

**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 required.
- (4) Atomic Weight (gm. Mole<sup>-1</sup>) :

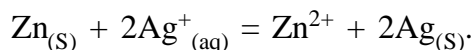
C = 12, N = 14, O = 16, Pb = 207, H = 1, S = 32

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

- (1) For what the value of  $\Delta G$  of a reaction is the measure ?
- (2) What is thermodynamically reversible process ?
- (3) Give two names of different forms of silicon dioxide.
- (4)  $\text{CH}_3\text{NH}_2$  is stronger base than  $\text{NH}_3$ . 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  $\text{CH}_3\text{COOH}$  in 100 ml. of a solution of the acid which has a pH of 3.00  $K_a$  of  $\text{CH}_3\text{COOH}$  is  $1.75 \times 10^{-5}$ .
- (2) Find out the change in free energy of the reaction.



which occurs in a standard cell at 25°C. The standard potential of the cell is 0.54 volt.

- (3) The ionization constant of methyl amine in aqueous solution is  $5.0 \times 10^{-4}$  at 25°C. 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)**

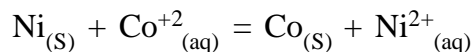
- (1) Define the terms internal energy and enthalpy, obtain  $\Delta H = q_p$  on the basis of first law of thermodynamic.
- (2) Discuss the relationship between radius ratio of ions and crystal lattice structure.
- (3) Explain Lewis acid base theory by suitable illustration.
- (4) (a) Discuss the effect of temperature on ionic product of water.  
(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  $\text{Th}^{233}$  is  $1.39 \times 10^{10}$  years. How many  $\alpha$ -particles would be emitted per minute from 5.0 gm.  $\text{Th}^{232}$ . Each  $\text{Th}^{232}$  atom emits one  $\alpha$ -particle on decomposition.
- (2) Calculate the equilibrium constants of the reaction.



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

- (3) Calculate the energy of a photon of a radiation having wavelength 6000  $\text{\AA}$ . Calculate the value of Einstein. Velocity of light =  $3.0 \times 10^{10} \text{ cm sec}^{-1}$ .

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

- (1) Derive equation of Arrhenius.
- (2) Give the diagrammatic representation of molecular orbitals of  $\text{F}_2$  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  $80^\circ\text{C}$  in presence of anhydrous  $\text{AlCl}_3$ .
- (2) Phenol cannot be neutralized by a weak base like sodium bicarbonate. Why ?
- (3) State the name of indicator obtained from phenol.
- (4) Give IUPAC name : (a)  $\text{C}_6\text{H}_5 - \text{O} - \text{C}_6\text{H}_5$  (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. (6)**  
**Also give the condition of the reaction, names and structural formula of the main organic compound (There should be only two step of each conversion)**

- (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 reaction 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)

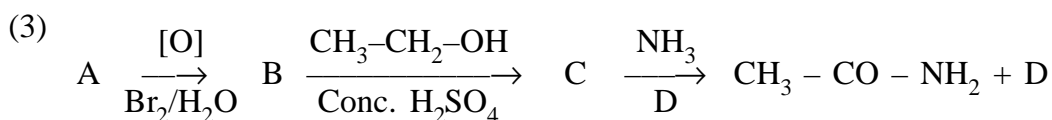
- (1) Give name and equation when dehydration of benzamide is carried out in presence of phosphorous pentoxide.

- (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 starch 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 acetyl 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.



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 oxidation state of vanadium exhibits low stability ?
- (3) How many coordination sites are present in bidentate and tridentate ligands ?
- (4) Give IUPAC (a)  $\text{Na}_4[\text{Co}(\text{NO}_2)_6]$  (b)  $\text{Fe}(\text{CO})_5$
- (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  $\text{ML}_6$  complexes giving examples.
- (2)  $\text{ZnSO}_4$  is colourless while  $\text{NiSO}_4$  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  $\text{K}_3[\text{Fe}(\text{CN})_6]$  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)  $\text{CuCl}_2$  is paramagnetic while  $\text{CuCl}$  is diamagnetic.  
 (b)  $\text{Ti}^{+4}$  is more stable than  $\text{Ti}^{+3}$  but  $\text{Ti}^{+4}$  ion does not exist.

\*\_\*\_\*

: ANSWER :

Q. 1. (A)

- (1)  $\Delta G$  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 system and surrounding would be infinitesimally small. Such process is known as thermodynamically reversible process.
- (3) Cristobelite, quartz and Tridimite are the different forms of silicon dioxide.
- (4) Because the  $K_b$  <sub>NH<sub>3</sub></sub> <  $K_b$  <sub>CH<sub>3</sub>NH<sub>2</sub></sub>. So CH<sub>3</sub>NH<sub>2</sub> is stronger base than NH<sub>3</sub>.
- (5) When the temperature is higher than the absolute zero, the crystal structure of any compound become unstable.

Q. 1. (B)

- (1)  $\text{pH} = -\log[\text{H}_3\text{O}^+]$   
 $3.0 = -\log[\text{H}_3\text{O}^+]$   
 $\therefore [\text{H}_3\text{O}^+] = \text{antilog } \bar{3}.00$   
 $= 1.0 \times 10^{-3} \text{ M.}$

But ionization of acetic acid is very little.



$$[\text{H}_3\text{O}^+] = \sqrt{K_a c_0}$$

$$1.0 \times 10^{-3} = \sqrt{1.75 \times 10^{-5} \times c_0}$$

$$1.0 \times 10^{-6} = \sqrt{1.75 \times 10^{-5} \times c_0}$$

$$= 1.75 \times 10^{-5} \times c_0$$

$$\therefore c_0 = 5.7 \times 10^{-2} \text{ M.}$$

$$\text{CH}_3\text{COOH's molarity} = \frac{1000 \times W}{60 \times 100}$$

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

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

$$\therefore W = 0.3429 \text{ CH}_3\text{COOH}$$

$$\therefore \text{CH}_3\text{COOH} = 0.342 \text{ gram.}$$



$$\Delta E^0 = E^0_{\text{ox}} (\text{Anode}) - E^0_{\text{ox}} (\text{Cathode})$$

$$= 0.76 - (-0.80)$$

$$\Delta E^0 = 1.56 \text{ volt} \quad \dots(1)$$

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

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

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

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

$$\therefore \log K_c = 52.70$$

$$K_c = \text{Antilog } 52.70$$

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

(3) Mol. weight of  $\text{CH}_3\text{NH}_2 = (1)(12) + 5(1) + 1(14) = 31 \text{ g/mol}$ .

$$\frac{\text{g}}{\text{liter}} \text{ of } \text{CH}_3\text{NH}_2 = \frac{6.2 \text{ g}}{\frac{500}{100} \text{ liter}} = 12.4 \frac{\text{g}}{\text{liter}}$$

$$\therefore \text{Conc. of } \text{CH}_3\text{NH} = \frac{12.4 \text{ g/liter}}{31 \text{ g/mole}} = 0.4 \frac{\text{mole}}{\text{liter}}$$

As  $\text{CH}_3\text{NH}_2$  is a weak base,

$$[\text{OH}^-] = \sqrt{K_b \times C_0}$$

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

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

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

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

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

$$= -\log 1.41 + 2$$

$$= 2 - 0.1492$$

$$= 1.85$$

$$\therefore P^{\text{H}} = 14 - 1.85$$

$$= 12.15$$

## 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 ( $\Delta H$ ) is expressed by,

$$\begin{aligned}\Delta H &= \Delta E + \Delta(PV) \\ &= \Delta E + P \Delta V + V \Delta P.\end{aligned}$$

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

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

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  $(w) = -P \Delta V$ .

