CAREERS360

GSEB HSC CHEMISTRY

Question Papers (All Sets)

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 25^0 C temperature. Calculate ionisation constant (Kb) of methyl amine.

(2) The standard free energies of formation of $NO_2(g_)$, $NO_{(g)}$ and $O_{3(g)}$ are 12.39, 20.72 and 39.06 K.cal/mole respectively at 25^0 C. Calculate the equilibrium constant of the reaction $NO_{(g)} + O_{3(g)} \rightarrow NO_{2(g)} + O_{2(g)}$ at 25^0. 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 $PbCl_2$ precipitate on mixing 5.0 ml 2.0×10^{-4} M $CaCl_2$ solution with 1.0 ml. 1.0×10^{-4} M $Pb(NO_3)_2$ solution ? Ksp of $PbCl_2$ is 2.0×10^{-4}.

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

(1) Derive a relation between the ionisation constant Ka and the concentration Co and H_3O^+ of given weak acid HA at 25^0C 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 CaF_2. Why solubility of AgCl decreases in aqueous solution of NaCl ?

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

(1) Define : Hybridization energy.

(2) Compare Ea and Ea^r for a given reversible thermochemical reaction.

(3) What is 'Electromotive force' ?

(4) Give two limitations of valance 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 $AgNO_3$ solution to reduce all $Ag^{+}_{(aq)}$ to $Ag_{(s)}$.

(2) The potential of the following cell is 0.54 Volts at 25^0C. Calculate pH of acid solution.

$Zn/Zn^{+2}_{(aq)}$ (1M) // $\mu^{+}_{(xM)}/H_{2(1\ atm)}$/Pt.

(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) $N_2O_{5(g)} \rightarrow 2NO_{2(g)} + \frac{1}{2}O_{2(g)}$ 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–Brogile equation.

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

(1) What is electrophile ? Give illustration.

(2) Give chemical equation showing hydrolysis of benzene triozonide.

(3) Give structural formula : Quinol, Anisol.

(4) Give chemical reaction between iodine and $KClO_3$. 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 followin g. **(9)**

(1) Discuss : (i) oxides of chlorine (ii) oxyacids of chlorine.

(2) Chlorination of nitrobenzene gives m–chloro nitrobenzene while nitration of chlobenzene 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) Fridle – 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) Industriall production of ABS.

(3) Explain condensation reaction of Aldehyde and Wolf– Krishner 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 $CuH_{0.96}$ prepared ? What is its character ?

(2) Give formula : Carbanato tetraammine chromium (III) nitrate

(3) How are activated nitrogen prepared ? State its function.

(4) Why Sc^{+3} gives colourless compounds.

(5) Define : Ligand

(B) Answer the following questions. **(6)**

(1) What is paramagnetism ? Calculate paramagnetic momentum (μ) for compound $Cr(CO)_6$

(2) $KMnO_4$ 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 HNO_2 as oxidising agent.

(2) Write a note on Interstitial and non–stochiometric compounds.

(3) $K_2[Ni(Cl)_4]$ is tetrahydral while $K_2[Ni(CN)_4]$ is square planner. Explain in detail.

(4) Write a note on complexes in nature.

_*_

: ANSWER :

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

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

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

(2) Kw is dissociation constant of pure water known as ionic product of purer water at 25^0c 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 repetation of $(Si_4O_{11})^{-6}$ 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_3NH_2 = 31.0 gram–mole^{-1}

$$\text{conc. of } CH_3NH_2 = \frac{\text{Wt. of Solute} \times 1000 \text{ ml}}{\text{Mole Wt.} \times \text{Volume of Sol}^n \text{ in ml}}$$

$$= \frac{6.2 \times 10^3}{31 \times 500}$$

$$= 0.4 \text{ M}$$

$$CH_3NH_2 + H_2O_{(l)} \rightleftharpoons CH_3NH_3{}^+{}_{(aq)} + OH^-{}_{(aq)}$$

pH = 12.15

$\therefore$ pOH = 14.0 – pH

= 14.0 – 12.15

= 1.85

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

$\therefore \log_{10}[OH^-]$ = – pH

= – 1.85

$\therefore [OH^-]$ = Antilog (–1.85)

= 1.41×10^{-2} M.

As weak base dissociate feebly, $[OH^-] = \sqrt{K_b.Co}$

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

$\therefore Kb = \frac{(1.41)^2}{4} \times 10^{-3}$

$= 5.0 \times 10^{-4}$

(2) $NO_{(g)} + O_{3(g)} \rightleftharpoons NO_{2(g)} + O_{2(g)}$

(i) ΔG^0 reaction = $\Sigma \Delta G^0$product – $\Sigma \Delta^0$ reactant

= $[\Delta G^0 + (NO_2) + \Delta G^0_f(O_2)] - [\Delta G^0_f(NO) + \Delta G^0_f(O_2)]$

= (12.39 + 0) – (2.72 + 39.06)

= 12.39 – 59.78

= – 47.39 k.cal.mole^{-1}

(ii) ΔG^0 = – RTlnkp

= – 2.303 RT log kp

$\therefore$ log Kp = $\frac{\Delta G^0}{-RT(2.303)}$

= $\frac{-47.39}{-2.303 \times 1.987 \times 10^{-3} \times 298}$

= 34.73

$\therefore$ Kp = Antilog 34.73 = 5.34×10^{34}

(iii) Now,

$\Delta H^0 = \Delta H^0_{product} - \Delta H^0_{reactant}$

= (8.09 + 0.0) – (21.60 + 34.0)

= 8.09 – 55.6

= – 47.51 K.cal/mole

(iv) Now,

$\Delta G^0 = \Delta H^0 - T\Delta S^0$

$\therefore \Delta S^0 = \frac{\Delta H^0 - \Delta G^0}{T}$

= $\frac{-47.51-(-47.39)}{298}$

= -4.02×10^{-4} k.cal.^{0}k^{-1}

(3) $CaCl_{2(g)} \rightleftharpoons Ca^{+2}_{(g)} + 2Cl^-_{(g)}$; $Pb(NO_3)_2 \rightleftharpoons Pb^{+2}_{(g)} + 2NO_3^-{}_{(g)}$

2.0×10^{-4} $2 \times 2 \times 10^{-4}$ 1.0×10^{-4} 1.0×10^{-4}

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 $M_1V_1 = M_2V_2$

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

= 1.67×10^{-5} M

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

= 3.33×10^{-4} M

Now, $PbCl_2 \rightleftharpoons Pb^{+2}_{(g)} + 2Cl^-_{(g)}$

$\therefore$ IP $PbCl_2$ $= [Pb^{+2}_{(g)}]\ [Cl^{-}_{(g)}]^2$

$= [1.67 \times 10^{-5}]\ [3.33 \times 10^{-4}]^2$

$= 1.85 \times 10^{-12}$

As IP < Ksp

$PbCl_2$ will not precipitate on mixing above solutions.

Q. (1) (C)

(1) Derivation of Ka for weak acid HA

Suppose a weak acid HA is dissolved in water,

Following equilibrium exists in the aqueous solution at 25^0C temperature

$HA_{(l)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + A^-_{(aq)}$

Let us calculate equilibrium constant K as under :

$$K = \frac{\text{product of concentrations of products}}{\text{product of concentrations of reactants}}$$

$$= \frac{[H_3O^+]\ [A^-]}{[H_2O][HA]}$$

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

Thus, $[H_2O]$ in above equation is considered as constant.

$$\therefore K\ [H_2O] = Ka = \frac{[H_3O^+]\ [A^-]}{[HA]}$$

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

$Ka[HA] = [H_3O^+]^2$ where, Ka = dissociation constant of given

$\therefore$ $KaCo = [H_3O^+]^2$ weak acid HA at 25^0c temperature

$\therefore$ $[H_3O^+] = \sqrt{Ka.Co}$ Co = Initial molar concentration of weak acid HA

(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 $ohm^{-1}cm^{-1}$ while that of some insulator is about 10^{-12} $ohm^{-1}cm^{-1}$ which is negligible.

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

Substances like pure alkalihalides are generally insulator.

The conductivity of semicondutors 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 : Tio ; CrO_2

Semi conductor : Ti_2O_3

Insulators : TiO_2, FeO, Fe_2O_3, CuO etc.

The appearance and conductivity of ReO_3 are like those of metallic copper.

(3) Characteristics entropy.

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

Entropy of a system is state function.

Absolute value of entropy can be calculated.

Change in entropy is given by

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

The total entropy change of a system is as under.

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

If ΔS_{total} is positive, the reaction should occure spontaneously while if ΔS_{total} is negative, the reaction cannot occure spontaneously. If ΔS_{total} is zero, the reaction enjoys a state of equilibrium i.e.

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

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

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

Q. 4. (C) Silicates

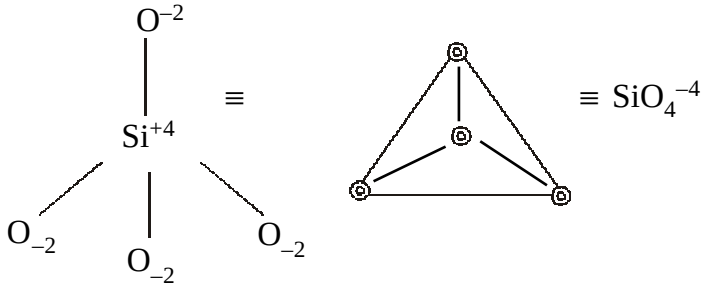
Silicates are derivatives of Silicic acid H_4SiO_4

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

$$2Na_2CO_3 + SiO_2 \xrightarrow[\Delta]{\text{fusion}} Na_2SiO_4 + 2CO_2 \uparrow$$

sodium carbonate — sand — sodium silicate

(1) Orthosilicate : * Basic unit = SiO_4^{-4}



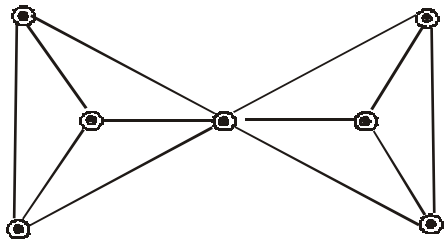
⇒ Orthosillicate has Tetrahedral SiO_4^{-4} unit; which is join with metalic ions to give various silicates founding Bessalt Rocks, from volacanic megma.

eg. Phenesite

Villemite

(2) Pyrosillicate :

* Basic unit → $Si_2O_7^{6-}$



⇒ Pyrosillicate has $Si_2O_7^{-6}$ common ion

eg. Thortveitite

Hemimorphit

⇒ Two SiO_4^{-4} ions combine to each other by one common 'O' atom form iland structure.

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

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

Derivation :

$$CaF_{2(s)} \rightleftharpoons Ca^{2+}_{(aq)} + 2F^{-}_{(aq)}$$

$$K = \frac{[Ca^{2+}][F^-]^2}{[CaF_2]}$$

$\therefore K[CaF_2] = [Ca^{2+}]\ [F^-]^2$

$\therefore Ksp = [Ca^{2+}]\ [F^-]^2$

$\therefore Ksp = [S]\ [2S]^2 = 4S^3$ at 25^0c temp.

Q. 2.(A)

(1) Hybridization energy :

⇒ 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 $Ea > Ea^r$ for endothermic reaction and

If $Ea < Ea^r$ 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) Limitions of V.B. Theory :

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

(ii) Paramagnetism of O_2 molecule cannot be explained.

(iii) delocatization of bonding electron cannot be explained.

(5) Advantages of fuel cell

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

(ii) Pure water is available as by product.

Q. 2.(B) (1) Moles of Ag^+ in 100 ml soln :

0.02M $AgNO_3$ = Molarity × Volume

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

$$= 0.002 \text{ mole}$$

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

(1) Cathode :

$Ag^+_{(aq)}$ + e^- → $Ag_{(s)}$

1 mole 1 mole 1 mole

1 Faraday : 1 mole

96500 coulomb–1 mole

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

$\therefore$ 0.002 Mole Ag^+ ions required.

$= 96500 \times 0.002$

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

Now, $Q = i \times t$

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

(2) ΔE cell = 0.54 V

$Zn/Zn^{+2}_{(aq)}$ (1M) // $H^+_{(aq)}$ (xM) /$H_{2(g)}$ (1.0 atm)./Pt.

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

now ΔE^0 cell $= E^0_{\text{oxi anode}} - E^0_{\text{oxi cathode}}$

$= 0.76 - 0.0$

$= 0.76$ V

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

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

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

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

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

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

$$\therefore pH = \frac{11}{2.96}$$

$= \text{Alog } (1.0414 - 0.4713)$

$= \text{Alog } (0.5701)$

$= 3.716$

(3) Let initial amount of sample be 100 unit = No

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

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

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

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

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

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

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

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

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

$\therefore t = \frac{2.303}{0.693} \times 120 = \frac{120}{0.3010}$ = Alog $(2.0792 - \bar{1}.4786)$

= Alog(2.6006)

= 398.7 Min

Q. 2. (C) (1)

(i) Consider first order reaction

$N_2O_{5(g)} = 2NO_{2(g)} + 1/2O_{2(g)}$

The differential rate law of the reaction is

$-\frac{d[N_2O_5]}{dt} = K.[N_2O_5]$

If the concentration of $N_2O_5 = C$

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

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

$\therefore$ If the initial conc. of the reactant isCo, above equation will have following limits for intigration

C = Co When t = 0

C = C When t = t

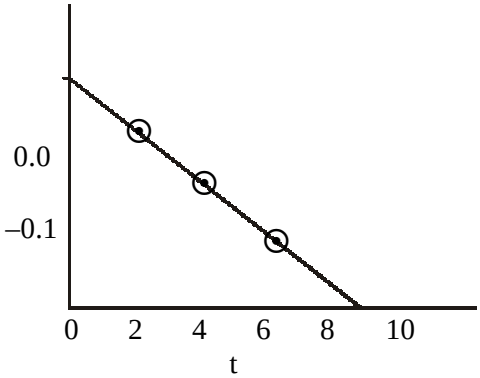
$\therefore -\int_{Co}^{C} \frac{dC}{C} = K \int_{0}^{t} dt$

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

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

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

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



$\left[\text{Slope} = -\frac{K}{2.303}\right]$

graph : log C $\rightarrow$ t

(ii) law of mass action :

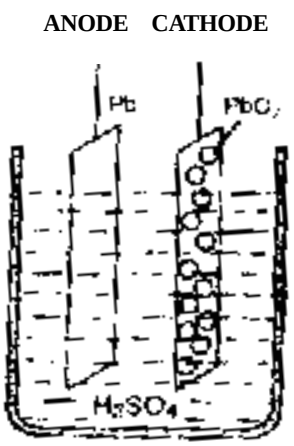
⇒ The driving force of a chemical reaction is proportional to the active masses of reactants

(2) Lead Storage Cell :

(ii) Lead Storage Cell : This cell consists of sponge– like lead plates and thin lead plates coated with PbO_2. These plates are dipped in approximately 30% (w/w) H_2SO_4 solution. The lead plates act as anode and the plates coated with PbO_2 act as cathode when they are connected. The following reactions occur at electrodes during the operation of the cell.

At anode : $Pb_{(s)} + SO_4^{2-}{}_{(aq)} = PbSO_{4(s)} + 2e^-$

At cathode : $PbO_{2(s)} + 4H^+ + SO_4^{2-}{}_{(aq)} + 2e^- = PbSO_{4(s)} + 2H_2O$



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 H_2SO_4 is consumed during the operation of the cell, the density of the cell goes on decreasing with its use. The initial density of H_2SO_4 solution is nearly 1.25 – 1.30 g ml^{-1}. This decreases to about 1.10 – 1.15 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) H_2SO_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) $\Psi_{\substack{n=1\\l=0}} = \frac{1}{\sqrt{\pi}} \left(\frac{1}{a_0}\right)^{\frac{3}{2}} e^{-\frac{r}{a_0}}$ is acceptable soln of Ψ

Where $a_0 = \frac{h^2}{4\pi me^2}$

⇒ 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 :

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

Cathode : $2MnO_2 + 2NH_4^+ + 2e^- \rightarrow Mn_2O_3 + 2NH_3 + H_2O$

(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 (λ) 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.

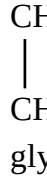
It was essential to verify this new concept of matter waves proposed by de Broglie. Radiations show properties of diffraction and interference due to their wave nature. If particles in motion are associated with waves, they should also show the property of diffraction. In 1927, Davisson and Germer, using 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)

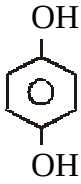
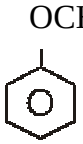
(1) Electrophile is reactant species capable of accepting electron pair and hence Lewis acid.

e.g. CH_3^+ , NO_2^+, SO_3H^+ etc.

(2) $C_6H_6(O_3)_3 + \xrightarrow[\text{hydrolysis}]{3H_2O/Zn} 3$  $+ 3H_2O_2$

Benzene Triozonide

glyoxal

(3)  = quinole ;  Anisole

(4) $2KClO_3 + I_2 \rightarrow 2KIO_3 + Cl_2$

Pottasium Chlorate — Pottasium Iodiate

(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**.

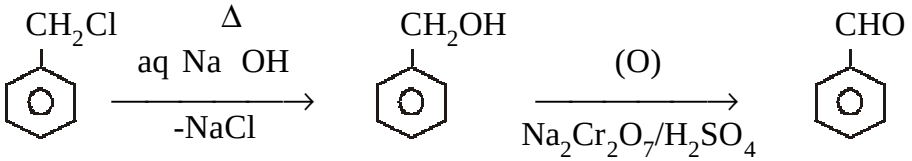
(B) Conversions :

(1) $CH_3CH_2–O–CH_2CH_3 + 2HI \xrightarrow[-H_2O]{\Delta} 2CH_3CH_2I$

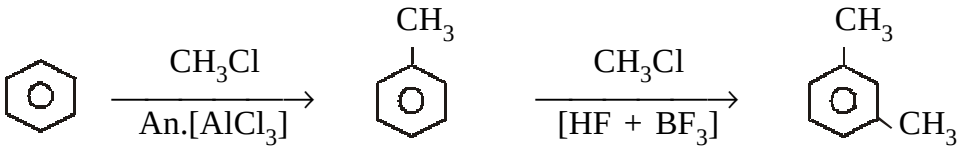
DiEthyl Ether — Ethyl Iodide

$2CH_3CH_2I + 2Na \xrightarrow[-2NaI]{\text{Anhydrous Ether}} CH_3CH_2CH_2CH_3$

Ethyl Iodide — Butane

(2) 

Benzyl Chloride — Benzyl Alcohol — Benzalde hyde

(3) 

Benzene — 80^0C –HCl — Toluene — 111^0C –HCl — m–xylene

(4) $CH_3CH_2Cl \xrightarrow[-NaCl]{NaOH_{(aq)}\Delta} CH_3CH_2OH$

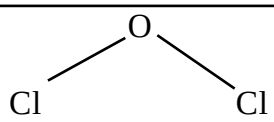
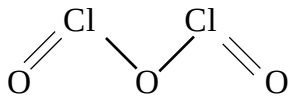
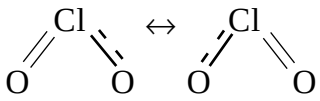
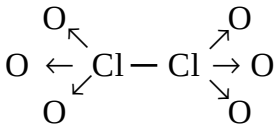
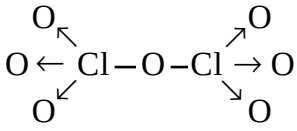
Ethyl chloride — Ethanol

$3CH_3CH_2OH \xrightarrow[-H_3PO_3]{PBr_3} 3\ CH_3CH_2Br$

Ethyl Bromide

(C) (A) (1)

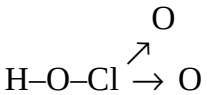
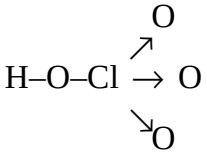
Oxides of chlorine

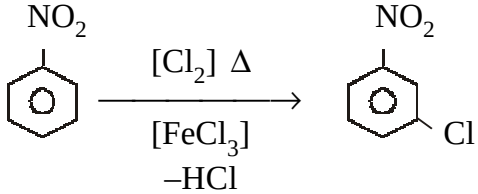
Name of oxide	**Molecular formula**	**Oxidation state**	**Structural formula**
Chlorine monoxide	Cl_2O	+1	
Chlorine trioxide	Cl_2O_3	+3	
Chlorine dioxide	ClO_2	+4	
Chlorine hexoxide	Cl_2O_6	+6	
Chlorine heptoxide	Cl_2O_7	+7	

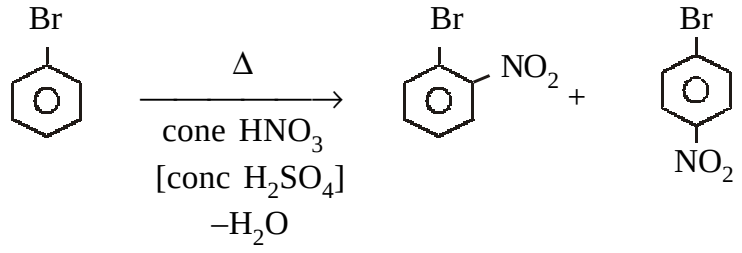
Oxyacids of chlorine :

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	HClO	+1	H–O–Cl
Chlorous acid	$HClO_2$	+3	H–O–Cl → O
Chloric acid	$HClO_3$	+5	
Perchloric acid	$HClO_4$	+7	

(2) 



⇒ $-NO_2$ grp of Nitrobenzene is m–directing, hence Nitrobenzene give m–chloro nitrobenzene

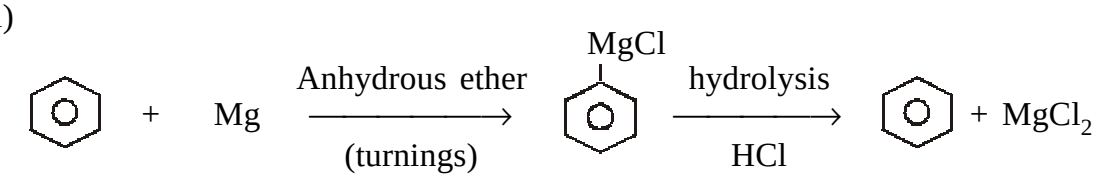
⇒ –Br grp of Bromobenzene is o–p directing, hence Bromobenzene gives o–p isomers.

(3) Griganard reactions

(i) $CH_3CH_2Cl + Mg \xrightarrow{\text{Anhydrous ether}} CH_3CH_2MgCl \xrightarrow[HCl]{\text{hydrolysis}} \underset{\text{ethane}}{CH_3CH_3} + MgCl_2$

Ethyl chloride (turnings) Ethyl Magnesium chloride

(ii)



Benzene Phenyl Magnesium chloride Benzene

⇒ 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_2

$4Li + O_2 \xrightarrow[\text{at low temp}]{\Delta} 2Li_2O$

limited supply — Lithium oxide

$2Na + O_2 \longrightarrow Na_2O_2$

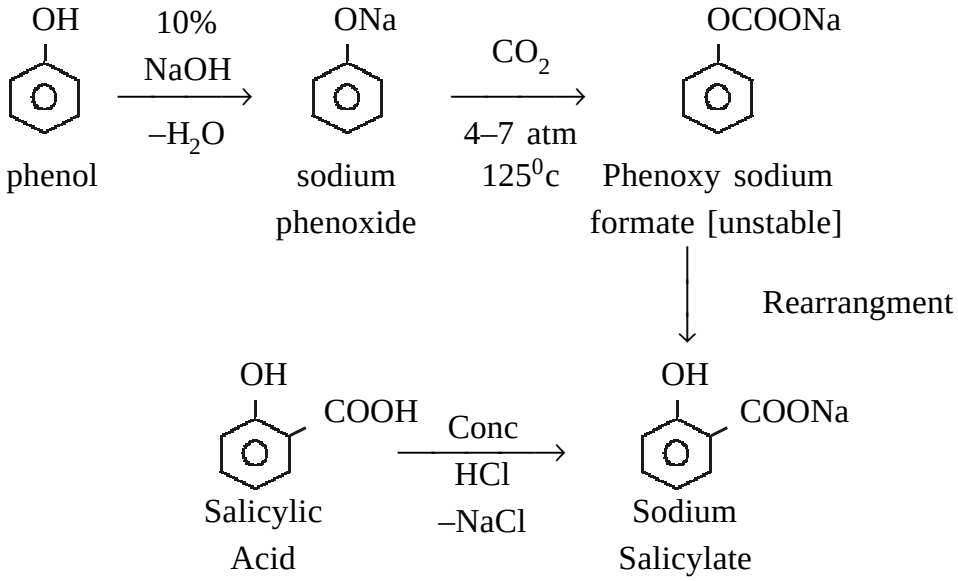
sufficient supply — sodium peroxide

$(Rb, Cs)\ K + O_2 \xrightarrow[\text{temp}]{\text{high}} KO_2$

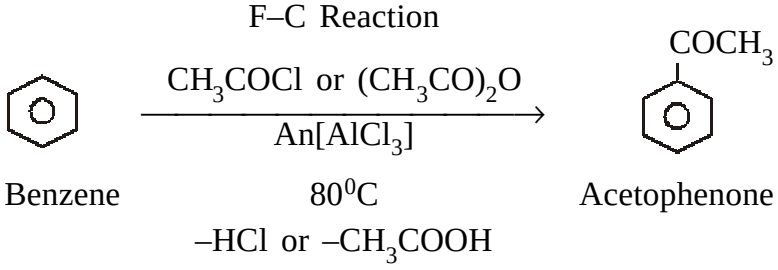
excess oxygen — potassium super oxide

(4) Kolbe Schmit Reaction :

(i)



(ii)



(4) (A)

(1) Formaldehyde is gas and its aqoues soln (30%) is known as formalin. It is used for the preservation of dead animal bodies, as well as an antiseptic.

(2) $C_6H_5NH_2 \rightarrow$ is capable of donating non–bonding electron pairs on Nitrogen to exhibit lewis base character.

eg. $C_6H_5NH_2 + H_2O_{(l)} \rightarrow C_6H_5NH_3^+{}_{(aq)} + OH^-_{(aq)}$

(3) Sources of Vitamin K :

$\Rightarrow$ Carrot, Cabbage, alpha–alpha leaves

function : $\rightarrow$ For normal Co–agulation of blood.

$\rightarrow$ It is used to stop bleeding.

(4) Due to formation of strong intermolecular H–bond, dimerization of carboxylic acid take place in organic solvent. Thus its M–wt. is twice.

(5) Organic compounds which make polymer flaxible are plastizers

eg. $\rightarrow$ TCP

$\rightarrow$ Glycerine Phthalate

$\rightarrow$ Oleic Acid etc.

4. (B)

(1) $(CH_3CO)_2O \xrightarrow[-CH_3COONH_4]{\Delta\ 2NH_3} CH_3CONH_2 \xrightarrow[Br_2/4NaOH\ -2NaBr\ -2H_2O\ -Na_2CO_3]{\Delta\ Hoffman} CH_3NH_2$

Acetic Anhydride — Acetamide — Methyl Amine

(2) $CH_3COCH_3 \xrightarrow[KMnO_4]{(O)} CH_3COOH \xrightarrow[LiAlH_4\ 2H_2\ -H_2O]{Reduction} CH_3CH_2OH$

Propanone — Acetic Acid — Ethanol

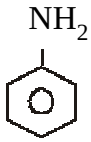
(3) $CH_3CHO \xrightarrow[Addition]{CH_3MgI} CH_3-\underset{\displaystyle OMgI}{\overset{\displaystyle H}{\underset{|}{\overset{|}{C}}}}-CH_3 \xrightarrow[aq.\ acid\ +H_2O]{Hydrolysis} CH_3-\underset{\displaystyle OH}{CH}-CH_3$

Acetaldehyde — Intermediate product — iso–propyl Alcohol + Mg(con)I

(4) $CH_3CHO \xrightarrow[KMnO_4]{(O)} CH_3COOH \xrightarrow[-H_3PO_3]{\Delta\ SOCl_2} CH_3COCl$

Ethanal — Acetic acid — Acetyl chloride

4. (C) (1) Diazotization :


Aniline

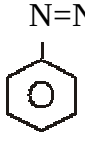
$+ NaNO_2 + 2HCl \xrightarrow[0–5^0C]{}$


Benzene diazonium chloride

$+ NaCl + 2H_2O$

$\Rightarrow$ Aniline when react with $NaNO_2$ + HCl at $0–5^0C$ to give Benzene diazonium chloride. Reaction is known as Diazotization.

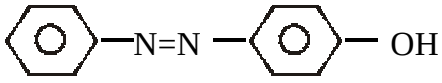
Preparation of Dyes :

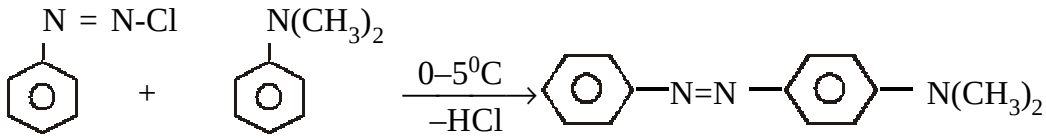

Benzene Diazonium Chloride

+


phenol

$\xrightarrow[-HCl]{0–5^0C}$


p–hydrozy–azo benzene (Orange Dye)



Diazonium chloride | N–N–Di Methyl Amino benzene | b–N–N di methyl Amino Azo benzene (Yellow dye)

(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 H_2SO_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.

