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.

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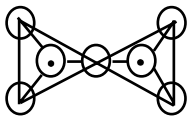
: ANSWER :

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.

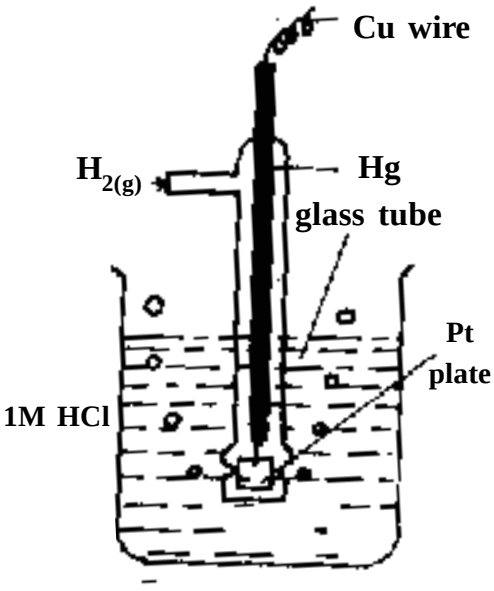
→ If H^+ ions are not available on cathode, O_2 dissolved in moisture gets reduced to $OH^-_{(aq)}$.

$$O_{2(g)} + 4H^+_{(aq)} + 4e^- \rightarrow 2H_2O_{(l)}$$

→ $Fe^{2+}_{(aq)}$ 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.

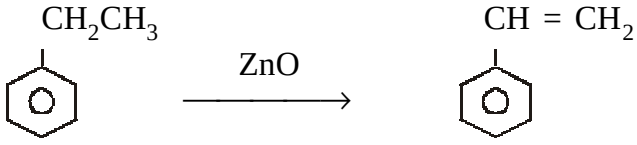
→ When such photon hits a microscopic particle, some unknown faction of its energy is transferred to the particle. As a result, the velocity of the particle increases suddenly to a high value. Thus, if the momentum of a particle is to be determined simultaneously with the determination of position of 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".

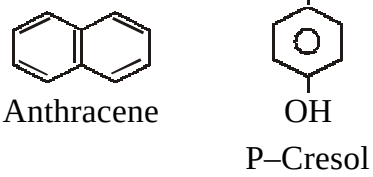
→ $\therefore \Delta\chi \times \Delta p \geq \frac{h}{4\pi}$ | Where h = Planck's constant
Δp = uncertainty in its momentum.
$\Delta\chi$ = uncertainty in the position of a particle.

→ 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) 

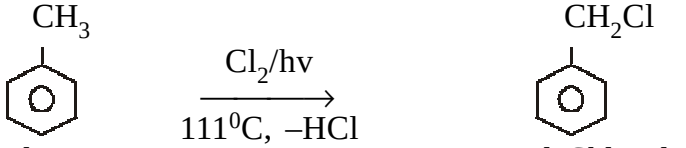
Ethyl benzene 630^0C, $-H_2$ Styrene

(2) 

Anthracene P–Cresol

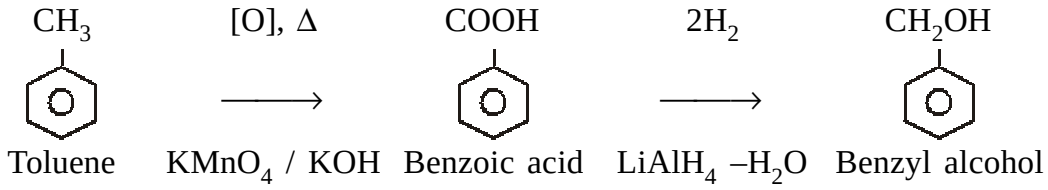
(3) Li_2C_2 and $HClO_4$

(4) Humphrey Davy

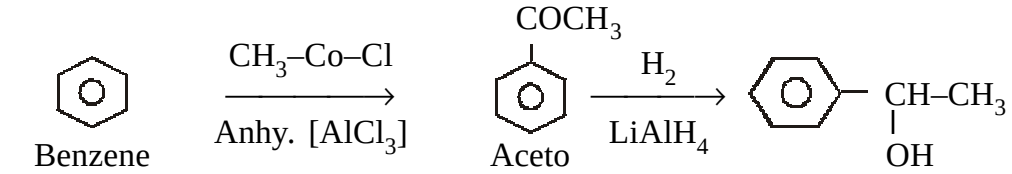
(5) 