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

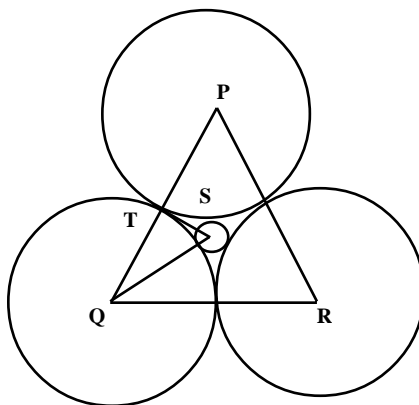
$$\therefore \Delta H = q - p \Delta v + p \Delta v$$

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

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.

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

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

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

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

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

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

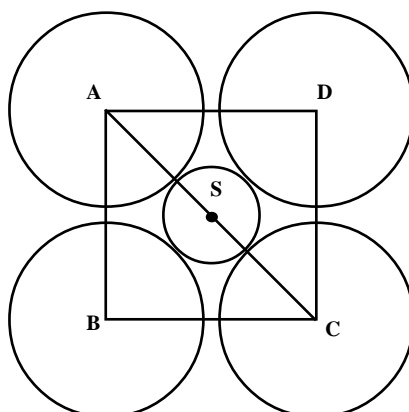
$$\therefore r_+ = \frac{2}{\sqrt{3}} r_- - r_-$$

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

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

(ii) Radius ratio in octahedral structure :

In the octahedral arrangement around 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 radii of cation and anion are  $r_+$  and  $r_-$  respectively.

$$AC = 2r_- + 2r_+$$

$$BC = 2r_-$$

Now in  $\Delta ABC$

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

$$\therefore AC \cos 45^\circ = BC$$

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

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

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

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

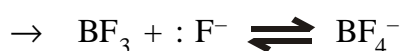
$$\therefore \frac{r_+}{r_-} = \sqrt{2} - 1$$

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

- (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.

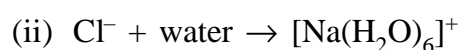
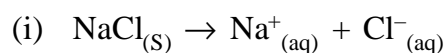
**Acid** : A compound which accepts an electron pair during reactions is known as an acids.

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



In above reactions  $\text{F}^-$  from bonds with  $\text{BF}_3$  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 acid base reaction.





In this hydration process,  $\text{Na}^+$  acts as an acid and  $\text{Cl}^-$  as a base.

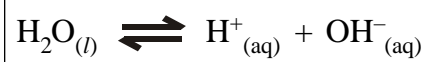
→ Negative ions and neutral molecules acting as ligands in the formation of complex salts are Lewis bases and metal-ions bonding to ligands are Lewis acids.

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

⇒ The value of ionic product of water  $K_w$  at  $25^\circ\text{C}$  is  $1 \times 10^{-14}\text{M}$ .

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

⇒ This process is an endothermic process.



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

⇒ Hence ionization of water increases.

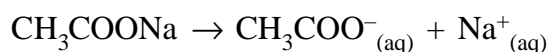
⇒ As a result the concentration of  $\text{H}^+$  and  $\text{OH}^-$  ions increases.

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

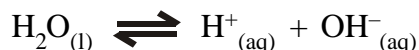
(b) Aqueous solution of sodium acetate is basic.

⇒ Sodium Acetate  $[\text{CH}_3\text{COONa}]$  is a salt formed from a weak acid  $\text{CH}_3\text{COOH}$  and strong base  $\text{NaOH}$ .

⇒ When it is dissolved in water it ionizes completely.



⇒ Moreover there exists following equilibrium in water.



⇒  $\text{CH}_3\text{COO}^-$  produced from  $\text{CH}_3\text{COONa}$  salt combine with  $\text{H}^+$  ions produced by self-ionization of water and form unionized weak acid  $\text{CH}_3\text{COOH}$ .

⇒ Due to this equilibrium of water gets disturbed.

⇒ As a result the equilibrium of water shifts in the forward direction and produces more  $\text{H}^+$  and  $\text{OH}^-$  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.



**Q. 2. (A)**

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

(2) **(n + l) rule :**

- ⇒ The order of energies 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**

$$t_{1/2} = 1.39 \times 10^{10} \text{ years}$$

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

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

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

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

**for K**

$$\log 0.693 = \bar{1} - 8407$$

$$\log 1.39 = 0.1430$$

$$10 \log 10 = 10.0000$$

$$+ \log 365 = 2.5623$$

$$+ \log 60 = 1.7782$$

$$\hline 15.8637$$

\* Calculation of N W = 5.0 gms.

$$N = \frac{6.023 \times 10^{23} \times W}{M \cdot \text{wt of Th}}$$

$$= \frac{6.023 \times 10^{23} \times 5.0}{232}$$

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

Now

$$-\frac{dN}{dt} = K \cdot N$$

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

$$= 61.55 \times 10^5$$

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

$$\bar{1}.8407$$

$$- 15.8607$$

$$\hline \bar{17}.9770$$

Antilog of  $\bar{17}.9770$

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

for N

$$\log 6.023 + 23 \log 10 + \log 5.0 - \log 232$$

$$= 0.7798 + 23$$

$$+0.6989 - 2.3655$$

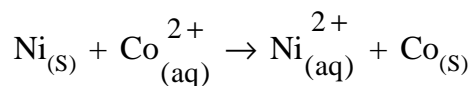
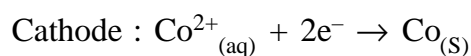
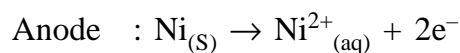
$$\propto 25.1776$$

$$- 2.3655$$

$$\hline 22.8121$$

$$\text{Antilog } 6.4889 \times 10^{22}$$

(2) Reactions for the cell :



$$\boxed{n = 2}$$

Cell potential  $\Delta E^0$

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

$$= 0.23 - 0.28$$

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

Calculation of  $K_c$  :

According to Nernst Equation :

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

Now cell is in equilibrium state

$$\therefore \Delta E = 0.01 \text{ volt}$$

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

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

$$\begin{aligned} \therefore \log K_c &= -\frac{0.05}{0.0296} \\ &= -(1.6900) \\ &= -1.6900 \\ &= -2 + 1 = 0.69 \\ &= -2 + 0.31 \end{aligned}$$

$$\log 0.05$$

$$\log 0.0296$$

$$\bar{2}.6990$$

$$- \bar{2}.4713$$

$$0.2217$$

$$\hline \text{Antilog } 0.2217 = 1.69$$

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

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

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

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

$$\begin{aligned} \therefore E &= \frac{6.626 \times 10^{-27} \times 3.0 \times 10^{10}}{6000 \times 10^{-8}} \\ &= \frac{6.626 \times 3}{6} \times 10^{-12} \times 10^{-12} \end{aligned}$$

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

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 Arrhenius rate constant.**Ans.**

⇒ Energy of activation of a reaction can be determined from Arrhenius equation using  $K$  values at different temperatures.

$$K = A \cdot e^{-E_a/RT} \quad \text{Where,} \quad A = \text{Arrhenius constant}$$

$$E_a = \text{activation energy}$$

$$K = \text{rate constant}$$

$$T = \text{Temp. (Kelvin)}$$

$$R = \text{gas constant}$$

$$K = A \cdot e^{-E_a/RT}$$

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

If ⇒  $K_1$  and  $K_2$  are rate constants

⇒  $T_1$  and  $T_2$  temperatures of respectively constants.