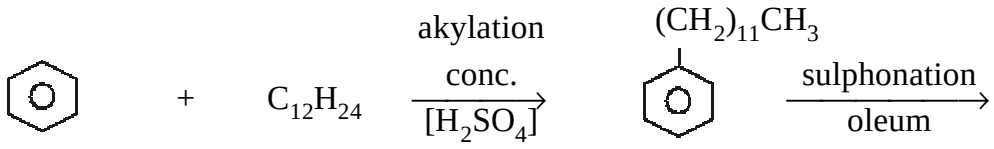
$$Ca_3(PO_4)_2 + 2\ H_2SO_4 \rightarrow Ca(H_2PO_4)_2 + 2\ CaSO_4$$

calcium phosphate | sulphuric acid | superphosphate of lime | calcium sulphate

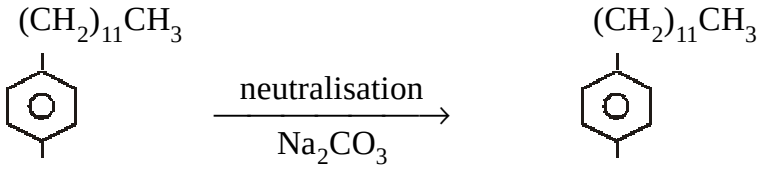
Superphosphate of lime is soluble in water and can be added to the soil as fertilizer, which supplies phosphorous and calcium nutrients to plants.

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

Tetramer of propylene reacts with benzene in presence of conc. H_2SO_4 to give alkyl benzene. Its sulphonation with oleum at 75^0 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 Na_2CO_3, it is obtained in the form of sodium alkyl benzene sulphonate. This is called ABS detergent



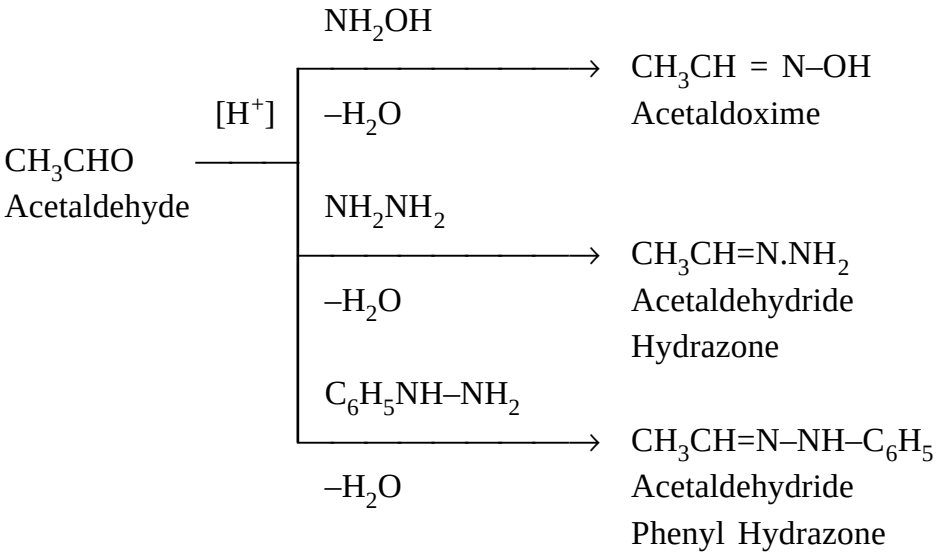
benzene | propylene tetramer | alkyl benzene | 75^0C



alkyl benzene sulphonic acid | sodium alkyl benzene sulphonate (ABS)

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

(i)



(ii) Wolf Kishner Red^{n} of Ketone :

$$CH_3COCH_3 \xrightarrow{N_2H_4/KOH} CH_3CH_2CH_3 + N_2 + H_2O$$

Acetone — Propane

⇒When Acetone react with basic hydrazine it gives propane.

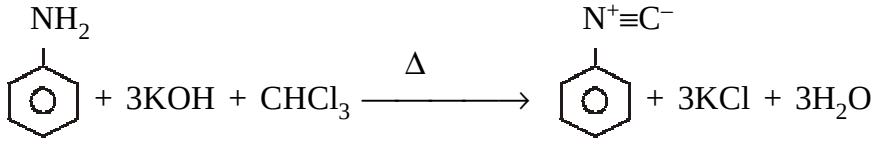
(4)

(i)

$$CH_3CONH_2 \xrightarrow[-H_2O]{\Delta\ ,\ P_4O_{10}} CH_3CN$$

Acetamide — Methyl cyanide

(ii)



Aniline — Phenyl Isocyanide

(iii) $CaCN_2 + 3H_2O \rightarrow CaCO_3 + 2NH_3$

Q. 5. (A)

(1) $CuH_{0.96}$ is prepared by reaction between $CuSO_4$ and sodium hypo phosphite.
⇒ It is brown colour and unstable.

(2) $[Cr(CO_3)\ (NH_3)_4]\ NO_3$

(3) $$N_{2(g)} \xrightarrow[\text{spark at low pressure}]{\text{electric}} 2N^* \text{ (activated Nitrogen)} + \text{orange glowing}$$

* N* nitrogen breaks some stable molecules.

(4) $Sc^{+3} \rightarrow [Ar]\ 3d^0 4s^0$
⇒ 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.
eg. $\ddot{N}H_3$, CN^-

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 ((μ) is calculated by equation,

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

As $Cr(CO)_6$ donot have any unpaired electrons,

$\mu = 0$

(2) In $KMnO_4$, Mn exibit +7 oxidation state.

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

$2KMnO_4 + 5H_2C_2O_4 + 3H_2SO_4 \rightarrow K_2SO_4 + 2MnSO_4 + 8H_2O + 10CO_2 \uparrow$

(3) Red phosphorous is prepared by heating white phosphorous in closed container at 250^0C temperature in presence of inert atmosphere caused by CO/N_2 and in presence of I_2 as catalyst

Red phosphorous donot ignite even at 400^0C temperature. It is poly atomic molecule.

Q. 5. (1)

(I) (i) $P_4 + 3NaOH + 3H_2O \longrightarrow \underset{\text{phosphine}}{PH_3} + 3NaH_2PO_2$

(ii) $Mg_3Sb_2 + 6HCl \longrightarrow \underset{\text{Stibia}}{2SbH_3} + 3MgCl_2$

(iii) $Mg_3Bi_2 + 3H_2SO_4 \longrightarrow \underset{\text{Bismathine}}{2BiH_3} + 3MgSO_4$

(ii) $2HNO_2 + 2HI \rightarrow I_2 + 2H_2O + 2NO$

Q. 5. (c) (2) Interstital 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. $ZrH_{1.92'}$ $TaH_{0.76}$ etc. The absorption of hydrogen expands or extends the metal lattic 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 $CuH_{0.96}$ 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 Cr_3C_2 and M_3C (where M = 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 lattic.

Like hydrides and carbides, the transition elements form interstitial nitrides with nitrogen. The example are Mn_4N, Fe_4N etc. in which the nitrogen aroms occupy the interstitial voids in Ihe 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 CrB. FeB, NIB, CrB etc. All these interstitial compounds are non-stoichiometric.

The formulas shown above are not competely 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 $K_2[NiCl_4] \Rightarrow$ Ni is Ni^{+2} state

	3d	4s	4p
$[NiCl_4]^{2-} = [Ar]\ ed^8\ 4s^0$	⇅ ⇅ ⇅ ↿ ↿	xx	xx xx xx
		sp^3	

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

In $K_2\ [Ni(CN)_4] \rightarrow$ Ni is +2 state

	3d	4s	4p
$[NiCl_4]^{2-} \rightarrow [Ar]\ 3d^8 4s^0$	⇅ ⇅ ⇅ ⇅ xx	xx	xx xx
		dsp^2	

$\Rightarrow$ due to dsp^2 hybridization it has square planner 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 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_{12} 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_{12} everday.

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.

*_*_ *

CHEMISTRY (052) E

Question Paper-II

Total Marks : 100 **Time : 3 Hours**

Instructions :

(1) There are FIVE questions in this question paper. All are compulsory.

(2) Give equations and diagrams wherever necessary.

(3) You may ask for log–table, if requried.

(4) Atomic Weight (gm. $Mole^{-1}$) :

C = 12, N = 14, O = 16, Pb = 207, H = 1, S = 32

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

(1) For what the value of ΔG of a reaction is the measure ?

(2) What is thermodynamically reversible process ?

(3) Give two names of different forms of silicon dioxide.

(4) CH_3NH_2 is stronger base than NH_3. Why ?

(5) When does the crystal structure of any compound become unstable ?

(B) Solve ANY TWO of the following numericals : **(6)**

(1) Calculate the weight of CH_3COOH in 100 ml. of a solution of the acid which has a pH of 3.00 Ka of CH_3COOH is 1.75×10^{-5}.

(2) Find out the change in free energy of the reaction.
$Zn_{(S)} + 2Ag^{+}_{(aq)} = Zn^{2+} + 2Ag_{(S)}$.
which occurs in a standard cell at 25^0C. The standard potential of the cell is 0.54 volt.

(3) The ionization constant of methyl amine in aqueous solution is 5.0×10^{-4} at 25^0C. At this temperature what would be pH of a solution containing 6.20 g. of methyl amine in 500 ml. solution ?

(C) Answer ANY THREE of the following : **(9)**

(1) Define the terms internal energy and enthalpy, obtain $\Delta H = q_p$ on the basis of first law of thermodynamic.

(2) Discuss the relationship betwen radius ratio of ions and crystal lattice structure.

(3) Explain Lewis acid base theory by suitable illustration.

(4) (a) Discuss the effect of temperature on ionic product of wter.

(b) Aqueous solution of sodium acetate is basic. Why ?

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

(1) On the basis of which principle can Nernst's equations be derived ?

(2) State (n + *l*) rule.

(3) Why does a gaseous fuel burn much faster than a solid fuel ?

(4) The potential of the cell depends on which factors ?

(5) Mention the characteristics of activated complex.

(B) Solve ANY TWO of the following numericals : **(6)**

(1) The half life period of radio active Th^{233} is 1.39×10^{10} years. How many α–particles would be emitted per minute from 5.0 gm. Th^{232}. Each Th^{232} atom emits one α–particle on decomposition.

(2) Calculate the equilibrium constants of the reaction.

$$Ni_{(S)} + Co^{+2}_{(aq)} = Co_{(S)} + Ni^{2+}_{(aq)}$$

$E^0\ Ni^{2+}/Ni = -0.23$ volt; $E^0\ Co^{+2}\ /\ Co = -0.28$ volt.

(3) Calculate the energy of a photon of a radiation having wavelength 6000 A^0. Calculate the value of Einstein. Velocity of light = 3.0×10^{10} cm sec^{-1}.

(C) Answer ANY THREE of the following : **(9)**

(1) Derive equation of Arrhenius.

(2) Give the diagrammatic representation of molecular orbitals of F_2 on the basis of Molecular Orbital Theory. Discuss the magnetic behaviour and bond order.

(3) (a) Explain the effect of temperature on the rates of reactions.

(b) Explain in brief : Half reaction time.

Q. 3. (A) Answer the following question in short. **(5)**

(1) Give the chemical equation when benzene and methyl chloride reacts at 80 ^{0}C in presence of anhydrous $AlCl_3$.

(2) Phenol cannot be neutralized by a weak bae like sodium bicarbonate. Why ?

(3) State the name of indicator obtained from phenol.

(4) Give IUPAC name : (a) $C_6H_5 - O - C_6H_5$ (b) Give structural formula of Dimethyl Ethylamine.

(5) State the limitations of Friedel – Craft reaction.

(B) Write chemical equations for ANY THREE of the following conversion. Also give the condition of the reaction, names and structural formula of the main organic compound (Tahere should be only two step of each conversion) **(6)**

(1) Ethanol from acetone.

(2) Glyoxal from Benzene.

(3) Toluene from phenol.

(4) m-chloro benzaldehyde from toluene

(C) Answer the following ANY THREE : **(9)**

(1) Explain :

(a) Metallic structure, hardness and cohesive energy of alkali metals.

(b) Electronegativity and bond type of alkali metals.

(2) Discuss the chlorination of toluene.

(3) Explain in detail giving equation the chlorination and oxidation reactoin of methyl group of toluene.

(4) Explain the structure of benzene on the basis of molecular orbital theory.

Q. 4. (A) Answer the following : **(5)**

(1) Give name and equation when dehydration of benzamide is carried out in presence of phosphorous pentoxide.

(2) How does hemoglobin supply oxygen to tissues ?

(3) Give the structural formulae of (a) 1–phenyl – 1– ethanol (b) Vegetable Oil

(4) Give preparation of Urea.

(5) How are sugars and stach obtained by body ?

(B) Write chemical equation for ANY THREE of the following conversions. (6) Also give the conditions of the reactions, names and structural formula of the main organic compound. (There should be only two step of each conversion)

(1) 2–methyl–2propanoic acid from acetone.

(2) Methylamine from acetyle chloride.

(3) p–Amino phenol from phenol.

(4) ABS from alkyl benzene.

(C) Answer the following ANY THREE : (9)

(1) Discuss the acetylation & alkylation of aniline.

(2) Write a note on nitrogen based fertilizer.

(3) $$A \xrightarrow[Br_2/H_2O]{[O]} B \xrightarrow[\text{Conc. } H_2SO_4]{CH_3–CH_2–OH} C \xrightarrow[D]{NH_3} CH_3 – CO – NH_2 + D$$

Give names and structural formulae of A, B, C & D for the above reaction.

(4) (i) Azo coupling Reaction (ii) Bromination of Aniline.

Q. 5. (A) Answer the following question in short : (5)

(1) How many maximum covalent bonds can P, As and Sb form ?

(2) Which oxidatin state of vanadium exhibits low stability ?

(3) How many co–ordination sites are present in bidentate and tridentate ligands ?

(4) Give IUPAC (a) $Na_4[Co(NO_2)_6]$ (b) $Fe(CO)_5$]

(5) Give the formulas (a) Chloro pentammine cobalt (III) sulphate

(b) Potassium pentacyano carbonyl ferrate (II)

(B) Answer the following question ANY THREE : (6)

(1) Explain the geometry of ML_6 complexes giving examples.

(2) $ZnSO_4$ is colourless while $NiSO_4$ is coloured.

(3) State names and electron configuration of the element of zero group.

(C) Answer the following question in ANY THREE. (9)

(1) The hybridization in complex $K_3[Fe(CN)_6]$ is d^2sp^3 and not sp^3d^2. Explain.

(2) Write a note on the allotropes of arsenic and antimony.

(3) Give electronic configuration of transition elements.

(4) Explain giving reasons :

(a) $CuCl_2$ is paramagnetic while CuCl is diamagnetic.

(b) Ti^{+4} is more stable than Ti^{+3} but Ti^{+4} ion does not exist.

_*_

: ANSWER :

Q. 1. (A)

(1) ΔG is a measure of energy available for doing useful work.

(2) If a change in state of a system occurs at an extremely slow rate, the differences between certain state functions of the systen and surrounding would be infinitesimaly small. Such process is known as thermodynamically reversible process.

(3) Cristobelite, quartz and Tridimite are the different forms of silicon dioxide.

(4) Because the $K_{b_{NH_3}} < K_{b_{CH_3NH_2}}$. So CH_3NH_2 is stronger base than NH_3.

(5) When the temparature is higher than the absolute zero, the crystal structure of any compound become unstable.

Q. 1. (B)

(1) $P^H = -\log[H_3O^+]$

$3.0 = -\log[H_3O^+]$

$\therefore \quad [H_3O^+] = \text{antilog } \bar{3}.00$

$= 1.0 \times 10^{-3}$ M.

But ionization of acetic acid is very little.

$\therefore \quad CH_3COOH_{(l)} + H_2O_{(l)} \rightleftharpoons CH_3COO^-_{(aq)} + H_3O^+_{(aq)}$

$[H_3O^+] = \sqrt{Kaco}$

$1.0 \times 10^{-3} = \sqrt{1.75 \times 10^{-5} \times Co}$

$1.0 \times 10^{-6} = \left(\sqrt{1.75 \times 10^{-5} \times Co}\right)^2$

$= 1.75 \times 10^{-}5 \times Co$

$\therefore \quad Co = 5.7 \times 10^{-2}$ M.

CH_3COOH's molarity $= \frac{1000 \times W}{60 \times 100}$

$\therefore \quad 5.7 \times 10^{-2} = \frac{1000 \times W}{60 \times 100}$

$\therefore \quad W = \frac{60 \times 100 \times 5.7 \times 10^{-2}}{1000}$

$\therefore \quad W = 0.3429 \ CH_3COOH$

$\therefore CH_3COOH = 0.342$ gram.

(2) $Zn_{(S)} + Ag^{+}_{(g)} \rightleftharpoons Zn^{2+}_{(aq)} + 2Ag_{(S)}$

$\Delta E^0 = E^0ox$ (Anode) $- E^0ox$ (Cathode)

$= 0.76 - (-0.80)$

$\Delta E^0 = 1.56$ volt ...(1)

Now, at equilibrium, $\Delta E = 0.00V$ and $n = 2$

$$\Delta E = \Delta E^0 - \frac{0.0592}{n} \times \log K_c \frac{\left[2n^{2+}\right]}{\left[Ag^{+}\right]^2}$$

$$0.00 = 1.56 - \frac{0.0192}{2} \times \log K_c$$

$$\therefore \frac{1.56}{.0296} = \log K_c \quad \text{... (1)}$$

$\therefore \log K_c = 52.70$

$K_c =$ Antilog 52.70

$K_c = 5.012 \times 10^{52}$ ... (1)

(3) Mol. weight of $CH_3NH_2 = (1)(12) + 5(1) + 1(14) = 31$ g/mol.

$$\frac{g}{\text{liter}} \text{ of } CH_3NH_2 = \frac{6.2 \text{ g}}{\frac{500}{100}\text{liter}} = 12.4 \frac{g}{\text{liter}}$$

$$\therefore \text{Conc. of } CH_3NH = \frac{12.4 \text{ g / liter}}{31 \text{ g / mole}} = 0.4 \frac{\text{mole}}{\text{liter}}$$

As CH_3NH_2 is a weak base,

$[OH^-] = \sqrt{K_b \times Co}$

$= \sqrt{5 \times 10^{-4} \times 0.4}$

$= 1.41 \times 10^{-2}$ M.

$P^{0H} = -\log [OH^-]$

$= -\log (1.41 \times 10^{-2})$

$= -\log (1.41 \times 10^{-2})$

$= -\log 1.41 + 2$

$= 2 - 0.1492$

$= 1.85$

$\therefore P^H = 14 - 1.85$

$= 12.15$

Q. 1. (C)

(1) Usually chemical reactions carried out in open containers occur at constant external pressure. A new state function called enthalpy is defined for the internal energy change taking place in such process.

Definition : "The sum of the internal energy (E) of the system and the work energy due to the product of pressure (P) and volume (V) of the system is known as enthalpy (H)."

$$H = E + PV$$

If the state of a system changes the enthalpy change (ΔH) is expressed by,

$\Delta H = \Delta E + \Delta(PV)$

$= \Delta E + P \Delta V + V \Delta P.$

Here, as the reaction occurs at constant external pressure, $\Delta P = 0$.

$\Delta H = \Delta E + P \Delta V$ ... (1)

Now, according to the first law of thermodynamics $\Delta = q = w$

But, the work done by the system due to the change in volume at constant external pressure is $(w) = -P \Delta V$.

$\Delta E = q - p \Delta v$

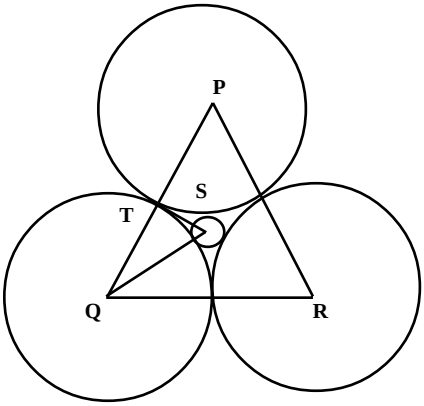
$\therefore \quad \Delta H = q - p \Delta v + p \Delta v$

$\therefore \quad \Delta H = qp.$

So "The change in enthalpy of a system in which reaction occurs at constant temperature and pressure, the volume of the system changes."

(2)

(i) In tetrahedral structure, three spheres of identical size are in mutual contact in the same plane.



→ In the tetrahedral void between these sphere is between these small spere of cation. This sphere is sufficiently small so as to be in contact with the spheres.

→ Lt P, Q and R be the centers of spheres of the anions and S that of the sphere of the cation. I is the contact point between the spheres with centers pond Cr. Now, as shown in figure.

→ Δ STQ is a right angled triangle in which $\angle$ STQ = 90^0 and $\angle$ TQS = 30^0. The side QS = $r_+ + r_-$ and QT = r_- Now in Δ STQ

$$\cos 30^0 = \frac{QT}{QS}$$

$$\therefore QS \cos 30^0 = QT$$

$$\therefore (r_- + r_+) \frac{\sqrt{3}}{2} = r_-$$

$$\therefore (r_- + r_+) \frac{\sqrt{3}}{2} = r_-$$

$$\therefore \frac{\sqrt{3}}{2} r_+ = r_- - \frac{\sqrt{3}}{2} r_-$$

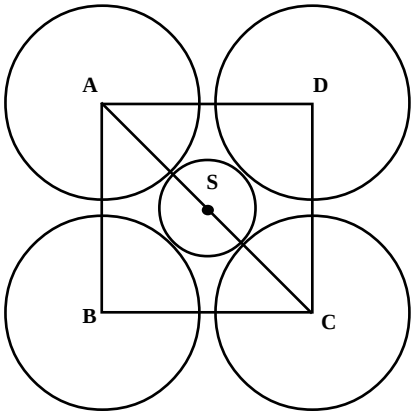
$$\therefore r_+ = \frac{2}{\sqrt{3}} r_- - r_-$$

$$\therefore r_+ = r_- \left[\frac{2}{\sqrt{3}} - 1\right]$$

$$\therefore \frac{r_+}{r_-} = 0.155$$

(ii) Radius ratio in octahedral structure :

In the octahedral arrangement arround each cation there are four anions in the same plane. Moreover there is one anion above and one below.



The figure shows the cation is surrounded by four anions in the same plane in which the raii of cation and anion are r_+ and r_- respectively.

$AC = 2r_- + 2r_+$

$BC = 2r_-$

Now in Δ ABC

$$\cos 45^0 = \frac{BC}{AC}$$

$$\therefore \quad AC \cos 45^0 = BC$$

$$\therefore \quad (2r_- + 2r_+) \frac{1}{\sqrt{2}} = 2r_-$$

$$2r_+ + 2r_- = \sqrt{2} \cdot 2r_-$$

$$\therefore (r_+ + r_-) = \sqrt{2} \cdot r_-$$

$$\therefore \quad r_+ = r_- (\sqrt{2} - 1)$$

$$\therefore \quad \frac{r_+}{r_-} = \sqrt{2} - 1$$

$$\therefore \quad \frac{r_+}{r_-} = 0.414.$$

(3) In 1923 a scientist named "Lewis" proposed acid– base theory on the basis of electron configuration, in which the idea of proton–transfer was abandoned.

Acid : A compound which accepts an electron pair during reactions is known as an acids.

Base : A compound which donates an electorn pair during reactions is known as a base.

→ $BF_3 + : F^- \rightleftharpoons BF_4^-$

In above reactions F^- from bonds with BF_3 by using their non–bonding electron pair.

→ When a salt is dissolved in water the ions formed in solution becomes hydrated. This process of hydration is an accid base reaction.

(i) $NaCl_{(S)} \rightarrow Na^+_{(aq)} + Cl^-_{(aq)}$

(ii) Cl^- + water $\rightarrow [Na(H_2O)_6]^+$

(iii) Cl^- + water $\rightarrow [Cl(H_2O)_6]^-$

In this hydration process, Na^+acts ass an acid and Cl^- as a base.

→ Negative ions and neutral molecule acting as ligands in the formation of complex salts are Lewis bases and metal–ions bonding t_0 ligands are Lewis acids.

(4) (a) The effect of temperature on ionic product of water.

⇒ The value of ionic product of water K_w at 25^0C is 1×10^{-4}M.

⇒ The process of formation of ions in small concentration by the dissociation of water is called self ionization of water.

⇒ This process is an endtothermic process.

$$H_2O_{(l)} \rightleftharpoons H^+_{(aq)} + OH^-_{(aq)}$$

⇒ Now, if the temperature is increased then according to Le–chatelier's principle the rate of forward reaction increases.

⇒ Hence ionization of water is increases.

⇒ As a result the concentration of H^+ and OH^- ions increases.

⇒ Thus the value of $[H^+]$ and $[OH^-]$ increases with the rise in temperature, K_w of water increases with increase in temperature.

(b) Aqueous solution of sodium acetate is basic.

⇒ Sodium Acetate $[CH_3COONa]$ is a salt formed from a weak acid CH_3COOH and strong base NaOH.

⇒ When it is dissolved in water it ionized completely.

$$CH_3COONa \rightarrow CH_3COO^-_{(aq)} + Na^+_{(aq)}$$

⇒ More over their exists following equilibrium in water.

$$H_2O_{(l)} \rightleftharpoons H^+_{(aq)} + OH^-_{(aq)}$$

⇒ CH_3COO^- produced from CH_3COONa salt combine with H^+ ions produced by self–ionization of water and form uniemised weak acid CH_3COOH.

⇒ Due to this equilibrium of water get disturbed.

⇒ As a result the equilibrium of water shift in the formward direction and produces more H^+ and OH^- ions.

⇒ However H^+ ions are removed by CH_3COO^- ions, hence the concentration of H^+ ions decreases.

⇒ Thus the concentration of OH^- ions exceeds the concentration of H^+ ions.

⇒ So the solution becomes basic.

⇒ The overall reaction is as follows.

$$CH_3COO^-_{(aq)} + H_2O_{(l)} \rightleftharpoons CH_3COOH_{(aq)} + OH_{(aq)}$$

Q. 2. (A)

(1) Nernst's equation can be derived on the basis of Thermodynamics.

(2) (n + l) rule :

⇒ The order of enrgies of orbitals of different energy level is determined by the sum of n and l quantum numbers of orbitals.

⇒ **An orbital having a higher value of (n + l) has higher energy.**

(3) Gaseous fuels have greater surface area than a solid fuel.

(4) The potential of cell depends on the following factors.

(i) Temperature of the cell.

(ii) Concentration of solution in the cell.

(ii) Nature of electrodes.

(5) Activated complex having very short life and the maximum potential energy.

Q. 2. (B)

(1) * Calculation of K

$t_{½} = 1.39 \times 10^{10}$ years

$= 1.39 \times 10^{10} \times 365 \times 24 \times 60$ mins.

$$K = \frac{0.693}{t_{½}}$$

$$= \frac{0.693}{1.39 \times 10^{10} \times 365 \times 24 \times 60}$$

$$K = \boxed{= 9.484 \times 10^{-17} \text{ min}^{-1}}$$

for K

log 0.693 = $\bar{1}$ – 8407

log 1.39 = 0.1430

10 log 10 = 10.0000

$_+$log 365 = 2.5623

$_+$log 60 = 1.7782

15.8637$^-$

*** Calculation of N W = 5.0 gms.**

$$N = \frac{6.023\times10^{23}\times W}{M\cdot \omega t \text{ of Th}}$$

$$= \frac{6.023\times10^{23}\times5.0}{232}$$

$N = 6.49 \times 10^{22}$ Th^{232} atoms.

Now

$$-\frac{dN}{dt} = K \,.\, N$$

$$= 9.484 \times 10^{-17} \times 6.49 \times 10^{22}$$

$$= 61.55 \times 10^{5}$$

$$-\frac{dN}{dt} = 6.155 \times 10^{6}\ \alpha\text{–particles/min.}$$ **Ans.**

$\bar{1}.8407$

$-\ 15.8607$

$\overline{17}.9770$

Antilog of $\overline{17}.9770$

$= 9.484 \times 10^{-17}$ mnt^{-1}

for N

log 6.023 + 23 log 10 + log 5.0 – log 232

= 0.7798 + 23 +0.6989 – 2.3655

$\propto$ 25.1776

$-\ 2.3655$

22.8121

Antilog 6.4889×10^{22}

(2) Reactions for the cell :

Anode : $Ni_{(S)} \rightarrow Ni^{2+}_{(aq)} + 2e^-$

Cathode : $Co^{2+}_{(aq)} + 2e^- \rightarrow Co_{(S)}$

$$Ni_{(S)} + Co^{2+}_{(aq)} \rightarrow Ni^{2+}_{(aq)} + Co_{(S)}$$

$\boxed{n = 2}$

Cell potential ΔE^0

$$\Delta E^0 = E^0_{Ni/Ni^{2+}} - E^0_{Co/Co^{+2}}$$

$$= 0.23 - 0.28$$

$$\Delta E^0 = -0.05 \text{ volt}$$

Calculation of K_c :

According to Nernst Equation :

$$\Delta E = \Delta E^0 - \frac{0.0592}{n} \log \frac{[Ni^{2+}]}{[Co^{2+}]}$$

Now cell is in equilibrium state

$\therefore$ $\Delta E = 0.01$ volt

$$\therefore \log \frac{[Ni^{2+}]}{[Co^{2+}]} = K_c$$

$$\therefore \quad 0.0 = 0.05 - \frac{0.0592}{2} \log K_c.$$

$$\therefore \quad \log K_c = -\frac{0.05}{0.0296}$$

$$= -(1.6900)$$

$$= -1.6900$$

$$= -2 + 1 = 0.69$$

$$= -2 + 0.31$$

$$\boxed{\log K = \bar{2}.31}$$

log 0.05
log 0.0296
$\bar{2}.6990$
$-\ \bar{2}.4713$
0.2217
Antilog 0.2217 = 1.69

$$\therefore \quad K = \text{Antilog of } \bar{2}.31 = 2.042 \times 10^{-2}$$

$$\boxed{K = 2.042 \times 10^{-2}}$$

(3) Energy of 1 photon = E = $\frac{hc}{\lambda}$

$$\therefore \quad E = \frac{6.626 \times 10^{-27} \times 3.0 \times 10^{10}}{6000 \times 10^{-8}}$$

$$= \frac{6.626 \times 3}{6} \times 10^{-12} \times 10^{-12}$$

$$E = 3.313 \times 10^{-12} \text{ erg.}$$

Now

$$\text{One einstein} = \frac{Nhc}{\lambda} = N \cdot E$$

$$= 6.023 \times 10^{23} \times 3.313 \times 10^{-12}$$

$$= 1.994 \times 10^{-12} \text{ erg. mole}^{-1} \text{ photon}$$

Q. 2. (C)

(1) Derive : The equation for E_a of Arhenious rate constant.

