Solutions to IIT JEE-2005 Mains Paper (Memory based)

Chemistry

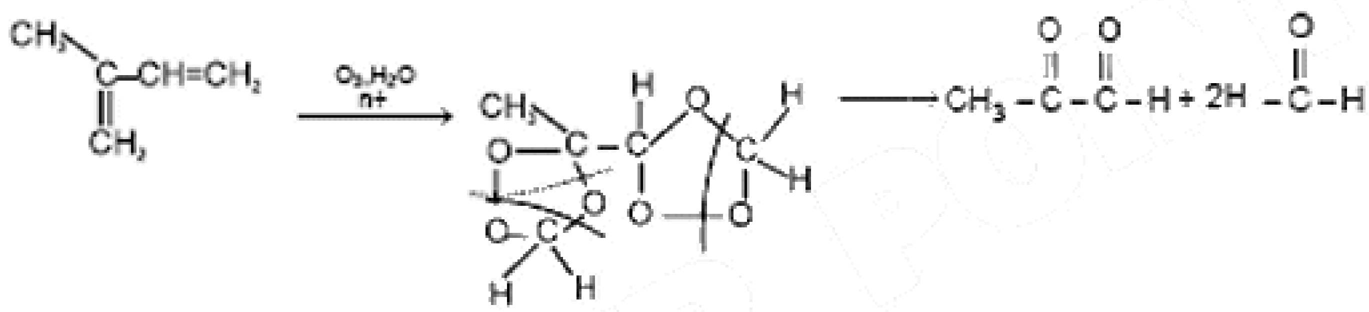
Q.1 HCHO and $CH_3-\overset{\overset{O}{||}}{C}-\overset{\overset{O}{||}}{C}-H$ are the products obtained on ozonolysis of a monomer (A) of a polymer.

(a) Give the structure of (A)

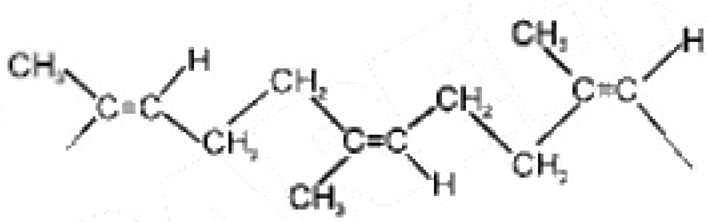
(b) Draw the "all-cis" form of a polymer of a monomer (A) **[2]**

Sol. (a) Since the products obtained are $\underset{\text{(two moles)}}{HCHO}$ and $\underset{\text{(One mole)}}{CH_3-\underset{\underset{O}{||}}{C}-\underset{\underset{O}{||}}{C}-H}$, it confirms the presence of two double bonds.

Therefore the structure will be :



(b)



Q.2 Fill in the blanks

(a) ${}^{236}U_{92} + {}_0n^1 \longrightarrow {}^{137}A_{52} + {}^{97}B_{40} +$ ....

(b) ${}^{82}Se_{34} \longrightarrow 2\,{}_{-1}\beta^0 +$ .... **[2]**

Sol. (a) ${}^{236}U_{92} + {}_0n^1 \longrightarrow {}^{137}A_{52} + {}^{97}B_{40} + 2\,{}_0n^1$

(b) ${}^{82}Se_{34} \longrightarrow 2\,{}_{-1}\beta^0 + {}^{82}Kr_{36}$

Q.3 For an element of FCC crystal lattice having edge length 400 pm, calculate the maximum diameter of an atom which can be placed in interstitial site so that the structure remain same. **[2]**

Sol. For FCC, interstitial

For octahedral voids and Tetrahedral voids

$\frac{r_1}{r_2} = 0.414$ $\qquad\qquad$ $\frac{r_1}{r_2} = 0.225$

r_1 = Radius of atomic interstitial site $\qquad$ r_2 = Radius of atom arranged in FCC.

$4r_2 = \sqrt{2}\,a$

Octahedral voids will be considered and for maximum diameter of atom in interstial sites

Diameter = $2r_1 = 2(\sqrt{2}\,r_2)$ $\qquad = 2 \times 0.414 \times \frac{400}{2\sqrt{2}} = 117.1$ pm.