$$\therefore \log K_1 = \log A - \frac{E_a}{2.303 RT_1}$$

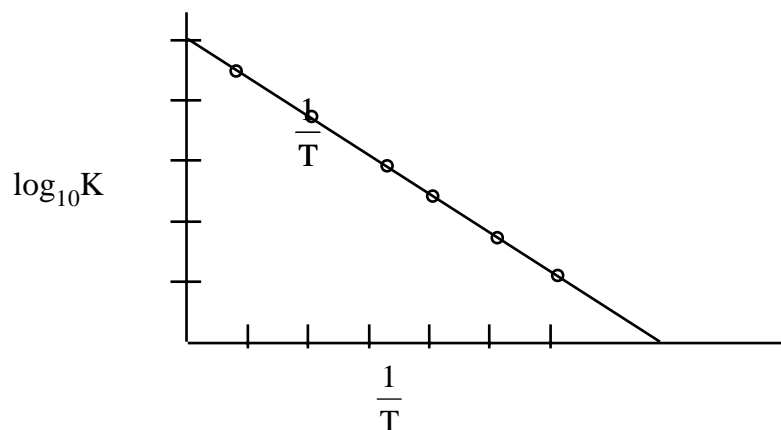
$$\log K_2 = \log A - \frac{E_a}{2.303 RT_2}$$

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

$$\therefore \log \frac{K_2}{K_1} = -\frac{E_a}{2.303 R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right) \dots (A)$$

⇒ Eq. (A) is a eq. of  $E_a$  of Arrhenius Rate constant.

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



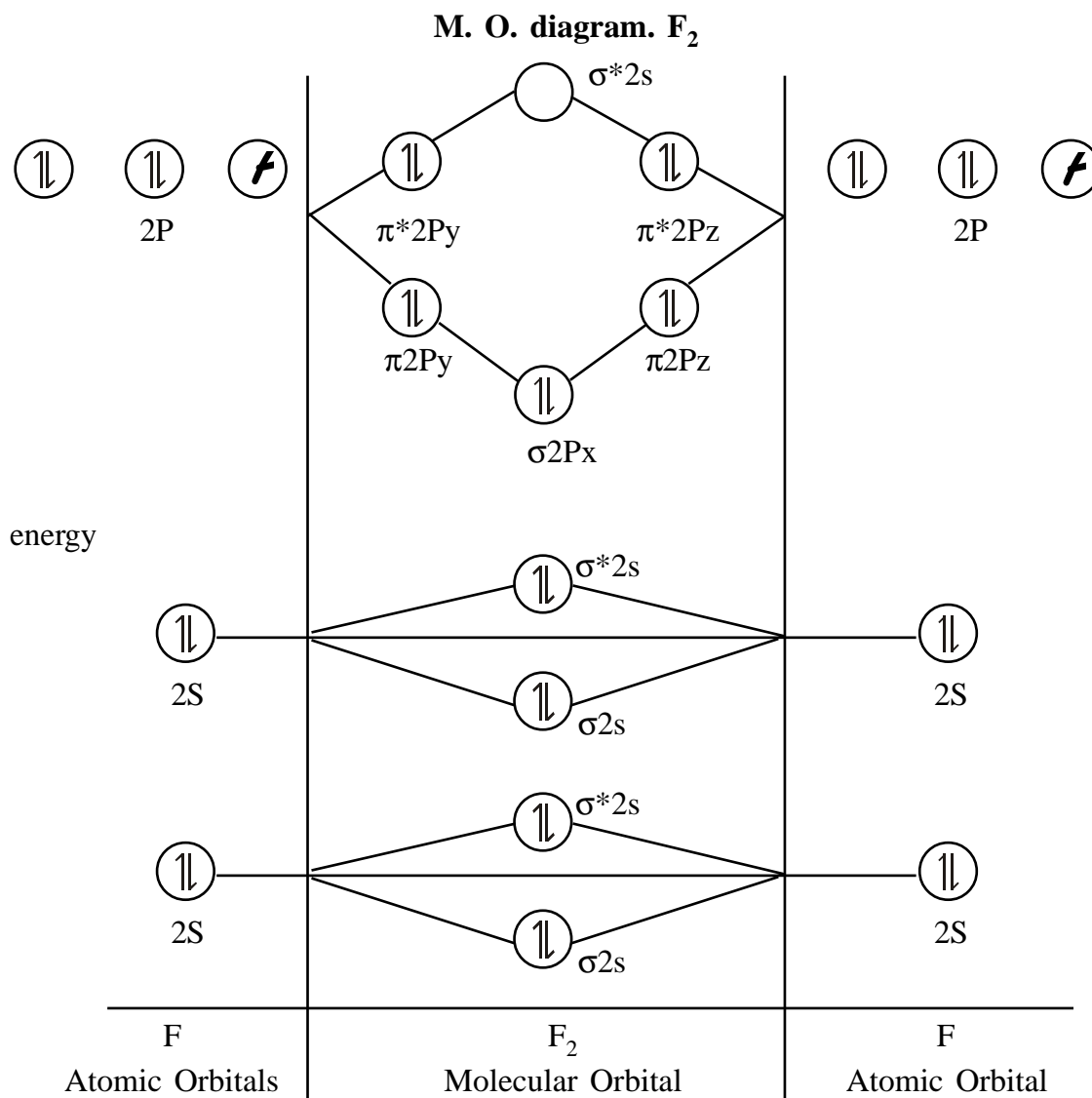
⇒ This graph has a negative slope equal to  $-\frac{E_a}{2.303R}$

⇒ The energy of activation can be calculated by determining slope.

(2) **Electron configuration of Flourine :**

$$F(z = 9) = 1S^2, 2S^2, 3P_x^2, 2P_y^2, 2P_z^1$$

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



**Bond Order :**

$$\begin{aligned} \text{Bond Order} &= \frac{1}{2} [N_b - N_a] \\ &= \frac{1}{2} [10 - 8] \\ &= \frac{2}{2} \\ \text{Bond order} &= 1 \end{aligned}$$

∴ F<sub>2</sub> molecule has a single bond

i. e. F-F

**Magnetic properties :**

⇒ since all electrons in F<sub>2</sub> are paired. **F<sub>2</sub> is a diamagnetic molecule.**

**Q. 2. (C)**

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

⇒ Arrhenius studied the rates of reaction at different temperature and established the following equation.

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

K = Rate constant

$$\therefore K = A \cdot e^{-E_a/RT}$$

R = Gas constant

T = Kelvin temp.

E<sub>a</sub> = activation energy

A = Arrhenous constant

⇒ The above equation indicates that K increases with a rise in temperature.

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

⇒ The rate of collisions also increases with a rise in temperature.

⇒ Both of these factors favour an **increase in the rate of reactions with a rise in temperature.**

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

⇒ Its relation with rate constant 'K' is as follows.

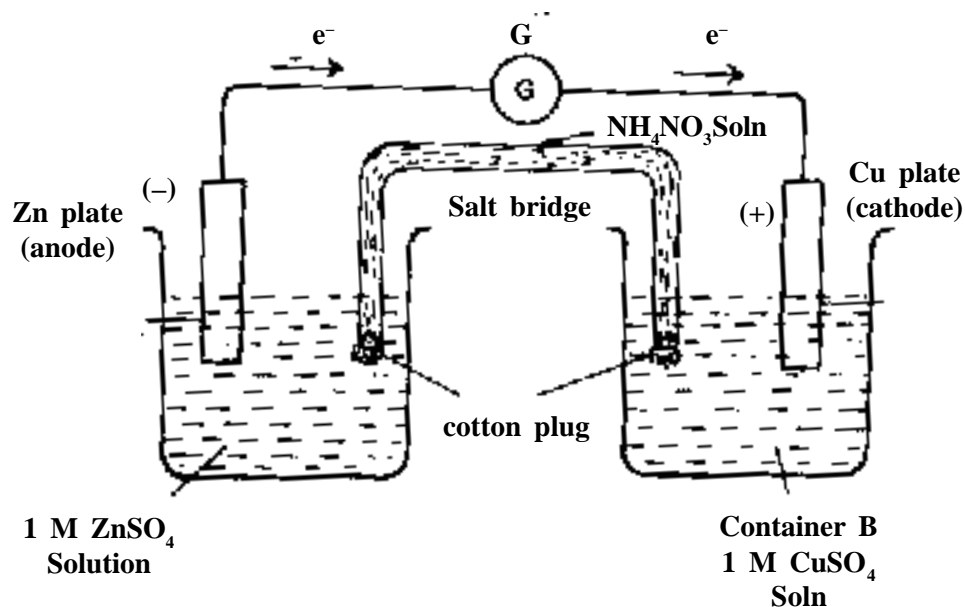
$$t_{1/2} = \frac{0.693}{K}$$

⇒ Above equation show that half-reaction time does not depend on the initial concentration of reactant.