Ans.

⇒ Energy of activation of a reaction can be determined from Arhenious equation using K values at different temparatures.

$K = A.e^{-Ea/RT}$ Where, A = Arhenious constant

E_a = activation energy

K = rate constant

T = Temp. (Kelvin)

R = gas constant

$K = A.e^{-Ea/RT}$

$$\therefore \log K = \log A - \frac{Ea}{2.303RT}$$

If ⇒ K_1 and K_2 are rate constants

⇒ T_1 and T_2 temperatures of respectively constants.

$$\therefore \quad \log K_1 = \log A = \frac{Ea}{2.303\ RT_1}$$

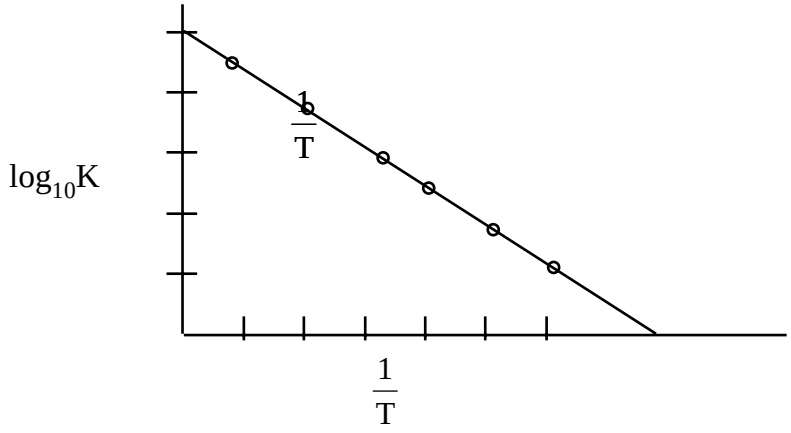
$$\log K_2 = \log A - \frac{Ea}{2.303\ RT_2}$$

$$\therefore \quad \log K_2 - \log K_1 = -\frac{Ea}{2.303\ R}\left[\frac{1}{T_2} - \frac{1}{T_1}\right]$$

$$\therefore \log \frac{K_2}{K_1} = -\frac{Ea}{2.303\ R}\left[\frac{1}{T_2} - \frac{1}{T_1}\right] \quad \text{... (A)}$$

⇒ Eq. (A) is a eq. of E_a f Arhenious Rate constant.

⇒ If the rate constant of a reaction are determined at several different temp. the plot of graph $\log K \to \frac{1}{T}$ should be straightline as below.



$\Rightarrow$ This graph has a negative slope equal to $-\frac{Ea}{2.303R}$

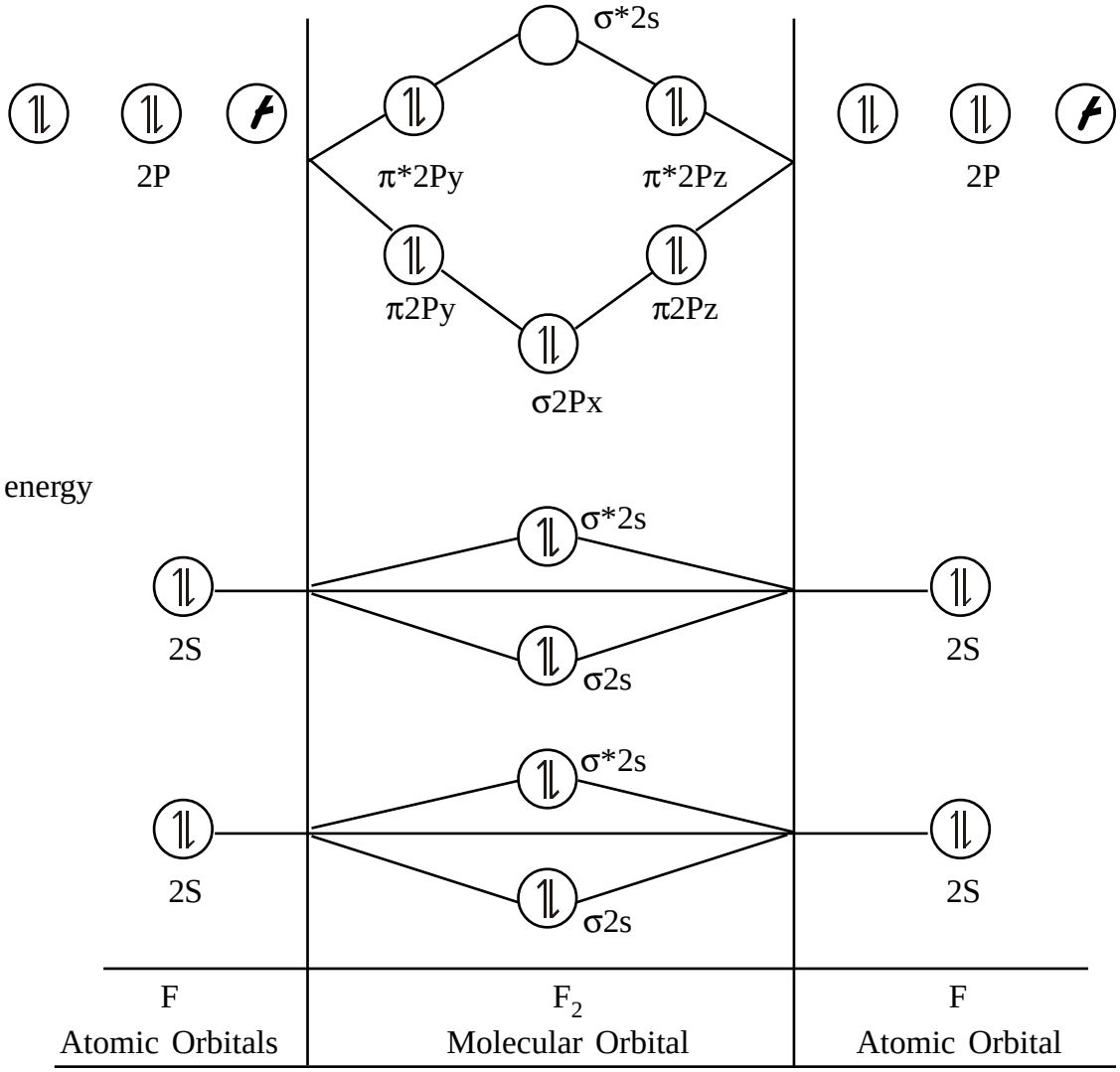
$\Rightarrow$ The energy of activation can be calculated by determining slope.

(2) Electron configuration of Flourine :

$F(z = 9) = 1S^2, 2S^2, 3Px^2, 2Py^2, 2Pz^1$

* When two flourine atoms combine, $18e^-$ are available and they are distributed in various M. O. as follows.

M. O. diagram. F_2



Bond Order :

Bond Order $= \frac{1}{2}$ [Nb – Na]

$= \frac{1}{2}$ [Nb – Na]

$= \frac{1}{2}$ [10 – 8]

$= \frac{2}{2}$

Bond order $= 1$

$\therefore$ F_2 molecule has a single bond

i. e. F–F

Magnetic properties :

$\Rightarrow$ since all electons in F_2 are paird. **F_2 is a diamagnetic molecule.**

Q. 2. (C)

(3) (a) Effect of temperature on the rates of reactions.

$\Rightarrow$ Arrhenius studeid the rates of reaction at different temperature and established the following equation.

$K \propto e^{-Ea/RT}$

$\therefore$ $K = A.e^{-Ea/RT}$

K = Rate constant

R = Gas constant

T = Kelvin temp.

E_a = activation energy

A = Arhenous constant

$\Rightarrow$ The above equation indicates that K increases with a rise in temperature.

$\Rightarrow$ As some of the molecules which do not possess enough energy for reaction gain sufficient energy.

$\Rightarrow$ The rate of collisions also increases with a rise in temperatutre.

$\Rightarrow$ Both of these factors favour an **increase in the rate of reactions with a rise in temparature.**

(b) $\Rightarrow$ The time taken by a reaction to consume 50% of initial concentration of reactant is called half-reaction time.

$\Rightarrow$ Its relation with rate constant `K' is as follows.

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

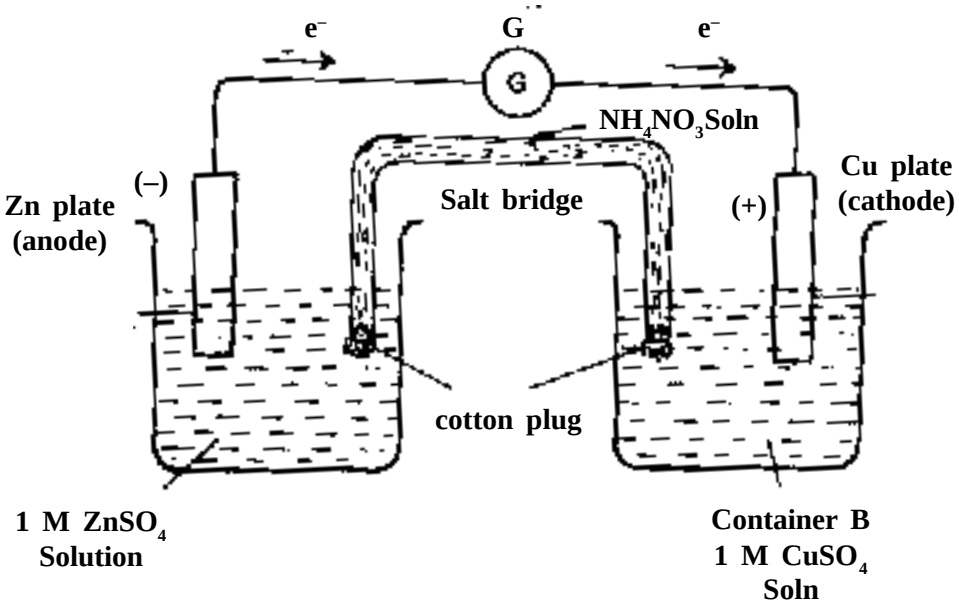
$\Rightarrow$ Above equation show that half-reaction time does not depend on the intial concentration of reactant.

(4) Construction & working of 'Daniel Cell'.

Principle :

⇒ Conversion of chemical energy to electrical energy.

Figure :



⇒ 1M aqueous $ZnSO_4$ solution is taken in container A in which a weighed Zn metal strip is placed as anode.

⇒ 1M aqueous $CuSO_4$ solution is taken in container B in which a weighed Cu metal strip is placed as cathod.

⇒ Zn and Cu strips are connected through a galvonometer using a thn conducting metal wire.

⇒ A salt bridge is placed between the two half cells.

⇒ The salt bridge is U–shaped hollow glass tube filled with NH_4NO_3 salt solution.

⇒ The functions of salt bridge is

(a) Maintaining electrical neutrality of solutions.

(b) It provides a connection between two solutions.

* **Functions : (Reaction)**

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

Cathode : $Cu^{+2}_{(aq)} + 2e^- \rightarrow Cu_{(S)}$

Cell Reaction : $Zn_{(S)} + Cu^{+2}_{(aq)} \rightarrow Zn^{2+}_{(aq)} + Cu_{(S)}$

* Direction of e^- : From Anode to Cathode.

* Working :

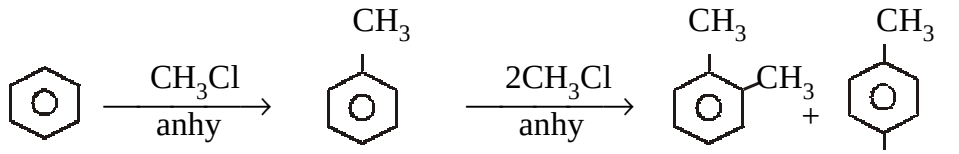
⇒ When circuit is completed cell is in working position and produced electric current of 1.10 volts.

⇒ According to reaction the weightaight of Zn strips decreases and teh weight of Cu strips increases.

⇒ SO_4^{-2} ions are flow from $CuSO_4$ soln through the salt bridge and maintain neutrality of the solutions of both the cells.

Q. 3. (A)

(1)



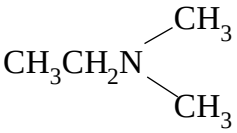
Benzene — o–xylene — O–xylene — P–xylene

(2) As acidity of phenol is as weak as that of HCN phenol can not be neutralised by weak base like sodium bicarbonate.

(3) Phenolpthalein indicator obtained from phenol.

(4) $C_6H_5 - O - C_6H_5$
Phenoxy benzene

→ Dimethyl Ethylamine



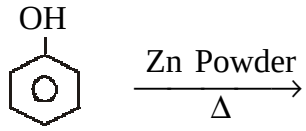
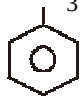
(5) Freidel – crafts reaction does not take place with aryl halide like chlorobenzene, acetophenone and nitrobenzene.

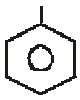
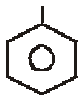
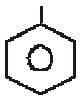
Q. 3. (B)

(1) $CH_3–CO–CH_3$ (Acetone) $\xrightarrow[-H_2O\ -CO_2]{\text{Oxidation } KMnO_4/KOH}$ $\xrightarrow[]{CH_3COOH}$ (Acetic Acid) $\xrightarrow[-H_2O]{\text{Direct Reduction } LiAlH_4/2H_2}$ CH_3CH_2OH (Ethanol)

(2) C_6H_6 (benzene) $+ 3O_3 \xrightarrow{\text{ozonolysis}}$ $C_6H_6(O_3)_3$ (benzene triozonide (unstable)) $\xrightarrow[+3H_2O]{\text{hydrolysis [Zn]}}$

$3\ \begin{matrix}CHO\\|\\CHO\end{matrix}$ (glyoxal) $+ 3H_2O_2$ (hydrogen peroxide)

(3)  (Phenol) $\xrightarrow[\Delta]{\text{Zn Powder}}$ -ZnO  (Benzene) $\xrightarrow[\text{anhy } [AlCl_3]]{\text{Alklyation } CH_3Cl}$ 80^0C –HCl  (Toluene)

(4)  (CH_3) $\xrightarrow[\Delta]{CrO_2Cl_2}$ [O]  (Benzaldehyde) $\xrightarrow[\Delta]{Cl_2}$ –HCl [$FeCl_3$]  (m–chloro benzaldehyde)

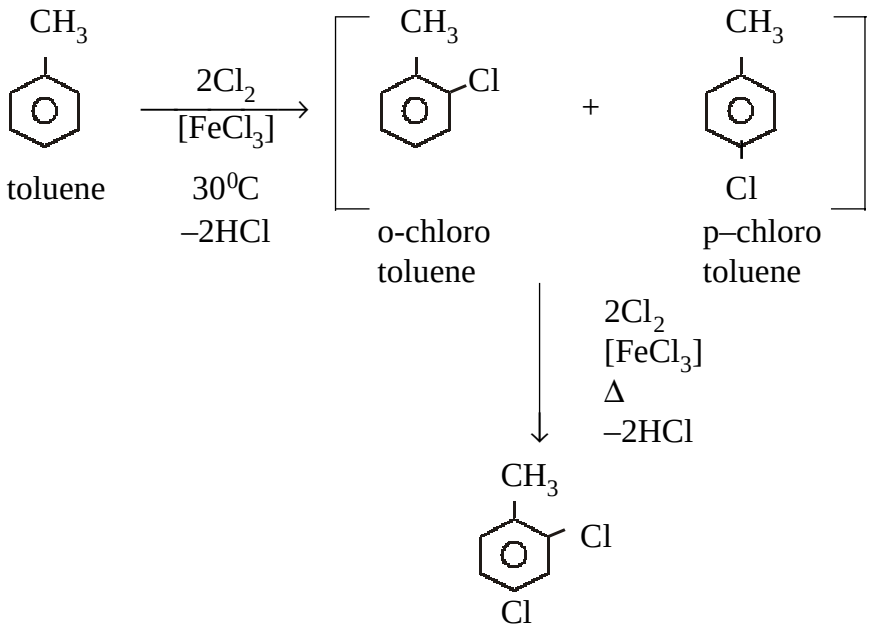
Q. 3. (C)

(1) (a) At ordinary temperature all he elements of alkali group exhibit body centered cubic type crystal structure with cordination number 8. AT very law temperatures lithium metal shows a hexa gonal close packed crystal structure having cordination number 12. The attractive force holding the atoms or ions to gether in the solid state is called the cohesive energy. Cohesive energy is also a measure of hardness. It depends on the number of bonding electgr5on and their binding energies. The progressive increse in atomic size on going from Li to Cs this electron becomes more and more weakly bound.

(b) The electron negativity of the alkali metal elements is extremely low, when these elements combine with other elements with high electro neativity they from ionic bonds. For example, the electronagetivity of Na is 0.9 and that of Cl is 3.0 owing to the relatively large electronegativity difference of 2.1, Nacl between two elements is about 1.7 – 1.8 then the nature of the bond formed between them is about 50% ionic. Example : LiF and KBr.

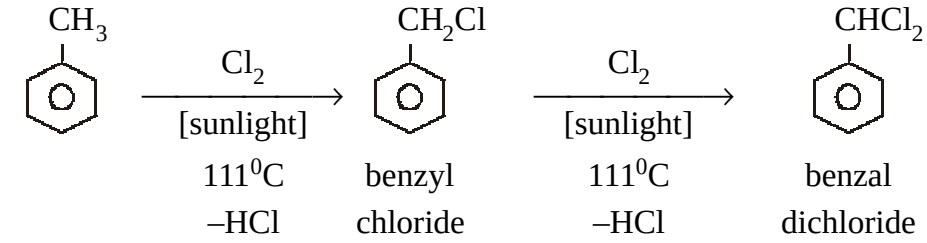
(2) Chlorination of Toluene :

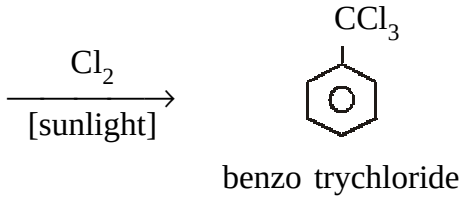
Toluene and chlorine at 30^0C in presence of catalyst $FeCl_3$ give a mixture of O–Chlorotoluene and P– Chlorotoluene by first chlorination. These two isomers can be separated by Fractional distillation. If temparature is raised in above reaction, second chlorination occurs giving 2, 4–dichlorotoluene.



2 : 4 – dichloro toluene.

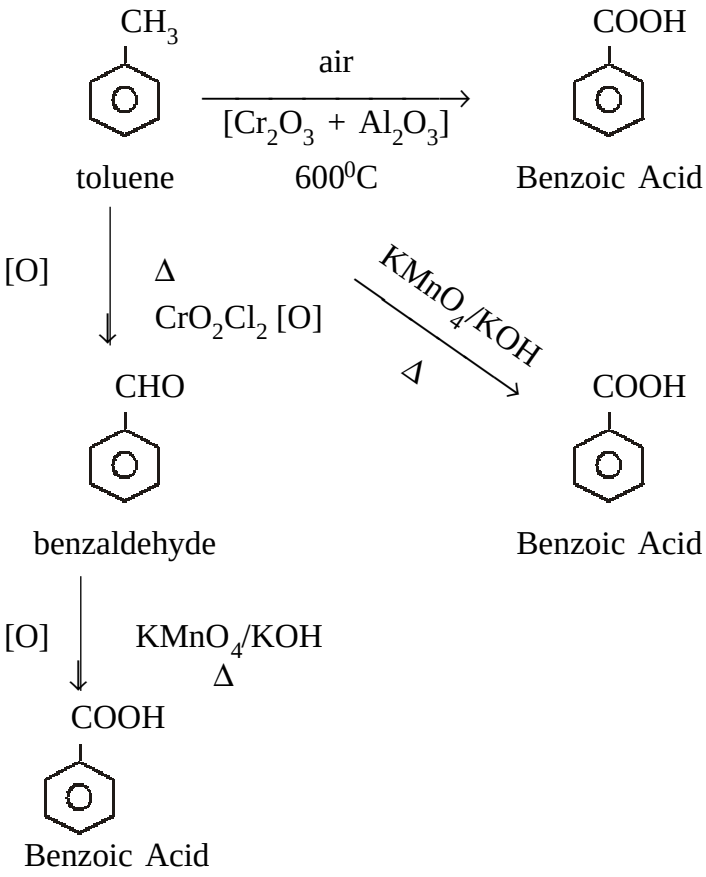
(3) Chlorination of Methyl group





benzo trychloride

→ Oxydation of Methyl group.



(4) Structure of benzene presented according to Molecular orbital theory.

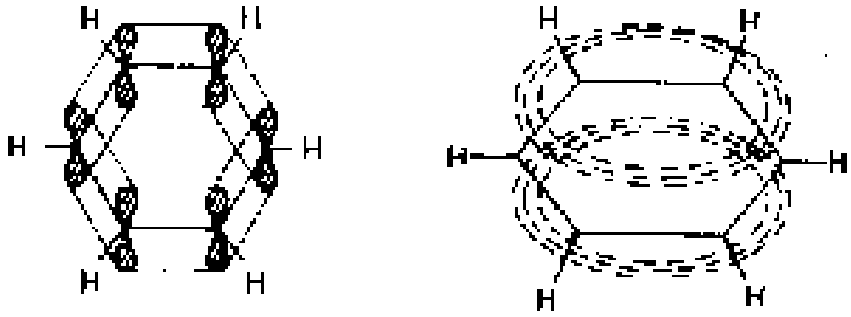
→ Benzene has each carbon sp^2 hybrid the three σ bonds are all planar at 120^0.

→ 6 carbon, 6 hydrogens, 6c–cσbonds and 6 C–Hσbonds are all in one palne.

→ Moreover an each six carbons we have $2P_z$ orbitals at right angels to the plane, containig on each of 6π electrons.

→ Molecular orbital theory suggests that due to over planing of six $2P_z$ orbitals of 6 carbon atoms a large circular shaped – molecular orbital is fermed and these 6π electorn are moving because of their dislocalitation. Thus all six carbon in Benzene are identical.

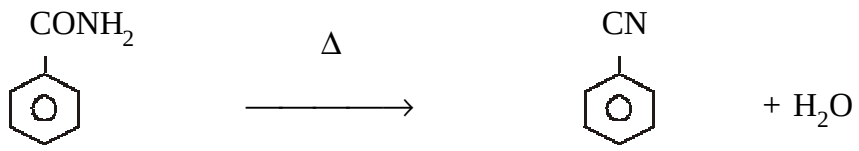
→ The charge cloud of benzene contaning 6π electrons also supports its lesser potential energy or justifies its resonance energy.



Molecular ring P_4O_{10} dehydration orbital shape of ring structure of benzene.

Q. 4. (A)

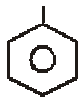
(1)



Benzamide Phenyl cyanide

(2) Hemoglobin is a complex combines with oxygen obtained through lungs and forms an intermediate compounds which supplies oxygen to tissues.

(3) S.F. $CH(OH)-CH_3$

(a)  1–phenyl 1–Ethanol

(b) Vegetable Oil

$$\begin{array}{l} CH_2OOC-C_{11}CH_{23} \\ | \\ CHOOC-C_{11}H_{22} \\ | \\ CH_2OOC-C_{11}H_{23} \end{array}$$

(4) Preparation of Urea :

$$2NH_3 + CO_2 \xrightarrow[\text{\& high pressure}]{\text{at high temp}} NH_2CONH_2 \xrightarrow[-H_2O]{\Delta} NH_2CONH_2$$

Ammonia; Carbon dioxide; Ammonium Carbamate; Urea

(5) Carbohydrates are the principal constituents of food, wheat, rice, maize etc. contains glucose in form of sugars and starch. Metabolism of glucose in body gives energy.

Q. 4. (B) Conversions :

(1) $CH_3COCH_3 + HCN \xrightarrow[NaCN + HCl]{\text{Addition}} CH_3-\underset{OH}{\overset{CH_3}{C}}-CN$

Acetone; cyanohydin of Acetone

$\xrightarrow[-NH_3]{aq-H_2SO_4}$ + $2H_2O$ hydrolysis

$$CH_3-\underset{OH}{\overset{CH_3}{C}}-COOH$$

2 Methyl 2 hydroxy propanoic acid

(2) CH_3COCl (Methyl Chloride) $\xrightarrow[-NH_4Cl]{2NH_3}$ CH_3CONH_3 (Acetamide)

Acetamide $\xrightarrow[\Delta]{-2NaBr,\ -Na_2CO_3,\ -2H_2O}$ CH_3NH_2 (Methyl Amine)

Hoffman Reaction: $Br_2 + 4NaOH$

(3) Phenol $\xrightarrow[\text{Nitration}]{\text{dil } HNO_3,\ -H_2O}$ P–Nitro phenol + ONP

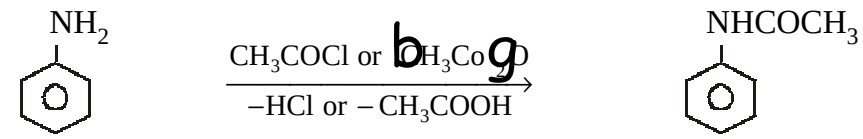
P–Nitro phenol $\xrightarrow[-2H_2O]{\text{Red } 3H_2/Ni}$ p–Amino phenol

(4) $(CH_2)_{11}CH_3$ (Alkyl Benzene) $\xrightarrow[\text{Oleum}]{\text{Sulphonation}}$ $(CH_2)_{11}CH_3$ (SO_3H) (Alkyl benzene sulphonic acid) $\xrightarrow[\text{Neutralization}]{Na_2CO_3}$ $(CH_2)_{11}CH_3$ (SO_3Na) (ABS)

Sulphonation: Oleum, 75^0C

Q. 4. (C) Acylation of Aniline :

(1) (i)

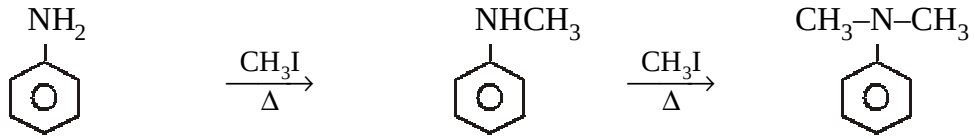


Aniline Acetanilide

⇒ Aniline when heated with acetyl chloride acetic anhydride gives Acetanilide by Acetylation.

(ii) Alkylation :

⇒ Excess of Methyl Iodide when heated with Aniline gives in sequence sec–N–methyl Aniline and tert – N–N dimethyl Aniline by **alkylation**.



Aniline | N–Methyl Aniline (2^0) | N, N-dimethyl Aniline (3^0)

(2) Nitrogen based fertilizer(Nitrolin) :

(a) When a mix of calcium oxide and carbon is heated in an electric furnace at 2000^0C. CaC_2 is formed

$$CaO + 3C \xrightarrow{2000\ ^oC} CaC_2 + CO$$

Calcium oxide Calcium Carbide

⇒ CaC_2 is then finely powdered and places in electric furnace having porcus walls at 1200^0C N_2 is passed n to thefurnato which give calcium.cyanamide.

$$CaC_2 + N_2 \xrightarrow{1200\ ^oC} CaCN_2 + C$$

⇒ Fine powder of calcium cyanamide is used as Nitrolim [Nitrogen + Lime]

⇒ In the soil containing moisture, Nitrolim hydrolyse giving $CaCO_3$ and NH_3.

$$CaCN_2 + 3H_2O \rightarrow CaCO_3 + NH_3$$

(b) Urea (NH_2CONH_2)

$$2NH_3 + CO_2 \xrightarrow[\text{high pressure}]{\text{high temp}} NH_2COONH_4$$

$$NH_2COONH_4 \xrightarrow{\Delta} -H_2O \; NH_2CONH_2 \text{ Urea}$$

(3) $CH_3CHO \xrightarrow[Br_2 / H_2O]{(O)} CH_3COOH$

Acetaldehyde (A) — Acetic Acid (B)

$$CH_3COOH \xrightarrow{\text{esterification}} + CH_3CH_3OH \;\; \text{Conc } [H_2SO_4]$$

Ethyl Acetate $CH_3COOCH_2CH_3$ (C)

$$CH_3COOCH_2CH_3 \xrightarrow{\Delta} NH_3$$

$$CH_3CONH_3 + CH_3CH_3OH$$

Acetamide [D]

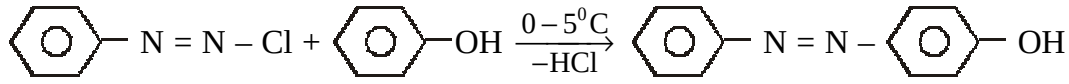
[A] = Acetaldehyde
CH_3CHO

[B] = Acetic Acid
CH_3COOH

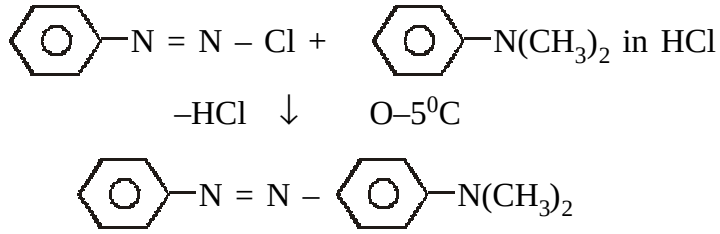
[C] = Ethyl Acetate
$CH_3COOC_2H_5$

[D] = Ethanol
C_2H_5OH

(4) Azo coupling Reaction :

(1) 

Benzene diazonium chloride | Phenol in NaOH | P–Hydroxy Azobenzene (orange Azodye)

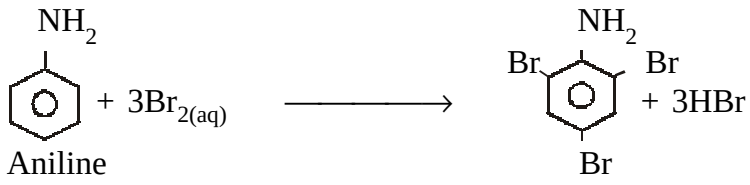
(2) 

p–Dimethyl Amino azo benzene (Yellow Dye)

⇒ When Benzene diazonium chloride react with phenol in NaOH at $0^0 - 5^0C$ give orange Azo dye by azo–coupling reaction.