Q.4 (a) What is the weight of calcium oxide when 852 gms of P_4O_{10} reacts with it.
(b) Draw the structure of P_4O_{10}. **[2]**

Sol. (a) The balanced chemical equations

$$6\,CaO + P_4O_{10} \longrightarrow 2Ca_3(PO_4)_2$$

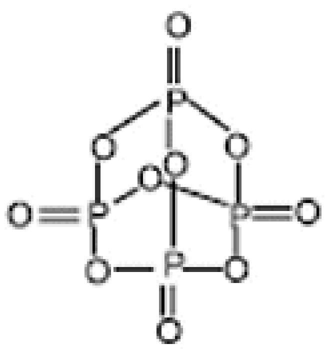
6 moles of CaO reacts with 1 mole of P_4O_{10}

$$\text{moles of } P_4O_{10} = \frac{852}{284} = 3$$

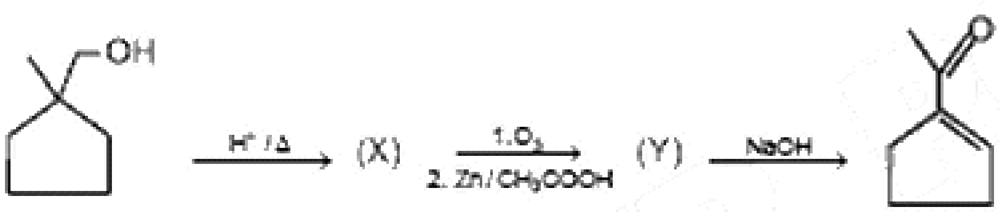
$\therefore$ Moles of CaO is equal to 18

$W_{CaO} = 18 \times 56 = 1000$ gm

(b)

