

**CHEMISTRY (052) E****Question Paper-I****Total Marks : 100****Time : 3 Hours****Instructions :**

- (1) There are Five questions in this question paper which all are compulsory.
- (2) Students can use only log books provided by school.
- (3) Figure to the right indicates full marks of the sub questions.  
(At. Wt. H = 1, C = 12, N = 14, O = 16, Cl = 35.5, Ca = 40.0, Pb = 207)

**Q. 1. (A) Answer the following questions in short. (5)**

- (1) How many atoms belongs to fcc unit cell ?
- (2) What is  $K_w$  ? Give effect of temperature on  $k_w$ .
- (3) Define : Adiabatic process.
- (4) What are amphiboles ?
- (5) How change in free energy is related to volume of an ideal gas ?

**(B) Calculate any Two of the following. (6)**

- (1) 500 ml aq. solution contain 6.20 gm.of Methyl amine dissolved in it. The solution has 12.15 pH at 25<sup>0</sup> C temperature. Calculate ionisation constant ( $K_b$ ) of methyl amine.
- (2) The standard free energies of formation of  $\text{NO}_2(\text{g})$ ,  $\text{NO}(\text{g})$  and  $\text{O}_3(\text{g})$  are 12.39, 20.72 and 39.06 K.cal/mole respectively at 25<sup>0</sup> C. Calculate the equilibrium constant of the reaction  $\text{NO}(\text{g}) + \text{O}_3(\text{g}) \rightarrow \text{NO}_2(\text{g}) + \text{O}_2(\text{g})$  at 25<sup>0</sup>. If the standard enthalpies of formation of above molecules are 8.09, 21.60 and 34.0 k.cal/mole respectively, what would be the change in entropy during the reaction ?
- (3) Will  $\text{PbCl}_2$  precipitate on mixing 5.0 ml  $2.0 \times 10^{-4}$  M  $\text{CaCl}_2$  solution with 1.0 ml.  $1.0 \times 10^{-4}$  M  $\text{Pb}(\text{NO}_3)_2$  solution ?  $K_{sp}$  of  $\text{PbCl}_2$  is  $2.0 \times 10^{-4}$ .

**(C) Answer any three of the following. (9)**

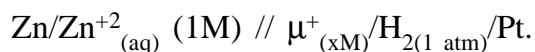
- (1) Derive a relation between the ionisation constant  $K_a$  and the concentration  $C_0$  and  $\text{H}_3\text{O}^+$  of given weak acid HA at 25<sup>0</sup>C in the aqueous solution.
- (2) Explain : (i) Classification of solids based on electrical conductivity.
- (3) Explain Characteristics of entropy.
- (4) Explain :
  - (i) What are silicates ? Explain ortho and pyro silicates.
  - (ii) Define sparingly soluble salt. Write equation for solubility product for the compound  $\text{CaF}_2$ . Why solubility of  $\text{AgCl}$  decreases in aqueous solution of  $\text{NaCl}$  ?

**Q. 2. (A) Answer the following : (5)**

- (1) Define : Hybridization energy.
- (2) Compare  $E_a$  and  $E_a^r$  for a given reversible thermochemical reaction.
- (3) What is 'Electromotive force' ?

- (4) Give two limitations of valence bond theory.
- (5) What are advantages of 'Fuel cell' ?
- (B) Calculate any Two of the following :** (6)

- (1) Calculate time for which 1.0 ampere current should be passed through 100 ml. 0.02 M  $\text{AgNO}_3$  solution to reduce all  $\text{Ag}^+_{(\text{aq})}$  to  $\text{Ag}_{(\text{s})}$ .
- (2) The potential of the following cell is 0.54 Volts at  $25^\circ\text{C}$ . Calculate pH of acid solution.



- (3) 50% of sample decomposes thermally in 120 minutes. How long will it take for 90% of compound to decompose for a first order reaction ?

- (C) Answer any Three of the following.** (9)

- (1) (i)  $\text{N}_2\text{O}_{5(\text{g})} \rightarrow 2\text{NO}_{2(\text{g})} + \frac{1}{2}\text{O}_{2(\text{g})}$  is first order reaction. Derive integrated rate law.

(ii) Give law of mass action.

- (2) Explain Lead storage cell.
- (3) Why do we believe that s-orbital is spherical ? Explain node and antinode.
- (4) (i) Give only chemical reaction occurring during operation of dry cell.
- (ii) Explain de-Broglie equation.

- Q. 3. (A) Answer the following questions.** (5)

- (1) What is electrophile ? Give illustration.
- (2) Give chemical equation showing hydrolysis of benzene triozone.
- (3) Give structural formula : Quinol, Anisol.
- (4) Give chemical reaction between iodine and  $\text{KClO}_3$ . What does the reaction suggest ?
- (5) What are photoelectrons ?

- (B) Give any Three of the following conversions. (only two steps).** (6)

- (1) Butane from diethyl ether.
- (2) Benzaldehyde from benzyl chloride.
- (3) m-xylene from benzene.
- (4) Ethyl bromide from ethyl chloride

- (C) Answer any Three of the following g.** (9)

- (1) Discuss : (i) oxides of chlorine (ii) oxyacids of chlorine.
- (2) Chlorination of nitrobenzene gives m-chloro nitrobenzene while nitration of chlorobenzene gives ortho chloro nitrobenzene and para chloro nitrobenzene. Explain on the basis of directive influence of function group.
- (3) Explain : (i) Grignard reaction for organic halides.  
(ii) Give reactions of alkali metals with oxygen.
- (4) Give : (i) Kolbe – Schmitt reaction.  
(ii) Friedle – Craft acylation of benzene.

- Q. 4. (A) Answer the following** (5)
- (1) How formalin is prepared ? What are its uses ?
  - (2) How aniline exhibit Lewis base character ?
  - (3) Give sources of vitamin K. What is its function ?
  - (4) Experimental molecular weight of carboxylic acid in non aqueous solvent is twice than actual. Why ?
  - (5) What are plasticizers ?
- (B) Give following conversions of any Three and write name of reaction, chemical condition, also give name of reactant, product and their structure.** (6)
- (1) Methyl amine from Acetic anhydride.
  - (2) Propanone to Ethanol.
  - (3) Iso-propanol from acetaldehyde.
  - (4) Acetyl chloride to Ethanol.
- (C) Answer any Three of the following.** (9)
- (1) Explain preparation of Benzene diazonium chloride. Give chemical reaction to prepare various dyes from Benzene diazonium chloride.
  - (2) Explain (i) Super phosphate of lime.  
(ii) Industrial production of ABS.
  - (3) Explain condensation reaction of Aldehyde and Wolf- Krishna reaction of ketone.
  - (4) Give only chemical reaction for : (i) Dehydration of acetamine. (ii) Carbylamine test for aniline (iii) Hydrolysis of Nitrolim.
- Q. 5. (A) Answer the following questions.** (5)
- (1) How is  $\text{CuH}_{0.96}$  prepared ? What is its character ?
  - (2) Give formula : Carbanato tetraammine chromium (III) nitrate
  - (3) How are activated nitrogen prepared ? State its function.
  - (4) Why  $\text{Sc}^{+3}$  gives colourless compounds.
  - (5) Define : Ligand
- (B) Answer the following questions.** (6)
- (1) What is paramagnetism ? Calculate paramagnetic momentum ( $\mu$ ) for compound  $\text{Cr}(\text{CO})_6$
  - (2)  $\text{KMnO}_4$  is strong oxidising agent. Give reason.
  - (3) How red phosphorus is prepared ? Give its characteristics.
- (C) Answer any Three of the following.** (9)
- (1) Answer :
    - (i) Give chemical reaction, one each to prepare phosphine, stibin, bismuthin.
    - (ii) Give only chemical reactions showing  $\text{HNO}_2$  as oxidising agent.
  - (2) Write a note on Interstitial and non-stoichiometric compounds.
  - (3)  $\text{K}_2[\text{Ni}(\text{Cl})_4]$  is tetrahedral while  $\text{K}_2[\text{Ni}(\text{CN})_4]$  is square planer. Explain in detail.
  - (4) Write a note on complexes in nature.

\*\_\*\*\_\*

: ANSWER :

Q. 1. (A) Answer the following in short :

$$(1) 8 \times \frac{1}{8} = 1$$

$$6 \times \frac{1}{2} = 3 \quad 1 + 3 = 4 \text{ Total 4 atoms belongs to fcc unit cell.}$$

(2) Kw is dissociation constant of pure water known as ionic product of purer water at 25<sup>0</sup>c temperature.

As ionisation is endothermic reaction, increase in temperature increases the value of kw.

(3) If a system doesnot gain energy from surrounding or given energy to the surrounding during change of its state, the process is known as an adiabatic process.