⇒ When Benzene diazonium chloride react with N–N– dimethyl Aminobenzene in HCl at $0–5^0C$ temp. obtained yellow azo–dye.

(2) Bromination of Aniline :



Aniline

2 : 4 : 6
Tribromo Aniline

⇒ Amino grp of Aniline is o–p directing grp.

⇒ When Br_2 water is added to Aniline and shaken.

⇒ Bromination iin the aromatic nucleus gives white precipitates of 2, 4, 6 tribromo Aniline.

Q. 5. (A) (1) P, As, Sb can form five (maxium) covelent bonds.

(2) The +4 oxidatin state of vanadium exhibits low stability.

(3) Two co–ordinate sites are present in Bidentate ligands and Three co–ordinate sites are present in Tridente ligands.

(4) **IUPAC Name :**

$Na_4[Co(NO_2)_6]$ = Sodium Hexanitrito Cobaltate (II)

$Fe(CO)_5 \Rightarrow$ Penta Carbonyl Iron (O)

(5) (i)Chloro pentamine cobalt (III) sulphate

$[Co(NH_3)_5Cl]SO_4$

Potassium Penta cyano carbonyl ferrate (II)

$K_3[Fe(CN)_5(Co)]$

Q. 5. (B) (1) ML_6 – complex : Geometry of ML_6 complex :

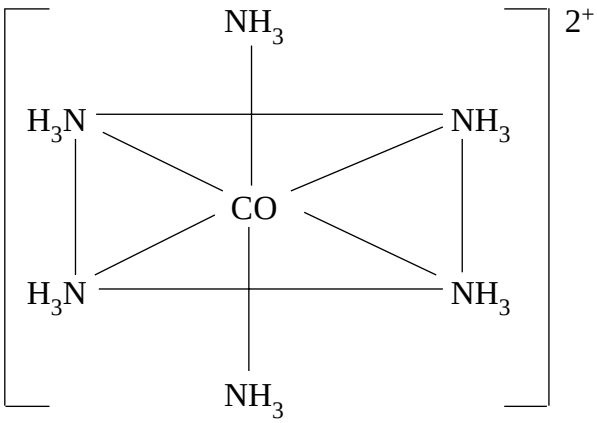
$\Rightarrow$ The co–ordination number of the central metal ion and the geometry of the complex can be known from the studies of magnetic proerties of the complexes.

$\Rightarrow$ ML_6 complex metalion having six–cordination number have octahedral geometry.

$\Rightarrow$ However the Oh is distroted of dofferent ligands are present in the complex.

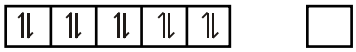
$\Rightarrow$ When two 3d, one 4s and three 4p orbitals or one 45, three 4p and two 4d orbitals of metal ions of ML_6 complex get six new equienergic d^2sp^3 or sp^3d^2 hybrid orbitals are formed and hence an octahedral geometry ligands donates loan pairs to thecentral metal ion.

e.q. $[Co(NH_3)_6]^{+2}$



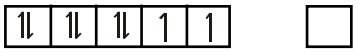
(2) In $ZnSO_4$ electronic configuration of Zn^{+2}

$3d^{10}$ $4S$

$_{30}Zn^{+2} = 3d^{10}\ 4S^0$ 

$\Rightarrow$ In $NiSC_4$, electronic configuration of Ni^{2+}

$3d^8$ $4S$

$_{28}Ni^{2-1} = 3d^8\ 4S^0$ 

$\Rightarrow$ In $NiSO_4$ d^8 arrangement contains unpaired electron. Hence d–d transition is possible. $\therefore$ So $NiSO_4$ is coloured.

$\Rightarrow$ In $ZnSO_4$ d^{10} configuration d–d transition is not possible. Hence $ZnSO_4$ is colourless.

(3) **Inert gases**

At. No.	**Symbol**	**Name**	**Electronic configuration**
2	He	Helium	$1s^2$
10	Ne	Neon	$1s^2\ 2s^2\ 2p^6$
18	Ar	Argon	$[Ne]3s^2\ 3p^6$
36	Kr	Krypton	$[Ar]\ 3d^{10}\ 4s^2\ 4p^6$
54	Xe	Xenon	$[Kr]\ 4d^{10}\ 5s^2\ 4p^6$
86	Rn	Radon	$[Xe]\ 4f^{14}\ 5d^{10}\ 6s^2\ 6p^5$

Q. 5. (C) (1) * In $K_3[Fe(CN)_6]$

$\Rightarrow$ Fe is present as Fe^{3+-}

$\Rightarrow$ Electronic configuration of Fe^{3+} as below :

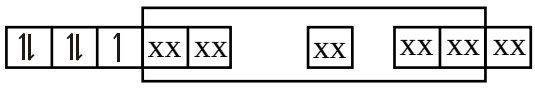
3d 4s 4p

$Fe^{3+} = [Ar]$ 

$(3d^5\ 4s^0)$

* For d^2sp^3 hybridization electronic configuration :

CN^- CN^- CN^- CN^- CN^- CN^-

$[Fe(CN)_6]^{3-} = [Ar]$ 

3d 4s 4p

$d^2\ sp^3$

$\Rightarrow$ For d^2sp^3 hybridization rearrangement of electrons take place in orbitals and make two vaccant orbitals.

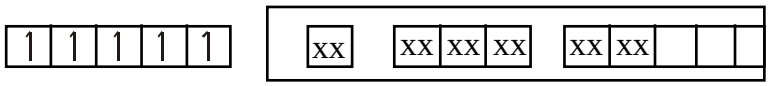
⇒ Now two 3d vacant orbitals, one 4s and three vacant 4p orbitals forming six equienergenic d^2sp^3 hybrid orbitals by d^2sp^3 hybridization in which six electron pair of ligand are accomodated.

⇒ There is 1 unpaired electron so $[Fe(CN)_6]^{-3}$ complex is paramagnetic.

Q. 5. (C)

(1) For Sp^3d^2 hybridization :

$[Fe(CN)_6]^{3-}$ = [Ar]



⇒ For sp^3d^2 hybridization rearrangement of electrons do not necessary.

⇒ Hence one 4s, three 4p and two 4d orbitals forms sp^3d^2 hybridization.

⇒ Six e^- pairs of ligands (CN^-) accomodate in six equal energenic hybrid orbitals to form Oh shape.

⇒ Here five electrons are unpaired

∴ So it is also paramagnetic.

But experimentally $K_3Fe(CN)_6$ is paramagnetic and its magnetic momentum is nearly 1–73 B–M, hence it indicates that $K_3Fe(CN)_6$ complex contain d^2sp^3 hybridization not sp^3d^2 hybridization.

(2) Allotropes of Arsenic & Antimony.

(1) Arsenic : (As)

Arsenic has three allotropes :

(a) Grey Arsenic : ⇒ It is crystalline and good conductor of electricity.

⇒ It has mettalic character.

(b) Yellow Arsenic : ⇒ It is a good electrical and thermal conductor.

(c) Black Arsenic : ⇒ It is a non conductor of heat and electricity.

⇒ It has mixed properties of a metal and non metal.

(2) Antimony : (Sb)

There are two Alltropes of Antimony.

(a) Yellow or α–Antimony

$\Rightarrow$ It is stable

(b) Mettalic or β–Antimony

$\Rightarrow$ It is silvery white.

(3) Electronic configuration of Transition Metals.

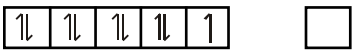
Scandium	Sc	21	[Ar] $3d^1\ 4s^2$
Titanium	Ti	22	[Ar] $3d^2\ 4s^2$
Vanadium	V	23	[Ar] $3d^3\ 4s^2$
Chromium	Cr	24	[Ar] $3d^5\ 4s^1$
Manganese	Mn	25	[Ar] $3d^5\ 4s^2$
Iron	Fe	26	[Ar] $3d^6\ 4s^2$
Cobalt	Co	27	[Ar] $3d^7\ 4s^2$
Nickel	Ni	28	[Ar] $3d^8\ 4s^1$
Copper	Cu	29	[Ar] $3d^{10}\ 4s^1$
Zinc	Zn	30	[Ar] $3d^{10}\ 4s^2$

(4) In $CuCl_2 \rightarrow Cu$ is $\rightarrow Cu^{+2}$

(a) $Cu^{2+}_{2a} \Rightarrow 3d^9\ 4s^0$

$\Rightarrow$ In $CuCl_2$ d^9 configuration has one unpaired electron. There fore it is paramagnetic

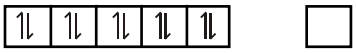
In $CuCl \rightarrow Cu$ is Cu^{+1}

$Cu^{+1} \rightarrow 3d^{10}\ 4s^0$ 

$\Rightarrow$ CuCl contains all paired electrons so it is diamagnetic

(b) The electron configuration of Ti^{3+} & Ti^{+4} are as below.

Ti^{3+} = [Ar] $4s^0\ 3d^1$

Ti^{+4} = [Ar] $4s^0\ 3d^0$ 

$\Rightarrow$ If transition elements or ions have d^0, d^5, d^{10} electronic configuration then it is stable.

$\Rightarrow$ Ti^{+4} is more stable.

$\Rightarrow$ Since removal of $4e^-$ from Ti atom requires very large amount of energy.

$\Rightarrow$ There fore Ti^{4+} ion is not possible but (+4) oxidation state is found in covalent compound. eq. $TiCl_4$

–*–

CHEMISTRY (052) E

Question Paper-III

Total Marks : 100 **Time : 3 Hours**

Instructions :

(1) This question paper contains FIVE questions and all are compulsory.

(2) Figure on the right indicates full marks of the questions.

(3) Answer the questions in short and to the point.

(4) Write equations of the reactions and draw figures wherever necessary.

Q. 1. (A) Answer in brief : **5**

(1) Why does a substance has kinetic energy ?

(2) Write the formula to calculate the change in entropy of system when a liquid evaporates at a constant temperature.

(3) Define : Degree of ionization.

(4) MgO remebles NaCl and TiCl resembles CsCl in their crystal structures. State the coordination number of positive ions in these crystals.

(5) What does $A_{1-x}/\square_A$ indicate ?

(B) Solve [any two] of the following : **6**

(1) Calcualte pOH of 4ml 2×10^{-6} HCl solution diluted to 500 ml.

(2) The concentration of OH^- in a sample of water is 1.75×10^{-8} M. Calculate the minimum quantity of solid $PbCl_2$ that should be added to water to precipitate $Pb(OH)_2$. (Ksp of $Pb(OH)_2 = 2.8 \times 10^{-16}$ molar mass of $PbCl_2$ = 278 g/mole)

(3) Calculate out the K_c of the reaction at 25^0C

$Cu_{(S)} + 2Ag^+_{(aq)} = Cu^{2+}_{(aq)}) + 2Ag_{(S)}$

The standard potential of the cell is 0.54 volt.

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

(1) A piece of ice in the atmosphere at 25^0C melts spontaneously; but liquid water does not get converted into ice spontaneously at this temperature. Account for this phenomenon on the basis of the second law of thermodynamics.

(2) What is hydrolysis of salt ? Discuss acidic and basic behaviour of the aqueous salt solution on this basis.

(3) (a) Explain crystalline structure of ZnS. (Figures are not required)

(b) In qualitative analysis to get precipitation of $Al(OH)_3$ NH_4Cl is added before adding NH_4OH solution. Explain.

(4) Explain BCC structure.

Q. 2. (A) Answer in brief :

(1) When two half–cells are connected with each other, electrons flow from anode to cathode. Why ?

(2) What does the following reaction indicate ? Explain on the basis of release of electrons.

$Zn_{(S)} + Cu^{2+}_{(aq)} = Zn^{2+}_{(aq)} + Cu_{(S)}$

(3) Give the usefulness of equation : $t_{1/2} = 0.693/K$.

(4) Give the type of hybrid orbitals and geometrical shape of PCl_5 molecule.

(5) How many orbitals are present if the principal quantum number of an energy level is 3 ?

(B) Solve [any two] examples : **6**

(1) Calculate the potential of the following cell at 25^0C.

Cd / Cd^{2+} (0.26M) // Ag^+ (0.06) / Ag

$E^0_{Cd/Cd^{2+}} = 0.40$ volt, $E^0_{Ag/Ag^+} = -0.80$ volt.

(2) A particle is moving with a kinetic energy of 3.1×10^{-13} erg. Calculate its wavelength. Mass of particle = 8.109×10^{-27} grams.

[Kinetic energy = $\frac{1}{2}mv^2$]

(3) At 300^0C temperature the differential rate of the reaction A + B $\rightarrow$ C, detemined in each of three sets of the experiments, were as under.

(i) Derive the differential rate law. (ii) State the order of the reaction.

(ii) Calculate the specific rate constant of the reaction.

Experiment number	Initial concentration of reactants mole–liter^{-1}		Initial rate of the reaction –d[B] / dt mole. lit^{-1} sec^{-1}
	[A]	[B]	
1	0.02	0.04	7×10^{-5}
2	0.04	0.04	2.8×10^{-4}
3	0.02	0.08	1.4×10^{-4}

(C) Answer the following in detail [any three] **9**

(1) Sketch a cell in which the following reaction occurs.

$Zn_{(S)} + 2Ag^{+}{}_{(aq)} = Zn^{2+}{}_{(aq)} + 2Ag_{(S)}$

Label different parts of the cell, write equations for oxidation and reduction reactions and indicate electrodes on which they occur.

(2) What is meant by order of reaction ? Explain in detail on the basis of the following general equation :

$n_1A + n_2B = n_3C + n_4D$

(3) (a) Explain bonding and anti–bonding molecular orbitals on the basis of molecular orbital theory.

(b) Sketch the shape of 2s orbital. How does 2s orbital differ from 1s orbital ?

(4) (a) Distinguish between covalent bond and coordinate covalent bond.

(b) Write a note on gas electrodes.

Q. 3. (A) Answer in brief : **5**

(1) On exposure to air, yellow phosphorus ignites spontaneously. Why ?

(2) Mention the names of compounds which are not soluble in benzene.

(3) Give the structural formulae of X & Y in following reaction.

$$X \xrightarrow[\text{Conc. } H_2SO_4,\ > 100^0C,\ -H_2O]{\text{Conc. } HNO_3} \begin{matrix} TNT \\ Y \end{matrix}$$

(4) Write the equation and name of product when ethyl cyanide is reduced with Ni or $LiAlH_4$.

(5) Give structural formual of DDT.

(B) Write chemical equation for ANY THREE of the following conversions. Also give the conditions of the reactions, names and structural formula of the main organic compounds. (There should be only two steps of each conversion). **6**

(1) P–methyl acetophenone from benzene.

(2) Isopropyl benzene from phenol

(3) Acetaldehyde from ethyl chloride.

(4) Propene from acetone.

(C) Answer the following [any three] **9**

(1) Compound A on heating with sodalime produced B, which on treatment with a mixture of conc. HNO_3 and conc. H_2SO_4 produced compound C. On reduction with Ni catalyst at 600^0C compound C produced compound D. Give reaction scheme and identify the compound A, B, C & D from the chemical reactions.

(2) Explain in detail about the preparations of the following from toluene.

(a) p–Toluene sulphonic acid (b) p–Dinitro toluene. (c) m–Xylene.

(3) Write a note on polyhalogen compounds.

(4) Give balanced equations of the following chemical reactions :

(a) The equation when potassium carbonate is reacted with nitric acid.

(b) The reaction when potassium hydroxide is reacted with nitric acid.

(c) Give the equation when potassium chlorate is treated with iodine.

Q. 4. (A) Answer in brief : **5**

(1) Which aldehyde is used to prepare various resin type plastics ?

(2) $X \xrightarrow[Br_2/H_2O]{[O]} CH_3COOH$

Give structural formula and IUPAC of X for the above reaction.

(3) Aqueous solutions of amines are basic. Why ?

(4) Which functional groups are present in amino acids ?

(5) Mention the name of inorganic fertilizers and their elements.

(B) Write chemical equations for ANY THREE of the following conversions. Also give the conditions of the reactions, names and structural formula of the main organic compounds. (There should be only two steps of each conversion). **6**

(1) Benzyl chloride from benzoic acid

(2) Ethyl benzoate from toluene

(3) Propane from Iso–propyl alcohol

(4) Ethyl iodide from acetaldehyde.

(C) Answer [any three] of the following : **9**

(1) Explain : Confirmative test of primary aromatic amines based on azo coupling.

(2) (a) What are vitamins ? Give sources and uses of vitamin C.

(b) Explain in detail about the role of Chloroform in human life.

(3) Disucuss Grignard reaction of aldehyde and ketones.

$$A \xrightarrow[Br_2/H_2O]{[O]} B \xrightarrow[Conc.[H_2SO_4]]{CH_3-CH_2-OH} C \xrightarrow[\Delta]{NH_3} CH_3-CO-NH_2 + D$$

Give names and structural formulae of A, B, C & D for the above reaction.

Q. 5. (A) Answer in brief : **5**

(1) Give the sources of $He_{(g)}$.

(2) The metals absorb hydrogen reversibly during electrolysis. Explain.

(3) Give electronic configuration of Cu_{29} & Cr_{24}

(4) What does secondary valency indicate ?

(5) Which orbitals will be utilized for the hybridization of complex $[Fe(H_2O)_6]^{3+}$? Why ?

(B) Answr the following : **6**

(1) Give the IUPAC of the following :

(a) $Na_4[Co(NO_2)_6]$ (b) $[Fe(CO)_6]$

(2) Why is the decrease in the energy of different orbitals irregular ?

(3) Give the names of the following :

(a) As_4O_6 (b) H_3SbO_4 (c) NaH_2AsO_4 (d) P_4O_8

(C) Answer the following : [any three]

(1) Discuss the various oxidation states observed in transition elements with suitable examples.

(2) Explain importance of complexes.

(3) Explain giving reasons :

(1) The formation of coordinate covalent bond is Lewis acid–base reaction.

(2) $K_4[Fe(CN)_6]$ is diamagntic while $[Fe(H_2O)_6]Cl_3$ is paramagnetic.

(4) Write a note on the allotropes of phsphorous and arsenic.

*_*_*

: ANSWERS :

Q. 1 (A) Answer in brief :

(1) Constituent particles of substance have translation, rotational and vibrational motions. Moreover, electrons and nuclei of these particles have different kind of motions. Therefor substance have kinetic energy.

(2) $\Delta S_{vaporisation} = \dfrac{\Delta H \text{ Vaporisation}}{T}$

(3) The fraction of dissolved compound inonised is known as degree of ionisation.

(4) Co–ordination number of Mg^{+2} and Na^{+} in MgO and NaCl respectively is six.

Co–ordination number of Ti^{+1} and C_s^{+1} in TiCl and C_sCl respcectively is eight.

(5) $A_{1-x/}\square_A$ shows that the atom A occupies $(1 - x)^{th}$ part of its normal site and the remaining part of its site is vacant.

(B) Solve the following :

(1) Given 4.0 ml 2.0×10^{-6}M HCl solution.

Above solution is diluted to 500.0 ml by ading water. Let us calculate concentration of diluted the solution.

$M_1V_1 = M_2V_2$ $\qquad M_1 = 2.0 \times 10^{-6}$ mole/lit.

$\therefore \quad M_2 = \dfrac{M_1V_1}{V_2}$ $\qquad V_1 = 4.0$ ml.

$= \dfrac{2.0 \times 10^{-6} \times 4.0}{500}$ $\qquad V_2 = 500.0$ ml.

$= 16 \times 10^{-9}$ M.

$\therefore$ Concentation of $H^{+}_{(g)}$ ion after diluting the solution is 16×10^{-9} M.

Since this concentration is less than the ceoncetration of $H^{+}_{(g)}$ ion produced due to self ionisation of water, the same i. e. 10^{-7} also has to be added.

$\therefore$ Concentration of $H^{+}_{(g)} = 16 \times 10^{-9} + 10^{-7}$

$= 1.16 \times 10^{-7}$ M

Now, pH $= -\log_{10} [H^+_{(g)}]$

$= -\log_{10} 1.16 \times 10^{-7}$

$= 6.9355$

Now pOH $= 14.0 - pH$

$= 14.0 - 6.9355$

$= 7.0645$

(2) Suppose x mole of $PbCl_2$ should be added to 1.0 lit. of water. Therefor the concentration of Ca^{+2} in water would be x M.

Let us now calcualte the value of x to get IP equal to Ksp.

$Pb(OH)_2 \rightleftharpoons Pb^{+2}_{(aq)} + 2OH^-_{(g)}$

$\therefore$ $Ksp = [Pb^{+2}] [OH^-]^2$

$\therefore$ $2.8 \times 10^{-16} = [x] [1.75 \times 10^{-8}]^2$

$\therefore$ $x = \frac{2.8 \times 10^{-16}}{1.75 \times 1.75 \times 10^{-16}}$

$= 0.9145$ M.

If littel more than 0.9145 mole of $PbCl_2$ i.e. 1.0 mole is added to 1.0 lit. of solution, Pb $(OH)_2$ will be precipitated.

$\therefore$ 1.0 mole i.e. 278.0 gm $PbCl_2$ must be added.

(3) As ΔG^0 in terms of electrical work done,

$\Delta G^0 = - nF\Delta E^0$.

Δ in terms of equilibrium constant $\Delta G^0 = - RTlnK$.

$\therefore$ $nF\Delta E^0 = RTlnK$.

$\therefore$ $\log K = \frac{nF\Delta E^0}{2.303 \times R \times T}$

$= \frac{2 \times 96500 \times 0.54}{2.303 \times 8.314 \times 298}$

$= 18.27$

$\therefore$ $K_c = 1.862 \times 10^{18}$

$Cu_{(s)} + 2Ag^+_{(g)} \rightarrow 2Ag + Cu^{+2}_{(aq)}$

$\Delta E^0 = 0.54V$

$n = 2$

$F = 96,500$

$R = 8.314$

$T = 298\ K^0$

Q. 1. (C)

(1) According to the second law of thermo dynamics in order to know whether a particular reaction will occure sportaneously or not the total entropy change is calcualted as under.

$\Delta S_{total} = \Delta S_{system} + \Delta_{srrounding}$.

(i) If $\Delta S_{total} > 0$ i.e. (+) reaction is spontaneous.

(ii) If $\Delta S_{total} < 0$ i.e. (–) reaction is non spontaneous

Now, molar heat of fusion of ice is 1440 cal. $mole^{-1}$.

$\therefore$ $\Delta H = 1440$ cal.$mole^{-1}$

$$\Delta_{system} = \frac{+\Delta H}{T}$$

$$= \frac{1440}{273} = 5.27 \text{ cal.}K^{-1}\text{mole}^{-1}$$

As heat is lost by atmosphere,

$$\Delta S_{surrounding} = \frac{-\Delta H}{T} = \frac{-1440}{298} = 4.83 \text{ cal.}k^{-1}\text{.mole}^{-1}$$

$\therefore$ $\Delta S_{total} = 5.27 - 4.83 = +0.44$ cal.k^{-1}.$mole^{-1}$

Thus ice melts spontaneously producing water at 0^0C.

For the conversion of water at 25^0C to ice at 0^0C, the system should release energy to atmosphere.

$$\Delta S_{system} = \frac{-1440}{273} = -5.27 \text{ cal}^0\text{K}^{-1}\text{.mole}^{-1}$$

$$\Delta S_{surronding} = \frac{+1440}{298} = +4.83 \text{ cal } {}^0\text{K}^{-1}\text{.mole}^{-1}$$

$\therefore$ For reversible process,

$\Delta S_{total} = \Delta S_{system} + \Delta_{surrounding} = -5.27 + 4.83 = -0.44$ cal.K^{0-1}.$mole^{-1}$

Thus, as ΔS_{total} is negative, liquid water does not get converted into ice spontaneously at 25^0C C temperature.

Q. 2. (2)

The aqueous solutions of salts are either acidic or basic because the ions formed from salts react with ions produced from water. This reaction is known as hydrolysis.

(i) Suppose a salt MA produced by a reaction between a strong base (MOH) and a weak acid (HA) is dissolved in water. The following equilibrium exists in water.

Further, all salts of above type ionize completely in aqueous solution as under :

$MA_{(aq)} \rightarrow M^{+}_{(aq)} + A^{-}_{(aq)}$

As HA is a weak acid, it ionizes only slightly. Therefore, the concentration of A^- present alongwith H^+ would be very low. When a salt dissolves in water, A^- ions are formed in large concentration. As a result, they combin with H^+ ions produced by the self–ionization of water and form undissociated HA. This disturbs the equilibrium in water. As a result, according to the Le Chatelier's principle the equilibrium of water shifts in the forward direction and produces more H^+ and OH^- ions. However as H^+ are removed by A^- the concentratin of OH^- ions exceeds the concentration of H^+ ions in the new state of equilibrium and, therefore the solution becomes basic. The overall reaction in solution may be represented as :

$A^{-}_{(aq)} + H_2O_{(l)} \rightleftharpoons HA_{(aq)} + OH^{-}_{(aq)}$

(ii) When a salt formed by a reaction between a weak base and a strong acid dissolves in waer, M^+ present in solution reacts with OH^- ions formed by the self– ionization of water. This reaction distrubs the equilibrium established between water and its ions. When the following net reaction reaches the state of equilibrium the concentration of H^+ ions exceeds the concentration of OH^- and the solution becomes acidic.

$M^{+}_{(aq)} + H_2O_{(l)} \rightleftharpoons MOH_{(aq)} + H^{+}_{(aq)}$

Q. 3. (A) Crystal Structure of Zinc Sulphide :

There are two crystal forms of zinc sulphide (ZnS) :

Zinc blend and Wurtzite

Just as the carbon atoms are joined tetrahedrally in diamond similarly in both the crystal forms of zinc sulphide Zn^{2+} and S^{2-} ions are arranged in a tetrahedral structure with four other ions surrounding are arranged in a tetrahedral structure with four other ions surrounding them. In Zinc blend, S^{2-} ions have, FCC structue while in Wurtzitee Zn^{2+} ions have hexagonal structure. ions around each S^{2-} ion and they are joined by covalent bonds. However the eight electrons

of the covalent bonds are not contributed equally by the zinc and sulphur atoms. The two valence electrons of zinc and the six valence electrons of sulphur together make up the eight electrons which form four covalent bonds. Each ion has a coordination number 4 in these crystal structures.

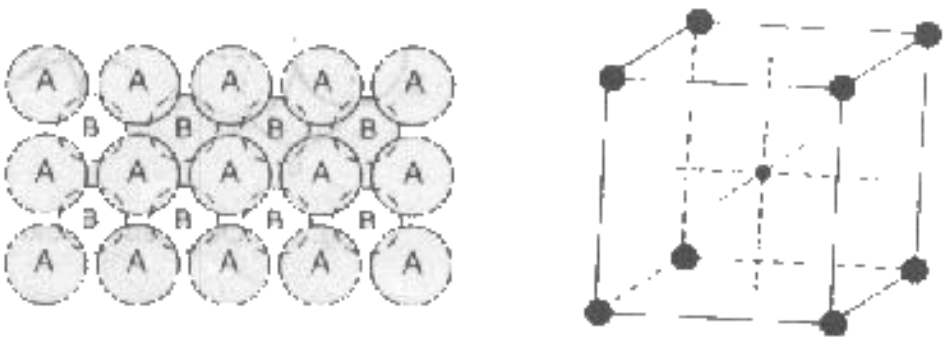
(b) $NH_4OH \rightleftharpoons NH_4^+ + OH^-$

$NH_4Cl \longrightarrow NH_4+ + Cl^-$ ...(1/2)

Thus, concentration of common ion NH_4^+ increases. So equilibrium of NH_4OH shifts in reverse direction. As a result, ionization ofr NH_4OH decreases. So the concentration of OH^- ion remains very low. The solubility of $AlCONL_3$ is very low compared to hydroxides of later groups III–B, IV and Mg^{2+}. So only $Al(OH)_3$ precipitate. ...(1)

Q. 1. (C) (4) Body–centered cubic close–packed structure :

In square structure, the spheres in the first layer A remain slightly away from one another. Each sphere is separated by some distance rather than being in mutual contact. Now when the second layer B is placed on the first layer A, then each sphere of the second layer comes in contact with four spheres of the first sphere. The third layer C is arrayed on the second layer B exactly the same way as is the first layehr A. The crystal structure generated by repetition of this ABABAB... kind of arrangement is called the body–centered cubic close– packed (BCC) structure.