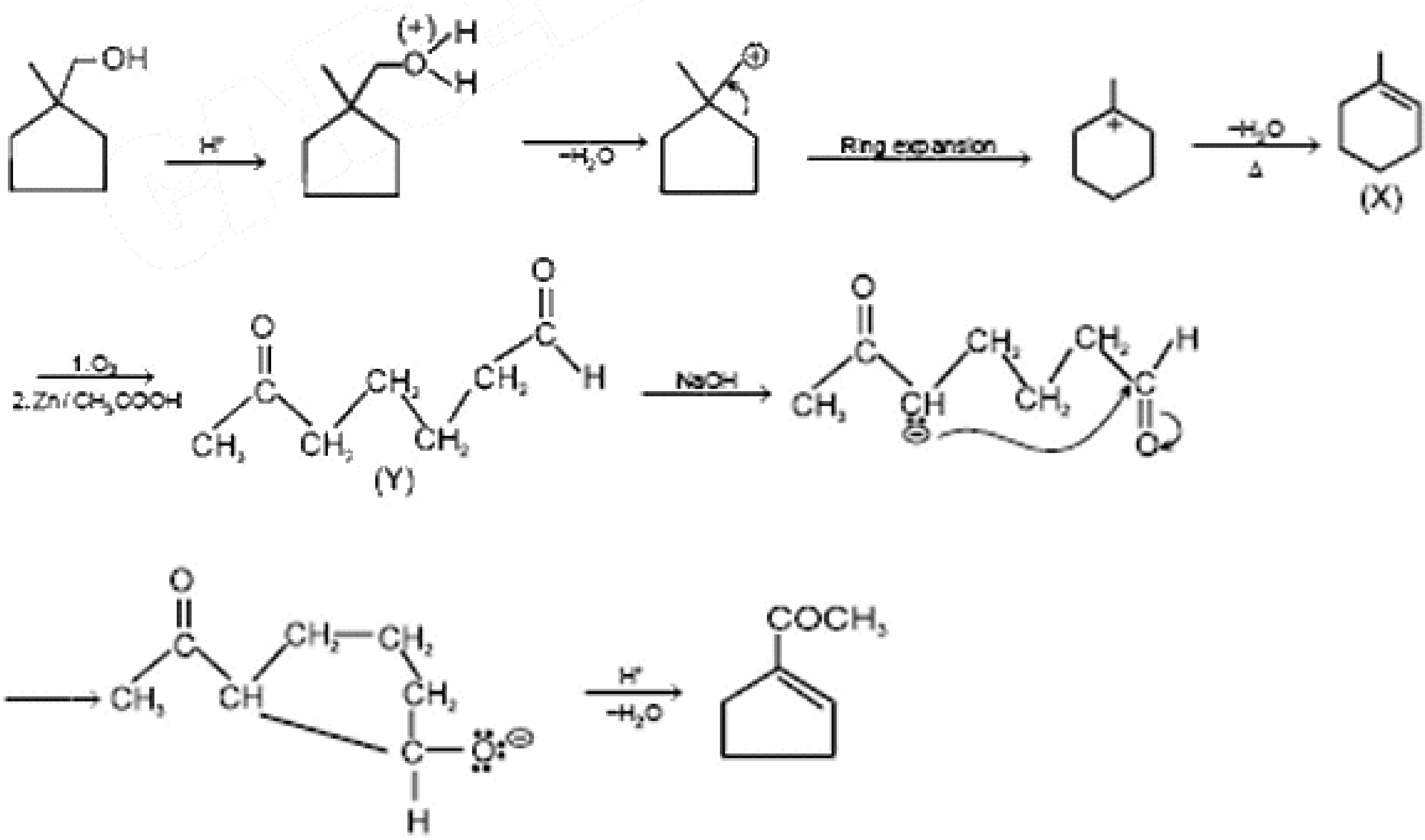


Q.5



Identify (X) and (Y). **[2]**

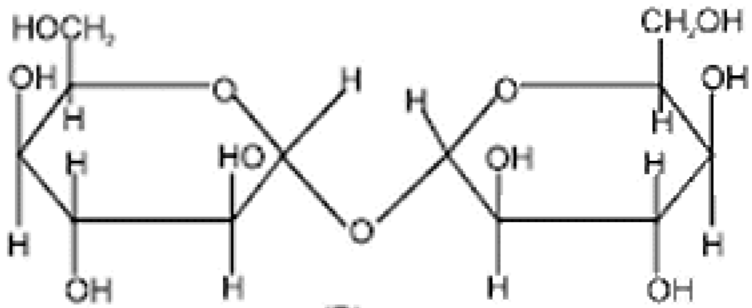
Sol.



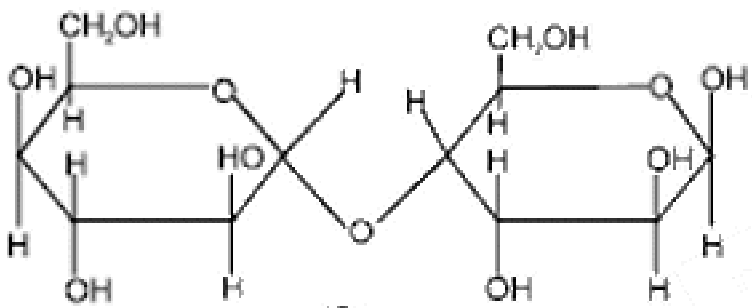
Q.6 Predict whether the following molecules are isostructural or not. Explain your answer.
(i) NMe_3
(ii) $N(SiMe_3)_3$ **[2]**

Sol. $N(Me)_3$ is trigonal pyramidal because of 3 – bond pairs and one lone pair. Because of back bonding ($p\pi$-$d\pi$ bonding). In $N(SiMe_3)_3$ the shape is trigonal planar.

Q.7 Which of the following disaccharide will not reduce Tollen's reagent ?



(P)



(Q)

[2]

Sol. In structure (Q) one ring is present in the form of hemiacetal. It will hydrolyse and reduce Fehling's solution.
In structure (P) both the rings are present in acetyl form it will not hydrolyse in solution hence no reaction with Fehling's solution.