(4) Silicates having repetition of (Si<sub>4</sub>O<sub>11</sub>)<sup>-6</sup> ion as the basic structural unit are amphiboles. For example, Trimolite.

$$(5) \Delta G = n.R.T. \ln \frac{V_1}{V_2}$$

Q. 1. (B) Solve the following examples.

Molecular wt of CH<sub>3</sub>NH<sub>2</sub> = 31.0 gram-mole<sup>-1</sup>

$$\begin{aligned} \text{conc. of CH}_3\text{NH}_2 &= \frac{\text{Wt. of Solute} \times 1000 \text{ ml}}{\text{Mole Wt.} \times \text{Volume of Sol}^n \text{ in ml}} \\ &= \frac{6.2 \times 10^3}{31 \times 500} \\ &= 0.4 \text{ M} \end{aligned}$$



$$\text{pH} = 12.15$$

$$\begin{aligned} \therefore \text{pOH} &= 14.0 - \text{pH} \\ &= 14.0 - 12.15 \\ &= 1.85 \end{aligned}$$

$$\text{Now, pOH} = -\log_{10}[\text{OH}^-]$$

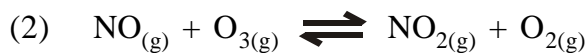
$$\begin{aligned} \therefore \log_{10}[\text{OH}^-] &= -\text{pOH} \\ &= -1.85 \end{aligned}$$

$$\begin{aligned} \therefore [\text{OH}^-] &= \text{Antilog}(-1.85) \\ &= 1.41 \times 10^{-2} \text{ M.} \end{aligned}$$

As weak base dissociate feebly,  $[\text{OH}^-] = \sqrt{K_b \cdot C_0}$

$$\therefore (1.41 \times 10^{-2})^2 = K_b \times 0.4$$

$$\begin{aligned} \therefore K_b &= \frac{(1.41)^2}{4} \times 10^{-3} \\ &= 5.0 \times 10^{-4} \end{aligned}$$



$$\begin{aligned} \text{(i)} \quad \Delta G^0_{\text{reaction}} &= \Sigma \Delta G^0_{\text{product}} - \Sigma \Delta G^0_{\text{reactant}} \\ &= [\Delta G^0_f(\text{NO}_2) + \Delta G^0_f(\text{O}_2)] - [\Delta G^0_f(\text{NO}) + \Delta G^0_f(\text{O}_3)] \\ &= (12.39 + 0) - (2.72 + 39.06) \\ &= 12.39 - 59.78 \\ &= -47.39 \text{ k.cal.mole}^{-1} \end{aligned}$$

$$\begin{aligned} \text{(ii)} \quad \Delta G^0 &= -RT \ln k_p \\ &= -2.303 RT \log k_p \end{aligned}$$

$$\begin{aligned} \therefore \log K_p &= \frac{\Delta G^0}{-RT(2.303)} \\ &= \frac{-47.39}{-2.303 \times 1.987 \times 10^{-3} \times 298} \\ &= 34.73 \end{aligned}$$

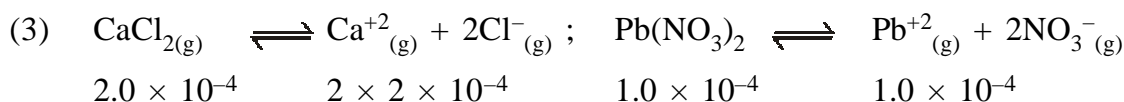
$$\therefore K_p = \text{Antilog } 34.73 = 5.34 \times 10^{34}$$

(iii) Now,

$$\begin{aligned} \Delta H^0 &= \Delta H^0_{\text{product}} - \Delta H^0_{\text{reactant}} \\ &= (8.09 + 0.0) - (21.60 + 34.0) \\ &= 8.09 - 55.6 \\ &= -47.51 \text{ K.cal/mole} \end{aligned}$$

(iv) Now,

$$\begin{aligned} \Delta G^0 &= \Delta H^0 - T\Delta S^0 \\ \therefore \Delta S^0 &= \frac{\Delta H^0 - \Delta G^0}{T} \\ &= \frac{-47.51 - (-47.39)}{298} \\ &= -4.02 \times 10^{-4} \text{ k.cal.}^0\text{k}^{-1} \end{aligned}$$

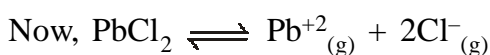


Total volume of mixture = 5.0 ml + 1.0 ml = 6.0 ml

Since total volume of mixture increases, concentration of ion in mixture decreases which is calculated by relation  $M_1V_1 = M_2V_2$

$$\begin{aligned} \therefore [\text{Pb}^{+2}] \text{ in mixture} &= \frac{1.0 \times 10^{-4} \text{ M} \times 1.0 \text{ ml}}{6.0 \text{ ml}} \\ &= 1.67 \times 10^{-5} \text{ M} \end{aligned}$$

$$\begin{aligned} \therefore [\text{Cl}^{-}] \text{ in mixture} &= \frac{5.0 \text{ ml} \times 4.0 \times 10^{-4} \text{ M}}{6.0 \text{ ml}} \\ &= 3.33 \times 10^{-4} \text{ M} \end{aligned}$$



$$\begin{aligned} \therefore \text{IP PbCl}_2 &= [\text{Pb}^{+2}_{(g)}] [\text{Cl}^{-}_{(g)}]^2 \\ &= [1.67 \times 10^{-5}] [3.33 \times 10^{-4}]^2 \\ &= 1.85 \times 10^{-12} \end{aligned}$$

As  $\text{IP} < \text{K}_{\text{sp}}$

$\text{PbCl}_2$  will not precipitate on mixing above solutions.

**Q. (1) (C)**

(1) Derivation of  $K_a$  for weak acid HA

Suppose a weak acid HA is dissolved in water,

Following equilibrium exists in the aqueous solution at  $25^\circ\text{C}$  temperature



Let us calculate equilibrium constant  $K$  as under :

$$\begin{aligned} K &= \frac{\text{product of concentrations of products}}{\text{product of concentrations of reactants}} \\ &= \frac{[\text{H}_3\text{O}^+] [\text{A}^-]}{[\text{H}_2\text{O}] [\text{HA}]} \end{aligned}$$

As decrease in concentration of water due to the dissolution of acid is negligible in comparison with the concentration of pure water.

Thus,  $[\text{H}_2\text{O}]$  in above equation is considered as constant.

$$\therefore K [\text{H}_2\text{O}] = K_a = \frac{[\text{H}_3\text{O}^+] [\text{A}^-]}{[\text{HA}]}$$

The concentration of undissociated weak acid HA is approximately equal to the initial concentration  $C_0$  of the same since it dissociates feebly. Moreover concentrations of positive and negative ions also are equal. Therefore above equation can be written as,

$$\begin{aligned} K_a [\text{HA}] &= [\text{H}_3\text{O}^+]^2 \quad \text{where, } K_a = \text{dissociation constant of given} \\ \therefore K_a C_0 &= [\text{H}_3\text{O}^+]^2 \quad \text{weak acid HA at } 25^\circ\text{C temperature} \\ \therefore [\text{H}_3\text{O}^+] &= \sqrt{K_a \cdot C_0} \quad C_0 = \text{Initial molar concentration of weak} \\ & \quad \text{acid HA} \end{aligned}$$

(2) Solids are classified into three types on the basis of their electrical conductivity.

(i) Good conductor (ii) Insulators and (iii) Semiconductors

The conductivity of metal is about  $10^8 \text{ ohm}^{-1}\text{cm}^{-1}$  while that of some insulator is about  $10^{-12} \text{ ohm}^{-1}\text{cm}^{-1}$  which is negligible.

The conductivity of solid metal which is referred as electronic conductivity is due to the easy mobility of electrons and hole in its crystal lattice.

Substances like pure alkali halides are generally insulator.

The conductivity of semiconductors and insulators is determined by the impurities and defects in their crystal lattice structure. Electrons and holes produced by these defects are responsible for the electronic conductor in these solids.

Electrical properties of some transition metal oxides are as under

Good conductor :  $\text{TiO}$  ;  $\text{CrO}_2$

Semi conductor :  $\text{Ti}_2\text{O}_3$

Insulators :  $\text{TiO}_2$ ,  $\text{FeO}$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{CuO}$  etc.

The appearance and conductivity of  $\text{ReO}_3$  are like those of metallic copper.

(3) Characteristics entropy.

Entropy is an extensive property. Value of entropy is directly proportional to quantity of substance.

Entropy of a system is state function.

Absolute value of entropy can be calculated.