Body–centered cubic close–packed structure (BCC)

In this structure, a sphere in any layer is in contact with a total of eight spheres, four of the layer above it and four of the layer beneath it. If we imagine a simple cube and place a Sphere at each of its eight corners and at the center inside the cube, then the structure that results is called the body–centered cubic close–packed (BCC) structure e. g. CsCl crystal in which coordination no. is 8.

Q. 2. (A) Answer in short : **(5)**

(1) Electrons flow from anode to cathode due to electrical pressure produced by a chemical reaction.

(2) Here Zn releases electrons. The tendency of Zn to release electons is greater than the tendency of Cu to release electrons.

(3) It is useful to recognise the first order of reactions.

(4) PCl_5 : Hybridization $\rightarrow sp^3d^2$

Shape $\rightarrow$ Trigonal bipyramidal

(5) Number of orbitals = $n^2 = (3)^2 = 9$

(B)

(1) Cd/Cd^2 (0.26M) || Ag^+ (0.06) / Ag

E^0 Cd/Cd^2 = 0.40V E^0Ag/Ag^+ = –0.80V

C_1 = 0.26M Co_2 = 0.06M

n = 2

ΔE^0 (ed) = E^0 – E^0

Oxi Anode Oxi Cathode

= 0.40 – (–0.8)

= 1.2 volt

$$\therefore \quad \Delta E = \Delta E^0_{cell} - \frac{0.0592}{n} \log \frac{c_1}{c_2}$$

$$= 1.2 - \frac{0.0592}{2} \log \frac{0.26}{0.06}$$

$$= 1.2 - 0.0296 \log \frac{13}{3}$$

$= 1.2 - 0.0296\ (1.1139 - 0.4771)$

$= 1.2 - 0296\ (0.6368)$

$= 1.2 - \text{A.log.}\ (0.4713 + 0.8040) \times 10^{-3}$

$= 1.2 - \text{A.log.}\ (1.2753) \times 10^{-3}$

$= 1.2 - 0.0188$

$= 2.1812$ volt.

$2\ ne = \frac{1}{2}\ mv^2 = 3.1 \times 10^{-13}$ erg. $M = 9.109 \times 10^{-27}$ gm.

$$v^2 = \frac{6.2 \times 10^{-13}}{8.109 \times 10^{-27}}$$

$$\therefore \quad v = \sqrt{\frac{6.2 \times 10^{-13}}{8.109 \times 10^{-27}}}\ \text{cm/s}$$

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

$$= \frac{6.626 \times 10^{-27}}{8.109 \times 10^{-27} \times \sqrt{\frac{6.626 \times 10^{-13}}{8.109 \times 10^{-27}}}}$$

$$= \frac{6.626 \times 10^{-27}}{\sqrt{8.109 \times 6.2} \times 10^{-20}}$$

$$= \text{A.log}\ (0.8213 - \frac{1}{2}\ (0.9090 + 0.7924)) \times 10^{-7}$$

$$= \text{A.log}\ (0.8213 - \frac{1}{2}\ (1.7014)) \times 10^{-7}$$

$= \text{A.log}\ (1.82113 - 0.8507) \times 10^{-8}$

$= \text{A.log}\ (0.9706) \times 10^{-8}$

$= 9.345 \times 10^{-8}$ cm

$= 9.345 \times 10^{-10}$ M

$= 9.345\ A^0$

(3) (i) differential rate law is Rate = $\frac{-d[A]}{dt} = \frac{-d[B]}{dt} = K[A]^x\ [B]^y$

(ii) From given table using different values in above eqn we get.

(1) $7 \times 10^{-5} = K[0.02]^x\ [0.04]^y$

(2) $2.8 \times 10^{-4} = K[0.04]^x\ [0.04]^y$

(3) $1.4 \times 10^{-4} = K[0.02]^x\ [0.08]^y$

$\therefore$ eqn $\frac{1}{2} \Rightarrow \frac{7\times10^{-5}}{2.8\times10^{-4}} = \left(\frac{0.02}{0.04}\right)^x$

$\therefore$ $\frac{.70}{2.8} = \left(\frac{1}{2}\right)^x$

$\therefore$ $2^2 = 2^x$

$\therefore$ $x = 2$

eqn. $\frac{1}{3} \Rightarrow \frac{7 \times 10^{-5}}{1.4 \times 10^{-4}} = \left(\frac{1}{2}\right)^y$

$\therefore$ $.50 = (0.5)^y$

$\therefore$ $y = 1$

$\therefore$ Net order of reaction = x + y = 2 + 1 = 3

putting value of x & g is eqn (1)

$\therefore$ $7 \times 10^{-5} = k[0.02]^2\ [0.04]$

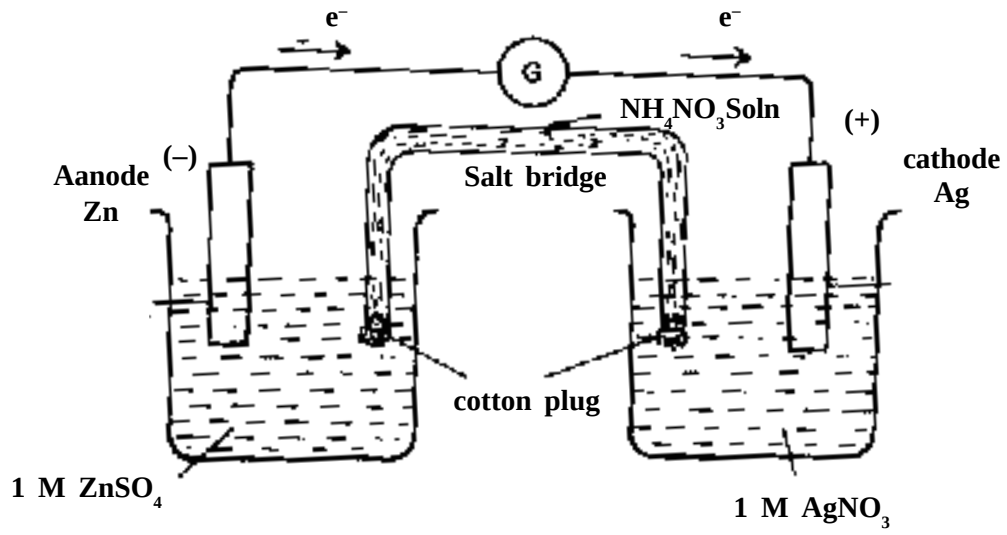
$\therefore$ $7 \times 10^{-5} = k \times [2 \times 10^{-2}]^2\ [4 \times 10^{-2}]$

$\therefore$ $7 \times 10^{-5} = k \times 8 \times 10^{-6}$

$\therefore$ $\frac{70}{8} = k$

$\therefore$ $k = 8.75\ lit^2\ mole^{-2}\ sec^{-1}$

Q. 3. (C) 1



Anode : $Zn_{(s)} \rightarrow Zn^{2+}_{(1M)} + 2e^-$ ... (2)

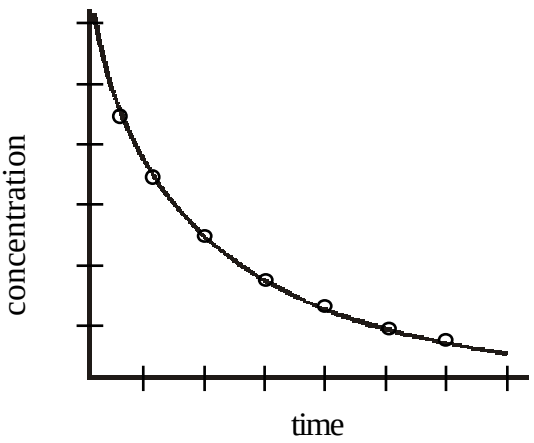
Cathode : $2Ag^+_{(1m)} + 2e^- \rightarrow 2Ag_{(s)}$ ... (1)

(2) The value of exponents of concentration term of reactants in differential rate law equation is known as order of reaction. ... (1)

Suppose a general reaction, $n_1A + n_2B = n_3C + n_4D$ occurs at a constant temperature. With the start of the reaction, concentrations of A and B begin to decrease as A and B are consumed in the reaction. The concentrations of C and D go on increasing as C andd D are formed in the reaction. If the decrease in concentrations of A and B are $\Delta[A]$ and $\Delta[B]$ respectively after time t, then the average rate of reaction of A in time interval $\Delta t = -\frac{\Delta A}{\Delta t}$ and, the average rate of reaction of B in time interval $\Delta t = -\frac{\Delta B}{\Delta t}$. Here negative (–), indicates the decreases in concentration of reactants.

Similarly, the rates of formation of C and D in time Δt can be represented by $+\frac{\Delta[C]}{\Delta t}$ and $+\frac{\Delta[D]}{\Delta t}$ respectively.

The rate of a chemical reaction at a particular moment is proportional to the concentrations of reactants, at the moment. As the concentrations of reactant, go on decreasing continuously the rate of a reaction decreases continuously as time passes; fig. indicates curved graph.



Above tems which indicate the rate of the reaction are related with each other as under :

$$-\frac{1}{n_1}\frac{\Delta[A]}{\Delta t} = -\frac{1}{n_2}\frac{\Delta[B]}{\Delta t} = +\frac{1}{n_3}\frac{\Delta[C]}{\Delta t} = +\frac{1}{n_4}\frac{\Delta[D]}{\Delta t}$$

Differential Rate Law :

The relation between the rate of a reaction and concentrations of reactant at any particular moment is known as the differential rate law of teh reaction. For example, the mathematical form of differential rate law of the general reaction mentioned above can be us under :

$$\frac{1}{n_1}\frac{d[A]}{dt} = -\frac{1}{n_2}\frac{d[B]}{dt} = K[A]^x\,[B]^y$$

Here $\frac{d[A]}{dt}$ is the rate of reaction of A at a moment at which the concentrations of A and B are [A] and [B] respectively. The exponents x and y are known as order of reaction with respect to A and B respectivley. x and y are not related with stoichiometric co–efficients n_1 and n_2 appearing in the balanced equation.

Q. 2. (C)

(3) (a) According to the principles of wave mechanics, a molecular orbital is constructed by the linear combinatin of atomic orbitals of two atoms between which a bond is formed. For example. When H_2 molecule is formed by bonding two H atoms, the acceptable wave function $\Psi_{1s(1)}$ and $\Psi_{1S(2)}$ combine linearly molecular wave functions, Ψ_{m0} and Ψ^0_{m0} are formed.

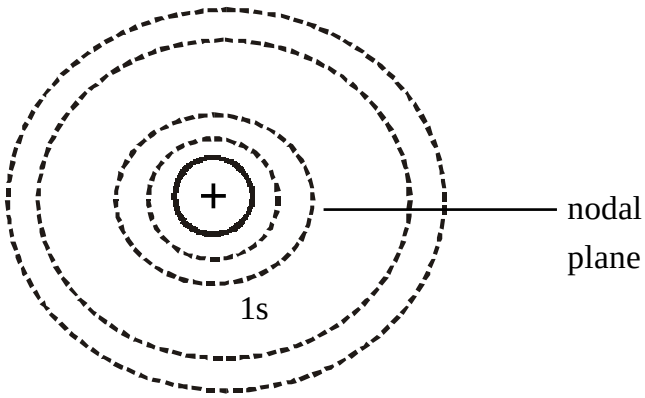
$$\Psi_{m0} = \Psi_{1S(1)} + \Psi_{1S(2)}$$

$$\Psi^*_{m0} = \Psi_{1S(1)} - \Psi_{1S(2)}$$

Here (1) and (2) are serial numbers used to distinguish between two hydrogen atoms. The energy of molecular orbital indicated by Ψ_{m0} is less than the energy of 1s atomic orbital. The energy of molecular orbital indicated by Ψ^*_{m0} has higher energy than the energy of 1s atomic orbital. Here Ψ_{m0} is bonding and Ψ^*_{m0} is antibonding molecular orbitals.

Symbols $\sigma$and π are used to indicate bonding molecular orbitals and σ^* and π^* symbols are used to indicate antibonding molecular orbitals.

(b)



... (1/2)

→ 2S orbital has one node while 1s orbital zero node. ... (1/2)

→ For ds, n = 2, while for 1s, n = 1. Thus, 2s orbital has higher energy than 1s.

(4) (a) The bond formed by overlaping of half–filled valence orbitals of combining atoms is called a covalent bond.

While if one of the two combining atoms has a fully filled valence orbital and another has vacant valence orbital, then the overlapping of these two orbitals forms the special bond is known as coordinate covalent bond.

→ In covalent bond, each atom shares its one electron with only one electron of another atom. While in coordinate bond one atom shares its pair of electron with another atom.

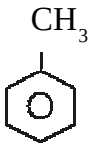
(b) (iii) Gas Electrode : These electrodes resemble inesrt electrodes to a large extent. In these electrodes, a gas is bubbled over the surface of a platinum plate dipped in a solution. For example, hydrogen gas is passed over a platinum plate dipped in a solution containing $H^+_{(aq)}$. In this case eigher $2H^+$ ions are reduced to H_2 by gaining electrons, on the surface of platinum of H_2 is oxidized to $2H_+$, by giving up electrons on the surface of the platinum plate. The platinum plate provides a contact surface for the exchagne of electrons. The reaction occuring on the surface can be represented as under :

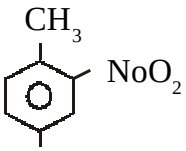
$$H_{2(g)} \rightleftharpoons 2H^+_{(a)} + 2e^- \qquad ...(3.4)$$

Q. 3. (A) Answer in brief : **(5)**

(1) The p–p bonds in P_4 are weak and p–p–p bond angle is very small. So there is strain in P_4 molecule. So it ignites.

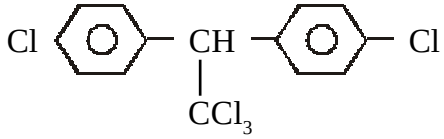
(2) Glucose, sugar and inorganic salts.

(3) X =  Toluene

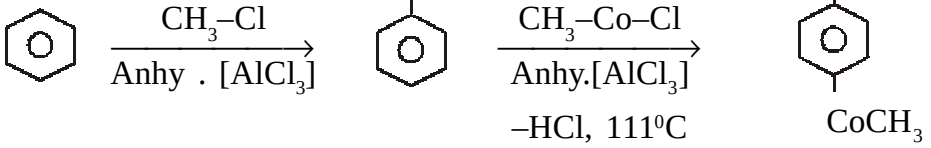
Y =  2,4,6–Triniitro toluene

(4) $CH_3–CH_2–CN \xrightarrow[Ni/LiAlH_4]{2H_2} CH_3–CH_2–CH_2–NH_2$

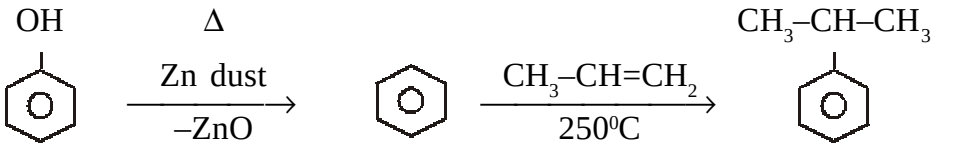
Ethyl cyanide — 1–amino propane

(5) 

(B) Give conversions (three) **(6)**

(1) 

Benzene — $CH_3–Cl$, Anhy . $[AlCl_3]$, –HCl — 80^0C — Toluene — $CH_3–Co–Cl$, Anhy.$[AlCl_3]$, –HCl, 111^0C — P–methyl acetophenone

(2) 

Phenol — Δ, Zn dust, –ZnO — Benzene — $CH_3–CH=CH_2$, 250^0C, $[H_3PO_4]$ — Iso–propyl benzene

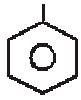
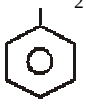
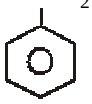
(3) $CH_3–CH_2–Cl \xrightarrow[\Delta,\ –NaCl]{Aq.NaOH} CH_3–CH_2–OH \xrightarrow[Na_2Cr_2O_7 + H_2SO_4]{[O]} CH_3–CHO + H_2O$

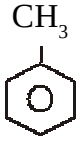
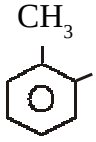
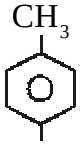
Ethyl Chloride — Ethanol — Acetaldeayde

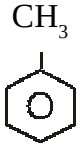
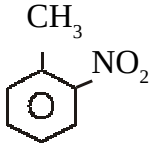
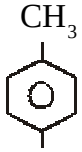
(4) $CH_3–CO–CH_3 \xrightarrow[[Ni]]{H_2} CH_3–\underset{OH}{CH}–CH_3 \xrightarrow[350 - 400^0C,\ –H_2O]{[Al_2O_3]} CH_3–CH=CH_2$

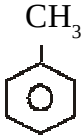
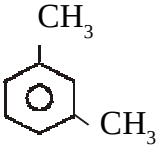
Acetone — 2–propanol — propene

(C)

(1)  Benzoic acid $\xrightarrow[–CO_2]{\Delta,\ Soda\ lime}$  Benzene $\xrightarrow[CeMe.[H_2SO_4],\ –H_2O,\ 50–60^0C]{Conc.\ HNO_3}$  Nitro benzene $\xrightarrow[600^0C,\ –2H_2O]{3H_2/[Ni]}$  Aniline

(2)  $\xrightarrow[–H_2O,\ 30^0C]{Firm.\ H_2SO_4}$  OTS +  PTS

 Toluene $\xrightarrow[–H_2O,\ 60–70^0C,\ conc.[H_2SO_4]]{conc.\ HNO_3}$  ONT +  PNT

 Toluene $\xrightarrow[–HCl,\ 111^0C,\ [HF + BF_3]]{CH_3–Cl}$  m–xylene

(3) Two or more halogen atoms of the same or different kind combine with a metal forming plyhalogen compounds, e.g. $CsBr_3$, CsI_3, $CsICl_2$, $CsIBr_2$. These polyhalogen compounds contain uninegative polyhalide ions like Br_3^-, I_3^-, ICl_3^-, ICl_3^-, IBr_2^- etc.

(4) $K_2CO_3 + HNO_3 \rightarrow KNO_3 + H_2O + CO_2$

$KOH + HNO_3 \rightarrow KNO_3 + H_2O$

$2KClO_3 + I_2 \rightarrow 2KIO_3 + Cl_2$

Q. 4. (A) Answer in brief : **(5)**

(1) Formaldehyde

(2) CH_3CHO – Ethanal

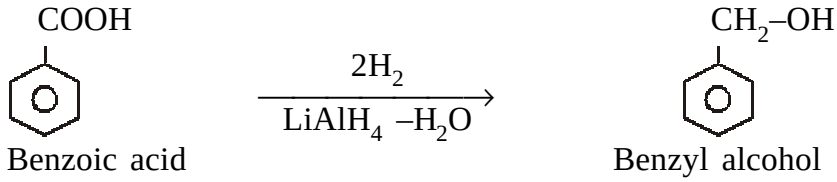
(3) Because, N–atom of amine has non–bonding electron pair and they produce OH^- ions in aqueous solutions.

(4) $–NH_2$ and –COOH

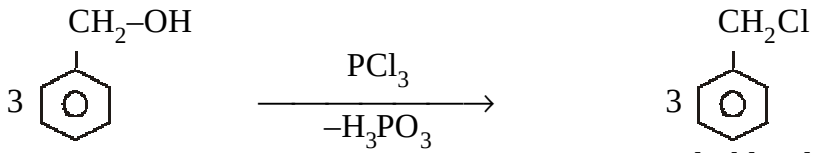
(5) Super phosphate of lime $\rightarrow$ Ca, P, S, O, H atoms

Nitrolime $\rightarrow$ Ca, C, N atoms.

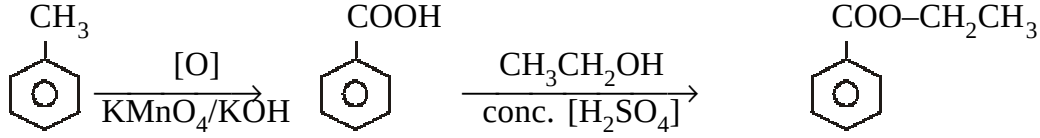
(B)

(1) 

Benzoic acid Benzyl alcohol



Benzyl chloride

(2) 

Toluene Benzoic acid Ethyl benzoate

(3) $CH_3–\underset{\underset{CH}{|}}{CH}–CH_3 \xrightarrow[KMnO_4 \mid KOH]{[O]} CH_3–\underset{\underset{O}{||}}{CH}–CH_3 \xrightarrow[-N_2,\ -H_2O]{N_2H_4/KOH} CH_3–CH_2–CH_3$

2–propanol — Acetone — Propane

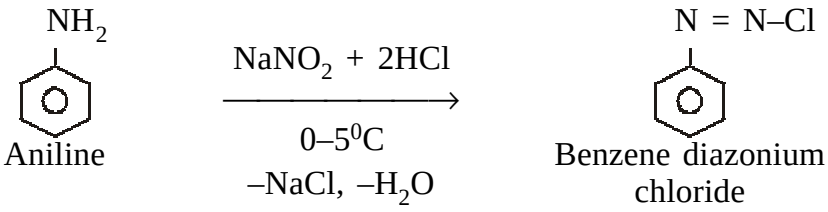
(4) $CH_3–CHO \xrightarrow[[Ni]]{H_2} CH_3–CH_2–OH$

Acetaldehyde — Ethanol

$3CH_3–CH_2–OH \xrightarrow[-H_3PO_3]{PI_3} 3CH_3–CH_2–I$ Ethyl iodide

(C) Answer any three **(6)**

(1) Solution of ailine in dilute hydrochloric acid is prepared and cooled to 0^0–5^0C. Maintaining this low temperature, cold solution of sodium nitrite is added to this very slowly. Benzene diazonium chloride salt is thus formed. Durign this reaction, nitrous acid produced by reaction of hydrochloric acid on sodium nitrite, reacts with amino group of aniline giving benzene diazonium chloride.

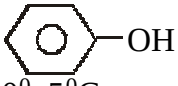


Aniline — Benzene diazonium chloride

phenyl hydrazine

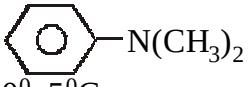
azo coupling

p–hydroxy azo–benzene (orange azo–dye)



0^0–5^0C

azo coupling



0^0–5^0C

p–dimethylamino azo–benzene (yellow azo–dye)

when benzene diazonium chloride is treated with phenol in NaOH at 0–5^{0}C it gives p–hydroxy azobene and with dimethyl aniline in HCl at 0–5^{0}C, it gives p–dimethyl amino azo benzene.

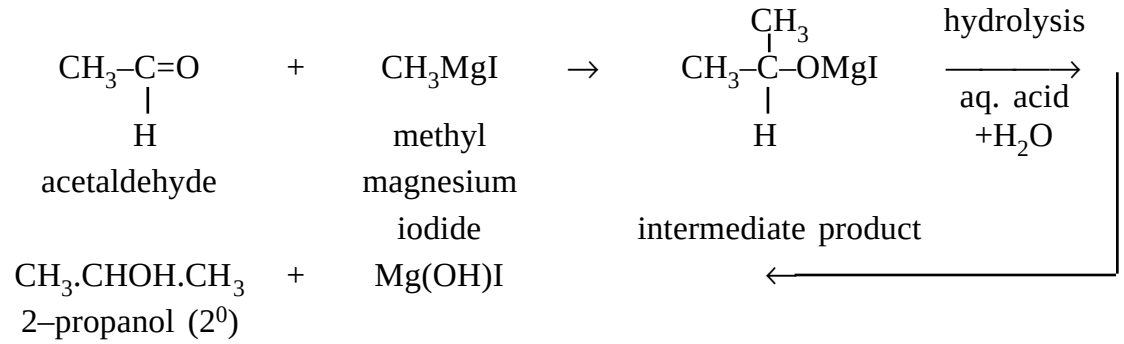
(2) For biochemical processes in body, for its normal growth and for the activity of its tissue cells, vitamins are necessary. Lack of vitamins produces defects in body, leading to deficiency dieseases.

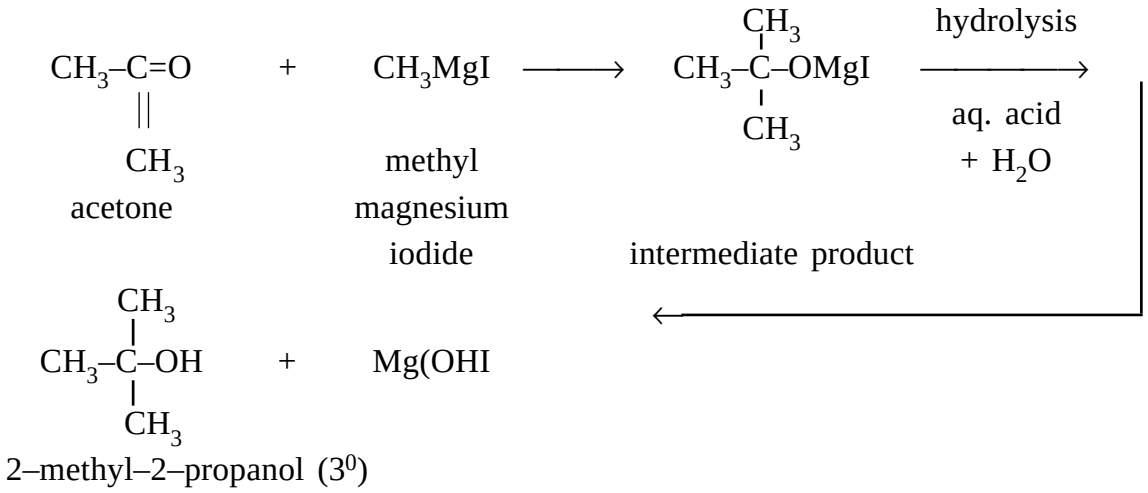
Vitamin C is called ascorbic acid. Citrus fruits, lemons, tomatoes and green vegetables contain this vitamin. Its deficiency produces a diseases called scury in which gums get swollen and start bleeding and ulcer occurs with teeth loosening. Vitamin C also gives resistance against common cold.

Chlorform :

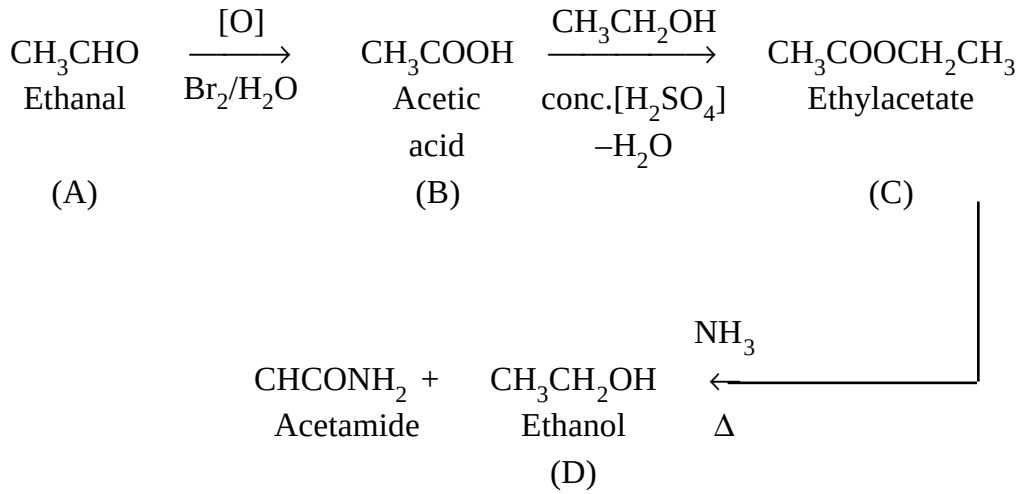
Drugs like opium, morphine etc. which lower the activity of central nervous system are called central nervous depressants (CND). Drugs like hashish, marijuana, ethanol etc. are called central newrvous stimulants (CNS). Chloroform is central nervous depressant. Its effect blocks the relay in central nervous system and therefore when body parts are operated, no pain is felt. In order to avoid pain during surgery, patient is given chloroform as an anaesthetic. Structure of chloroform is $CHCl_3$ and it is prepared from acetaldehyde or acetone.

Chloroform is a colourless, sweet smelling liquid, heavier than water and sparingly soluble in water. In presence of sunlight it combines with atmospheric oxygen giving cabonyl chloride or phosgene. Hence chloroform used as an anaesthetic containig impurity of phosgene will be fatal. In order to avoid this difficulty, chloroform used in hospitals is mixed with 1% ethanol, which converts phosgene into harmless diethyl carbonate.





When acetaldehyde and Ketones are reacted with CH_3MgI, they give intermediate products. They an hydrolysis by aqueous acid gives alcohol. By these reactions acetaldehyde gives 2–propanol and acetone give 2–methyl 2–propanol.

(4) 

Q. 5. (A) Answer in brief : **(5)**

(1) He is preseent about 7% in volcanic gases.

(2) Ni metal absorbs H atoms in interstitial voids and reversibly releases hydrogen. So Ni metal is used as catalyst.