Q.8 N_2 is adsorbed in 20% of the surface sites. N_2 gas evolved on heating was collected at 0.001 atm and 298 K in a container of volume 2.46 cm^3. Find out the no. of surface sites occupied per molecule of N_2. If the density of surface sites is $6.023 \times 10^{14}/cm^2$ and surface area is 1000 cm^2. **[2]**

Sol. For nitrogen gas
$P(N_2) = 0.001$ atm
$T = 298$ K; $V = 2.46$ cm^2
Applying ideal gas equation $PV = nRT$

$$\therefore \quad n_{(N_2)} = \frac{0.001 \times 2.46 \times 10^{-3}}{0.0821 \times 298} = 1 \times 10^{-7}$$

N_2 molecules $= 6.023 \times 10^{23} \times 10^{-7} = 6.023 \times 10^{16}$
Surface sites $= 6.023 \times 10^{14} \times 1000 = 6.023 \times 10^{17}$

Since 20% of the sites are used to adsorb $= \frac{20}{100} \times 6.023 \times 10^{17} = 12.04 \times 10^{16}$

$$\Rightarrow \text{ Site occupied per molecule } = \frac{12.04 \times 10^{16}}{6.02 \times 10^{16}} = 2$$

Q.9. For developing black and white photographic film, give the balanced chemical equation. Sodium thiosulphate on acidification turns milky. Give the balanced chemical equation. **[4]**

Sol. For developing photographic film, reactions are
$AgBr + 2Na_2S_2O_3 \longrightarrow Na_3[Ag(S_2O_3)_2]$. The milkiness appears because of sulphur
$Na_2S_2O_3 + 2H^+ \longrightarrow 2Na^+ + H_2SO_3 + S$.

Q.10 For a reaction

$2X_{(g)} \longrightarrow 3Y_{(g)} + 2Z_{(g)}$

the data of partial pressure of X with time is given below (assume ideal gas conditions)

Time (Min)	0	100	200
P_x (mm of Hg)	800	400	200

Calculate -

(a) Order of reaction

(b) Rate constant

(c) time required to complete 75% of reaction

(d) Total pressure of reaction mixture if p_x = 700 mm **[4]**

Sol. $2X_{(g)} \longrightarrow 3Y(g) + 2Z_{(g)}$

(a) $t_{1/2}$ is independent of initial conc. of X, hence reaction is first order. ($t_{1/2}$ = 100 min)

(b) $K = \dfrac{0.693}{t_{1/2}} = \dfrac{0.693}{100} = 6.93 \times 10^{-3}\ \text{min}^{-1}$

(c) Time required $= 2\,t_{1/2} = 2 \times 100 = 200$ min.

(d)
$$\begin{array}{lcll} 800 & & 0 & 0 \\ 2X_{(g)} & \longrightarrow & 3Y(g) + & 2Z_{(g)} \\ 800 - 2p & & 3p & 2p \end{array}$$

$800 - 2p = 700$

$2p = 100$

$p = 50$ mm

Total pressure (P_T) = 800 + 3 p = 950 mm.

Q.11 In the given reaction sequence. Identify (A) and (B)

$Fe^{3+} + \xrightarrow[\text{(Excess)}]{SCN^-} \underset{\text{Blood red}}{(A)} \xrightarrow{F^-\text{(excess)}} \text{colourless (B)}$

(a) Write the IUPAC name of (A) and (B)

(b) Find out the spin only magnetic moment of B. **[4]**

Sol. $Fe^{3+} + \underset{\text{(excess)}}{SCN^-} \xrightarrow{\text{aqueous}} [Fe(SCN)(H_2O)_5]^{2+}$

$\underset{\text{(Blood Red)}}{\underset{(A)}{[Fe(SCN)(H_2O)_5]^{2+}}} + 6F^- \longrightarrow \underset{\text{(Colourless)}}{\underset{(B)}{[FeF_6]^{3-}}} + SCN^- + 5H_2O$

(a) IUPAC name of

(A) is Pentaaquathiocyanato iron (III) ion

(B) is Hexafluroferrate (III)

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

$= \sqrt{35} = 5.92$ B.M. Where n = 5

(No. of unpaired electron).