Change in entropy is given by

$$\Delta S = S_{(\text{final})} - S_{(\text{initial})}$$

The total entropy change of a system is as under.

$$\Delta S_{\text{total}} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}}$$

If  $\Delta S_{\text{total}}$  is positive, the reaction should occur spontaneously while if  $\Delta S_{\text{total}}$  is negative, the reaction cannot occur spontaneously. If  $\Delta S_{\text{total}}$  is zero, the reaction enjoys a state of equilibrium i.e.

$$\Delta S_{\text{system}} + \Delta S_{\text{surrounding}} > 0 ; \text{(spontaneous reaction)}$$

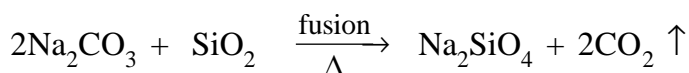
$$\Delta S_{\text{system}} + \Delta S_{\text{surrounding}} < 0 ; \text{(Non-spontaneous reaction)}$$

$$\Delta S_{\text{system}} + \Delta S_{\text{surrounding}} = 0 ; \text{(Reaction is in equilibrium)}$$

**Q. 4. (C) Silicates**

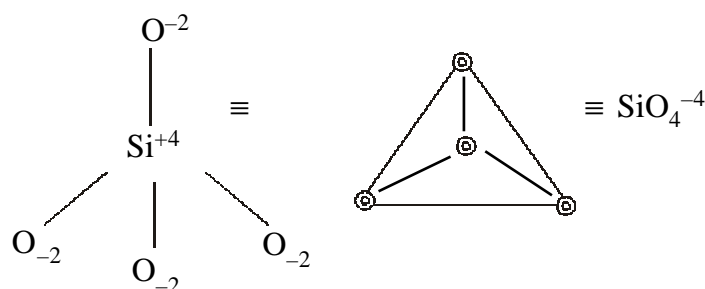
Silicates are derivatives of Silicic acid  $\text{H}_4\text{SiO}_4$

Alkali silicates are prepared by fusing the oxide or carbonate with sand at a very high temperature.



sodium carbonate      sand      sodium silicate

(1) Orthosilicate : \* Basic unit =  $\text{SiO}_4^{-4}$



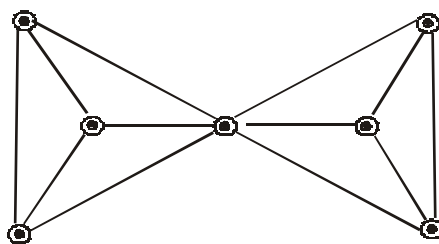
⇒ Orthosilicate has Tetrahedral  $\text{SiO}_4^{-4}$  unit; which is join with metallic ions to give various silicates founding Bessalt Rocks, from volacanic megma.

eg. Phenosite

Villemite

**(2) Pyrosilicate :**

\* Basic unit  $\rightarrow \text{Si}_2\text{O}_7^{6-}$



$\Rightarrow$  Pyrosilicate has  $\text{Si}_2\text{O}_7^{6-}$  common ion

eg. Thortveitite

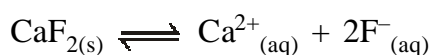
Hemimorphit

$\Rightarrow$  Two  $\text{SiO}_4^{4-}$  ions combine to each other by one common 'O' atom form island structure.

**Q. 1 (C) (i) Sparingly soluble salt :**

$\Rightarrow$  Salts which form aq. saturated soln. having less than  $0.01 \text{ ML}^{-1}$  concentration are called sparingly soluble salt.

Derivation :



$$K = \frac{[\text{Ca}^{2+}][\text{F}^{-}]^2}{[\text{CaF}_2]}$$

$$\therefore K[\text{CaF}_2] = [\text{Ca}^{2+}][\text{F}^{-}]^2$$

$$\therefore K_{sp} = [\text{Ca}^{2+}][\text{F}^{-}]^2$$

$$\therefore K_{sp} = [S][2S]^2 = 4S^3 \text{ at } 25^\circ\text{C temp.}$$

**Q. 2.(A)****(1) Hybridization energy :**

$\Rightarrow$  The difference between the energy of an atom in the ground state and the energy of hypothetical structure at the moment of bond formation is known as Hybridization energy :

(2) If  $E_a > E_a^f$  for endothermic reaction and

If  $E_a < E_a^f$  for exothermic reaction

(3) The potential of a cell measured relative to a standard hydrogen electrode is known as Electromotive Force (EMF) of the electrodes combine with the Hydrogen electrode.

(4) Limitations of V.B. Theory :

(i) It is difficult to explain molecular spectra of molecules

(ii) Paramagnetism of  $\text{O}_2$  molecule cannot be explained.

(iii) delocalization of bonding electron cannot be explained.

(5) Advantages of fuel cell

(i) It does not create pollution of air & noise.

(ii) Pure water is available as by product.



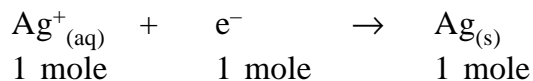
**Q. 2.(B) (1) Moles of  $\text{Ag}^+$  in 100 ml soln :**

$$0.02\text{M AgNO}_3 = \text{Molarity} \times \text{Volume}$$

$$= 0.02 \times \frac{100}{1000}$$

$$= 0.002 \text{ mole}$$

$\therefore$  0.002 mole  $\text{Ag}^+$  ions are to be reduced.

**(1) Cathode :**

1 mole                      1 mole                      1 mole

1 Faraday : 1 mole

96500 coulomb–1 mole

$\therefore$  96500 coulombs required to reduced 1 mole  $\text{Ag}^+$

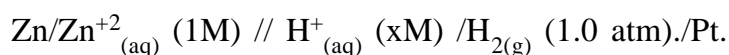
$\therefore$  0.002 Mole  $\text{Ag}^+$  ions required.

$$= 96500 \times 0.002$$

$\therefore$  Q = 193.0 coulomb    **Ans.**

Now, Q = i  $\times$  t

$$\therefore t = \frac{Q}{i} = \frac{193.0}{1.0} = 193 \text{ seconds} \quad \text{Ans.}$$

**(2)  $\Delta E$  cell = 0.54 V**

$$\Delta E \text{ cell} = \Delta E^0 \text{ cell} - \frac{0.0592}{n} \log \frac{C_1}{C_2}$$

$$\begin{aligned} \text{now } \Delta E^0 \text{ cell} &= E^0_{\text{oxi anode}} - E^0_{\text{oxi cathode}} \\ &= 0.76 - 0.0 \\ &= 0.76 \text{ V} \end{aligned}$$

$$\therefore 0.54 = 0.76 - \frac{0.0592}{2} \log \frac{1}{(\text{x})^2}$$

$$\therefore -0.22 = -0.0296 \log \frac{1}{(\text{x})^2}$$

$$\therefore \frac{0.22}{0.0296} = \log \frac{1}{(\text{x})^2} \quad \text{Where } \text{x} = [\text{H}^+_{(\text{aq})}]$$

$$\therefore \log \frac{1}{[\text{H}^+_{\text{aq}}]^2} = \frac{22}{2.96}$$

$$\therefore -\log_{10} [\text{H}^+_{(\text{aq})}]^2 = \frac{22}{2.96}$$

$$\therefore -2\log_{10} [\text{H}^+_{(\text{aq})}] = \frac{22}{2.96}$$

$$\begin{aligned} \therefore \text{pH} &= \frac{11}{2.96} \\ &= \text{Alog} (1.0414 - 0.4713) \\ &= \text{Alog} (0.5701) \\ &= 3.716 \end{aligned}$$

(3) Let initial amount of sample be 100 unit =  $N_0$

$\therefore$  50% of sample decay in 120 min

$$\therefore t_{1/2} = 120 \text{ min}$$

$$\therefore \lambda = \frac{0.693}{t_{1/2}} = \frac{0.693}{120} \text{ min}^{-1}$$

Suppose at time  $t$ , 90% of sample has decayed, at that time 10% of the initial sample will be remaining  $\therefore N_{(t)}$  units

$$\therefore \frac{N_0}{N_{(t)}} = e^{\lambda t}$$

$$\therefore \frac{100}{10} = e^{\lambda t}$$

$$\therefore 10 = e^{\lambda t}$$

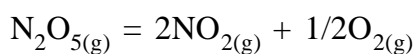
$$\therefore 10 = e^{\frac{0.693}{120}t}$$

$$\therefore 2.303 = \frac{0.693}{120}t$$

$$\begin{aligned} \therefore t &= \frac{2.303}{0.693} \times 120 = \frac{120}{0.3010} = \text{Alog}(2.0792 - \bar{1}.4786) \\ &= \text{Alog}(2.6006) \\ &= 398.7 \text{ Min} \end{aligned}$$