Toluene 111^0C, $-HCl$ Benzyl Chloride

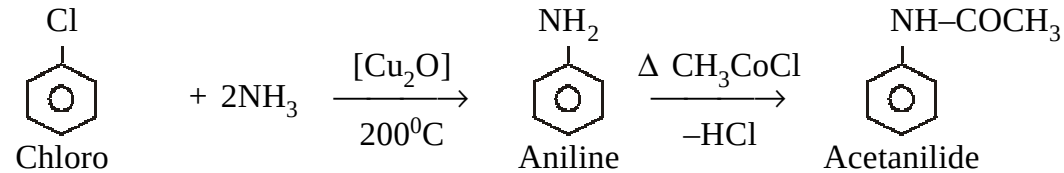
(B) Any three conversions : **(6)**

(1) 

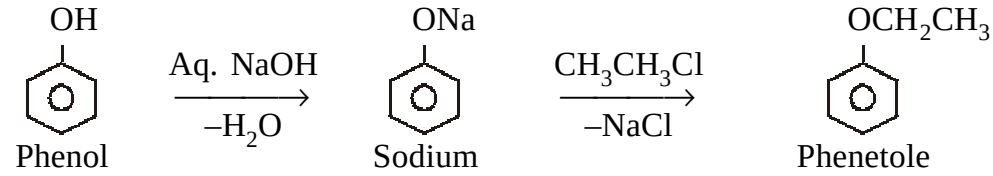
Toluene $KMnO_4$ / KOH Benzoic acid $LiAlH_4$ $-H_2O$ Benzyl alcohol

(2) 

Benzene Aceto Phenone 1–Phenyl, 1–Ethanol

(3) 

Chloro benzene Aniline Acetanilide

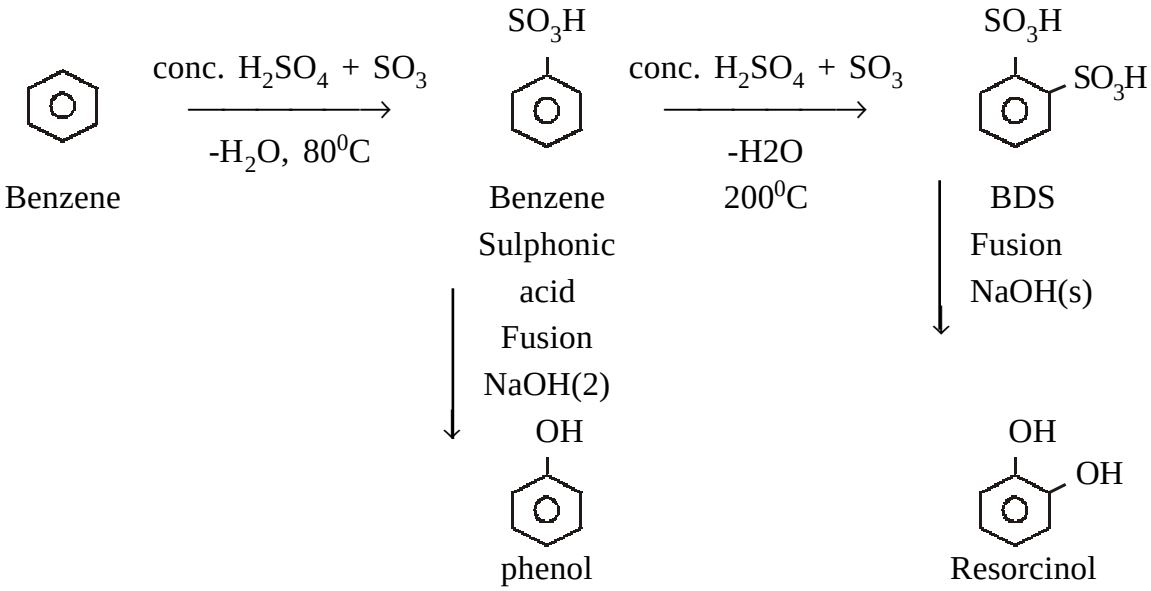
(4) 

Phenol Sodium Phenoxide Phenetole

Q. 3. (C) Answer in the following (three) **9**

(1) Sulphonation of benzene

$H_2SO_4 + H_2SO_4 \rightleftharpoons SO_3H^+ + HSO^-_4 + H_2O$



Benzene

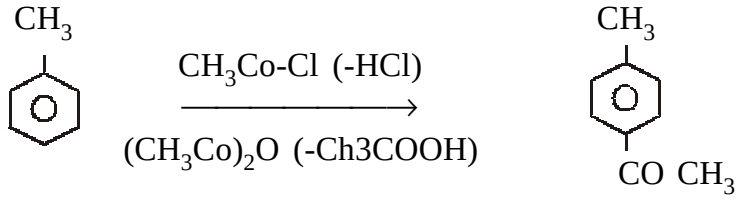
→ When benzene is heated with conc. H_2SO_4 and SO_3 at 80^0C, it gives benzene sulphonic acid. If more H_2SO_4 is taken and temperature is increased to 200^0C for long time then it gives benzene m-disulphonic aid.