## (4) Construction &amp; working of 'Daniel Cell'.

**Principle :**

⇒ Conversion of chemical energy to electrical energy.

**Figure :**

⇒ 1M aqueous ZnSO<sub>4</sub> solution is taken in container A in which a weighed Zn metal strip is placed as anode.

⇒ 1M aqueous CuSO<sub>4</sub> 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<sub>4</sub>NO<sub>3</sub> salt solution.

⇒ The functions of salt bridge is

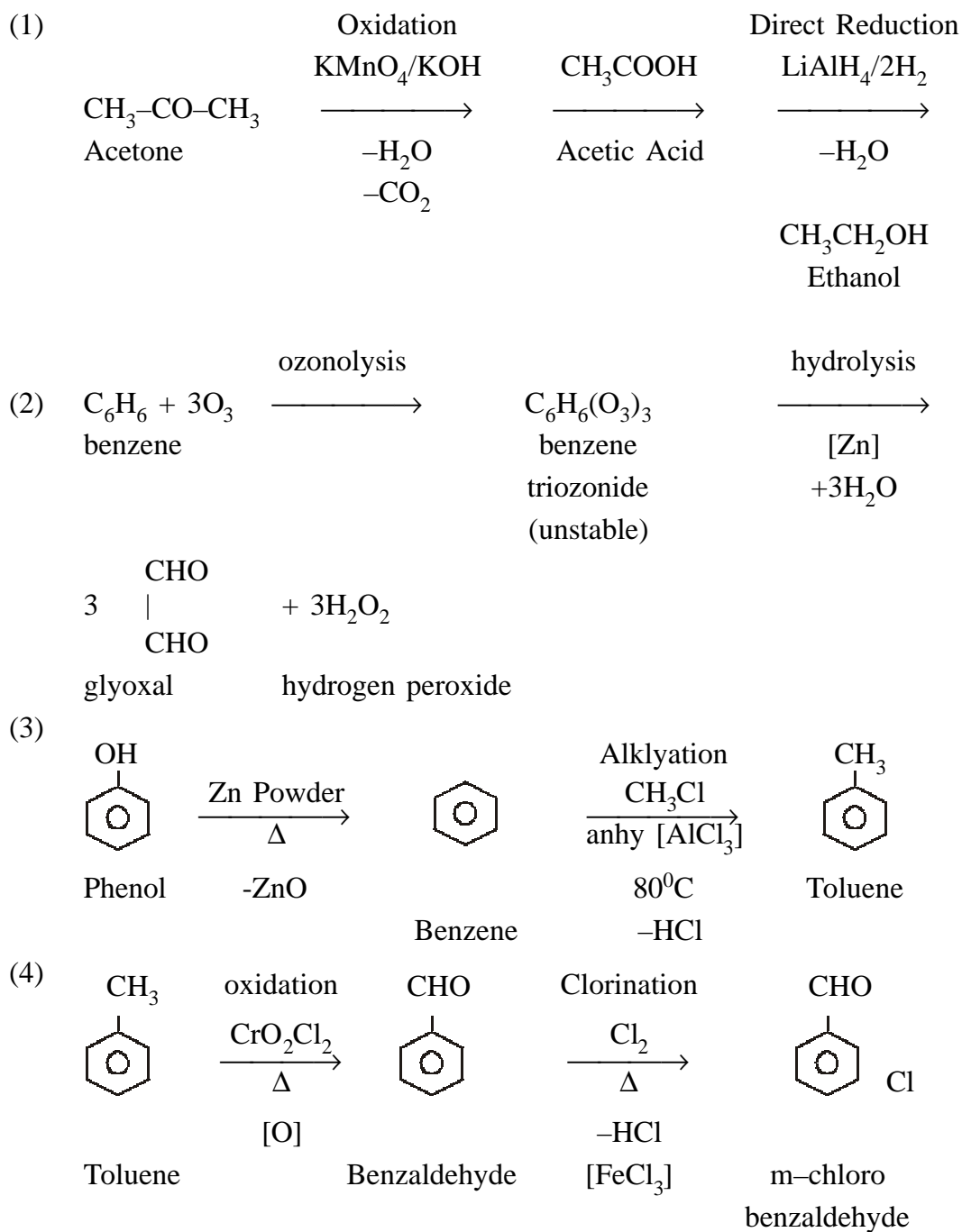
(a) Maintaining electrical neutrality of solutions.

(b) It provides a connection between two solutions.





## Q. 3. (B)

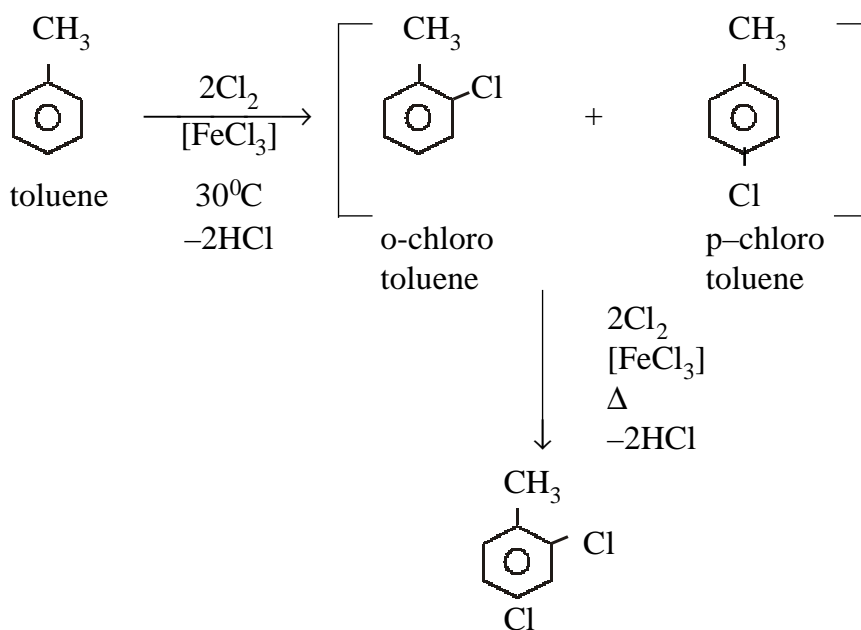


## Q. 3. (C)

- (1) (a) At ordinary temperature all the elements of alkali group exhibit body centered cubic type crystal structure with coordination number 8. At very low temperatures lithium metal shows a hexagonal close packed crystal structure having coordination number 12. The attractive force holding the atoms or ions together in the solid state is called the cohesive energy. Cohesive energy is also a measure of hardness. It depends on the number of bonding electrons and their binding energies. The progressive increase 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 electronegativity they form ionic bonds. For example, the electronegativity 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.