### Q. 2. (C) (1)

(i) Consider first order reaction



The differential rate law of the reaction is

$$-\frac{d[\text{N}_2\text{O}_5]}{dt} = K[\text{N}_2\text{O}_5]$$

If the concentration of  $\text{N}_2\text{O}_5 = C$

$$\therefore -\frac{dC}{dt} = K.C \quad K = \text{rate constant}$$

$$\therefore -\frac{dC}{C} = K.dt$$

$\therefore$  If the initial conc. of the reactant is  $C_0$ , above equation will have following limits for integration

$$C = C_0 \text{ When } t = 0$$

$$C = C \text{ When } t = t$$

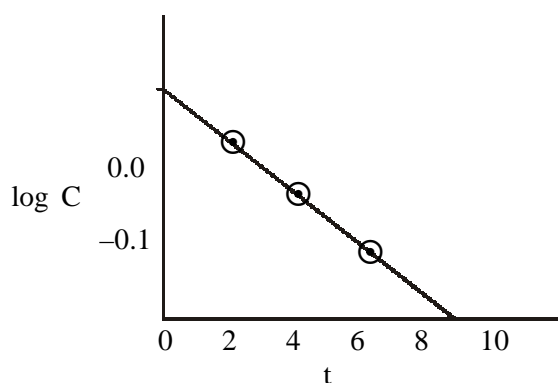
$$\therefore -\int_{C_0}^C \frac{1}{C} = K \int_0^t dt$$

$$\therefore -[\ln C]_{C_0}^C = K[t]_0^t$$

$$\therefore -\ln \frac{C}{C_0} = Kt$$

$$\therefore -2.303 \log \frac{C}{C_0} = K.t$$

$$\therefore K = \frac{2.303}{t} \log \frac{C_0}{C}$$



$$K = -\frac{K}{2.303}$$

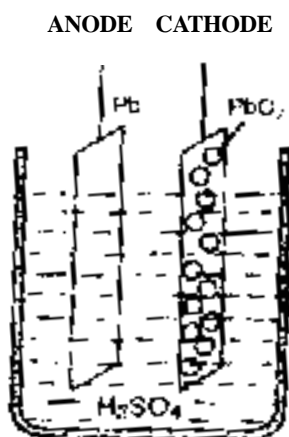
graph :  $\log C \rightarrow t$

**(ii) law of mass action :**

⇒ The driving force of a chemical reaction is proportional to the active masses of reactants

**(2) Lead Storage Cell :**

**(ii) Lead Storage Cell :** This cell consists of sponge-like lead plates and thin lead plates coated with  $\text{PbO}_2$ . These plates are dipped in approximately 30% (w/w)  $\text{H}_2\text{SO}_4$  solution. The lead plates act as anode and the plates coated with  $\text{PbO}_2$  act as cathode when they are connected. The following reactions occur at electrodes during the operation of the cell.



Lead Storage Cell

Lead sulphate formed during reaction remains on the surface of the electrodes. The potential of the cell is nearly 2 volts. As water is produced and  $\text{H}_2\text{SO}_4$  is consumed during the operation of the cell, the density of the cell goes on decreasing with its use. The initial density of  $\text{H}_2\text{SO}_4$  solution is nearly  $1.25 - 1.30 \text{ g ml}^{-1}$ . This decreases to about  $1.10 - 1.15 \text{ g ml}^{-1}$  when the cell becomes dead. If this dead cell is connected with another cell having higher opposing potential, the reactions at electrodes are reversed and again it becomes charged and capable of generating current. However, the efficiency of recharging process is not 100%. Therefore, 30% (w/w)  $\text{H}_2\text{SO}_4$  solution has to be added to the cell periodically. After a long use, the cell has to be discarded.

By using more than one anodes and cathodes and connecting them in series a potential higher than 2.0 volt can be generated.

$$(3) \Psi_{n=1} = \frac{1}{\sqrt{\pi} a_0} e^{-\frac{r}{a_0}} \text{ is acceptable soln of } \Psi$$

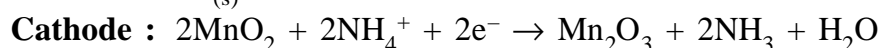
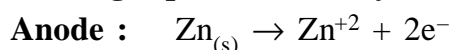
$$\text{Where } a_0 = \frac{h^2}{4\pi m e^2}$$

⇒ Since  $r$  is constant, electron is probable in all direction at equi distance.

⇒ Thus shape of  $s$ -orbital is spherical.

**Node :** The space around nucleus, probability of finding electron is almost zero is called node.

**Antinode :** The space around nucleus where probability for finding electron cloud is more than 95% is called Antinode.

**(4) (i) During Operation of dry cell :**

**(ii) de Broglie Equation :**

After acceptance of a dual nature i.e. a particle nature and a wave nature of radiations, de Broglie, a French scientist, proposed the idea of matter waves in 1924. He argued that if radiations which were accepted to have a wave nature, also showed a particle nature, a moving matter which was accepted as a particle should also have a wave nature. He derived the following equation correlating the mass (m) and velocity (v) of particle and wavelength ( $\lambda$ ) associated with it.

$$\lambda = \frac{h}{mv}$$

Above equation is derived as under.

According to Planck's equation, the energy of a photon (E) is related to the frequency of a radiation as  $E = hv$ . According to Einstein's theory of relativity, the energy of a photon is related to its momentum p. The relation is  $E = cp$  in which c is the velocity of the photon. Correlating these two equations, we get the relation.

$$E = hv = cp$$

As  $v = \frac{c}{\lambda}$ , equation can be written as,

$$\frac{hc}{\lambda} = cp \text{ or } \lambda = \frac{h}{p}$$

de Broglie suggested that if the momentum of a photon is replaced by the momentum (mv) of a particle in motion, the equation can be written as,

$$\lambda = \frac{h}{mv}$$

Where v is the velocity of the particle, and m is the mass of the particle.

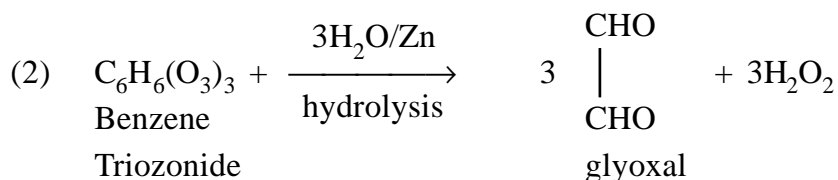
It was essential to verify this new concept of matter waves proposed by de Broglie. Radiations show properties of diffraction and interference due to their wave nature. If particles in motion are associated with waves, they should also show the property of diffraction. In 1927, Davisson and Germer, using a crystal of nickel, showed that the electrons in motion could be diffracted like x-rays.

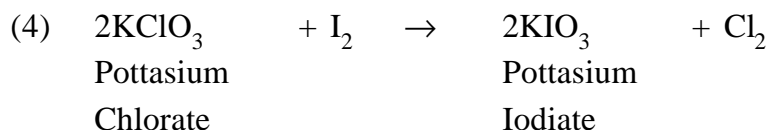
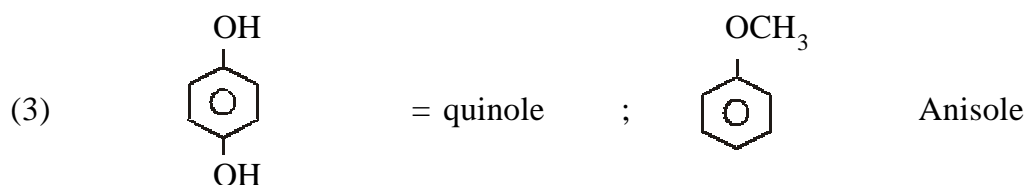
These experiments proved that the concept of matter waves proposed by de Broglie is correct.

**Q. 3. (A)**

- (1) Electrophile is reactant species capable of accepting electron pair and hence Lewis acid.

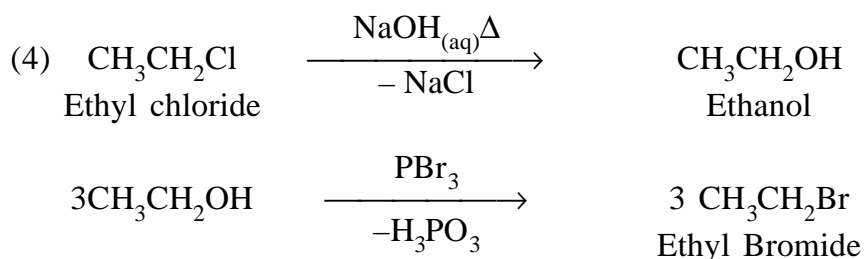
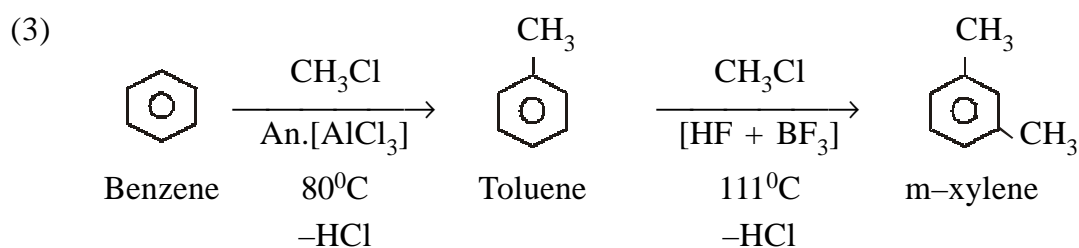
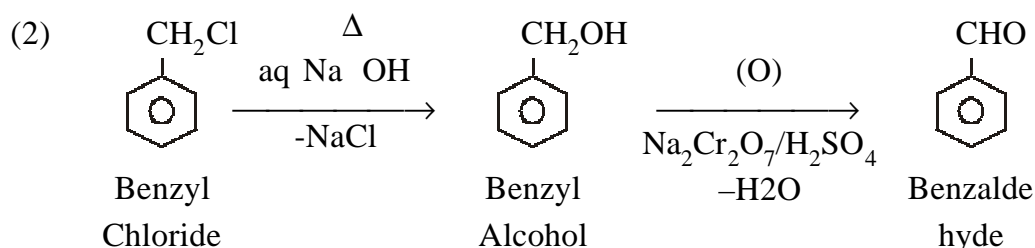
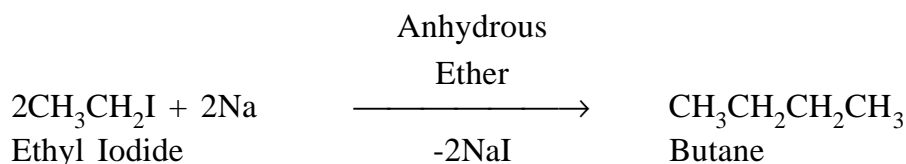
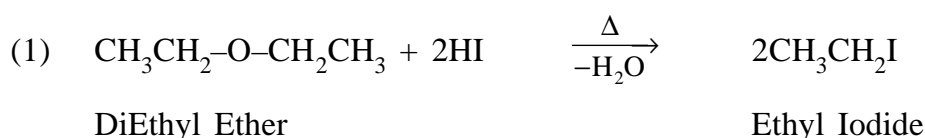
e.g.  $\text{CH}_3^+$ ,  $\text{NO}_2^+$ ,  $\text{SO}_3\text{H}^+$  etc.





