAL SWEETNING AGENTS-These are the chemical compounds which give sweetening effect to the food without adding calorie.**

They are good for diabatic people eg- aspartame, saccharin, alitame , sucrolose.

14. **FOOD PRESERVATIVES- They prevents spoilage of food to microbial growth.eg-salt, sugar, and sodium benzoate.**
15. **CLEANSING AGENTS-**

(i) *SOAPS*- They is sodium or potassium salts of long chain fatty acids.They are obtained by the soapnification reaction, when fatty acids are heated with aqueous sodium hydroxide.

They do not work well in hard water.

(iii) *TOILETS SOAP*-That are 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) *MEDICATED SOAPS*- Substances of medicinal value are added.eg- Buthional , dettol.

16. SYNTHETIC DETERGENTS-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)*ANIONIC DETERGENTS*-They are sodium salts of sulphonated long chain alcohols or hydrocarbons.eg- sodium lauryl sulphonate . They are effective in acidic solution.

$CH_3 (CH_2) CH2OH \rightarrow CH_3 (CH_2)_{10}CH_2OSO_3H$

(laurylalchol)
$\rightarrow CH_3 (CH_2)_{10}CH_2SO_3^-Na^+$

(Sodium lauryl sulphonate)

(ii)*CATIONIC DETERGENTS*- They are quarternary ammonium salts of amines with acetates , chlorides, or bromides.They are expensive used tolimited extent.eg- cytyltrimethylammoniumbromide

(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.- Treatment of diseases using chemicals is called chemotherapy.

Q-2 why do we require artificial sweetening agents?

Ans.- To reduce calorie intake.

Q-3 what are main constiuent of Dettol?

Ans.- Choloroxylenol & Terpinol .

Q-4 what type drug phenaticinis?

Ans.- It is antipyretics.

Q-5 Name the drug that are used to control allergy?

Ans.- Antihistamines.

Q-6Why is the use of aspartame limited to cold food and drinks?

Ans.- It is unstable at cooking temperature and decompose.

Q-7What is tranquilizers? Give an example?

Ans.- They is the drug used in stress, mild severe mental disease.

Q-8 what type of drug chloramphenicol?

Ans.- It is broad spectrum antibiotic.

Q-9Why is bithional is added to the toilet soap?

Ans.-It acts as an antiseptic.

Q-10 what are food preservatives?

Ans- The substances which 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- (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- (i) Antipyretics- Those drugs which reduce the temperature of feveral body are called Antipyretics.

Eg - Paracetamol

(ii) Antibiotics-The drugs which prevent the growth of other micro-organisms. Eg- Pencillin.

Q-3 what are tincture of iodine?

Ans- 2-3% iodine solution of alcohol water is called tincture of Iodine. It is a powerful antiseptics and is applied on wounds.

Q- 4 What is artificial sweetening agent? Give two examples?

Ans- The substances which give sweetening to food but don't add calorie to our body .

Eg- Saccharin, alitame.

Q-5 How is synthetic detergents better than soaps?

Ans- (i) Detergents can be used in hard water but soaps cannot be used.

(ii) Detergents have a stronger cleansing action than soaps.

Q-6 what are sulpha drugs? Give two examples?

Ans- A group of drugs which are derivatives of sulphanilamide and are used in place of antibiotics is called sulpha drugs.

Eg- Sulphadizine, Sulphanilamide.

Q-7 what forces are involved in holding the active sites of the enzymes?

Ans- 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-8 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-9 Give two examples of organic compounds used as antiseptics?

Ans- 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- 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- 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- (i) Antihistamines

(ii) Preservatives

(iii) Antifertility drug

Q-4 Identify the type of drug-

(i) Ofloxacin (ii) Aspirin (iii) Cimetidine

Ans- (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.

Chapter-5

Surface Chemistry

Q1.Gelatine is generally added to ice creams. Why?

Ice cream is an emulsion of milk or cream in water (o/w type). Gelatine is generally added to act as emulsifiers to form the stable emulsion.

Q2. Why is chemisorption called activated absorption?

For a chemisorption to take place ,reactants should acquire

minimum energy of activation.

Q3. Why is desorption necessary in catalytic reaction?

Desorption is necessary in catalytic reaction to maintain the flow of reaction.

Q4. In chemical reaction can a product formed act as catalyst? If so give example.

Yes, Example: hydrolysis of ester. Ester hydrolysis is catalysed by acid. In the course of the reaction carboxylic acid is produced which catalyses the reaction.

Q5. What is colloidion solution?

Colloidion solution is the solution which is used to impregnate the filter paper to make it an ultra filter.

Q6. Give conditions for Tyndall effect to take place?

The refractive indices of dispersion medium & dispersed phase should not be same. The wavelength of the light should not be too low.

Q7 Why is the ester hydrolysis slow in the beginning & becomes faster after sometime?

The ester hydrolysis slow in the beginning & becomes faster after sometime

because the carboxylic acid produced acts as the catalyst.

Q8. What are the reasons for charge on sol particles?

Frictional electrification

Electron capture

Preferential adsorption of ions from solutions

Dissociation of surface molecules

Q9. Why colloidal medicines are more effective?

Colloidal medicines have large surface area for the reaction. Hence colloidal medicines are more effective.

Q10.Give the factors governing colour of colloidal solution?

Wavelength of light scattered, the manner in which light is received by observer, particles size.

Q11. Why are Lyophylic colloids self stabilized?

Due to the force of attraction between dispersion medium & dispersed phase.

Q12. State one application ZSM-5.

Used for the conversion of alcohol to gasoline.

Q13. Explain the role of catalyst in a chemical reaction.

It lowers the activation energy & hence increases the rate of the reaction.