→ 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.

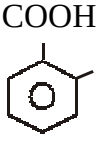
(2) $–OH \rightarrow$ O and p–directing group

(3) $–SO_3H$, $–NO_2 \rightarrow$ m–directing group

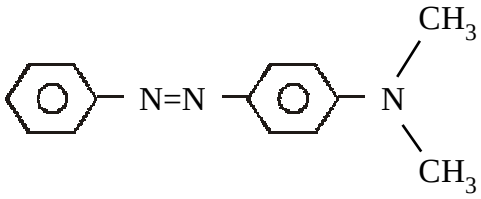
Q. 4. (A) Answer following in shrot : **(5)**

(1) IUPAC name : $C_6H_5–NH–CH_3 \rightarrow$ N–methyl amino benzene
$C_2H_5–CN \rightarrow$ cyano ethane

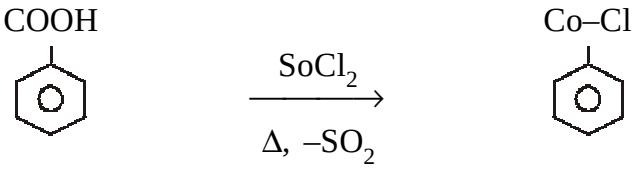
(2) If in 100 ml the amount of glucose is more than 130 miligram it is called hyperglycemia or diabetes and amount of glucose is less than 65 miligram it is called hypoglycemia.

(3) 

, chemical name : acetyle solicylic acid

(4) 

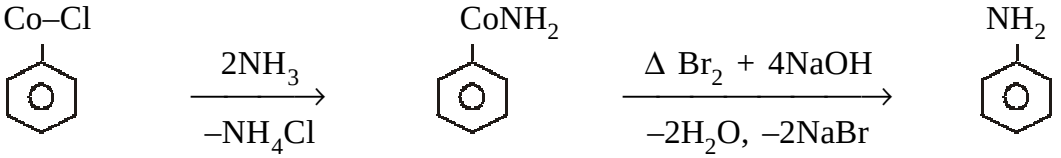
P–dimethyl amino azobenzene

(5) 

Benzoic acid –HCl Benzoly Chloride

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

(1) Aniline from benzoly chloride



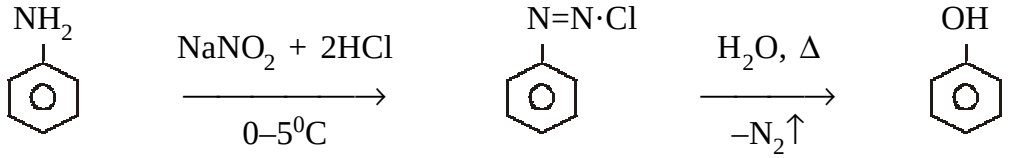
Benzoly Chloride — Benzamide — $-Na_2CO_3$ — Aniline

(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.

$$CH_3CHO \xrightarrow[KOH]{NH_2.NH_2} CH_3CH_3 + H_2O + N_2$$

Acetaldehyde — Ethane

$$CH_3COCH_3 \xrightarrow[KOH]{NH_2.NH_2} CH_3CH_2CH_3 + H_2O + N_2$$

Acetone — Propane

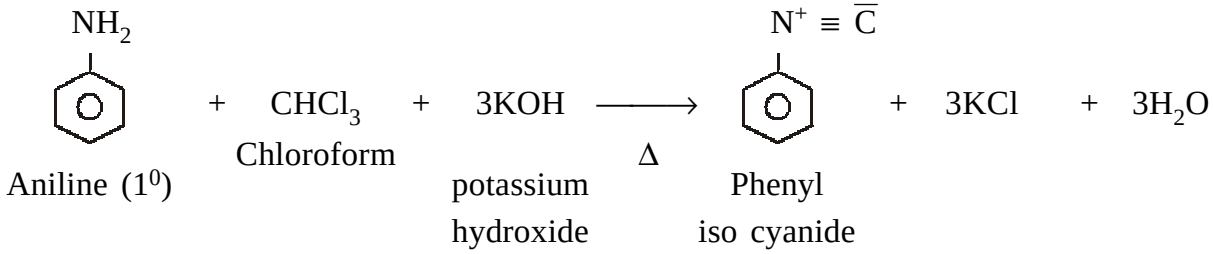
(2) Explain : Carbyl Amine Test. Short note :