(3) Cu[29] : [Ar] $3d^{10}$ $4s^1$

Cr[24] : [Ar] $3d^5$ $4s^1$

(4) It indicates co–ordination number of metal ion.

(5) one 4s, three 4p and two 4d orbitals giving sp^3d^2 hybridized orbitals.

(B) Answer the following : (6)

(1) (a) Sodium hexanitrito cobaltate (II)

(b) Hexa carbonyl iron (O)

(2) Because the screening effect of the electrous in the inner filled shells is different on different orbitals of the same shell.

(3) (a) $AS_4O_6 \rightarrow$ Arsenic trioxide

(b) $H_3SbO_4 \rightarrow$ Orthoantimonic acid

(c) $P_4O_8 \rightarrow$ Phosphorous tetraoxide

Q. 5. (d)

(1)

Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
+3*	(+2)	(+2)	+2	+2*	(+1)	(+1)	+1	+2*	
	+3	+3	+3*	+3	+2	+2	+2*	+2*	
	+4*	+4*	(+4)	+4	+3*	+3*	(+3)		
		+5	(+5)	(+5)	+4	(+4)	(+4)		
			(+6)	(+6)	+6				
				+7					

In the table, the most stable oxidation states are shown by asterisk, while the unstable or rare states are placed in brackets. The oxidation states shown in brackets are the ones found in unstable compound.s These oxidation states are found in common compounds but there are cases known +1, 0 and even negative oxidation states.

The oxidation state of the transition metal atom can be easily calculated in the compounds where the electronegativity difference between the transition element atom and the other atoms combined with it is appreciably large. Generally the ligands possessing N, O, or a halogen form compounds by forming σ–bonds with the metal atom. In the compounds of this type, the oxidation state of the metal atom is positive. But in the compounds of the transition metals with ligands which can accept π–electrons of the metal, the oxidation state of the metal atom is negative but stable. Such liigands are fluoride, cyanide, phosphate, etc.

(2) Complex compounds are of great importance. They are resent in plants, animals and minerals and play a very important role in them. For example, chlorophyll, a magnesium complex present in green plants is important for photosynthesis. Hemoglobin, an iron complex present in animal blood, serves to carry oxygen to the muscles and to remove CO_2 from the blood. The complexes present in minerals are useful as catalysts in the metallurgical industries and as analytical reagents in the laboratory.

The first systematic study of complex compounds was done by Werner in 1892. He prepared several complex compounds by the reaction between cobalt chloride and ammonia and from their exhaustive studies proposed his theory of complex compounds.

(3) (a) The neutral atoms or the cation of the transition elements occupying the centers of the molecules of the complex compounds aer linked with the surrounding anions or neutral molecules by co–ordinate bonds, and these anions or neutral molecules co–ordinated to the central metal ion are called ligands. Ligands function as Lewis bases, sincce they donate electron pairs and the central metal ion of the complex being the acceptor of electron–pairs acts as a Lewis acid.

$CO^{3+} + 6NH_3 \rightarrow [Co(NH_3)_6]^{3+}$

(b) $[Fe(CN)_6]^{4-}$ 

$[Fe[H_2O]_6]^{1+}$ 

→ As Cn^- is strong ligand. So pairing of electorns in 3d–orbitals gives all electrons paird. So it is diamagnetic.

While H_2O is weak ligand. So pairing of electrons does not take place. It gives five unpaired electrons. So it is paramagnetic.

(4) **Phosphorus :** There are three different forms (allotropes) of phosphorus : (1) Yellow phosphorus (2) Red phosphorus and (3) Black phsphorus.

All the three allotropes are solid at ordinary temperature. The yellow phosphorus is wax–like soft and reactive. In air it spontaneously ignites at 35^0C and, therefore has to be kept under water. It causes burns. The tetrahedral P_4 molecules of the solid, liquid nad vapour states decompose into P_2 molecules. When yellow phosphorus is heated to a temperature of 250^0C or lower in presence of sunlight with I_2 as a catalyst and under an inert atmosphere of CO or N_2 red phosphorus is obtained.

Red phosphorus is a plymolecular solid. It does not ignite on exposure to air or on being heated to 400^0C.

Black phosphorus is obtained on heting yellow phosphorus under high pressure. It is a polymolecular solid. It is the most stable form of phosphorus.

Arsenic : There are three allotropic forms of arsenic : (1) grey (2) yellow and (3) black. All three forms are solids at ordinary temperatures. The grey arsenic is crystalline and is a good conductor of electricity showing that this form has a metallic character. Yellow arsenic is a good thermal and electrical condusctor but it is unstable. Black arsenic possesses mixed properties of a metal and a non–metal. It is a non–conductor of heat and electricity.

*_*_*

CHEMISTRY (052) E

Question Paper-IV

Total Marks : 100 **Time : 3 Hours**

Atomic weights : Na = 23, Mg = 24, Cl = 35.5 gm/mole

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

(1) Why absolute value of free energy G^0 cannot be determined ?

(2) Give conjugate base of HPO_4^{2-} and NH_3.

(3) Give importance of $E = mc^2$ equation.

(4) How are double chain structures in silicate compounds formed ?

(5) What does symbol $A_{(1-x)}$ / $\square_A$ indicate ?

(B) Solve any two examples. **[6]**

(1) Calculate free energy change and equilibrium constant of following cell. if standard potential of the cell is 0.78 volt at 25^0C.

$Fe_{(s)}$ / Fe^{2+}(1M) // Cu^{2+} (1M) / $Cu_{(s)}$

$E^0_{Fe/Fe^{+2}} = 0.45V$; $E^0_{Cu/Cu^{+2}} = 0.34V$

(2) Calculate pH of 0.25 M CH_3COONa solution. Ka of CH_3COOH is 1.75×10^{-5} at 25^0C.

(3) 0.1 mole solid $Ca(NO_3)_2$ and 0.001 mole solid $Ba(NO_3)_2$ are added in 9.92×10^{-8} M H_2SO_4 solution such that its volume does not change. Which salt $BaSO_4$ or $CaSO_4$ will precipitate ?

Ksp of $BaSO_4 = 9.9 \times 10^{-11}$ and Ksp of $CaSO_4 = 2.4 \times 10^{-5}$

(C) Explain the following questions. (Any three) **[9]**

(1) State first law of thermodynamics. Explain its relation with work.

(2) Explain (i) Hydration of NaCl

(ii) Hydrolysis of $CuSO_4$ in water

(3) Explain (i) Ultra marines.

(ii) Importance of first law of thermodynamics.

(4) Explain (i) Amorphous solids

(ii) Crystal structure of ZnS (figs. not required)

Q. 2. (A) Answer the following questions in short. [5]

(1) What is called one faraday ?

(2) What is known as electrolytic cell ?

(3) Define : specific rate constant of reaction.

(4) What is called nodal plane ? Which type of molecular orbitals possess nodal plane ?

(5) Why SF_6 is stable through it is formed from excited state ?

(B) Solve any two examples. [6]

(1) Fused $MgCl_2$ and NaCl are connected in series and same current is passed through them. During this period, 142 gm. of Cl_2 gas is evolved. How much Mg and Na would be produced during this period ?

(2) In a first order reaction, the concentration of reactant decreases from 0.8 M to 0.6 M in 2700 seconds. Calculate half–life of the reaction.

(3) Calculate wavelength of particle weighing 500 milligram and moving with a velocity of 3600 km/second ($h = 6.626 \times 10^{-27}$ erg.)

(C) Explain any three of following. [9]

(1) Explain : ''Fuel cell''.

(2) Derive integrated rate law equation for first order reaction.

(3) Explain (i) Energy barrier

(ii) Difference between BMO and ABMO

(4) Give molecular orbital diagram of O_2 molecule. Calculate its bond order and predict its magnetic property.

Q. 3. (A) Answer the following objectives. [5]

(1) Why the temperature for the bromination of benzene is maintained higher ?

(2) Give structural formula of glycerol and DDT.

(3) Give the equation of reaction when ethanol is reacted with PI_3.

(4) What is half–life of francium ? Why does it not occure free in nature ?

(5) Which of the following reaction is possible ? Why ?

(i) $Cl_2 + 2KF \rightarrow 2KCl + F_2$

(ii) $F_2 + 2KCl \rightarrow 2KF + Cl_2$

(B) Give equations of following conversions (any three). Mention name, structures of organic compounds and necessary conditions. (only in two steps) [6]

(1) Benzene into TNT.

(2) Toluene into Benzoyl chloride

(3) Di ethyl ether into n–butane.

(4) Chlorobenzene into sodium phenoxide

(C) Explain any three of following. [9]

(1) Explain (1) Ozonolysis of benzene and its importance

(2) Toluene has one isoner while xylene has three isomers.

(2) Explain (1) B–elimination reaction

(2) Classification alkyl halides

(3) Explain (i) Crystal structures of alkali metal elements.

(ii) Density of alkali metals.

(4) Explain : Preparation of halogen acids.

Q. 4. (A) Answer the following objectives [5]

(1) Give structural formula of diethyl ketone and acetone cyanohydrine.

(2) What is called formaline ? Give its use.

(3) Give equation of bromination of aniline.

(4) What are called optical brightners ?

(5) Give two different names of iso cyanide compounds.

(B) Give equations of any three conversions. Mention names, structures of organic compounds. Also state necessary reaction conditions. (only in two steps) [6]

(1) Acetophenone into Ethyl benzoate

(2) Acetic acid into ethene.

(3) Nitro benzene into acetanilide

(4) Benzene diazonium chloride into phenyl acetate.

(C) Explain the following questions (any three) [9]

(1) Explain (i) Condensation of ethanal

(ii) Wolf–kishner reduction

(2) Explain preparation of amide. Give its two different chemical properties with equations.

(3) Explain (i) Degree of polymerisation

(ii) preparation of polystyrene and its uses.

(4) Explain (i) Hormones and its importance

(ii) CNS and CND drugs.

Q. 5. (A) Answer the following objectives. **[5]**

(1) Give two characteristics of black arsenic.

(2) Give the compound of manganese in highest oxidation state. What is its characteristic ?

(3) Give IUPAC name.

(i) $K_3\ [Co(OX)_2\ (CN)_2]$

(ii) $[Mn(en)_2\ Br_2]\ NO_3$

(4) Give the molecular formula of calcium phosphide and stibine

(5) Give electron configuration of Bi (Z = 83) Br (z = 35) elements.

(B) Answer the following questions. **[6]**

(1) Explain allotropes of phosphorous

(2) Explain properties of interstitial compounds.

(3) Give only importance of chlorophyl and hamoglobin

(C) Explain the following questions. (any three) **[9]**

(1) Explai : bi dentate and hexadentate ligands with illustrations.

(2) Explain coloured ions of transition elements.

(3) Explain Wenner's theory.

(4) Explain nature of bonding of V–A group elements.

*_*_*

Marking Scheme

Q. 1. (A) Answer the following objectives **(5)**

(1) According to equation G = H–TS, the value of G depends on enthalpy and absolute value of enthalpy cannot be determine. ∴ G cannot be determine

(2) Conjugate base : $HPO_4^{2-} \rightarrow H_2PO_4^{3-}$

$NH_3 \rightarrow NH_2^-$

(3) Importance of $E = mc^2$ equation.

(i) mass is itself is one form of energy

(ii) Thus, if mass is converted into heat energy, extremely large amount of heat can be produced

(4) When half the Si atoms in chain silicates shares with more O–atoms, then bent or double chain silicates are formed

(5) This symbol indicates that atom A occupies (1–x)th part of its normal lattice site and remaining site being vacant

(B) Solve any two examples (Each of 3 marks) **(6)**

(1) Here, n = 2 mole and $\Delta E^0 = 0.78$ V

$\therefore \Delta G^0 = -nF\Delta E^0$ (total mark 1 1/2)

$= -2 \times 96500 \times 0.78$ volt. quolomb

$= -88140$ joules

But 4.183 j $\rightarrow$ 1 cal

– 88140 j $\rightarrow$ (?)

$\therefore \Delta G^0 = -21071$ cal

Now $\Delta G^0 = -2.303\ RT \log Kc$

$-21.071 = -2.303 \times 1.987 \times 10^{-3} \times 298 \times \log Kc$

$$\therefore Kc = \frac{21.70}{2.303 \times 1.987 \times 10^{-3} \times 298}$$

$$= \frac{21.70}{1363.7 \times 10^{-3}}$$

$= 15.4513$

$\therefore$ Kc = Anti (15.4513)

$Kc = 2.8 \times 10^{15}$

(2) Here, total volume V = 1 litre = 1000 ml

$\therefore$ Molar solubility of $Ca(NO_3)_2 = 0.1 \times \frac{1000}{V_{ml}} = 0.1 \times \frac{1000}{1000}$

Similarly, molarity of $Ba(NO_3)_2 = \frac{0.001 \times 1000}{1000} = 0.0001$ M

Now,

$Ca(NO_3)_{2(aq)} \rightarrow Ca^{2+}_{(aq)} + 2\ NO_3^-{}_{(aq)}$

0.1M 0.1 M 0.2 M

$Ba(NO_3)_{2(aq)} \rightarrow Ba^{2+}_{(aq)} + 2NO_3^-{}_{(aq)}$

0.001 M 0.001 M 0.002 M

$H_2SO_{4(aq)} \rightarrow 2H^+_{(aq)} + SO_4^{2-}{}_{(aq)}$

9.92×10^{-8} M 9.92×10^{-8} M

Now : IP of $CaSO_4$:

$CaSO_{4(s)} \rightleftharpoons Ca^{2+}_{(aq)} + SO_4^{-2}{}_{(aq)}$

$Ip = [Ca^{2+}]\ [SO_4^{2-}]$

$= (0.1)\ (9.92 \times 10^{-8})$

$IP = 9.92 \times 10^{-9}$

But $Ksp = 2.4 \times 10^{-5}$ $\therefore$ IP < Ksp

$\therefore$ $CaSO_4$ will not precipitate

Similarly, IP of $BaSO_4$:

$BaSO_{4(s)} \rightleftharpoons Ba^{2+}_{(aq)} + SO_4^{2-}{}_{(aq)}$

$Ip = [Ba^{2+}]\ [SP_4^{2-}] = (0.001) \times (9.92 \times 10^{-8}) = 9.92\ 10^{-11}$

$\therefore$ Ip > Ksp $\therefore$ $BaSO_4$ will precipitate

(2) CH_3COONa is a salt of NaOH and CH_3COOH Thus, it undergoes hydrolysis

$CH_3COONa_{(aq)} \rightarrow CH_3COO^-_{(aq)} + Na^+{}_{(aq)}$

$CH_3COO^- + H_2O_{(l)} \rightleftharpoons CH_3COOH_{(aq)} + OH^-{}_{(aq)}$

$\therefore \frac{Kw}{Ka} = \frac{[\overline{OH}]^2}{Co}$ $\therefore [OH^-] = \sqrt{\frac{Kw \cdot Co}{Ka}} = \sqrt{\frac{1 \times 10^{-14} \times 0.25}{1.75 \times 10^{-5}}}$

$\therefore$ $[OH^-] = 1.2 \times 10^{-5}$ M

$\therefore$ pOH = $-\log [OH^-] = -\log [1.2 \times 10^5] = -[5 - 0.0969]$

pOH = 4.9031 c $\therefore$ pH + pOH = 14.00

$\therefore$ pH = 14 – 4.9031 = 9.0969

Q. 1. (C) Answer any three (Each of 3 marks) **(9)**

(1) First law :

(i) Energy is neither created nor destroyed

(ii) Total energy in the world is constant

Work : If a force acts on a body and the point on which the force acts is displaced in any direction, we say that the work is done.

There are two types of work in chemistry

(i) Electrical work and (ii) Mechanical work

→ Electrical work is importance in reactions involving ions. While mechanical work is important in reactions involving gase.

→ In gaseous process, the volume of the system changes under constant external pressure Thus, if volume increases, work is done by the system and if volume decreases, work is done on the system.

$\therefore$ work done $W = P(V_2 - V_1) = P\Delta V$

Now : If only P.V type work is done, then, at constant pressure q = q(v) and $W = -P\Delta V$. $\therefore$ According to $\Delta E = q + w$, $\Delta E = q(v) - P.\Delta V$. But if volume does not change then $P\Delta V = 0$. $\therefore$ $\boxed{\Delta E = qv}$

This indicates that "internal energy change of reaction at constant volume is equal to the heat lost or gain by the system.

(2) Hydration of NaCl

(1) → When a salt dissolves in water, some definite no. of water molecules attaches to the ions of salt.This is known as hydration. e.g. NaCl in water.

$$NaCl_{(s)} \xrightarrow{12H_2O_{(l)}} [Na(H_2O)_6]^+_{(aq)} + [Cl(H_2O)_6]^-_{(aq)}$$

This, Na^+ is Lewis acid and H_2O is Lewis base.

Similarly Cl^- is Lewis base and H_2O is Lewis acid.

(2) **Hydrolysis of $CuSO_4$:** $CuSO_4$ is a salt of base $Cu(OH)_2$ and acid H_2SO_4. It hydrolysis as follows :

$$H_2O_{(l)} \rightleftharpoons H^+_{(aq)} + OH^-_{(aq)}$$

$$CuSO_{4(aq)} \rightarrow Cu^{2+}_{(aq)} + SO_4^{2-}$$

$$Cu^{2+}_{(aq)} + 2H_2O \rightleftharpoons Cu(OH)_2 + 2H_3O^+$$

Explanation : According to text book.

(3) Explain :

(1) Ultramarines

They are known as for their attractive colours

Blue $\rightarrow S_2^{2-}$, Green : S_2^{2-}, S_3^{2-} and Red : S_2^{2-}, S_3^{2-} and S_4^{2-} ions.

(2) Importance of first law of thermodynamics.

(i) Bond energy (ii) Heat of formation of compounds (iii) heat of combustion (iv) Enthaly charge and internal energy changes can be determined.

(4) Explain : (1) Amorphorus solids :

$\rightarrow$ Solids which do not have ordered arrangement or definite pattern of symmetry of their constituent particles like atoms, ions or molecules are called amorphous solids.

Explain : acc. to text book page no.

(2) Crystal structure of Zns :

There are two forms of Zns. (i) Zinc bend (ii) Wrutzite.

$\rightarrow$ As C–atoms are arranged in tetrahedral shape, Zn^{2+} and S^{2-} ions are also arranged in tetrahedral shape.

$\rightarrow$ In Wurtzite, Zn^{+2} ions ... hexagonal str.

Zinc blene, S^{2-} ions ... Face centered cubic str.

$\rightarrow$ In Zns, Zn shares its two Valence $\bar{e}$s and s shares its six Valence $\bar{e}$s making total 8 es. for four covalent bond.

$\therefore$ Each ions has co–ordination number $\rightarrow$ 4

Q. 2. (A) (1) The quantity of electricity carried by 1 mole electrons is called one Faraday. 1 F = 96500 C = 6.023×10^{23} electrons

(2) The device in which redox reaction is carried out by passing current through fused or aqueous solutions of electrolytes is called electrolytic cell.

(3) When concentration of each of the reactant in a reaction is 1M i.e. unity, then rate of reaction becomes equal to the rate constant. Such rate constant is called specific rate constant.

(4) The surface or plane having zero probability of electron is called nodal plane.

π and π^* molecular orbital possess nodal planes.

(5) Because energy released during formation of more no. of bonds in SF_6 is greater than energy absorbed in unpairing of electrons.

(B) Solve any two examples (Each of three marks) **(6)**

(1) Molecular weight of Cl_2 = 71 gm/mole

$\therefore$ mole of $Cl_2 = \frac{142}{71} = 2.0$

Anode : $2Cl^-_{(l)} \rightarrow Cl_{2(g)} + 2e^-$ | 1 mole cb $\rightarrow$ 2F
1 mole 2F | 2 mole $\rightarrow$?

$\therefore$ Faraday = 4.0 = 4 × 96500 coulombs

Now Cathode : $Mg^{2+}_{(l)} + 2e^- \rightarrow Mg_{(s)}$
2F 1 mole

2 F $\rightarrow$ 1 mole Mg

4 F $\rightarrow$? $\therefore$ moles of Mg = 2.0 $\therefore$ wt. of Mg = 2 × 24 = 48 gms

Similarly : Cathode : $Na^+_{(l)} + e^- \rightarrow Na_{(s)}$
1 mole 1 mole
(1F)

Thus, 1F $\rightarrow$ 1 mole Na

4F $\rightarrow$ (?) $\therefore$ moles of Na = 4 $\therefore$ weight of Na = 4 × 23 = 92 gm.

(2) $K = \frac{2.303}{t} \times \log \frac{C}{C_o}$

$= \frac{2.303}{2700} \times \log \frac{0.8}{.6}$

$= \frac{2.303}{2700} \times (9.9031 - \bar{1}.778)$

$= \frac{2.303}{2700} \times 0.1253$

$K = 383.4 \text{ second}^{-1}$

Now : $t_{½} = \frac{0.693}{K} = \frac{0.693}{3834}$

$t_{½}$ = 6504 seconds

(3) Velocity V = 3600 km/second = 3600×10^5 cm/second

$$\lambda = \frac{h}{mv} = \frac{6.626\times10^{-27}}{500\times10^{-3}\times3600\times10^{5}} = \frac{6.626\times10^{-27}}{1800000\times10^{2}} = \frac{6.626\times10^{-27}}{1.8\times10^{8}}$$

$\lambda = 3.68 \times 10^{-5}$ cm $= 3.68 \times 10^{-27}$ A^0

→ Such extremely small λ cannot be determined by experiment.

∴ wave nature concept cannot be applied to such particle.

(C) Answer any three : (Each of 3 marks) **(9)**

(1) Fuel cell : fig. and construction of cell

Equations at electrodes

→ importance of the cell

(2) Integrated rate law :

$$N_2O_{5(g)} \rightarrow 2NO_{2(g)} + \frac{1}{2}O_{2(g)} \quad \therefore -\frac{d[N_2O_5]}{dt} = K.[N_2O_5]$$

$$\therefore \text{ But } [N_2O_5] = C \ \therefore -\frac{dc}{dt} = K.C \ \therefore -\frac{dc}{c} = K.dt$$

→ **Now** : Integrating this equation

$$-\int_{c_o}^{c}\frac{dc}{c} = K\int_{0}^{t}dt \ \therefore -\left[\ln C^1\right]_{C_o}^{C} = K[t]_0^t \ \therefore -\ln\frac{c}{Co} = \mathbf{Kt}$$

$$\therefore 2.303 \times \log\frac{w}{c} = Kt \ \therefore K = \frac{2.303}{t} \times \log\frac{Co}{C} \text{ time}^{-1}$$

(3) Explain : (1) Energy barrier

→ There is a presence of energy barries between molecules of reactant and product during reaction.

→ The height of energy barier is an important factor determining rate of reaction.

→ If height is more, rate is less and height is less, rate is more.

→ Energy barrier decreases in presence of catalyst. ∴ rate of reaction increases.

(2) Difference between BMO and ABMO (each point 1/2 mark)

BMO	ABMO
→ lower energy	→ higher energy
→ indicated as	→ Indicated as σ^*, π^*
→ helps in bonding	→ opposes in bonding

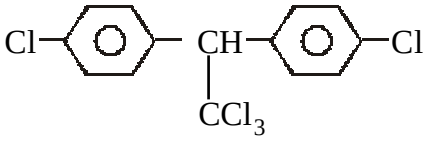
(4) → Molecular orbital diagram with labbels and es.

→ Calculation of bond order B.O. = 1/2[10–6] = 2.0

→ Magnetic property : two unpd. es. Paramagnetic

Q. 3. (A) Answer the following questions (Each of 1 mark) **5**

(1) Because rate of bromination of benzene is very slow.

(2) $CH_2(OH)-CH(OH)-CH_2(OH)$ 

(3) $3CH_3CH_2OH + PI_3 \rightarrow 3CH_3CH_2I + H_3PO_3$

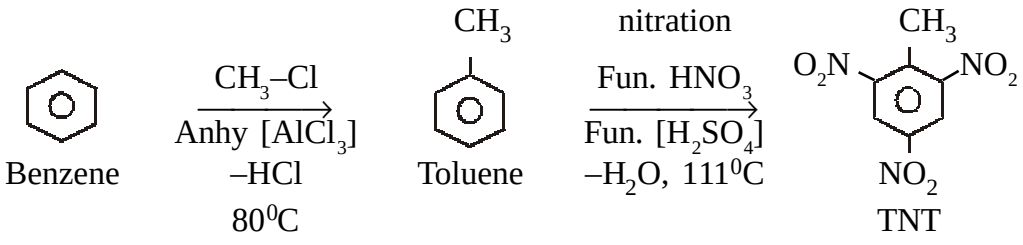
Ethanol Ethyl iodide

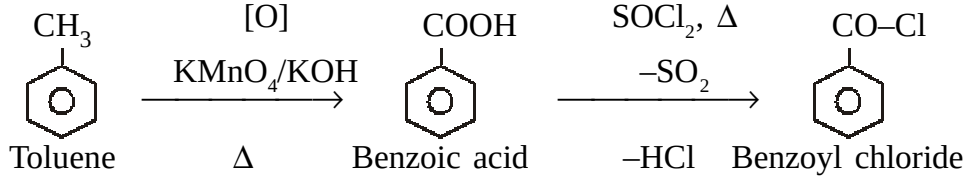
(4) Fr, $t_{1/2}$ = 21 minutes. It is radio active therefore does not occur in nature.

(5) $F_2 + 2KCl \rightarrow 2KF + Cl_2$ is possible.

Because reactivity of F > Cl ∴ F can displace Cl.

(B) Conversions (any three) (Each of two mark) **6**

(1) 

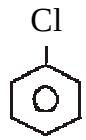
(2) 

(3)

$$\underset{\text{Di–Ethyl ether}}{CH_3CH_2–O–CH_2CH_3} + \underset{\text{conc.}}{2HI} \xrightarrow{\Delta} \underset{\text{Et–iodide}}{2CH_3CH_2I} + H_2O$$

$$\underset{\text{Et–iodide}}{2CH_3CH_2I} + \underset{\text{sodium}}{2Na} \xrightarrow[\text{Wurt}]{\text{Dry ether}} \underset{\text{n–butane}}{CH_3–CH_2–CH_2–CH_3} + 2NaI$$

(4)



Chloro benzene

$\xrightarrow[6–8\%]{\text{Aque + NaOH}}$

$\xrightarrow[360^0C]{300\text{ atm}}$ (Dow) –NaCl

Phenol ...(1)

$\xrightarrow[-H_2O]{\text{Aq.NaOH}}$

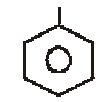
Sodium Phenoxide ...(1)

(C) Answer the following (any three) (Each of 3 marks) **(9)**

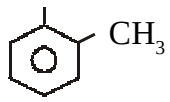
(1) Explain : $\underset{\text{Benzene}}{C_6H_6} + \underset{\text{Ozone}}{3O_3} \longrightarrow \underset{\text{BTO}}{C_6H_6(O_3)_3} \xrightarrow[-3H_2O_2]{Zn/3H_2O} 3$ $\underset{\text{Glyoxal}}{\overset{\overset{CHO}{|}}{CHO}}$

Importance (i) Three C–C single bonds, three C = C double bond
(ii) benzene has hexagonal cyclic structure

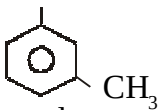
(2) Acc. to M.O. theory 6C and 6H atoms are indentical



Toluene



o–xylene (1:2)



m–xylene (1:3)

p–xylene (1:4)

→ Explain of one isomer of toluene

→ Explanation of three isomers of xylenes

[2](1) β–elimination :

$CH_3–CH_2–Cl + KOH \xrightarrow[-KCl\ -H_2O]{Ethanol} CH_2=CH_2$

Et–chloride — ethene

$CH_4–CH_2–CH_2–Cl + KOH \xrightarrow[-KCL\ -H_2O]{Ethanol} CH_3–CH = CH_2$

1–chloro propane — Propene

OR

$CH_3–\underset{\underset{Cl}{|}}{CH}–CH_3 + KOH \xrightarrow[-KCl,\ -H_2O]{Ethanol} CH_3–CH=CH_2$

2–chloro propane — Discription — propene

(2) Classification of alkyl halides

primary ... $CH_3–CH_2–Cl$

secondary ... $CH_3–\underset{\underset{Cl}{|}}{CH}–CH_3$

tertiary ... $CH_3–\underset{\underset{Cl}{|}}{\overset{\overset{CH_3}{|}}{C}}–CH_3$

[3] (1) Crystal str. of alkali metals

→ 8 coordination no. and BCC–str.

→ Li at V. low temp., 12 co–ordi. no. & hcp str.

(2) Alkali metals have very large size. So they have remarkably low density

Li → half the density of water

Na → slightly less density than water

[4] Preparation of halogen acids (Discription is required)

(i) $CaF_2 + \underset{\text{conc.}}{H_2SO_4} \xrightarrow[\Delta]{} CaSO_4 + 2HF$

(ii) $NaCl + \underset{\text{Conc.}}{H_2SO_4} \xrightarrow{\Delta} NaHSO_4 + HCl$

$H_2 + Cl_2 \xrightarrow{\text{direct}} 2HCl$

(iii) $H_2 + Br_2 \xrightarrow[\Delta]{[pt]} 2HBr$

(iv) $3KI + H_3PO_4 \longrightarrow 3HI + K_3PO_4$

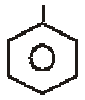
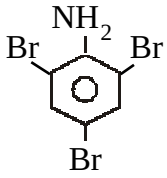
Q. 4. (A) Answer following in short (Each of half–mark) **(5)**

(1) $CH_3–CH_2–\underset{\underset{O}{||}}{C}–CH_2–CH_3$ Di–Et–Ketone

$CH_3–\underset{\underset{OH}{|}}{\overset{\overset{CH_3}{|}}{C}}–CN$

(2) Formaldehyde is gas but its aqueous solution is known as formaline

Uses : In preservation of dead bodies of animals

(3)  + $3Br_2$ water $\xrightarrow[\text{bromination}]{\text{Direct}}$ 

Aniline $\quad -3HBr$ $\quad$ 2,4,6 Tri bromo aniline

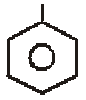
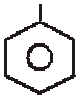
(4) Some colourless organic compounds have affinity toward the fabric. Moreover, they have fluorescent properly in presence of sunlight. Such compounds are called optical brightness.