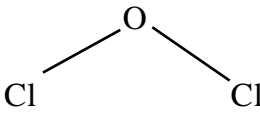
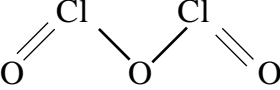
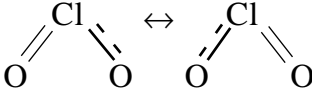
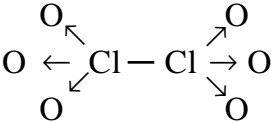
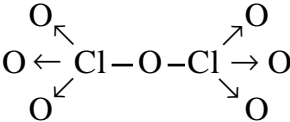
- (5) Due to low ionization energy Cs and K absorbs energy from the incident visible light and get excited and tend to set free electron of the outer most shell. electrons thus liberated are called Photoelectrons and this effect is called **Photoelectric effect**.

**(B) Conversions :**



(C) (A) (1)

## Oxides of chlorine

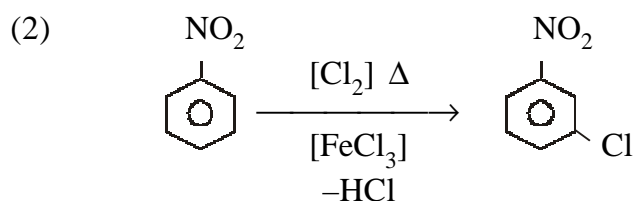
Name of oxide	Molecular formula	Oxidation state	Structural formula
Chlorine monoxide	$\text{Cl}_2\text{O}$	+1	
Chlorine trioxide	$\text{Cl}_2\text{O}_3$	+3	
Chlorine dioxide	$\text{ClO}_2$	+4	
Chlorine hexoxide	$\text{Cl}_2\text{O}_6$	+6	
Chlorine heptoxide	$\text{Cl}_2\text{O}_7$	+7	

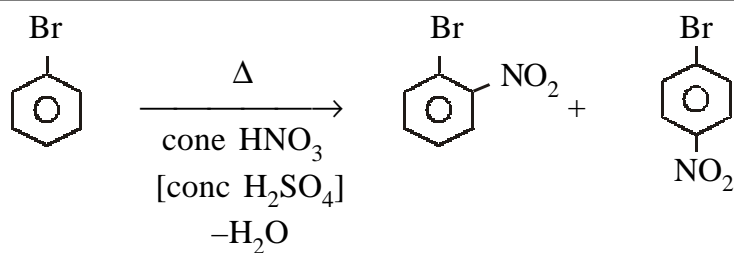
**Oxyacids of chlorine :**

There are different oxyacids formed by chlorine in different oxidation states. These oxyacids are given in table.

## Oxyacids of chlorine

Name of oxyacid	Molecular formula	Oxidation state	Structural formula
Hypochlorous acid	$\text{HClO}$	+1	$\text{H}-\text{O}-\text{Cl}$
Chlorous acid	$\text{HClO}_2$	+3	$\text{H}-\text{O}-\text{Cl} \rightarrow \text{O}$
Chloric acid	$\text{HClO}_3$	+5	$\text{H}-\text{O}-\text{Cl} \begin{matrix} \nearrow \text{O} \\ \rightarrow \text{O} \end{matrix}$
Perchloric acid	$\text{HClO}_4$	+7	$\text{H}-\text{O}-\text{Cl} \begin{matrix} \nearrow \text{O} \\ \rightarrow \text{O} \\ \searrow \text{O} \end{matrix}$

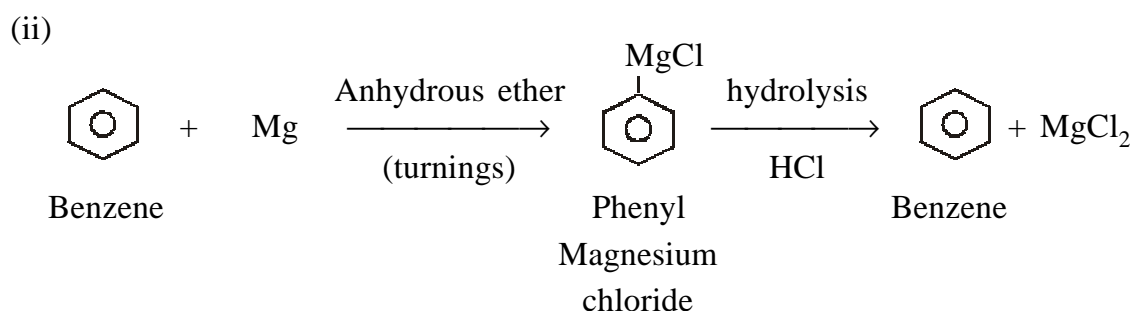
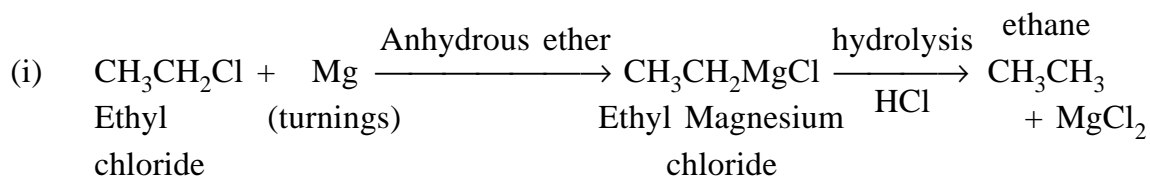




⇒ -NO<sub>2</sub> grp of Nitrobenzene is m-directing, hence Nitrobenzene give m-chloro nitrobenzene

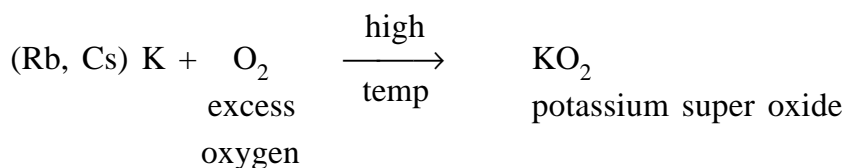
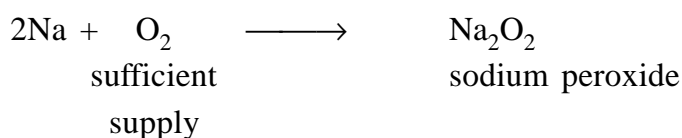
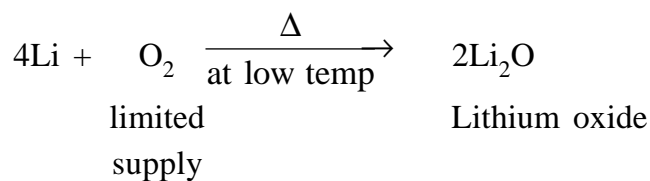
⇒ -Br grp of Bromobenzene is o-p directing, hence Bromobenzene gives o-p isomers.