Q14. Adsorption is always exothermic. Why?

During adsorption, the bonding takes place between adsorbate &

adsorbent and there is a decrease in surface area & decrease in entropy.

Q15. Define weeping of gels. Give the other name of weeping?

When gels are allowed to stand for a long time they give out small quantity of trapped liquid which accumulates on its surface. This action of gels is called as weeping, other name is syneresis.

Q16. What is Thixotrophy?

Conversion of sol to gel is called thixotrophy.

Q17. Why is $FeCl_3$ preferred over KCl for a cut leading to bleeding?

$Fecl_3$ has more positive charge and causes coagulation of blood

quickly.

Q18. Why is silica gel used as dehumidifier?

Silica gel adsorpes moisture on its surface quickly.

Q19. Give the kinetics of adsorption of gases on metal surfaces.

Adsorption of gases on metal surfaces follows zero order kinetics.

Q20. $\triangle G$ is negative for adsorption process. Why?

Adsorption is exothermic & decrease in entropy occurs in adsorption.

Q21. Give the significance of Brownian movement.

It gives stirring effect to the colloid. Hence colloidal particles do not aggregate. The colloid becomes stable.

Q22. What happens when blood charcoal is shaken with conc. Kcl

in one case and its dilute KCl solution in other case?

In conc. KCl positive adsorption occurs & in dilute Kcl negative adsorption occurs.

Q23.Give the principle used in gas masks?

Competing adsorption

Q24. Gold sol appears red , purple & also golden in colur Why?

Colour of the gold sol changes with its particle size.Its' colour is red

& becomes puple when size increases & finally becomes golden.

Q25. Give the sign of ΔH & ΔS when Br_2 gas gets adsorbed on charcoal. ΔH = negative & ΔS = positive

Q26. What is Argyrol?

Colloid of Ag with proteine(mild silver protein)

Antiseptic & used for treating gonoria (a disease)

Q27. What happens when NaCl is added to ferrichydroxide sol?

When NaCl is added to ferrichydroxide sol coagulation occurs.

Q28.Differentiate dilute soap solution & concentrated soap solution.

Dilute soap solution behaves like a true solution & concentrated soap solution behaves like a colloid.

Q29. Comment: Colloid is not a substance but it is a state of a substance.

The nature of the sub whether colloid or crystalloid depends upon the particle size.When the size of the solute particles lies between 1000 – 10000 pm , it behaves as a colloid & whenit is less than this value it behaves as a crystalloid. Thus Colloid is not a substance but it is a state of a substance which depeds upon the particle size.

Q30. What happens when $Fe(OH)_3$ is added to Gold sol?Why?

The Gold sol is negatively charged, $Fe(OH)_3$ is positively charged

& so coagulation occurs.Color of Gold sol changes from red to blue. Gold sol changes from red to blue due to the change in the particle size.

(AS THIS CHAPTER HAS NO NUMERICALS HOTS MAY INCLUDE THE QUESTIONS OF THE ABOVE TYPE)

Chapter-8

d and f block Elements

1. Silver atom has completely filled d orbitals in its ground state. How can you say that it is a transition element?

Ans: It forms AgF_2 a dark brown crystalline solid

2. Transition elements exhibit their highest oxidation state in their oxides not in Flourides.Why?

Ans: Because oxygen can form covalent multiple bonds.

3. Explain why, Zn (II) salts are white while Mn (VII) are deep purple in colour?

Ans: due to charge transfer between O^{2-} ion to Mn^{7+}

4. KMnO4 is used in acidic medium quite frequently than in its aqueous or alkali for oxidizing purpose. Why?

Ans: In acidic medium MnO_4^- involves the addition of $5e^-$ or $E^o = +1.52v$

5.Inspite of low enthalpy of atomiza

6.Give reasons:

i) Zr and Hf have identical sizes

ii) In the titration of $FeSO_4$ with $KMnO_4$ in the acidic medium dil.H_2SO_4 is used instead of dil HCl

Ans: i) Due to lanthanoid contraction

ii) dil.HCl is reducing agent and liberates chlorine on reacting with $KMnO_4$ soln.

7.Calculate the spin only magnetic moment of Iron present in the following compound.

$[Fe(H_20)_5NO]^{2+}$

Ans: 5.92 BM

8. K_2 [$PtCl_6$] is a well known compound whereas the corresponding Ni compound is not known. State the reason for it.

Ans: The oxidation state of Pt in K_2 [$PtCl_6$] is +4, which is a stable oxidation state for Pt. The same oxidation state Ni is very difficult because of ($I.E_1 + I.E_2 + I.E_3 + I.E_4$)

9. Among the ionic species Sc^{3+} ,Ce^{4+} and Eu^{2+} Which one is a good oxidizing agent?

Ans: Ce^{4+} is a good reducing agent because it can readily change to the most stable oxidation state by gaining one electron. Others cannot do so.

10. Why are Fe^{3+} and Cu^{2+} prominent in their aqueous solutions?

Ans: Because of high hydration enthalpies.

11. There is a dip in the melting point curve at Mn, though the preceding element also has similar electronic configuration. Why?

Ans: Due to $3d^5$ half filled configuration which are tightly held by more effective nuclear charge of Mn

12. CrO_3 is an acid anhydride. Explain.

Ans: It dissolves in water to give chromic acid.

$$CrO_3 + H_2O \longrightarrow H_2CrO_4$$

13. Though both Cr^{2+} and Mn^{3+} have d^4 configuration, yet Cr^{2+} is reducing and Mn^{3+} is oxidizing. Explain Why?

Ans: Because of the stable half filled configuration of t_2g sets of Cr^{3+}

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