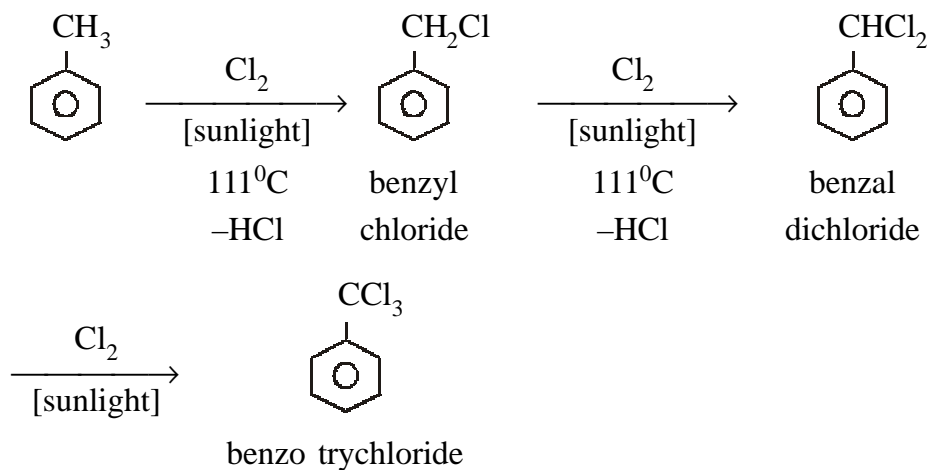
## (2) Chlorination of Toluene :

Toluene and chlorine at 30°C in presence of catalyst FeCl<sub>3</sub> give a mixture of o-Chlorotoluene and p-Chlorotoluene by first chlorination. These two isomers can be separated by Fractional distillation. If temperature is raised in above reaction, second chlorination occurs giving 2, 4-dichlorotoluene.

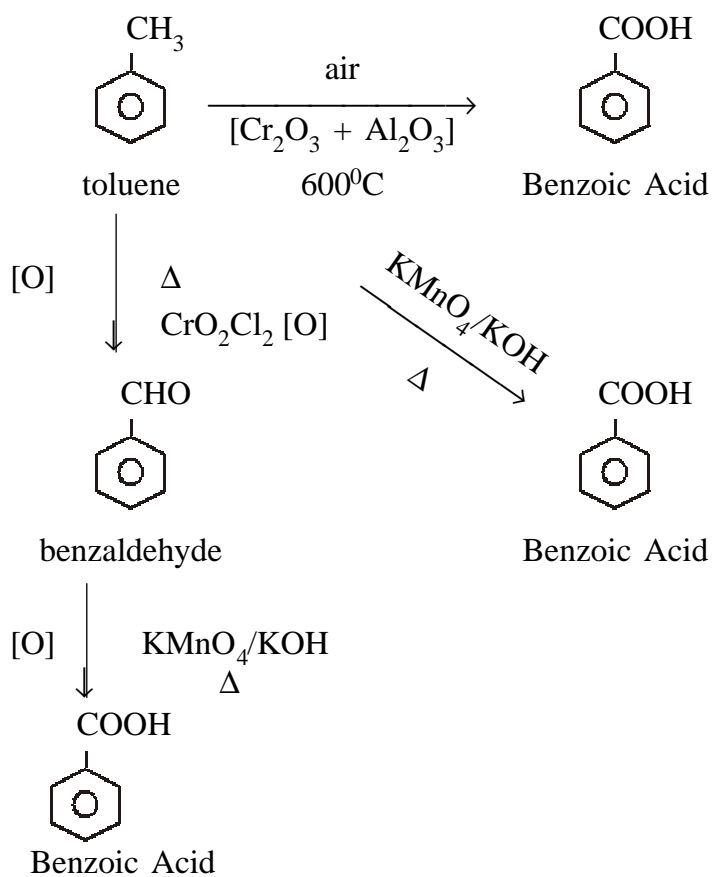


2 : 4 – dichloro toluene.

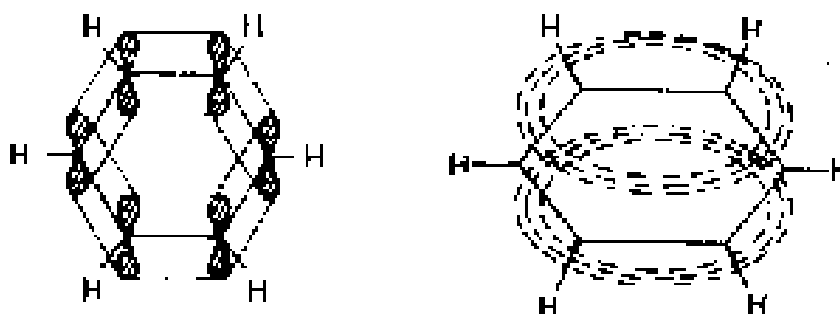
## (3) Chlorination of Methyl group



## → Oxidation of Methyl group.

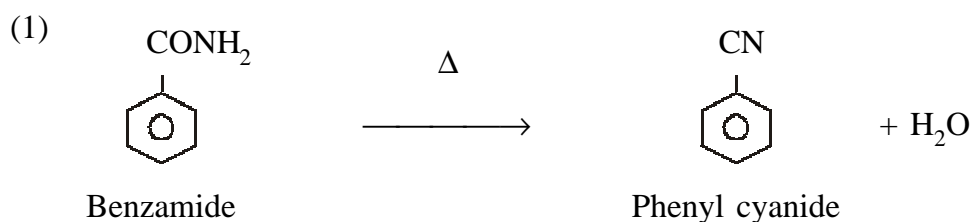


- (4) Structure of benzene presented according to Molecular orbital theory.
- Benzene has each carbon  $sp^2$  hybrid the three  $\sigma$  bonds are all planar at  $120^\circ$ .
  - 6 carbon, 6 hydrogens, 6 C-C bonds and 6 C-H bonds are all in one plane.
  - Moreover on each six carbons we have  $2P_z$  orbitals at right angles to the plane, containing on each of  $6\pi$  electrons.
  - Molecular orbital theory suggests that due to overlap of six  $2P_z$  orbitals of 6 carbon atoms a large circular shaped – molecular orbital is formed and these  $6\pi$  electrons are moving because of their delocalisation. Thus all six carbon in Benzene are identical.
  - The charge cloud of benzene containing  $6\pi$  electrons also supports its lesser potential energy or justifies its resonance energy.

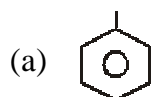
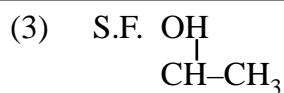


Molecular ring       $P_4O_{10}$  orbital shape of ring structure of benzene.  
dehydration

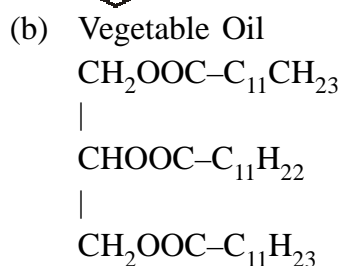
**Q. 4. (A)**



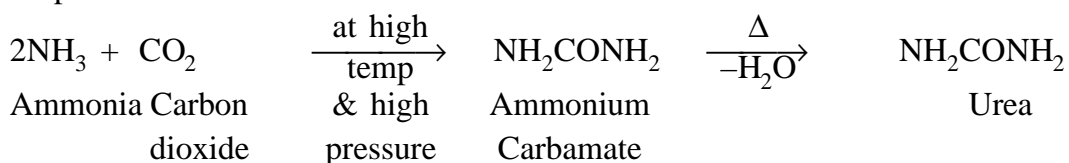
- (2) Hemoglobin is a complex combines with oxygen obtained through lungs and forms an intermediate compounds which supplies oxygen to tissues.