### (3) Grignard reactions



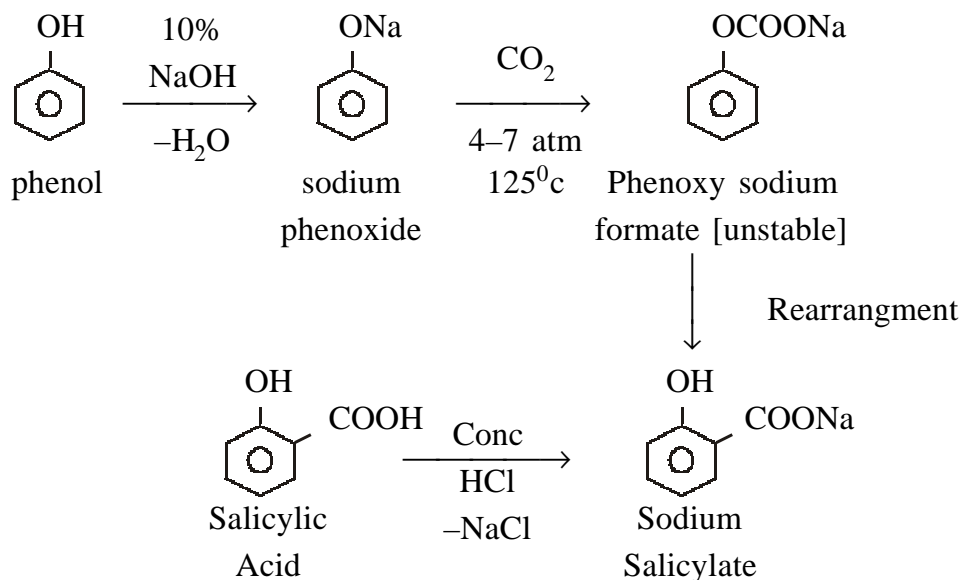
⇒ When alkyl and aryl halide react with Mg turning in presence of anhydrous Ether Alkyl or Aryl Magnesium halide is produced which on hydrolysis gives Ethane and Benzene respectively.

### (II) Reactions with O<sub>2</sub>

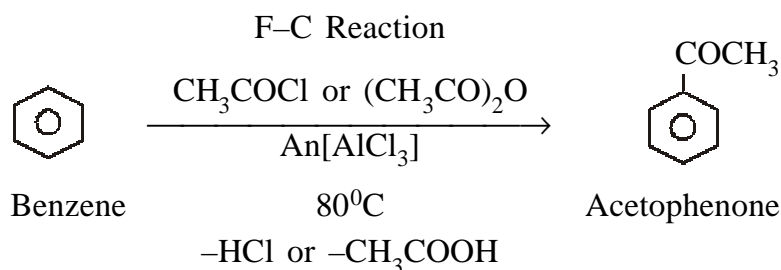


**(4) Kolbe Schmit Reaction :**

(i)



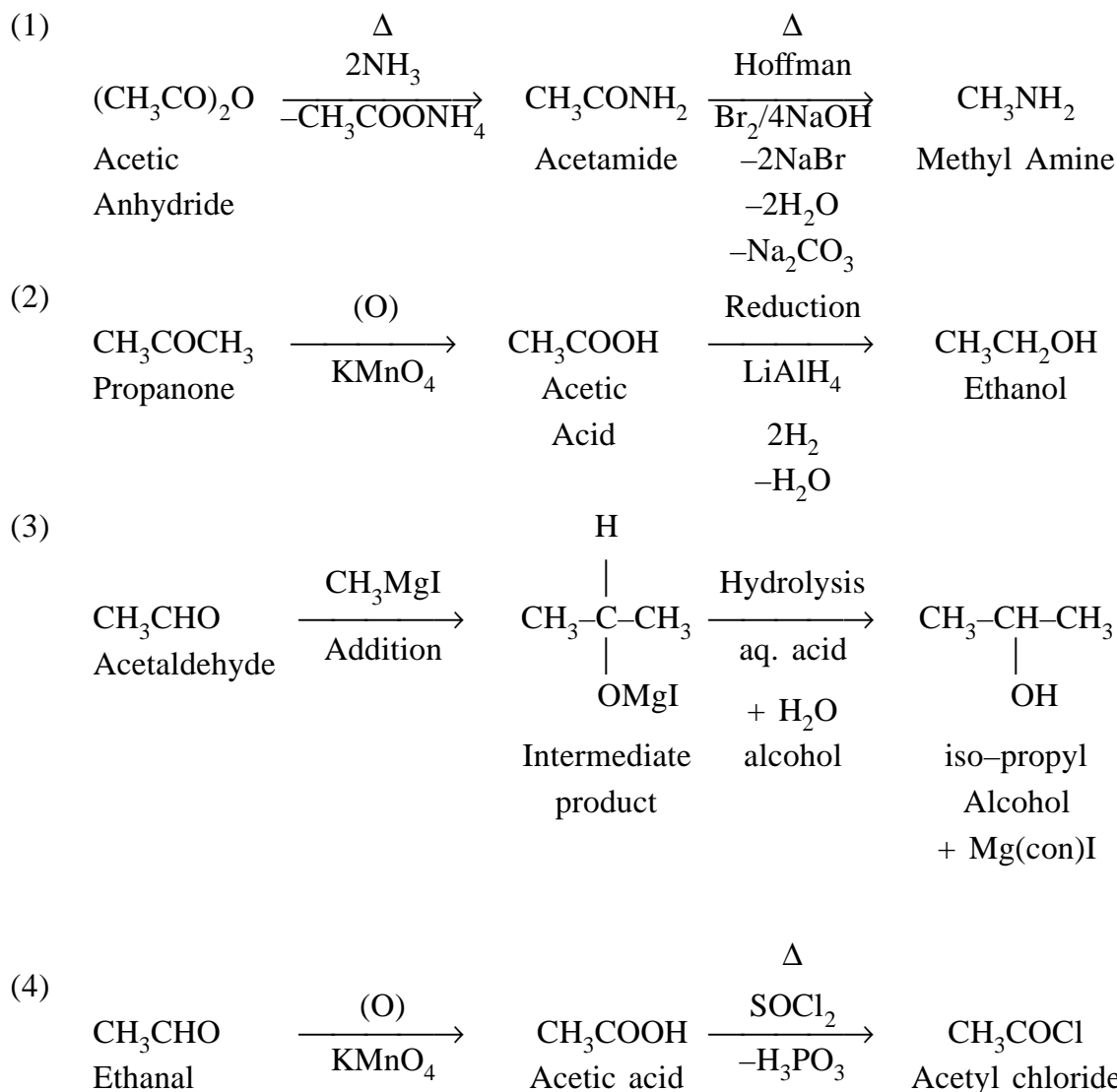
(ii)

**(4) (A)**

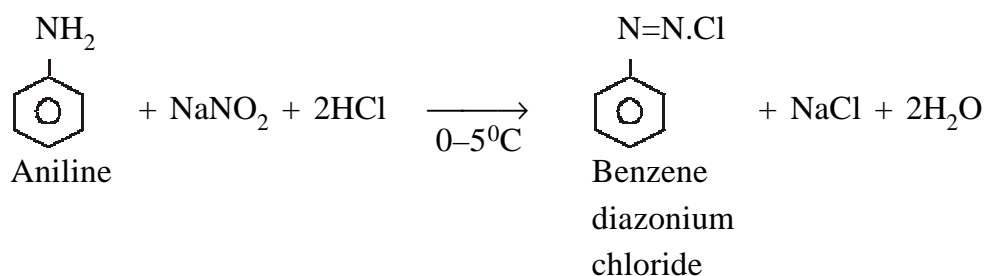
- (1) Formaldehyde is gas and its aqueous soln (30%) is known as formalin. It is used for the preservation of dead animal bodies, as well as an antiseptic.
- (2) C<sub>6</sub>H<sub>5</sub>NH<sub>2</sub> → is capable of donating non-bonding electron pairs on Nitrogen to exhibit Lewis base character.  
 eg. C<sub>6</sub>H<sub>5</sub>NH<sub>2</sub> + H<sub>2</sub>O<sub>(l)</sub> → C<sub>6</sub>H<sub>5</sub>NH<sub>3</sub><sup>+</sup><sub>(aq)</sub> + OH<sup>-</sup><sub>(aq)</sub>
- (3) Sources of Vitamin K :  
 ⇒ Carrot, Cabbage, alpha-alpha leaves  
 function : → For normal Coagulation of blood.  
 → It is used to stop bleeding.
- (4) Due to formation of strong intermolecular H-bond, dimerization of carboxylic acid takes place in organic solvent. Thus its M-wt. is twice.
- (5) Organic compounds which make polymer flexible are plasticizers  
 eg. → TCP  
 → Glycerine Phthalate  
 → Oleic Acid etc.