Q.12 (a) For first orbit of hydrogen atom, calculate the velocity of electron ($r = a_0 = 0.529$ Å)

(b) Calculate the de-broglie wavelength of electron in first Bohr orbit

(c) Calculate the orbital angular momentum of 2p orbital in terms of $h/2\pi$ units **[4]**

Sol. (a) $V = 2.18 \times 10^8 \times Z/n$ cm/sec $= 2.18 \times 10^8$ cm/sec

(b) $2\pi R = n\lambda$

$$\lambda = \frac{2\pi R}{n} = 2\pi \times 0.529\ \text{Å}$$
$$= 3.3\ \text{Å}$$

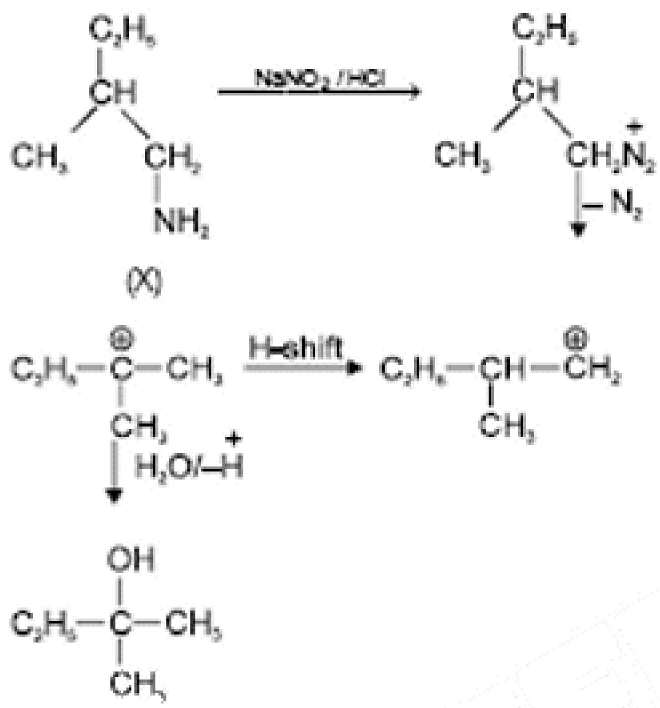
(c) for 2p, $\ell = 1$

orbital angular momentum = $\frac{h}{2\pi}\sqrt{\ell(\ell+1)} = \sqrt{2} \times \frac{h}{2\pi}$.

Q.13 $C_5H_{13}N \xrightarrow[-N_2]{NaNO_2/HCl}$ Tertiary alcohol + other products

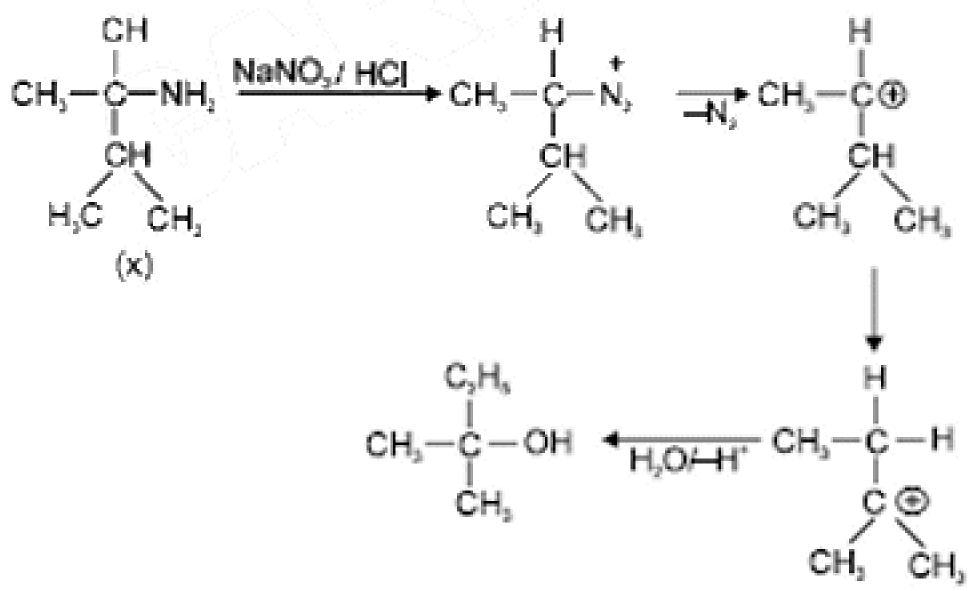
X is optically active. Find X and Y. Is Y optically active ? write all intermediate steps. **[4]**

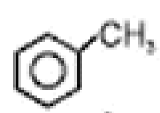
Sol. There are 2-possibilities of X.