(5) Two difference names of isocyanides are

(i) Carbyl amine compounds and

(ii) Iso-nitriles

(B) Any three conversions (Each of 2 marks) **6**

(1)  $CO-CH_3$ $\xrightarrow[KMNO_4/KOH]{[O],\ \Delta}$  $COOH$ $\xrightarrow[CH_3CH_2OH]{\text{Esterification}}$  $COO-CH_2CH_3$ $+ H_2O$

Aceto–phenone $-CO_2, -H_2O$ Benzoic acid conc.$[H_2SO_4]$, Δ Et.–benzoate

(2) $CH_3COOH \xrightarrow[LiAlH_4]{2H_2} CH_3CH_2OH \xrightarrow[350-400^0C]{[Al_2O_4]} CH_2=CH_2$

Acetic acid –H2O Ethanol $-H_2O$ Ethene ...(1)

(4)  $N=N-Cl$ $\xrightarrow[-N_2\uparrow]{\Delta, H_2O}$  OH $\xrightarrow[-HCl]{\Delta, CH_3CO-Cl}$  $OCOCH_3$

Benzene diazonium chloride –HCl phenol ...(1) Acetylation Phenyl acetate ...(1)

[C] Answer any three (Each of three mark) **9**

(1) Explain (1) Condensation of ethanal

CH_3-CHO – Ethanal

- $\xrightarrow[[H^+], -H_2O]{NH_2OH}$ $CH_3-C(=N-OH)-H$ Acetaldoxime
- $\xrightarrow[[H^+], -H_2O]{NH_2-NH_2}$ $CH_3-C(=N-NH_2)-H$ Acetaldehyde hydrazone
- $\xrightarrow[[H^+], -H_2O]{NH_2-NH-C_6H_5}$ $CH_3-C(=N-NH-C_6H_5)-H$ Acetaldehyde Phenyl hydrazone ...

(2) $CH_3–CHO \xrightarrow{N_2H_4 \mid KOH} CH_3–CH_3 + N_2 \uparrow + H_2O$
Acetaldehyde

$CH_3–Co–CH_3 \xrightarrow{N_2H_4 \mid KOH} CH_3–CH_2–CH_3 + N_2 \uparrow + H_2O$
Propane

Explanation is required acc. to text book.

[2] Preparation of amide :

$CH_3CO–Cl + 2NH_3 \rightarrow CH_3CONH_2$ OR

*** Any two chemical reactions**

[3] Explain :

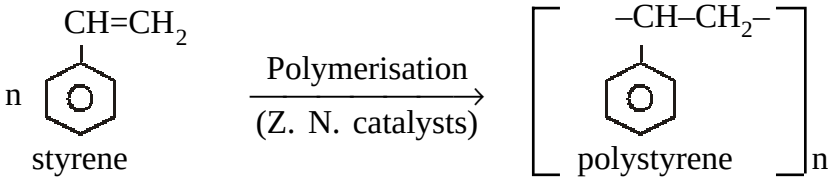
(i) Degree of polymerisation

→ No. of repeating units is called d. p.

→ If d. p. > 25 ... heavy polymers

→ If d. p. < 25 ... light polymers

(ii)



styrene (n–molecules)

Uses : In buttons, tooth brush handes, cock of botle, pipes, In cabinates of radio, freez, TV etc.

(4) Explain :

(1) Hormones :

→ Secretion of chemical messanger in ductless glands.

→ Inhibites circulation

(2) CNS and CND durgs :

→ some compounds like opium, morphin etc. decreases the activity of CNS

→ Some compounds like hashish, marijuana, Ethanol increase the activity to CNS

Q. 5. (A) Answer the following in short (Each one mark) (5)

(1) Black As : (i) Mixed properties of metal and non metals.
(ii) Non–conductor of heat adnd electric current.

(2) $KMnO_4$, strong oxidizing property

(3) (i) Potassium dicyano bis (oxalato) cobaltate (III)

(ii) Dibromo bis (ethylene diamine) manganese (III) nitrate

(4) Ca_3P_2 and SbH_3

(5) Bi(Z = 83) [Xe] to $4f^{14}5d^{10}6s^26p^3$

Br(Z = 35) . [Ar] $3d^{10}$ $4s^2$ $4p^5$

[B] Answer the following : (Each of two marks) **(6)**

(1) Allopropes of phosphorous yellow phospherous and its characteristics

(2) Properties (any four)

(i) Bonding forces increase (ii) m.p. and b.p. increases.

(iii) Hardness increases (iv) good electrical conductors.

(v) lusture like metal

(3) Chlorophy : → essential for photosynthesis.

→ responsible for geen colour of plants.

Hemoglobin : → Provides O_2 to the muxles.

→ resoponsible for red colour of blood.

Q. 5 (C) Answer the following (any three) (Each three mark) **(9)**

(1) Didentate : two co–ordination sites

eq. $CH(-\ddot{N}H_2)-CH_2-\ddot{N}H_2$, CO_3^{2-}, SO_4^{2-} etc

Hexadentate : Six co–ordination sites

give example of Edta with structure

(2) Coloured ions : (i) coloured property (ii) colourless property

(according to text book)

(3) Werner's theory : Each two points 1 mark.

(according to text book)

(4) Nature of bonding : → electron configuration

(i) Covalent bonding → sharing of $3e^-$s ... NH_3, PH_3

→ sharing of $5e^-$s ... PCl_5, NH_4^+ etc.

(ii) ionic bonding : → ions in +5 state not possible

→ ions in +3 state ... Sb^{3+}, Bi^{3+}

→ ions in –3 state ... Li_3N, Na_3P

(Write acc. to text book)

*_*_*

CHEMISTRY (052) E

Question Paper-V

Total Marks : 100 **Time : 3 Hours**

Note : This Question paper contains five questions and all are compulsory.

Q. 1 (A) Answer the following objective questions : **5**

(1) Define : Entropy.

(2) Give dimeric structure of silicate compounds.

(3) Which sulphides are water insoluble.

(4) What is change in pH value during 99.9 to 100% Neutralization of Acid with Base.

(5) What is the name of compound used to prepare magnetic taps.

(B) Solve any two Numericals : **6**

(1) Calculate equilibrium constant for given reaction at 25^0C.

$2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)}$

ΔG^0 for So_3 and So_2 at 25^0 C are –71.89 Kcal mole^{-1} and –88.52 cal. mole^{-1}.

(2) Calculate PH value of solution on adding 24 ml 0.1M NaOH solution to 25 ml 0.1 M Hcl solution.

(3) Solubility of $PbSO_4$ is 1×10^{-4} M at 25^0C temp. How many grm. of $PbSO_4$ can be dissolved in 2 lit 0.02 M K_2So_4 solution at this temp.

Pb = 208, S = 32,

K = 39, 0 = 16

(C) Answer any three of the given : **(9)**

(1) Explain giving defination enthalpy and internal energy.

(2) How are defects produced in crystals ? Give no of atoms in perunit cell of F. C. C. and B. C. C.

(3) Prove the relation $[OH^-] = \sqrt{KbCo}$ for aq. solution of methylamine.

(4) (1) Explain diamagnetic properties.

(2) Give common Ion effect with one use in Qualitative analysis.

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

(1) What is half life time (t 1/2)

(2) Write cathodic reaction of fuel cell.

(3) Give factours on which products of electrolysis depends.

(4) Give type of hybridization and shape of SF_6

(5) Write schrodingers wave equation.

(B) Solve any two Examples : **6**

(1) An electron is moving with a velocity of 3×10^7 cm sec^{-1}. Calculate its wave length. Mass of an electron is 9.1×10^{-28} grm. and h = 6.626×10^{-27} erg.

(2) The Con. of a first order reaction's reactant becomes 40% of its initial Con. in 1600 sec. calculate time to complete 60% of this reaction.

(3) Calculate equilibrium constant of the reaction.

$Ni_{(s)} + Co^{+2}{}_{(aq)} \rightarrow Ni^{+2}{}_{(aq)} + Co_{(s)}$

$E^0Ni/Ni^{+2} = 0.23V$

$E^0Co/Co^{+2} = 0.28V$

(C) Answer any three question from the following : 9

(1) Explain chemistry of Rusting of Iron. How it can be stop ?

(2) Describe the construction. Working and uses of standard hydrogen electrode.

(3) Derive the equation for rate constant of a first order reaction. Using Integrated rate law method.

(4) Explain Heisenberg's principle.

Q. 3. (A) Answer the following objective questions : 5

(1) Write the reaction when Ethyl Benzene is healted at 630^0c with Zinc Oxide.

(2) Give structure of Anthracene, p–cresol.

(3) Give formula of Lithium Carbide. Perchloric Acid.

(4) Give the name of scientist who first isolated Na and K.

(5) Give Equation of the reaction when toluene reactwith Cl_2 at 111^0C in presnece of sunlight.

(B) Write the chemical Equation for any three of to following conversions (two steps) 6

(1) Benzyl Alcohol from toluene.

(2) 1 phenyl–1 Ethanol from Benzene.

(3) Acetanilide from chloro Benzene.

(4) Phenetol from phenol.

(C) Answer any three question from the following : 9

(1) Explain the following reactions with equations.

(a) Sulphonation of Benzene

(b) Acetylation of Benzene

(2) Write short note on : (1) Lucas test (2) Wurtz reaction

(3) Give the properties in which Li differ's from the other elements of it's group.

(4) Explain : (1) Benzene does not oxidize

(2) Classify in Ortho and meta directing groups

–OH, $–SO_3H$, $–NO_2$

Q. 4. (A) Answer the following objective questions : 5

(1) Give IUPAC name $C_6H_5NHCH_3$, C_2H_5CN

(2) What is Hyperglycemia and Hypoglycemia

(3) Give Chemical name and structure of Asprin.

(4) Give name and structureof yellow azodye.

(5) Give the reaction when Benzoic Acid is heated with thionyl chloride.

(B) Write the chemical Equation for any three conversions (two steps) 6

(1) Aniline from Benzoyl chloride

(2) Lactic Acid from Acetaldehyde

(3) Phenol from Aniline

(4) Triethyl amine from ethy amine.

(C) Answer the three questions from the following : 9

(1) Give classification of polymers on the bases of structure.

(2) Give short note on : (1) Wolff kishnes reduction (2) Carbyl amine test

(3) Write preparation and uses of : Nitrolim, PVC

(4) What is diazotization ? Write the reaction to prepare. Iodobenzene from diazoniam salt.

Q. 5. (A) Answer the following objective questions : **5**

(1) How is Red phosphorous prepared.

(2) Define Co–ordination site of ligand.

(3) Give name of complex compound.

$[Cr(en)_2Co_3]NO_3$

(4) What are vanadates ?

(5) How much vitamin B_{12} is required perday to a person.

(B) Answer the following questions : **6**

(1) Why Inert gas do not forms compounds.

(2) Explain most stable oxidation state of Ti is 4 but Ti^4 Ion does not exist.

(3) Give the physical properties of transition elements.

(C)Answer any three questions from the following : **9**

(1) Explain importance of complex occuring in nature

(2) Discuss the shape and magnetic properties of complex $[NiCl_4]^{2-}$

(3) Give the structure of : (1) Pyrophosphoric Acid (2) hypophosphoroous Acid

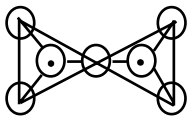
(4) “Transition metal Ions have high tendency to form complex compounds” Explain.

_*_

: ANSWER :

Q. 1. (A) Anser in short **(5)**

(1) The measure of randoness in a system is called entropy

(2) 

(3) Sulphides of alkali metals and alkaline earth metals

(4) From 4.30 to 7.00

(5) CrO_2

(B) Solve any two numericals **(6)**

(1) $\Delta G^0 = \Sigma \Delta G^0 f_{(products)} - \Sigma \Delta G^0 f_{(reactants)}$

$= [2\Delta G^0 fSO_3] - [2\Delta G^0 fSO_2 + \Delta G^0 fO_2]$

$= [2(-88.52)] - [2(-71.79) + 0]$

$= -177.04 + 143.58]$

$\Delta G^0 = -33.46$ Kcal

Now

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

$-33.46 = -2.303 \times 1.987 \times 10^{-3} \times 298 \times \log Kp$

$\therefore \log Kp = \dfrac{33.46}{2.303 \times 1.987 \times 10^{-3} \times 298}$

$= \dfrac{33.46}{1363.7}$

$\log Kp = 24.53$

$\therefore Kp = \text{Antilog } (24.53)$

$Kp = 3.44 \times 10^{24}$

(2) 1000 ml HCl $\rightarrow$ 0.1 mole HCl

25 ml HCl $\rightarrow$ (?)

$\therefore$ moles of HCl = 0.0025

Similarly, moles of NaOH = $\dfrac{0.1 \times 24}{1000}$ = 0.0024 mole

$NaOH + HCl = NaCl + H_2O$

Thus, 0.0024 mole NaOH will neutralize 0.0024 moles of HCl

$\therefore$ Unneutralized moles of HCl = 0.0025 – 0.0024

= 0.0001 mole

Now, total volume = 24 + 25 = 49 ml

$\therefore$ Molarity of HCl = $\dfrac{1 \times 10^{-4} \times 1000}{49}$

$[HCl] = 2.04 \times 10^{-3}$ M

Now, HCl is strong acid, ionizes completely

$HCl + H_2O \rightarrow Cl^- + H_3{}^+O$

$\therefore \quad [H_3{}^+O] = 2.04 \times 10^{-3}$ M

$\therefore \quad pH = -\log [H_3{}^+O] = -\log 2.04 \times 10^{-3}$

$= 3 - 0.3096$

$pH = 2.6904$

(3) $PbSO_{4(s)} \rightleftharpoons Pb^{2+}{}_{(aq)} + SO_3{}^{2-}{}_{(aq)}$

$K_2SO_{4(aq)} \rightarrow 2K^+{}_{(aq)} + SO_4{}^{2-}{}_{(aq)}$

$2(0.02)M \quad 0.02$ M

$\therefore$ In solution, $[Pb^{2+}] = S = ?$

$[SO_4{}^{2-}] = (S + 0.02)$

$\cong 0.02$ M $[\because S < < < 0.02)$

Now,

$\therefore \quad Ksp = [Pb^{2+}] [SO_4{}^{2-}]$

$1 \times 10^{-4} = (S) (0.02)$

$S = 5 \times 10^{-3}$ mole/litre

Now, Molecular weight of $PbSO_4 = 208 + 32 + 64$

$= 304$ gm/mole

$$\text{Molar solubility} = \frac{\text{Solubility in gm}}{\text{Molecular weight}} \times \frac{1000}{\text{Volume in ml}}$$

$$5 \times 10^{-3} = \frac{W}{304} \times \frac{1000}{2000}$$

$w = 5 \times 10^{-3} \times 608$

$w = 3.04$ gm

(C) Answer any three : **(9)**

(1) Internal energy :

Each substance is a huge store of energy. The energy stored in any substance is known as internal energy.

This energy is stored as potential energy and kinetic energy.

The absolute energy of internal energy can not be calculated. It is a state function and extensive properties.

Enthalpy :

Usually chemical reactions are carried out in an open container under constant pressure. Thus, a new state function called enthalpy (H) is defined.

$H = E + PV$

If the state of a system changes, the enthalpy change ΔH is as below :

$\Delta H = \Delta E + \Delta(PV)$

$= \Delta E + P\Delta V + V\Delta P$

but at constant pressure, $\Delta P = 0$

$\therefore \Delta H = \Delta E + P\Delta V$

Now, according to first law of thermodynamics. $\Delta E = q + w$ and under constant pressure $q = q(p)$ and $w = -P\Delta V$

$\Delta H = (q(p) - P\Delta V) + P\Delta V$

$\therefore \quad \Delta H = q(p)$

(2) (i) At a temperature higher than absolute zero, the ions or atoms vibrate and the arrangement becomes slightly random. Due to this, the displacement of cations and anious from their proper positions causes defects in the crystal.

(ii) Moreover, the introduction of some impurities in the crystal also produces defects.

Number of atoms in FCC $= \left[8 \times \frac{1}{8}\right] + \left[6 \times \frac{1}{2}\right]$

$= 1 + 3$

$= 4$ atoms

Number of atms in BCC $= \left[8 \times \frac{1}{8}\right] + (1)$

$= 1 + 1$

$= 2$ atoms

(3) $CH_3–NH_2 + H_2O \rightleftharpoons CH_3NH_3^+ + O\overline{H}$

$\therefore$ Ke $= \dfrac{\left[CH_3 - NH_3^+\right]\left[O\overline{H}\right]}{\left[CH_3 - NH_2\right]\left[H_2O\right]}$

When methyl amine dissolves in water, the decrease in concentration of water is negligible compare to concentration to pure water. So the concentration of water is accepted as constant. This constant $[H_2O]$ is combined with Ke and new constant Kb is written.

$\therefore$ Ke $\times [H_2O] =$ Kb $= \dfrac{\left[CH_3 - NH_3^+\right]\left[O\overline{H}\right]}{\left[CH_3 - NH_2\right]}$

$\rightarrow$ Now CH_3NH_2 is weak base. Thus, if ionizes only slightly. Moreover, $CH_3NH_3^+$ and OH^- ions are produce in equal mole ratio.

$\therefore \quad [CH_3NH_3^+] = [OH^-]$ and $[CH_3NH_2] =$ Co

$\therefore \quad$ Kb $= \dfrac{\left[O\overline{H}\right]}{\left[CH_3NH_3\right]}$

Kb $[CH_3NH_2] = [OH^-]^2$

$\therefore$ Kb.Co $= [OH^-]^2$

$\therefore \quad [OH^-] = \sqrt{Kb \cdot Co}$ ...(1)

(4) (1) Diamagnetic Substances :

$\rightarrow$ The substance which are repelled by an external magnetic field are called dia-magnetic substances.

$\rightarrow$ When such substances are place in external magnetic field, they tend to move away from the stronger part to the weaker part of the applied magnetic field e.g. TiO_2

→ Diamagnetic property is due to the substances having atoms with closed shells of electrons or with all electrons paired.

→ The magnetic susceptibility of such substances is negative.

→ Larmor circulation : Under the influence of an external magnetic field, the electrons in the closed shells of every substance experience a force. This force sets them into motion about the direction of applied magnetic field as the axis and as a result another magnetic field is induced with its direction opposite to that of the applied field. The induced field acts against the applied field. So the substances are repelled. This kind of motion of electrons is Known as "Larmor Circulation"

(2) In III–A group of qualitative analysis, NH_4Cl is added before NH_4OH to the given solution.

e.g. $NH_4OH_{(aq)} \rightleftharpoons NH_4^+{}_{(aq)} + OH^-{}_{(aq)}$

$NH_4Cl_{(aq)} \rightarrow NH_4^+{}_{(aq)} + Cl^-{}_{(aq)}$

common ion

→ Here, NH_4Cl being strong electrolyte, ionizes completly and produces large connections of NH_4^+ ions. So the concentration of NH_4^+ ions increases. So the equilibrium of NH_4OH shifts in the reverse direction. As a result, ionization of NH_4OH decreases. Here the concen. of OH^- ions decrease to a large extent.
$\therefore$ $[OH]^-$ remains very low.

→ Now, the solubilities of hydroxides of group III–A ions Al^{3+}, Fe^{3+}, Cr^{3+} and Fe^{2+} are very low compared to the hydroxides of later groups i.e. III–B, IV and Mg^{2+}. So under low concentration of OH^- ion, only Al^{3+}, Fe^{3+}, Cr^{3+} and Fe^{2+} ions are precipitated as hydroxides.

→ While the solubility of hydroxides of group III–B, IV and Mg^{2+} are comparatively high. So under low concen. of OH^- ions these groups ions do not precipitate as hydroxides.

Q. 2. (A) Answer the following objectives ...(5)

(1) The time taken by the reaction to consume half (50%) of initial concentration of reactant is known as half– life time of reaction

(2) $O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$

(3) Factors : (i) Nature of electrodes
(ii) Concentration of electrolytes

(4) SF_6 : Hybridization $\rightarrow sp^3d^2$
shape $\rightarrow$ Octahedral

(5) $\frac{d^2\psi}{dx^2} = \frac{d^2\psi}{dy^2} = \frac{d^2\psi}{dz^2} = \frac{8\pi^2 m}{h^2}(E - V)\,\Psi = 0$

(B) Solve any two examples : (6)

(1) $\lambda = \frac{h}{mv} = \frac{6.626 \times 10^{-27}}{9.1 \times 10^{-28} \times 3 \times 10^7} = 24.25A^0$

(2) $K = \frac{2.303}{t} \times \log \frac{a}{a-b}$

$t_{40\%} = \frac{2.303}{K} \times \log \frac{100}{60}$

$\therefore\ t_{40\%} = \frac{2.303 \times 0.2219}{K}$

Now,

$t_{60\%} = \frac{2.303}{K} \times \log \frac{100}{40}$

$= \frac{2.303 \times 0.3980}{K}$

Now,

$\frac{t_{60\%}}{t_{40\%}} = \frac{2.303 \times 0.3980}{K} \times \frac{K}{2.303 \times 0.2219}$

$\frac{t_{60\%}}{1600} = \frac{0.3980}{0.2219}$

$\therefore\ t_{60\%} = 2871$ seconds

(3) Equilibrium constant

$Ni_{(s)} + CO^{2+}_{(aq)} \rightleftharpoons NI^{2+}_{(aq)} + Co_{(s)}$

$\Delta E^0 = E^0 Ni/Ni^{2+} - E^0 ColCo^{2+}$

$= 0.23 - 0.28$

$\Delta E^0 = -0.05$ volt

Now, At equilibrium $\Delta E = 0.000$, Kc = ?

$\Delta E = \Delta E^0 - \frac{0.0592}{n} \times \log \frac{[Ni^{2+}]}{[Co^{2+}]}$

$0.00 = -0.05 - \frac{0.0592}{2} \times \log Kc$

$\therefore \log Kc = \frac{0.05}{0.0296}$

$\therefore = -1.690$

$\therefore\ Kc = \text{Antilog } (-1.690)$

$= \text{Antilog } (2.310)$

$Kc = 2.042 \times 10^{-2}$

Q. 2. (C) Explain following (any three) **9**

(1) Corrosion of metal :

→ The formation of the rust on the surface of some metals by a chemical rreaction between **oxygen of air and atoms of metals** lying in contact with air is known as corrosion.

→ e.g. Rusting or ison, formation green salts of utensils of copper and brass, tarnishing of shing silver etc. are examples of corrosion.

→ **Anodic Oxidation :** The arrangement of atoms in an iron rod or a container can never be perfect. Whenever even a slight bent in a rod exists, the microscopic

imperfection is created in the crystalinc structure. Moreover, the crystal structure of metal is **never perfect**. In addition, impurity of **Cu** metal is also present in minute proportion in iron. So the surface of microstal is **very reactive**. Due to this, the atoms present in this surface **can lose** the electrons easily and get converted into positive (+ve) ions. Thus, metal at bent acts as an anode. Water molecules needed in this reaction are available from moisture of air.

Anode : (At bent) : $Fe_{(s)} \rightarrow Fe^{2+}_{(aq)} + 2e^-$

Cathodic Reduction : The electrons set free by anode are conducted by the rod and reach to a such point where they can reduce O_2 of air in presence of H^+ ions. This point on the surface acts as a cathode.

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

→ H^+ ions required in this reaction are produced by the dissociation of H_2CO_3. This H_2CO_3 is formed on the surface of the rod by dissolution of CO_2 gas in the moisture present on the surface of the rod.

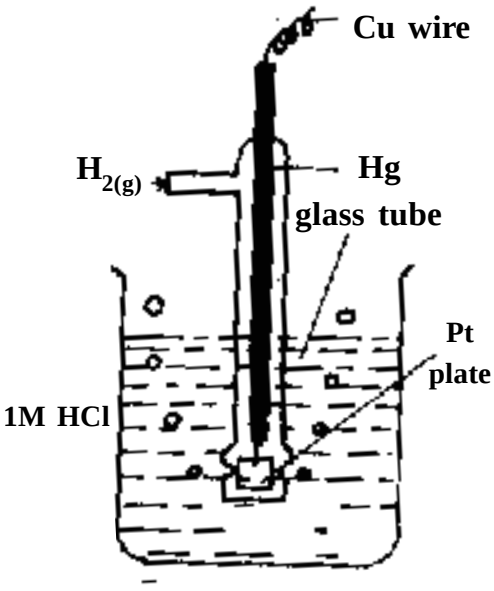
→ If H^+ ions are not available on cathode, O_2 dissolved in moisture gets reduced to $OH^-_{(aq)}$.

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

→ $Fe^{2+}_{(aq)}$ formed by the oxidation are further oxidized to Fe^{3+} by atmospheric oxygen. These Fe^{3+} ions migrate towards cathode and eventually fron $Fe_2O_3.xH_2O$.

→ Corrosion of Fe can be prevented : (i) by avoiding the contact of metal surface with moisture. (ii) For this purpose the surface of iron is coated with thin layer of Zn metal, (iii) by attaching iron plates with metals like Mg or Zn. Thus, Fe becomes cathod and Mg or Zn acts as an anode. Because $E^0_{Mg/Mg^{2+}} > E^0_{Fe/Fe^{2+}}$

(2) Standard Hydrogen Electrode. (SHE)



→ **Construction :** 1 M aqueous solution of HCl (H_3O^+) is filled in a container. A platinum plate coated with **platinum black** is dipped in 1 M $HCl_{(aq)}$ solution.

→ This platinum plate is connected with a small piece of platinum wire and it is sealed in a glass–tube. The another end of this Pt wire is in contact with a small quantity of mercury A thin copper wire which is also in contact with mercury is used to connect external circuit. This half cell is known as standard hydrogen electrode. $H_{2(g)}$ is bubbled over platinum plate at 25^0 C and 1 atm pressure.

→ **Working :** This electrode is connected with another half–cell to form a complete cell. It acts either as an anode or a cathode. When it acts as an anode H_2 gas gets oxidized into H^+ ions. When it acts as a cathode $2H^+$ ions gets reduced to H_2 gas on the plate.

Anode : $\frac{1}{2}H_2(g.1\ atm) \rightarrow H^+_{(aq.1M)} + e^-$

Cathode : $H^+_{(aq,1M)} + e^- \rightarrow \frac{1}{2}\ H_{2\ (g,1atm)}$

→ Thus, this electrode has a tendency either to accept electrons or to release electrons. However, the intensity of this tendency is assigned arbitarily a value of 0.00 volt. So the relative tendency of other electrodes to release or gain the electrons can be determined easily.

→ **Use :** This electrode is used to determine the standard potential of another electrodes. The electrode of which potential is to be determined is connected with a standard hydrogen half cell. Then using a salt bridge an electrochemical cell is completed. And ΔE^0 of the cell is measured by potentiometer and using following formula potential of another electrode can be calculated.

$\Delta E^0_{cell} = E^0_{ox(anode)} - E^0_{ox\ (cathode)}$

(3) Integrated rate law.

Following reaction occurs in forward direction and it isfirst order.

$N_2O_{5(g)} \rightarrow 2NO_{2(g)} + \frac{1}{2}\ O_{2(g)}$

$-\frac{d[N_2O_5]}{dt} = K\ [N_2O_5]$

if $[N_2O_5] = C$ mole/litre

$\frac{dc}{dt} = K\ .\ C$

$\therefore \quad -\frac{dc}{c} = K\ .\ dt$

Now, integrating this equation between following limits.

Initial concentration c = co when t = to and concentration c = c when t = t.

$-\int_{co}^{c}\frac{dc}{c} = K\int_{0}^{t}dt$

$-[\ln c]_{Co}^{C} = K[t]_0^t$

$-\ln\frac{C}{Co} = K\ .\ t$

$2.303\ \log\ \frac{Co}{C} = K\ .\ t$

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

→ The unit of K forfirst order is time^{-1} i. e. second^{-1}, minute^{-1} etc.

(4) State the explain Heisenberg's Uncertainty Principle.

Ans. The speed and the position of a plane flying in sky can be determine accurately at any moment.

→ But "it is not possible to determine simultaneously the position and the speed

of moving microscopic particles like electron, proton, neutron in a space with high accuracy." It is known as a Heisenberg's uncertainty principle.

→ If a radiation having λ wavelength is used to locate a microscopic particle in space, the minimum uncertainly in the measured value sould be $\pm\lambda$. Therefore to minimize the value ofuncertainty in the measured value of position of the partcile, the wavelength of radiation used in the experiment should be very small as far as possible. Since the momentum (p) of a photon is given by $P = \frac{h}{\lambda}$, the momentum of a photon of radiation having very small wavelength is very large.