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**.

$$CH_3–CH_2NH_2 + CHCl_3 + 3KOH \xrightarrow{\Delta} CH_3 – CH_2 – N^+ \equiv \overline{C} + 2KCl + 3H_2O$$

Ethylamine (i) — Chloroform — Potassium hydroxide — Ethyl iso cyanide

→ 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.

$$\underset{\text{calcium oxide}}{CaO} + \underset{\text{carbon}}{3C} \xrightarrow{2000^0C} \underset{\text{Calcium carbide}}{CaC_2} + \underset{\text{Carbon monoxide}}{CO}$$

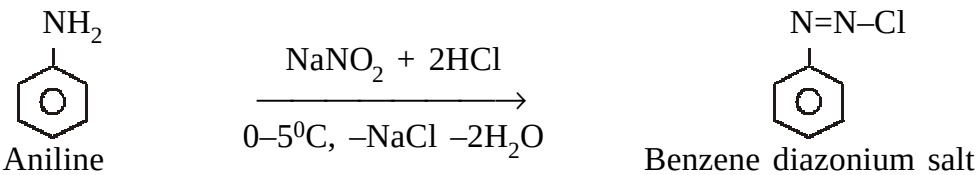
$$\underset{\text{Calcium carbide}}{CaC_2} + \underset{\text{nitrogen}}{N_2} \xrightarrow{1200^0C} \underset{\text{Calcium cyanamide}}{CaCN_2} + \underset{\text{Carbon}}{C}$$

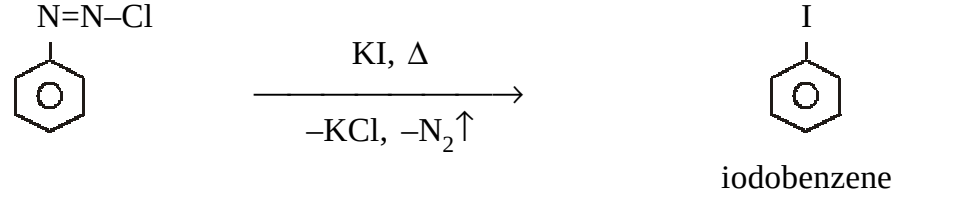
$$CaCN_2 + 3H_2O \xrightarrow{\text{hydrolysis}} \underset{\text{calcium carbonate}}{CaCO_3} + \underset{\text{ammonia}}{2NH_3}$$

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.

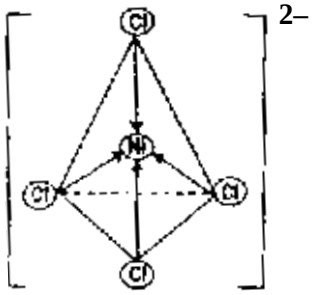
$Ni^{2+}_{(z=28)}$ = [Ar] $3d^8 4s^0$ 3d 4s 4p

$[Ni(Cl)_4]^{2-}$ =

tetrahedral n = 2 sp^3 hybridization

$[Ni(Cl_4]^{2-}$ =

square planar n = 0 dsp^2 hybridization



TETRAHEDRAL

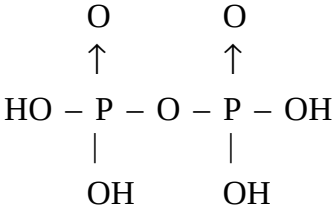
→ Magnetic property : This complex has two unpaired electrons in 3d orbitals; the complex is paramagnetic. Its μ expt. = 2.80 BM which is near to its μ theor = 2.83 BM for n = 2 electrons. This suggests sp^3 hybridization and tetrahedral shape

μ_{expt} = 2.90 BM

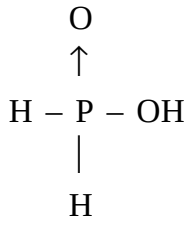
μ_{theor} = 2.83 BM, for n = 2

→ 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.

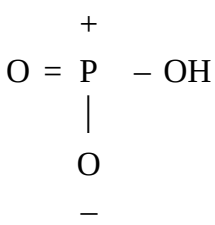
(3) pyrophosphoric acid →



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

*_*_*