(Y)

(Y is optically inactive)

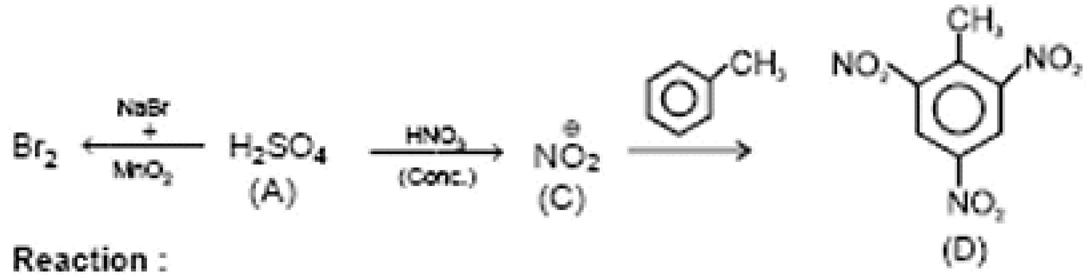


Q.14 (B) $\xleftarrow{NaBr + MnO_2}$ (A) $\xrightarrow{Conc.\ HNO_3}$ (C)  $\longrightarrow$ (D) (Explosive Product)

(Brown fumes & Pungent smell) (Intermediate)

Identify the missing compounds. Give the equation from A to B and A to C. **[4]**

Sol.



Reaction :

$$2\,NaBr + MnO_2 + 2H_2SO_4 \longrightarrow Br_2\uparrow + Na_2SO_4 + MnSO_4 + 2H_2O$$

(A) (B)

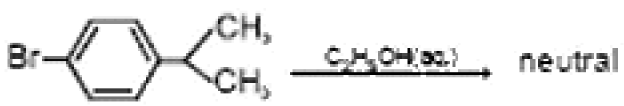
$$H_2SO_4 + HNO_3 \longrightarrow HSO_4^- + \overset{\oplus}{N}O_2 + H_2O$$

(A) (C)

Q.15 Give reasons :

(a) (i)

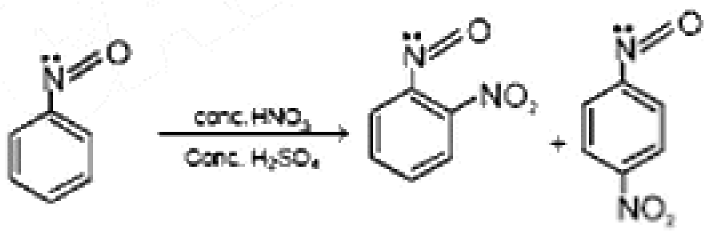
(ii)



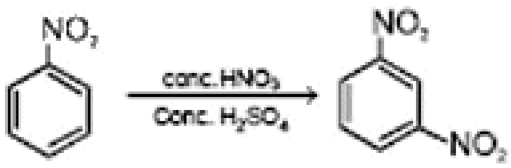
(b) (i)

(ii)

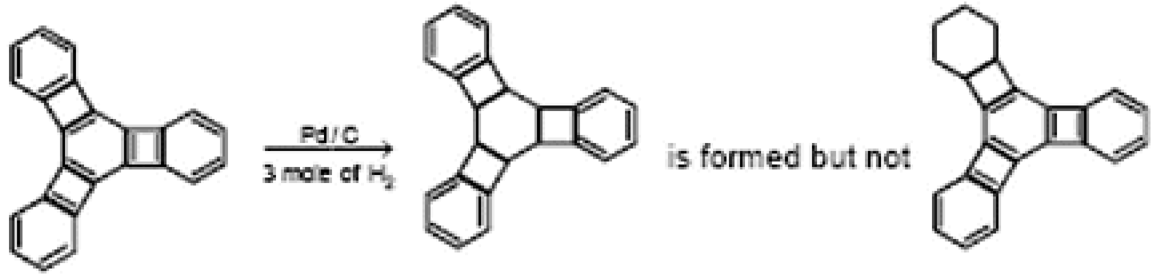
(c) (i)