## 4. (B)

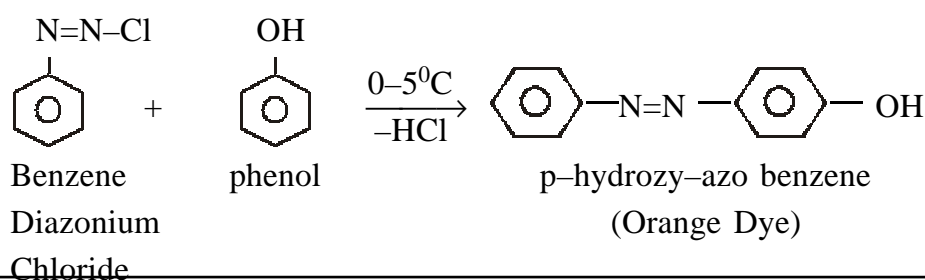


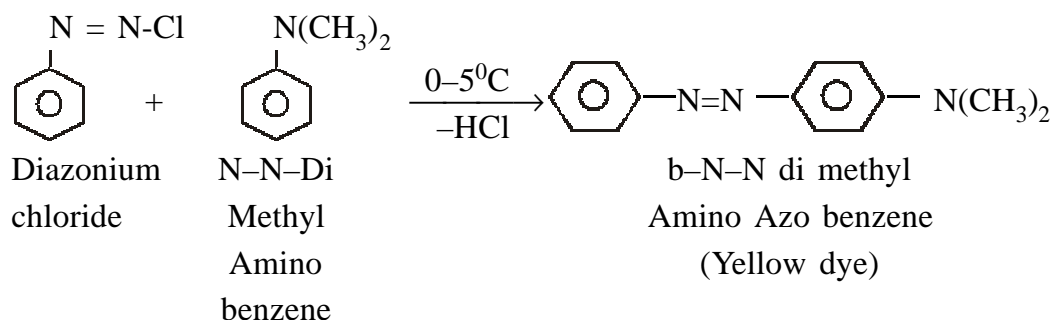
## 4. (C) (1) Diazotization :



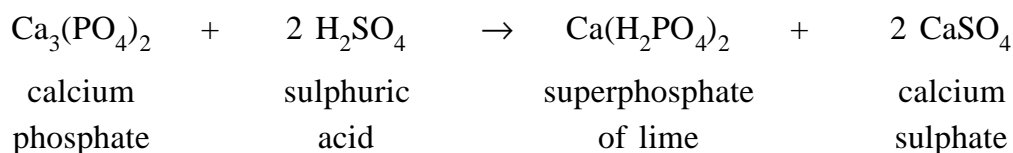
⇒ Aniline when react with  $\text{NaNO}_2 + \text{HCl}$  at  $0-5^\circ\text{C}$  to give Benzene diazonium chloride. Reaction is known as Diazotization.

## Preparation of Dyes :



(2) (1) **Superphosphate of lime :****Superphosphate of Lime :**

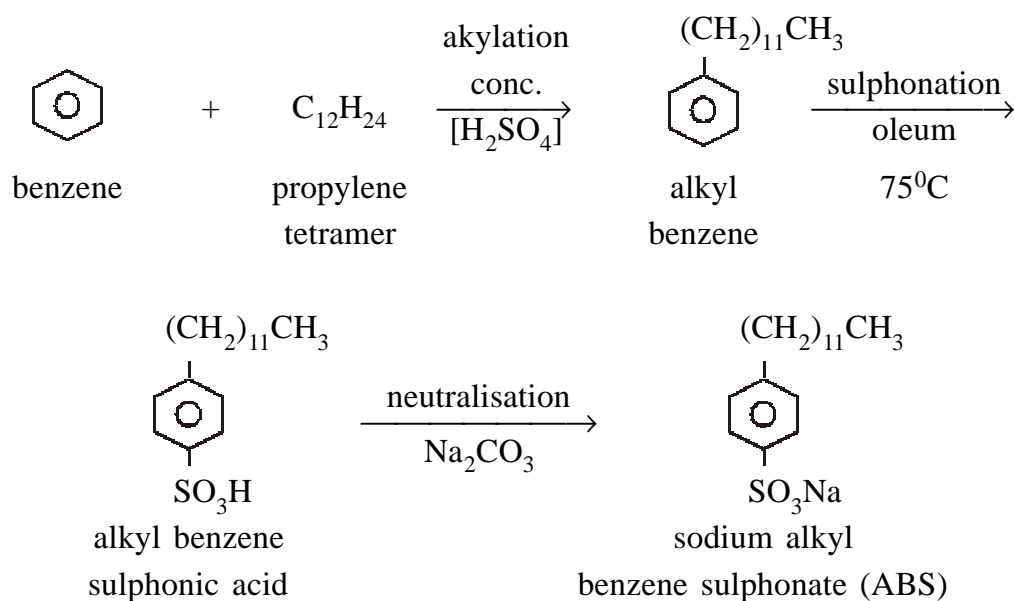
Calcium phosphate is found in nature as a mineral but this being insoluble in water is not useful as fertilizer. This needs to be converted into soluble phosphate. In a big closed vessel, finely pulverized calcium phosphate mineral is mixed with 80–90% conc  $\text{H}_2\text{SO}_4$ , chemical reaction is very slow and calcium dihydrogen phosphate is formed. This has large phosphorous content than calcium phosphate. Hence calcium dihydrogen phosphate is called superphosphate of lime.



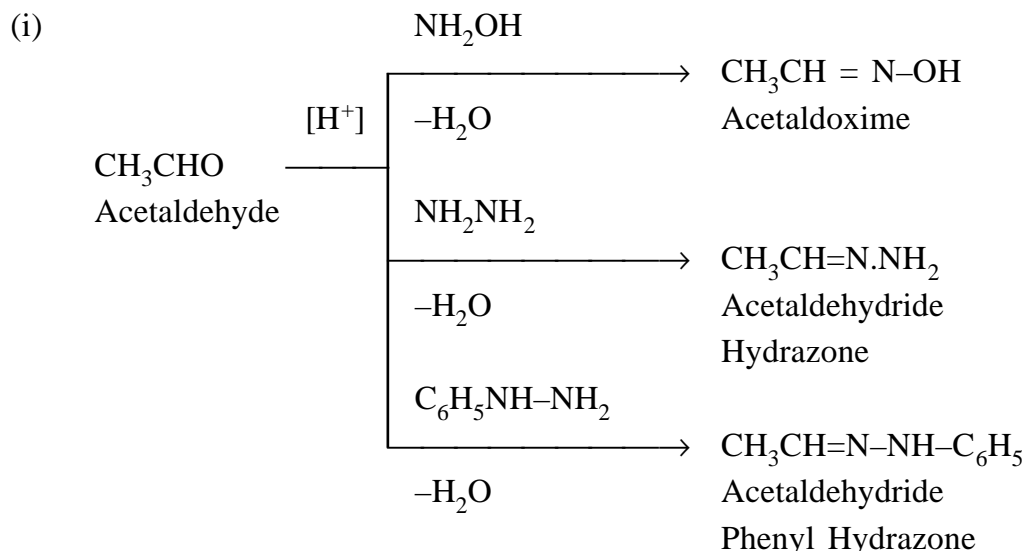
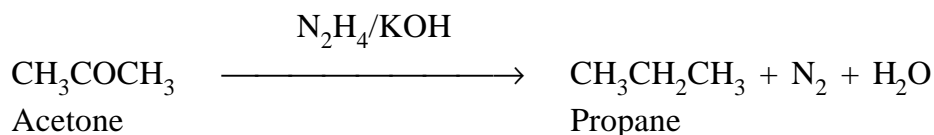
Superphosphate of lime is soluble in water and can be added to the soil as fertilizer, which supplies phosphorous and calcium nutrients to plants.

(2) **Industrial Production of ABS or Alkyl Benzene Sulphonates :**

Tetramer of propylene reacts with benzene in presence of conc.  $\text{H}_2\text{SO}_4$  to give alkyl benzene. Its sulphonation with oleum at  $75^\circ\text{C}$  gives alkyl benzene sulphonic acid. By allowing the reaction mixture to settle for some time, alkyl benzene sulphonic acid being lighter separates out as upper layer. After separation and neutralisation with  $\text{Na}_2\text{CO}_3$ , it is obtained in the form of sodium alkyl benzene sulphonate. This is called ABS detergent

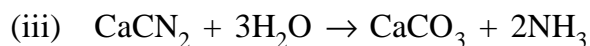
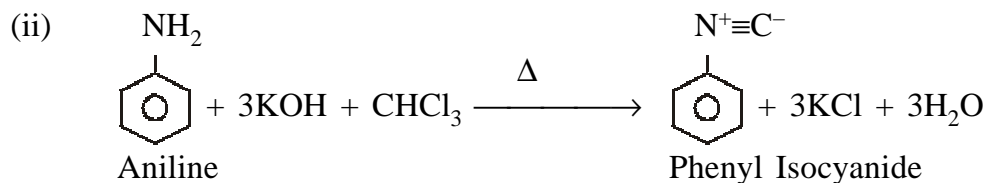
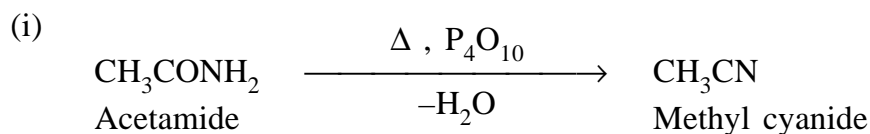


## Q . 4. (C) (3) Condensation Reactions of Acetaldehyde

(ii) Wolf Kishner Red<sup>n</sup> of Ketone :

⇒ When Acetone react with basic hydrazine it gives propane.