1-phenyl 1-Ethanol

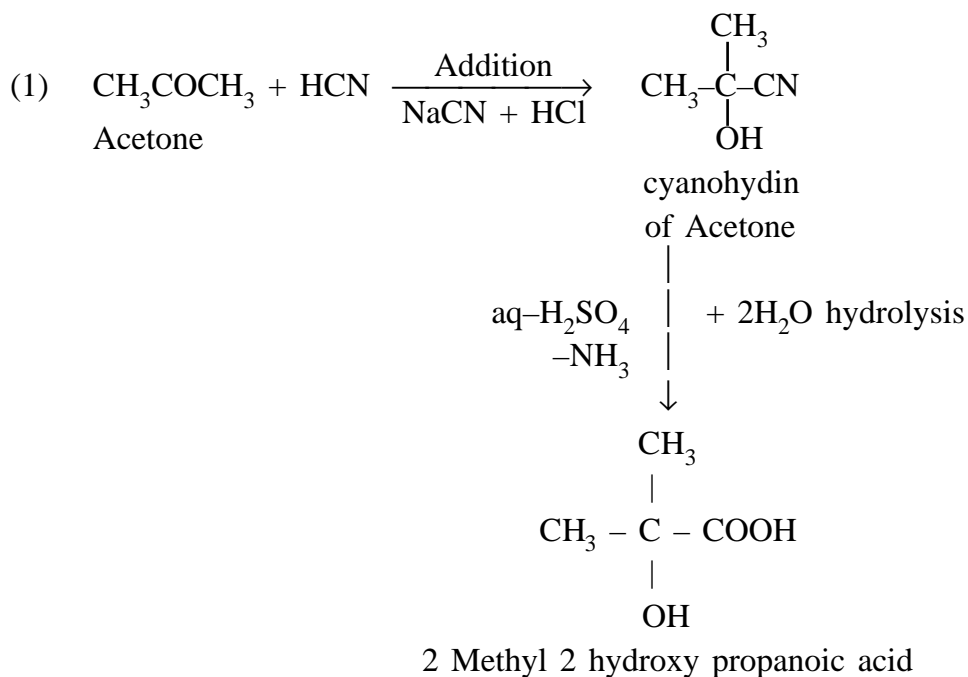


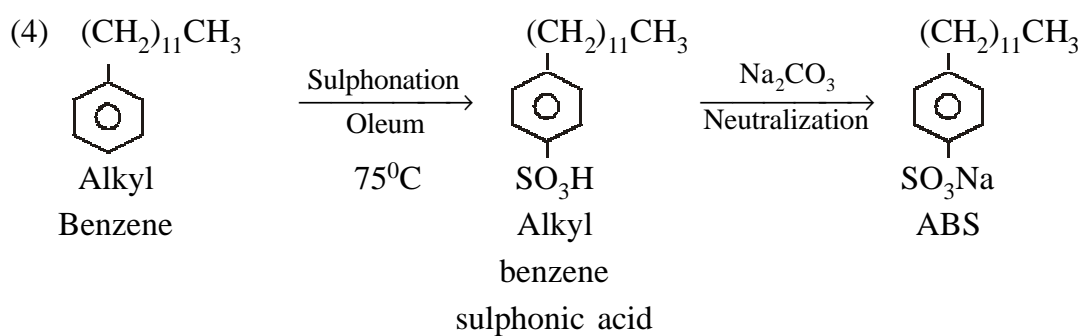
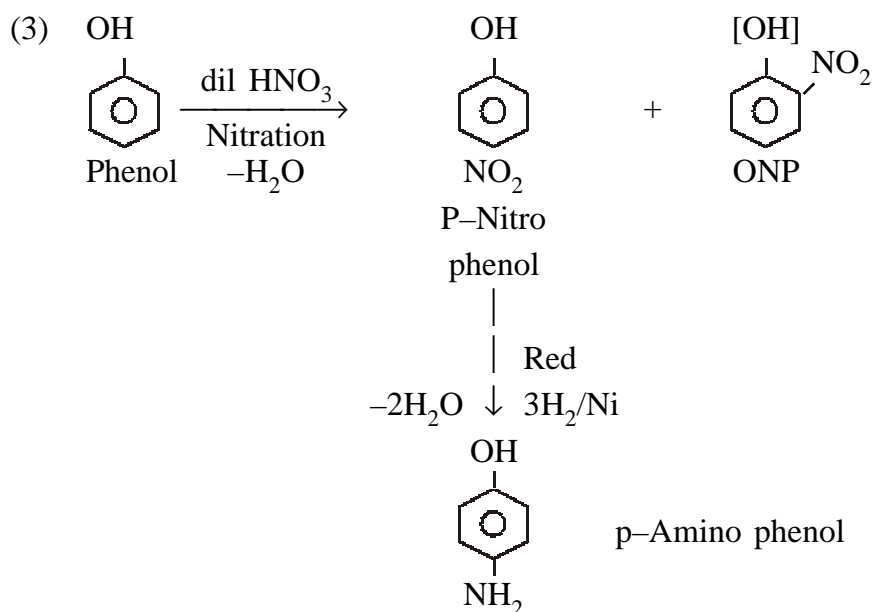
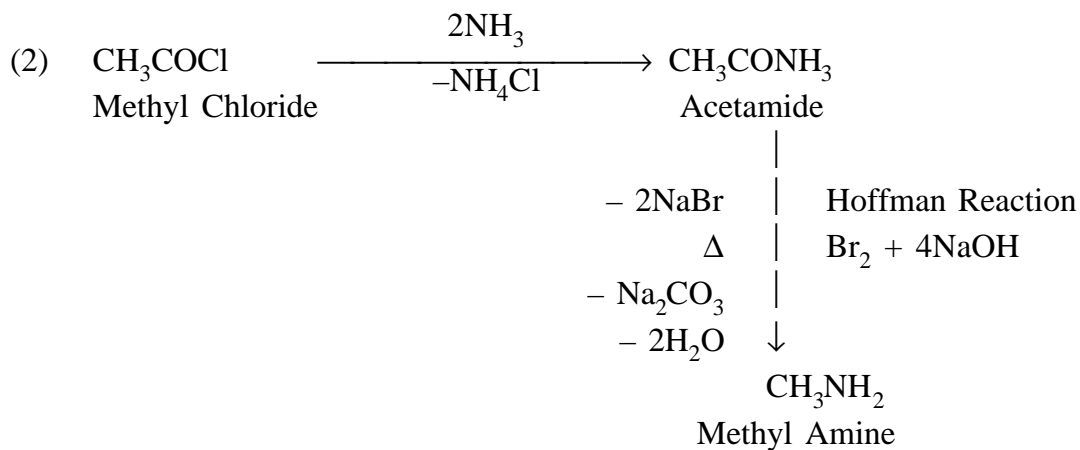
(4) Preparation of Urea :



(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.