(ii)

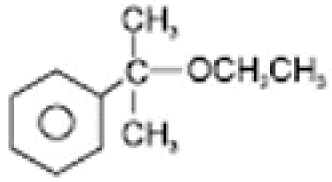


(d)

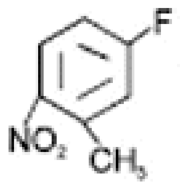


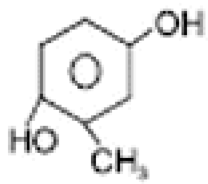
[4]

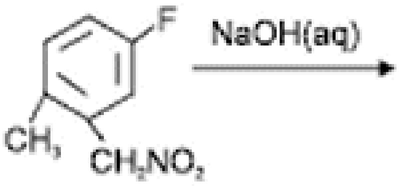
Sol. (a) (i) The products formed are



and HBr by nucleophilic substitution and because of presence of HBr, the solution is acidic.
(ii) There will be no reaction because Br group is directly attached to the Bengene ring (no possibility of S_N reaction)

(b) (i)  will undergo nucleophilic substitution as NO_2 group makes benzene ring electron deticient and

the product formed B 

(ii)  F^- is not liberated because the ring does not become electron deficient and will not undergo SN^2 reaction

(c) (i) Because of presence of lone pair of electrons, the ring gets attacked and gives ortho and para products.
(ii) Because of –I effect, NO_2 is strongly deactivating group, hence m-director.
(d) Three- four membred
Anti aromatic rings becomes stable due to the reduction of central ring and only on antiaromatic ring can be stabilized on reduction of terminal ring.

Q.16 (B) $MCl_4 \xrightarrow{Zn}$ (A)
(white fumes pungent smell) (M = transition colourless) (Purple colour)
Identify the metal M and MCl_4
Explain the colour difference of MCl_4 and (A). **[4]**

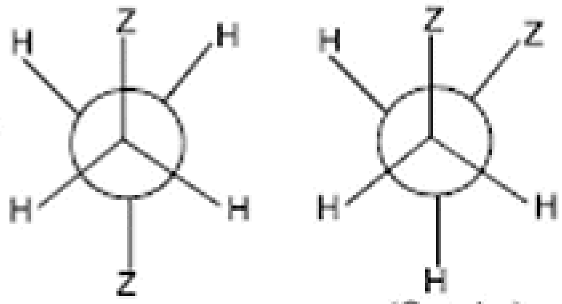
Sol. $TiO_2 \xleftarrow{\text{MOist: air}} TiCl_4 \xrightarrow{Zn} (Ti(H_2O)_6)^{3+}$
(B) (A)
(Purple colour)
d – d transition of single electron of Ti (III) will cause color change and Ti (iv) contains no d- electrons.

Q.17 (a) $\mu_{observed} = \sum \mu_i x_i$
where μ_i is the dipole moment of stable conformes and x_i is mole fraction of that conformer.
(i) Draw the New man's projection for stable
conformers of $Z–CH_2–CH_2–Z$.
(ii) If $\mu_{observed}$ = 1.0 D and mole fraction of anti form = 0.82, find μ_{gauche}

(b) Draw most stable meso conformer of $\begin{matrix} CHDY \\ | \\ CHDY \end{matrix}$

if (i) Y= CH_3 about $C_2 – C_3$ rotation and
(ii) Y = OH about $C_1 – C_2$ rotation **[6]**

Sol. (a)



(Anti) (Gauche)