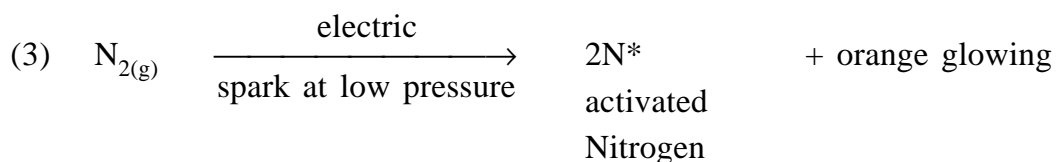
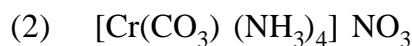
(4)



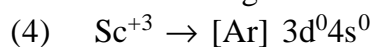
## Q. 5. (A)

(1)  $\text{CuH}_{0.96}$  is prepared by reaction between  $\text{CuSO}_4$  and sodium hypo phosphite.

⇒ It is brown colour and unstable.

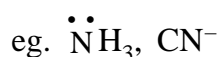


\* N\* nitrogen breaks some stable molecules.



⇒  $d^0$  configuration does not allow d-d transition giving colourless compounds.

(5) Ligands are Lewis base characterised reactant species capable of donating electron pair either electrical neutral molecule or negatively charged ion.



**Q. 5. (B)**

- (1) If the molecules, atoms or ions contain unpaired electron(s) then the substance is paramagnetic.

Substance is attracted by external magnetic field.

Value of para magnetic momentum ( $\mu$ ) is calculated by equation,

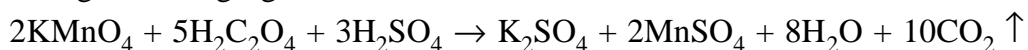
$$\mu = \sqrt{n(n+2)} \quad \text{Where } n = \text{no. of unpaired electrons}$$

As  $\text{Cr}(\text{CO})_6$  donot have any unpaired electrons,

$$\mu = 0$$

- (2) In  $\text{KMnO}_4$ , Mn exhibit +7 oxidation state.

Due to small ionic radius and intense charge, it attract, electrons and act as strong oxidising agent.

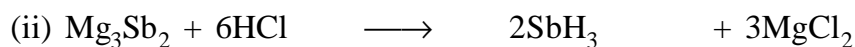


- (3) Red phosphorous is prepared by heating white phosphorous in closed container at  $250^\circ\text{C}$  temperature in presence of inert atmosphere caused by  $\text{CO}/\text{N}_2$  and in presence of  $\text{I}_2$  as catalyst

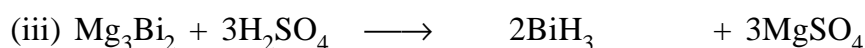
Red phosphorous donot ignite even at  $400^\circ\text{C}$  temperature. It is poly atomic molecule.

**Q. 5. (1)**

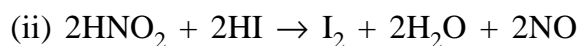
phosphine



Stibia



Bismathine

**Q. 5. (c) (2) Interstitial and non-stoichiometric compounds:**

Transition elements form interstitial compounds. By accomodating the atoms of the non-metals like H, C, N, B which are relatively small in size into the voids in their lattices and forming bonds with them, these elements form the interstitial compounds hydrides, carbides, nitrides and borides respectively. The metals absorb hydrogen reversibly. It has been established experimentally that, when the metal is used as a cathode in electrolysis of aqueous solutions hydrogen is absorbed on the cathode. Nickel, palladium, platinum metals absorb hydrogen. Nickel absorbs hydrogen which is liberated from it reversibly and, therefore, it is used as a catalyst in hydrogenation of unsaturated organic substances.

The hydrides formed by a absorption of hydrogen by the transition metals are non-stoichiometric compounds, e.g.  $\text{ZrH}_{1.92}$ ,  $\text{TaH}_{0.76}$  etc. The absorption of hydrogen expands or extends the metal latic and the small hydrogen atoms enter the intersitial voids. The brown coloured unstable compound is formed when aqueous solution of copper sulphate is reduced with sodium hypophosphide has the formula  $\text{CuH}_{0.96}$  Similarly, Cr, Fe, Co, Ni, form non-stoichiometric hydrides which are interstitial compounds.

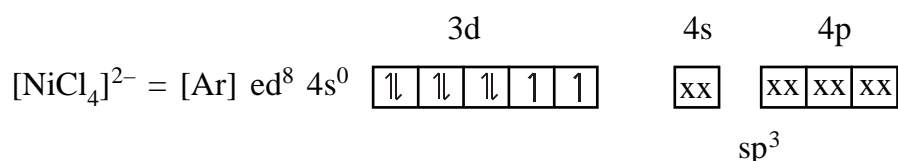
The transition elements Cr, Mn, Fe, Co, Ni. etc. combine with carbon forming carbides  $\text{Cr}_3\text{C}_2$  and  $\text{M}_3\text{C}$  (where  $\text{M} = \text{Mn, Fe, Co, Ni}$ ). These give hydrocarbons by reaction with water or dilute acid. These carbides are interstitial compounds, in which the carbon atoms occupy the interstitial voids in the metal lattice.

Like hydrides and carbides, the transition elements form interstitial nitrides with nitrogen. The example are  $\text{Mn}_4\text{N}$ ,  $\text{Fe}_4\text{N}$  etc. in which the nitrogen atoms occupy the interstitial voids in the metal lattice. These are also non-stoichiometric compounds.

The transition elements form non-stoichiometric interstitial compounds like borides with boron also. The boron atoms fill the interstitial voids in the metal lattice. The examples of borides are interstitial  $\text{CrB}$ ,  $\text{FeB}$ ,  $\text{NiB}$ ,  $\text{CrB}$  etc. All these interstitial compounds are non-stoichiometric.

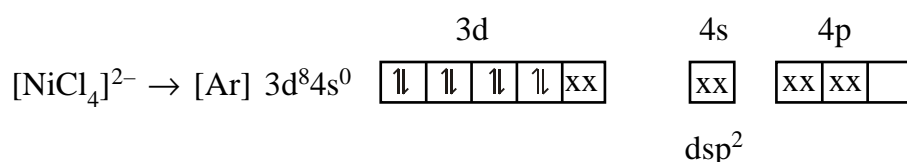
The formulas shown above are not completely correct. The metal hydrides, carbides, nitrides or borides involve formation of interstitial compounds which increases the bonding forces of the metal and results in changes in the properties of the metal. All these compounds possess high melting points and boiling points. They are very hard substances, with a metallic lustre, and are good conductors of electricity. They are useful in industry and in making tools.

(3) In  $\text{K}_2[\text{NiCl}_4] \Rightarrow \text{Ni}$  is  $\text{Ni}^{+2}$  state



$\Rightarrow$  due to  $sp^3$  hybridization it has Tetrahedral shape.

In  $\text{K}_2 [\text{Ni}(\text{CN})_4] \rightarrow \text{Ni}$  is +2 state



$\Rightarrow$  due to  $dsp^2$  hybridization it has square planar geometry.

#### (4) Complexes in nature:

Complexes play important roles in nature. They are specially needed in many chemical reactions occurring in plants and animals. Chlorophyll is responsible for the green colour of the leaves of plants. The red colour of the animal blood is due to hemoglobin. Chlorophyll is a magnesium complex and hemoglobin is a complex of iron. Both these complexes contain very large molecules. They have similar molecular structures. Mg and Fe in these complexes are coordinated with four nitrogen atoms present in the ligand.

Hemoglobin serves to carry the oxygen entering through lungs to different parts of the body. The  $\text{Fe}^{2+}$  of hemoglobin combines with oxygen forming a complex which releases this oxygen in the body cells. The liberated oxygen combines with the organic substances in the body and produces carbon dioxide and energy. The carbon dioxide is exhaled in respiration. Hemoglobin thus provides energy to our body.

Chlorophyll is inevitable for photosynthesis in plants. It absorbs solar energy and prepares starch from water and carbon dioxide. The magnesium needed by our body is obtained through chlorophyll from green leafy vegetables. Magnesium deposits in bones. It is also useful for muscles and nervous system. The body of a grown-up person contains on an average 25 milligrams of magnesium.

Vitamin B<sub>12</sub> curing in nature is a complex of cobalt metal. It is present in animals but not in plants. A grown-up person requires about 1.5 microgram of vitamin B<sub>12</sub> everyday.

Several metals and non-metals are present in our body in the form of compounds. Vegetables also contain many elements in trace amounts. These elements are essential for different chemical reactions that sustain life. These elements occur as complexes with proteins and enzymes, which are necessary in many complicated reactions in the body.

\*\_\*\_\* \*