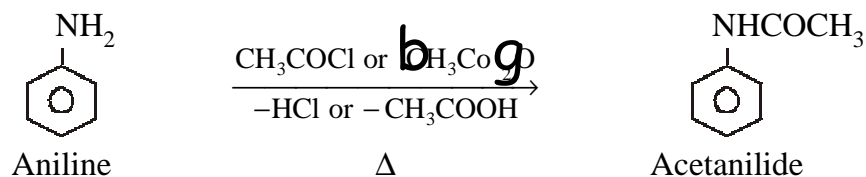
**Q. 4. (B) Conversions :**





**Q. 4. (C) Acylation of Aniline :**

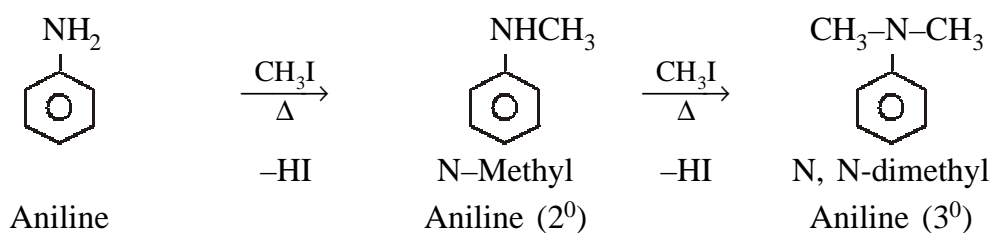
(1) (i)



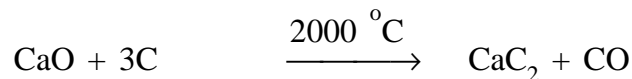
⇒ Aniline when heated with acetyl chloride acetic anhydride gives Acetanilide by Acetylation.

**(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**.

**(2) Nitrogen based fertilizer(Nitrolin) :**

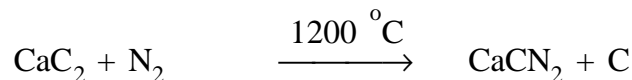
(a) When a mix of calcium oxide and carbon is heated in an electric furnace at 2000°C. CaC<sub>2</sub> is formed



Calcium oxide

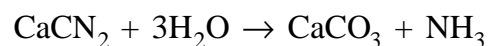
Calcium Carbide

⇒ CaC<sub>2</sub> is then finely powdered and places in electric furnace having porous walls at 1200°C N<sub>2</sub> is passed n to thefurnato which give calcium.cyanamide.

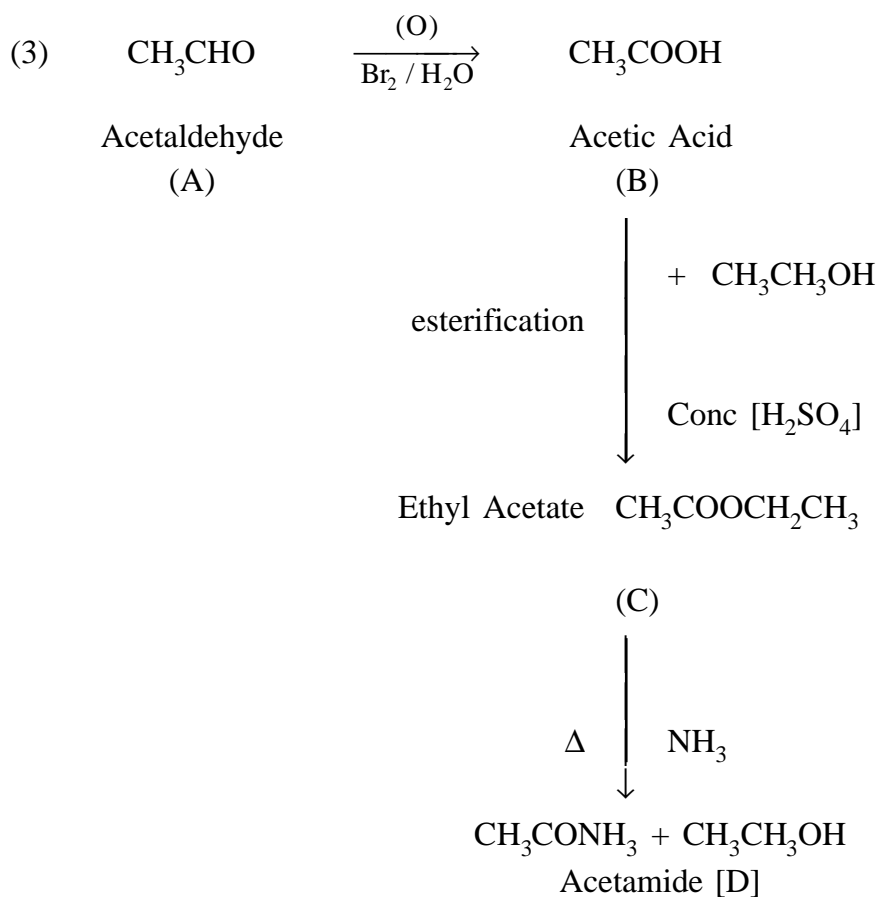
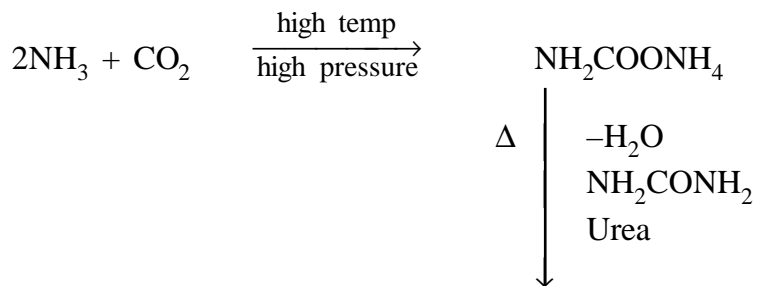


⇒ Fine powder of calcium cyanamide is used as Nitrolim [Nitrogen + Lime]

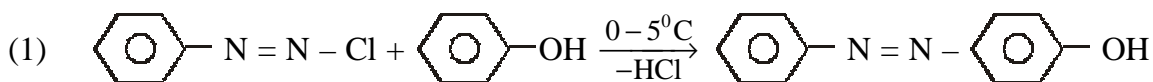
⇒ In the soil containing moisture, Nitrolim hydrolyse giving CaCO<sub>3</sub> and NH<sub>3</sub>.





(b) Urea ( $\text{NH}_2\text{CONH}_2$ )

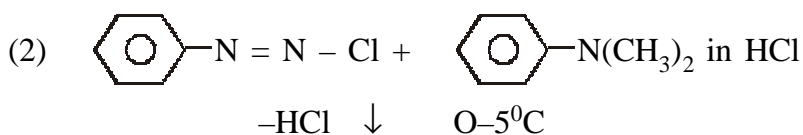
- [A] = Acetaldehyde  
 $\text{CH}_3\text{CHO}$
- [B] = Acetic Acid  
 $\text{CH}_3\text{COOH}$
- [C] = Ethyl Acetate  
 $\text{CH}_3\text{COOC}_2\text{H}_5$
- [D] = Ethanol  
 $\text{C}_2\text{H}_5\text{OH}$

**(4) Azo coupling Reaction :**

Benzene  
diazonium  
chloride

Phenol  
in NaOH

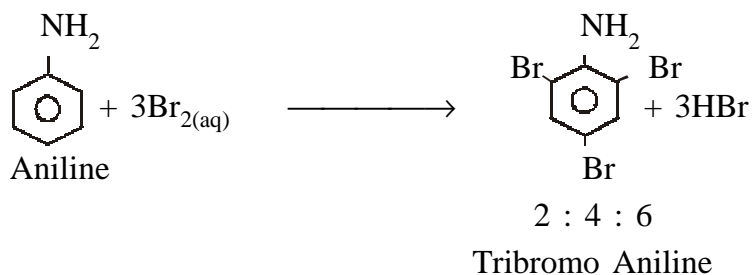
p-Hydroxy  
Azobenzene  
(orange Azodye)



p-Dimethyl Amino azo benzene (Yellow Dye)

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

⇒ When Benzene diazonium chloride react with N-N- dimethyl Aminobenzene in HCl at  $0-5^\circ\text{C}$  temp. obtained yellow azo-dye.

**(2) Bromination of Aniline :**

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

⇒ When  $\text{Br}_2$  water is added to Aniline and shaken.