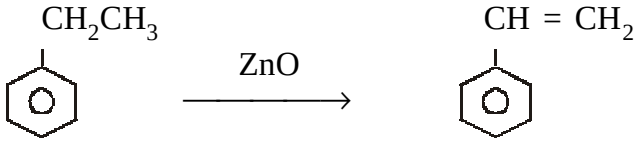
→ When such photon hits a microscopic particle, some unknown faction of its energy is transferred to the particle. As a result, the velocity of the particle increases suddenly to a high value. Thus, if the momentum of a particle is to be determined simultaneously with the determination of position of the particle, the measured value of the momentum would be highly uncertain.

→ It is possible to show that "the product of uncertainties in values of position and momentum determined simultaneously is atleast equal to $h/4\pi$ or more".

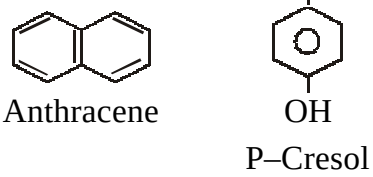
→ $\therefore \Delta\chi \times \Delta p \geq \frac{h}{4\pi}$ | Where h = Planck's constant
Δp = uncertainty in its momentum.
$\Delta\chi$ = uncertainty in the position of a particle.

→ Above equation indicates that if, any attempt is made to reduce uncertainty of one kind then there increases the uncertainty of another kind. Thus, it is understood that the path of a particle going from one point to another point cannot be predicted with a very high accuracy.

Q. 3 (A) Answer in short : **(5)**

(1) 

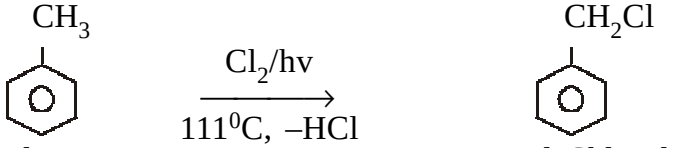
Ethyl benzene 630^0C, $-H_2$ Styrene

(2) 

Anthracene P–Cresol

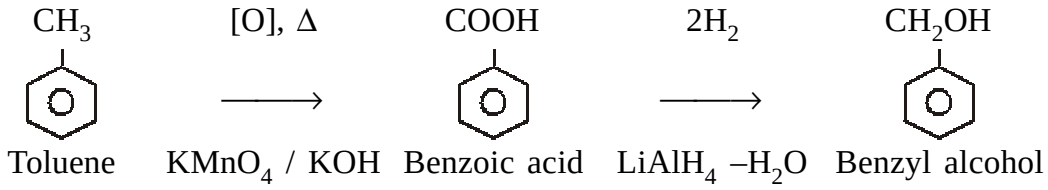
(3) Li_2C_2 and $HClO_4$

(4) Humphrey Davy

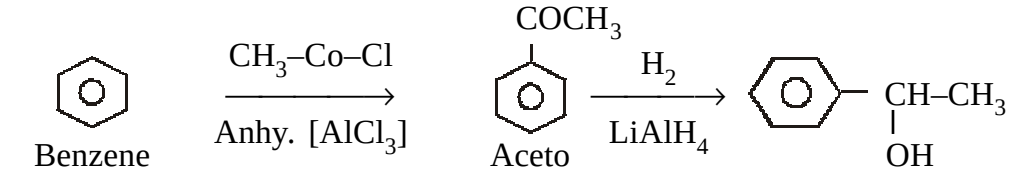
(5) 

Toluene 111^0C, $-HCl$ Benzyl Chloride

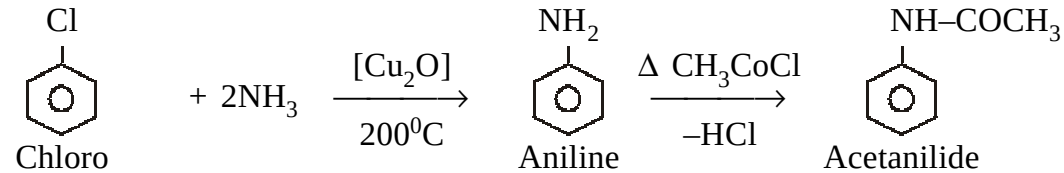
(B) Any three conversions : **(6)**

(1) 

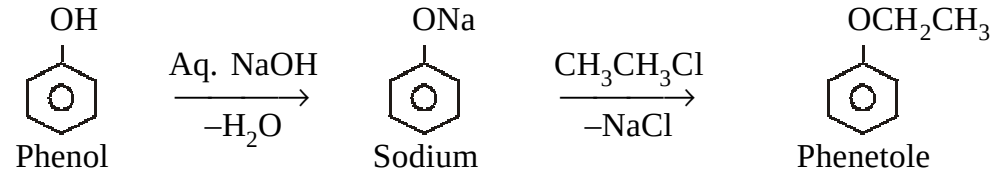
Toluene $KMnO_4$ / KOH Benzoic acid $LiAlH_4$ $-H_2O$ Benzyl alcohol

(2) 

Benzene Aceto Phenone 1–Phenyl, 1–Ethanol

(3) 

Chloro benzene Aniline Acetanilide

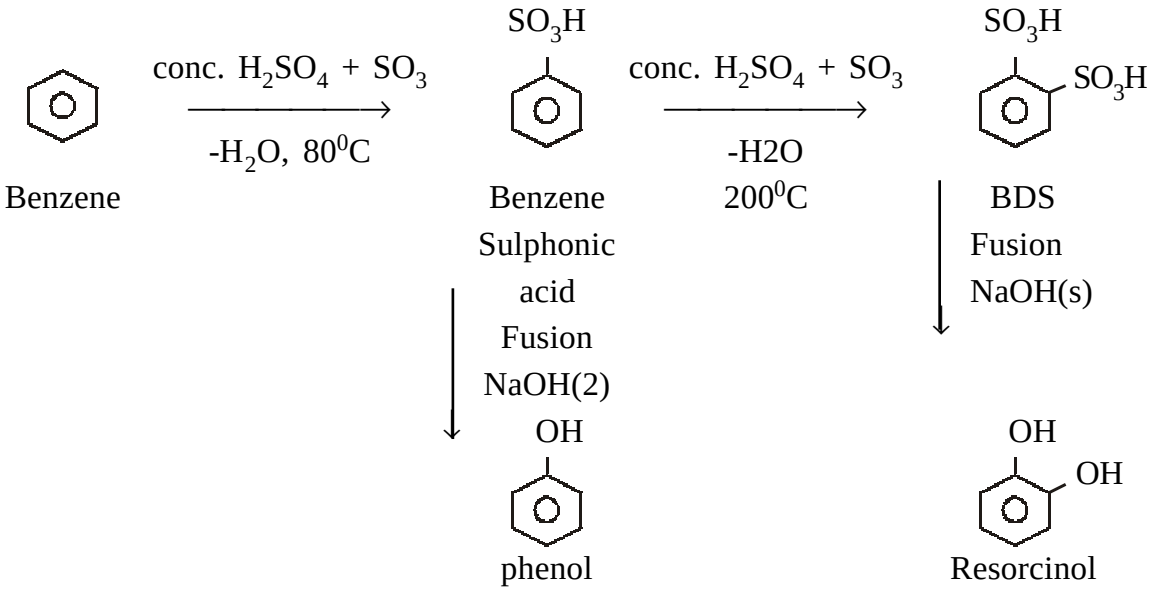
(4) 

Phenol Sodium Phenoxide Phenetole

Q. 3. (C) Answer in the following (three) **9**

(1) Sulphonation of benzene

$H_2SO_4 + H_2SO_4 \rightleftharpoons SO_3H^+ + HSO^-_4 + H_2O$



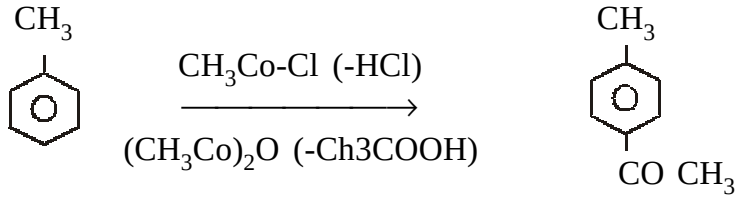
→ When benzene is heated with conc. H_2SO_4 and SO_3 at 80^0C, it gives benzene sulphonic acid. If more H_2SO_4 is taken and temperature is increased to 200^0C for long time then it gives benzene m-disulphonic aid.

→ Here, $-SO_3H$ group is m-directing, so second incoming $-SO_3H$ goes to m-position giving BDS.

→ When these products are fused with solid NaOH, give phenol and resorcinol.

→ In sulphonation, SO_3H^+ is attracted by π-electron cloud of benzene and it displaces aromatic substitution reaction.

Acylation of toluene :



Toluene 111^0C. Anhy. [AlC;$_3$] p=methyl acetophenone

Where toluene is heated with acetyl chloride or acetic anhydride at 111^0C, in presence of anhy. $AlCl_3$ it gives p-methyl acetophenone. Here CH_3 grp is o+p directing. So-$COCH_3$ grp is attached to p-position.

(2) (1) Explain : Lucas Test : **(Imp.)**

$$\underset{\text{alcohol}}{R\text{–}OH} + \underset{\text{hydrochloric acid}}{\text{conc. HCl}} \xrightarrow[\Delta]{\text{anhy. } [ZnCl_2]} \underset{\text{alkyl chloride}}{R\text{–}Cl} + H_2O$$

→ When alcohol is heated with conc. HCl in presence of anhydrous $ZnCl_2$, it gives alkyl chloride. This reaction is fast with tertiary alcohol, Slow with secondary alcohol and difficult with primary alcohol. Thus, Primary, Secondary and tertiary alcohol can be distinguished by this reaction. This test is called Lucas test.

→ Test and Observations :

→ In this test, a given sample of alcohol is mixed with conc HCl and anhydrous $ZnCl_2$ and shaken well and the mix. is kept for observation.

(i) If in few minutes, oily drops are appeared on the upper layer of the mixture, it must be a tertiary alcohol. (3^0)

(ii) If it takes about five minutes for the solution to become milky, it must be a secondary (2^0) alcohol.

(iii) And if mixture remains clear i.e. no reaction occur. It must be a primary (1^0) alcohol.

(2) Wurtz reaction :

$$\underset{\text{Methyl Iodide}}{2CH_3I} + \underset{\text{Powder}}{2Na} \xrightarrow[\text{ether}]{\text{anhy.}} \underset{\text{Ethane}}{CH_3\text{–}CH_3} + \underset{\text{Sodium Ionide}}{2NaI}$$

$$\underset{\text{Ethyl chloride}}{2CH_3–CH–Cl} + \underset{\text{Sodium}}{2Na} \xrightarrow[\text{ether}]{\text{anhy.}} \underset{\text{n–Butane}}{CH_3–CH_2–CH_2–CH_3} + 2NaCl$$

→ When alkyl halide is reacted with powdered sodium metal taken in anhydrous ether, it gives an alkane. This alkane contains double number of C–atoms compared to initial alkyl halide. This reaction is known as Wurtz reaction. By this reaction methyl iodide give ethan and Ethyl chloride gives butane.

(3) Explain how Li differs from other alkali metals. (Specific)

Ans. (1) The under lying closed shell in Li contains only 2 **electrons ($2S^2$)** while the underlying closed shell of other alkali metals contains **8 electrons** of **ns^2np^6** type.

(2) Li directly combines with nitrogen giving lithium nitride while other alkali metals do not form nitrides. $6Li + N_2 \xrightarrow{\Delta} 2Li_3N$ (Lithium nitride)

(3) Only Li can combine with carbon and silicon to from a carbide and a silicide respectively while other alkali metals do not form carbides and silicides.
$2Li + 2C \rightarrow Li_2C_2$ (Lithium Carbide)
$2Li + 2Si \rightarrow Li_2Si_2$ (Lithium Silicide)

(4) The nitrate of Li when heated gives nitrogen dioxide and oxygen while other alkali metal nitrate heating give on nitrites.

$$4LiNo_3 \xrightarrow{\Delta} \underset{\text{nitrogen dioxide}}{2Li_2O + 4NO_2} + O_2, \qquad 2NaNO_3 \xrightarrow{\Delta} \underset{\text{sodium nitrite}}{2NaNO_2} + O_2$$

(4) (1) Give reasion : Benzene resists oxidation.

→ Due to a resonance in benzene its energy state (potential energy) decreases by 36.0 K.cal/mole. The lower resonance energy of benzene indicates its specific type of higher stability and somewhat less chemical reactivity.

→ Thus, inspite of having three double bonds in benzene, it is more stable and much less reactive compared to alkene. Hence, it behaves like stable alkanes. So benzene resists oxidation with strong oxidizing agent like $KMnO_4$ at room temperature.

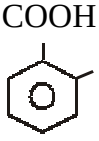
(2) $–OH \rightarrow$ O and p–directing group

(3) $–SO_3H$, $–NO_2 \rightarrow$ m–directing group

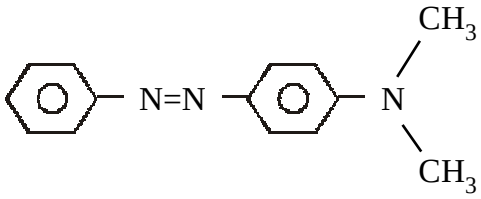
Q. 4. (A) Answer following in shrot : **(5)**

(1) IUPAC name : $C_6H_5–NH–CH_3 \rightarrow$ N–methyl amino benzene
$C_2H_5–CN \rightarrow$ cyano ethane

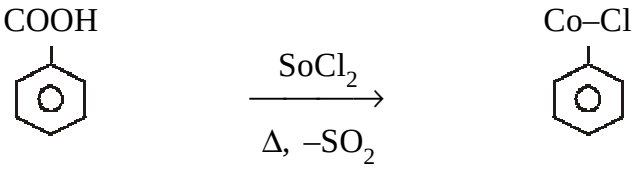
(2) If in 100 ml the amount of glucose is more than 130 miligram it is called hyperglycemia or diabetes and amount of glucose is less than 65 miligram it is called hypoglycemia.

(3) 

, chemical name : acetyle solicylic acid

(4) 

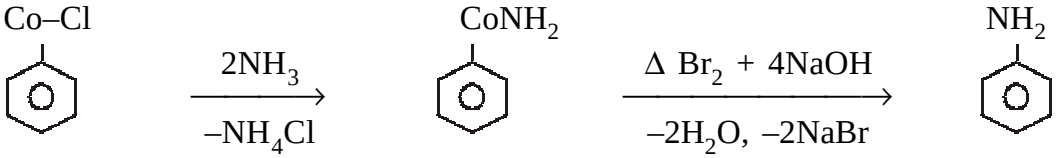
P–dimethyl amino azobenzene

(5) 

Benzoic acid –HCl Benzoly Chloride

(B) Give conversions (three) : **(6)**

(1) Aniline from benzoly chloride



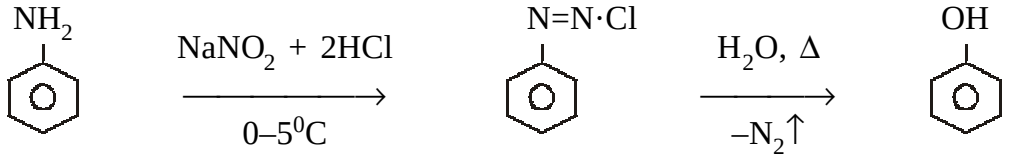
Benzoly Chloride — Benzamide — $-Na_2CO_3$ — Aniline

(2) Lactic acid from acetaldehyde

$$CH_3–CHO + HCN \rightarrow \underset{OH}{CH_3–CH–CN} \xrightarrow[+2H_2O]{\text{Aq. } H_2SO_2} \underset{OH}{CH_3–CH–COOH}$$

Acetaldehyde — Acetaldehyde Cyanohydrin — $-NH_3$ — Lactic acid

(3) Phenol from qniline



$NaNO_2 + 2HCl$, $0–5^0C$, $-NaCl, -2H_2O$ — BDAC Salt — H_2O, Δ, $-N_2\uparrow$, $-HCl$

✍ Tri ethyl amine from ethyl amine

$$\underset{\text{Ethyl amine}}{CH_3CH_2–NH_2} \xrightarrow[-HCl]{CH_3CH_2–Cl} \underset{\text{Diethyl amine}}{CH_3CH_2–NH–CH_2CH_3} \xrightarrow[-HCl]{CH_3CH_2–Cl} \underset{\text{triethyl amine}}{CH_3–CH_2–N(CH_2–CH_3)(CH_2–CH_3)}$$

(C) Answer the following (three) **(9)**

(1) Classification of polymers :

(i) Linear plymers : If monomers are jointed to each other in a continuous long chain, it gives linear polymers.

→ Natural fibers like cotton, wool, silk, etc. are also linear polymers. Linear polymers are thermoplastic polymers. eq. Nylon, terylene etc.

– A – A – A – A – A – A – A – A –

– A – B – A – B – A – B – A – B –

linear plymers

(ii) Branched polymers :

→ When a long chain is formed from monomers contain branching, we get branched polymers. Branched polymers can be called Thermosetting polymers. eg. PVC polystyrenes aer branched polymers.

```
– A – A – A – A – A – A –
          |
          A – A – A – A – A – A –
                  |
                  A – A – A – A – A – A –
```

branched polymer

(iii) Cross – Linked Polymers :

→ If several linear long chains of monomer units are chemically joined to each other at several points by mixed bonding, we get Cross–linked polymers.

→ These polymers can be called thermo setting polymers. e.g. Bakelite melamine etc. They are solid, hard and resistant to wear and tear.

```
– A – A – A – A – A – A – A – A –
– A – A – A – A – A – A – A – A –
– A – A – A – A – A – A – A – A –
```

cross–linked polymers

(2) (1) Wolf–Kishner Reduction : When aldehydes and ketones are reduced by hydrazine and potassium hydroxide givs hydrocarbons. In this reaction carbonyl group C = O is directly reduced in methylene – CH_2 – group. This reaction is known as wolf–kishner reduction. e.g. Acetaldehyde gives ethane and acetone gives propane by this reduction.

$$\underset{\text{Acetaldehyde}}{CH_3CHO} \xrightarrow[KOH]{NH_2.NH_2} \underset{\text{Ethane}}{CH_3CH_3} + H_2O + N_2$$

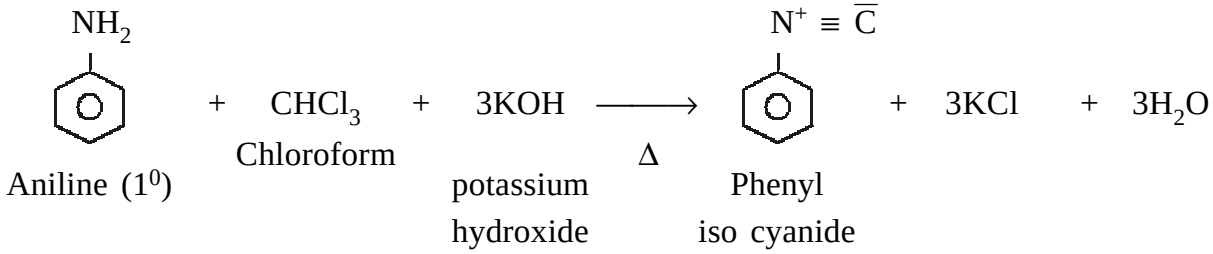
$$\underset{\text{Acetone}}{CH_3COCH_3} \xrightarrow[KOH]{NH_2.NH_2} \underset{\text{Propane}}{CH_3CH_2CH_3} + H_2O + N_2$$

(2) Explain : Carbyl Amine Test. Short note :

Ans. Primary amines (1^0) can be detected in laboratory by carbyl amine test. In this test, ethyl amine is heated with alcoholic KOH and chloroform. It forms ethyl isocyanide or carbyl amine. This product is **very toxic** and **foul smelling**.

$$\underset{\text{Ethylamine}}{CH_3–CH_2NH_2} + \underset{\text{(i) Chloroform}}{CHCl_3} + \underset{\text{Potassium hydroxide}}{3KOH} \xrightarrow{\Delta} \underset{\text{Ethyl iso cyanide}}{CH_3 – CH_2 – N^+ \equiv \overline{C}} + 2KCl + 3H_2O$$

→ While secondary and tertiary amines do not give this test. So 1^0 amine can be distinguished from 2^0 and 3^0 amines.



→ Similarly when aniline is heated with alcoholic KOH and chloroform, it gives very foul smelling toxic compound phenyl isocyanide or carbil amine.

(3) Nitrolim : (Nitrogeneous Fertilizer)

Ans. When a mixture of calcium oxide (quick lime) and carbon is heated in an electric furnace at 2000^0C, it gives calcium carbide.

→ This is then finely powdered and placed in electric furnace having porous walls. At 1200^0C, nitrogen is passed into the furnace which gives calcium cyanamide.

→ Fine powder of this mixture (nitrogen + lime) is used as nitrolim fertilizer. In the soil containing moisture, nitrolim hydrolyze giving $CaCO_3$ and ammonia.

$$\underset{\text{calcium oxide}}{CaO} + \underset{\text{carbon}}{3C} \xrightarrow{2000^0C} \underset{\text{Calcium carbide}}{CaC_2} + \underset{\text{Carbon monoxide}}{CO}$$

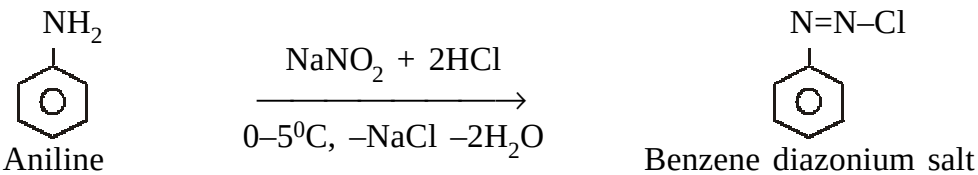
$$\underset{\text{Calcium carbide}}{CaC_2} + \underset{\text{nitrogen}}{N_2} \xrightarrow{1200^0C} \underset{\text{Calcium cyanamide}}{CaCN_2} + \underset{\text{Carbon}}{C}$$

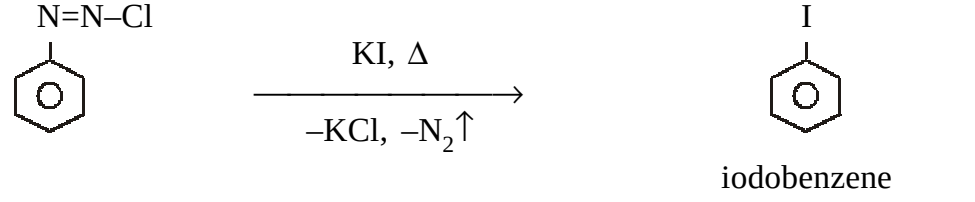
$$CaCN_2 + 3H_2O \xrightarrow{\text{hydrolysis}} \underset{\text{calcium carbonate}}{CaCO_3} + \underset{\text{ammonia}}{2NH_3}$$

Uses : It supplies Nitrogen to plants.

(4) Diazotiazation of Aniline :

Ans. The reaction of primary aromatic amine with HNO_2 at low temperature ($O - 5^0C$) gives diazonium chloride salt. This reaction is known as Diazotiation.





When BDAC salt is heated with KI, it gives iodobenzene.

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

(1) When yellow phosphorous is heated at 250^0C in presence of sunlight and I_2 as catalyst and in inert atmosphere of N_2 or CO, it gives red phosphorous

$$nP_4 \xrightarrow[[I_2],\ N_2 \text{ or } Co]{250,\ hv} (P_4)_n$$

Yellow red (polymolecular)

(2) The electron pair donar atom of the ligand is called coordination site of ligand.

eq. $\overset{\bullet\bullet}{N}$–atom in $\overset{\bullet\bullet}{N}H_3$, $\overset{\bullet\bullet}{N}O$ and $CH_3\overset{\bullet\bullet}{N}H_2$ molecule is co–ordination site.

(3) IUPAC name : Carbonato bis (ethylene diamine) chromium (III) nitrate.

(4) The highest oxidation state of vanadium is +5. The compounds in +5 state are called vanadates eq. V_2O_5.

(5) 1.5 microgram of vitamin B_{12}.

(B) Answer the following : **(6)**

(1) The inert gases other than helium possess an electron octet in their valence shells. This closed shell configuration is very stable. Owing to very high ionization energies, inert gases possess a negligible tendency of exchanging electrons and so they do not form ionic compounds. All the electrons being paired in these elements, they are unavailable for sharing. Moreover the expansion of the valence shells of these elements being not possible, even covalent compounds cannot be formed.

(2) The most stable oxidation state of Ti is +4. Which is more stable than Ti^{3+} and Ti^{3+}

$$Ti + \underset{\text{(Large)}}{\text{energy}} \rightarrow Ti^{4+} + 4e^-$$

Thus Ti^{4+} is expected to be stable due to $3d^0$ but the removal of four electrons from Ti atom requires very large energy, the Ti^{4+} ion does not exist but this oxidation state is found in compounds containing covalent bonds. Therefore, $TiCl_4$ contains covalent bonds.

(3) Physical Properties : (any four)

(1) They are all metallic elements. They easily form positive ions losing the electrons from the outermost valence shells and combine with non–metals.

(2) These metals possess high melting points and boiling points.

(3) They are good conductors of heat and electricity.

(4) They combine with oxygen forming oxides. They form alloys with other metals.

(5) They react with acids giving ionic compounds.

(6) These elements can be drawn into wires and beaten into sheets and they have a shining surface.

(C) (1) Importants of complex :

(1) Chlorophyl, a magnesium complex present in green plants is important for photosynthesis.

(2) Hemoglobin, an iron complex present in animal blood, serves to carry oxygen to the muscles and to remove Co_2 from the blood.

(3) The complexes present in minerals are useful as catalysts in the metallurgical industries and as analytical reagents in the laboratory.

(2) Geometry and Magnetic property of $[NiCl_4]^{2-}$ OR $K_2[NiCl_4]$, (Tetra chloro nickelate (II) ion).

Ans. This complex contains Ni^{2+} which is co–ordinated with four weak Cl^- ligands. The relatively weak Cl^- ligands are attracted weakly by Ni^{2+} ion. So they cannot approach very close to it. As a result, the rearrangement of the 3d electrons of the Ni^{2+} ion does not become necessary.

→ The electron configuration of Ni^{2+} ion = [Ar] $3d^8 4s^0 0$

→ If complex involvex Sp^3 hybridization then the one 4s and the three 4p orbitals hybridize and produces four equienergic Sp^3 hybrid orbitals. These four vacant sp^3 hybrid orbitals acomodate four electron – pairs donated by four Cl^- ions which are shown as xx.

→ These four Sp^3 hybrid orbitals are directed toward the four corners of a tetrahedron. So the geometry of $[NiCl_4]^{2-}$ is tetrahedral.

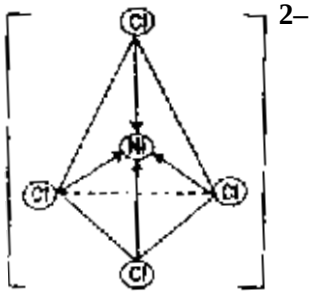
$Ni^{2+}_{(z=28)}$ = [Ar] $3d^8 4s^0$ 3d 4s 4p

$[Ni(Cl)_4]^{2-}$ =

tetrahedral n = 2 sp^3 hybridization

$[Ni(Cl_4]^{2-}$ =

square planar n = 0 dsp^2 hybridization



TETRAHEDRAL

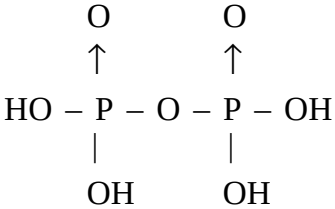
→ Magnetic property : This complex has two unpaired electrons in 3d orbitals; the complex is paramagnetic. Its μ expt. = 2.80 BM which is near to its μ theor = 2.83 BM for n = 2 electrons. This suggests sp^3 hybridization and tetrahedral shape

μ_{expt} = 2.90 BM

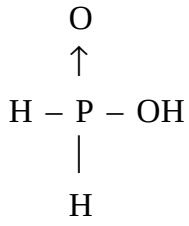
μ_{theor} = 2.83 BM, for n = 2

→ If complex has dsp^2 hybridization then its μ = 0.00 BM for n = 0. But these is not in agreement with value μ = 2.83 BM. This proves that complex ion contains. sp^3 hybridization and not dsp^2 hybridization.

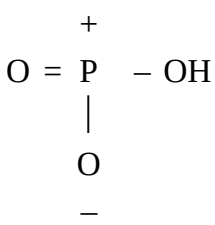
(3) pyrophosphoric acid →



hypo phosphorous acid →



meta phosphoric acid →



The transition Metal Ions have a greater tendency to form complexes than other elements. Explain giving reason.s

Ans. (1) Transition metal cations are small in size compared to cations of other elements.

(2) The nuclear and ionic charges of transitional metal ions are relatively large.

(3) The electronic configurations of these cations are suitable for complex formation. The 3d orbitals of the ions are either vacant or can become vacant, which can accomodate the incoming electron – pairs.

(4) There are very small energy separations between 3d, 4s, 4p and 4d orbitals of these ions. This make the possible various types of hybridization of these orbitals.
e.g. sp^3, dsp^2, d^2sp^3, sp^3d^2 etc.

(5) Due to different types of hybridizations and the directional character of co–ordinate bonds, complexes with different geometries can be formed.
e.g. (i) Tetrahedral $K_2[NiCl_4]$ (i) Square planar $K_2[Ni(CN)_4]$
(iii) Octahedral $[Co(NH_3)_6]Cl_3$

(6) These metal ions being capable of existing in several oxidation states, different types of complexes are formed.
e.g. The oxidation states of Fe = +2, +3 and Mn = +2, +3, +4, +5, +6, +7

*_*_*