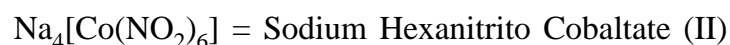
⇒ Bromination in the aromatic nucleus gives white precipitates of 2, 4, 6 tribromo Aniline.

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

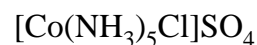
(2) The +4 oxidatin state of vanadium exhibits low stability.

(3) Two co-ordinate sites are present in Bidentate ligands and Three co-ordinate sites are present in Tridentate ligands.

(4) **IUPAC Name :**



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



Potassium Penta cyano carbonyl ferrate (II)



**Q. 5. (B) (1)  $\text{ML}_6$  – complex : Geometry of  $\text{ML}_6$  complex :**

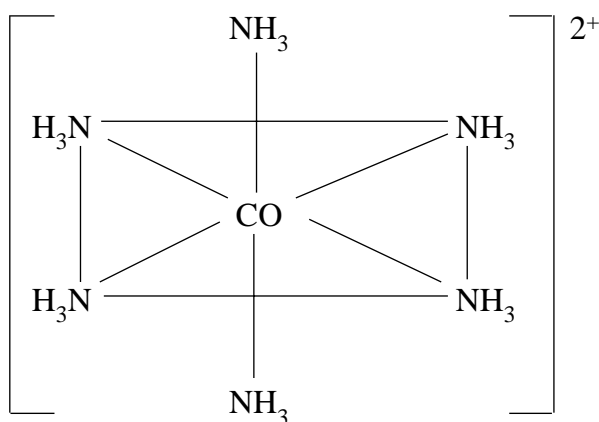
$\Rightarrow$  The co-ordination number of the central metal ion and the geometry of the complex can be known from the studies of magnetic properties of the complexes.

$\Rightarrow$   $\text{ML}_6$  complex metal ion having six-ordination number have octahedral geometry.

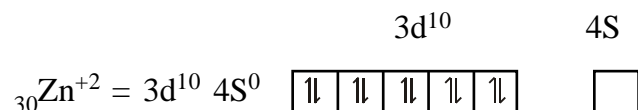
$\Rightarrow$  However the Oh is distorted if different ligands are present in the complex.

$\Rightarrow$  When two 3d, one 4s and three 4p orbitals or one 4d, three 4p and two 4d orbitals of metal ions of  $\text{ML}_6$  complex get six new equienergetic  $d^2sp^3$  or  $sp^3d^2$  hybrid orbitals are formed and hence an octahedral geometry ligands donate lone pairs to the central metal ion.

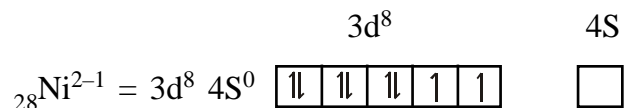
e.g.  $[\text{Co}(\text{NH}_3)_6]^{+2}$



(2) In  $\text{ZnSO}_4$  electronic configuration of  $\text{Zn}^{+2}$



$\Rightarrow$  In  $\text{NiSO}_4$ , electronic configuration of  $\text{Ni}^{2+}$



$\Rightarrow$  In  $\text{NiSO}_4$   $d^8$  arrangement contains unpaired electron. Hence d-d transition is possible.  $\therefore$  So  $\text{NiSO}_4$  is coloured.

$\Rightarrow$  In  $\text{ZnSO}_4$   $d^{10}$  configuration d-d transition is not possible. Hence  $\text{ZnSO}_4$  is colourless.

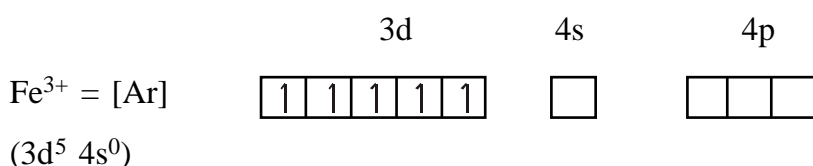
(3) **Inert gases**

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

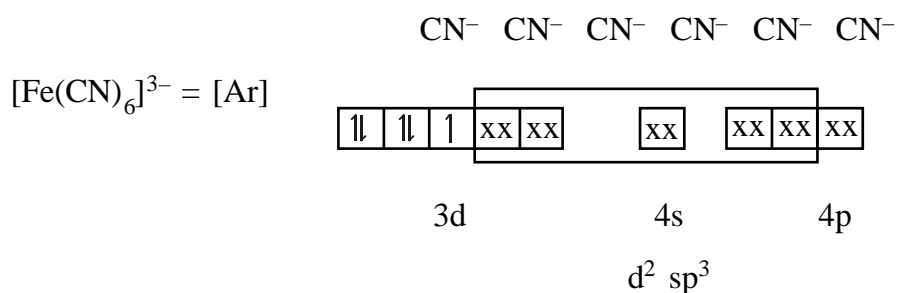
**Q. 5. (C) (1) \*** In  $\text{K}_3[\text{Fe}(\text{CN})_6]$

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

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



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



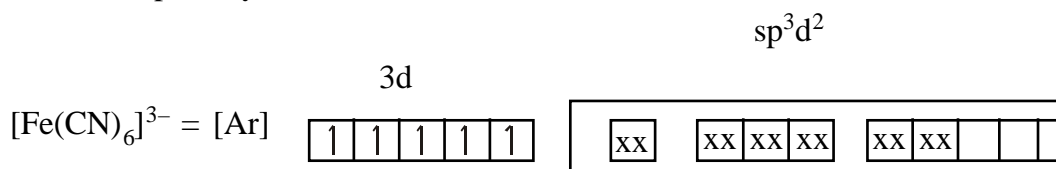
$\Rightarrow$  For  $d^2sp^3$  hybridization rearrangement of electrons take place in orbitals and make two vacant orbitals.

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

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

**Q. 5. (C)**

(1) For  $sp^3d^2$  hybridization :



⇒ 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 ( $\text{CN}^-$ ) accomodate in six equal energenic hybrid orbitals to form Oh shape.

⇒ Here five electrons are unpaired

∴ So it is also paramagnetic.

But experimentally  $\text{K}_3\text{Fe}(\text{CN})_6$  is paramagnetic and its magnetic momentum is nearly 1–73 B–M, hence it indicates that  $\text{K}_3\text{Fe}(\text{CN})_6$  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 Alltrops of Antimony.

(a) Yellow or  $\alpha$ -Antimony

$\Rightarrow$  It is stable

(b) Mettalic or  $\beta$ -Antimony

$\Rightarrow$  It is silvery white.

(3) Electronic configuration of Transition Metals.

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

(4) In  $\text{CuCl}_2 \rightarrow \text{Cu}$  is  $\rightarrow \text{Cu}^{+2}$

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

$\Rightarrow$  In  $\text{CuCl}_2$  d<sup>9</sup> configuration has one unpaired electron. There fore it is paramagnetic

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

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

↑↓	↑↓	↑↓	↑↓	↑↓
----	----	----	----	----

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

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

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

↑↓	↑↓	↑↓	↑↓	↑
----	----	----	----	---

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

↑↓	↑↓	↑↓	↑↓	↑↓
----	----	----	----	----

$\Rightarrow$  If transition elements or ions have d<sup>0</sup>, d<sup>5</sup>, d<sup>10</sup> electronic configuration then it is stable.

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

$\Rightarrow$  Since removal of 4e<sup>-</sup> from Ti atom requires very large amount of energy.

$\Rightarrow$  There fore  $\text{Ti}^{4+}$  ion is not possible but (+4) oxidation state is found in covalent compound. eq.  $\text{TiCl}_4$

—\*—