(ii) $X_{anti} = 0.82$

$x_{gauche} = 0.18$

$\mu_{observed} = \mu_{anti} \times 0.82 + \mu_{gauche} \times 0.18$

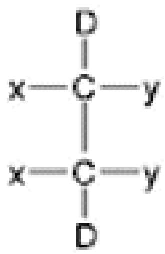
$\mu_{anti} = 0$ {due to symmetry}

$\therefore$ $1 = \mu_{gauche} \times 0.18$

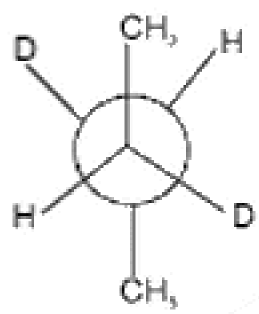
$\mu_{gauche} = 1/0.18$

$= 5.55$ D

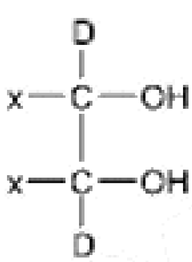
(b) (i)

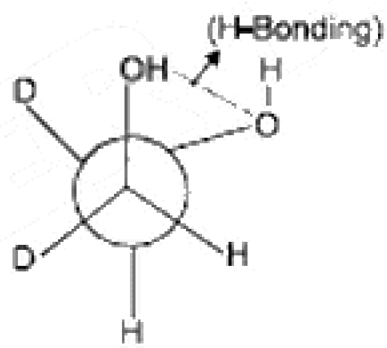


(y = CH_3)



(ii)





Q.18 (a) (i) Represent the following reaction in the form of a cell

$Ag^+ (aq) + Cl^- (aq) \longrightarrow AgCl(s)$

(ii) Calculate $\Delta G°$ of the above reaction from the following data :

$\Delta G°_f$ (AgCl) = –109 kJ/ mol

$\Delta G°_f$ (Cl^-) = –129 kJ/ mol

$\Delta G°_f$ (Aq) = 77 kJ/ mol

(iii) Calculate E° of the cell.

(iv) Calculate $\log_{10} K_{sp}$ for AgCl

(b) 6.539×10^{-2} g of metallic Zn (65.39 amu.) was added to 100 ml of saturated solution of AgCl. Calculate

$\log_{10} \frac{[Zn^{2+}]}{[Ag^+]^2}$, given

$Ag^+ + e^- \longrightarrow Ag$ E° = 0.80 V

$Zn^{2+} + 2e^- \longrightarrow Zn$ E° = –0.76 V

Also find how many moles of Ag will be formed. [6]

Sol. Cell Reactions :-

(1) $Ag(s) + 1/2\ Cl_2(g) \longrightarrow AgCl(s)$

(2) $Ag(s) + \longrightarrow Ag^+\ (aq) + e^-$

(3) $1/2\ Cl_2(g) + e^- \longrightarrow Cl^-(aq)$

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(1) – (2) – (3): $Ag^+(aq) + Cl^-(aq) \longrightarrow AgCl\ (s)$

(i) Cell Representation

$Ag/Ag^+/AgCl/Cl^-/Cl_2\ Pt.$

$Ag+(aq) + Cl–(aq) \longrightarrow AgCl(s)$

(ii) $\Delta G^\circ = \sum \Delta G^\circ(P) - \sum \Delta G^\circ(R)$

$= (-109) - (-129 + 77) \quad = -57\ kJ$

(iii) $\Delta G^\circ = -nFE^\circ\ (n = 1,\ F = 96500)$

$$E^\circ = \frac{-57 \times 1000}{96500 \times 1} = 0.59 \text{ volts}$$

(iv) $Ag+(aq) + Cl^-(aq) \rightleftharpoons Ag\ Cl(s)\ K_{eq}$

$\Delta G^\circ = -\ 2.303\ RT\ \log K_{eq}$

$-57 = -2.303\ RT\ \log K_{eq}$

$$\log K_{eq} = \frac{57000}{2.303 \times 8.314 \times 298} = 10$$

$$K_{eq} = 10^{10} = \frac{1}{[Ag^+][Cl^-]}$$

$K_{sp} = 10^{-10}$

$K_{sp} = s^2 = 10^{-10} \Rightarrow s = 10^{-5}\ mol/L$

(b) (1) $2\ Ag^+_{eq} + 2e^- \longrightarrow 2Ag(s)\ E^\circ = 0.80\ V$

(2) $Zn(s) \longrightarrow Zn^{2+}(aq) + 2e^-\ E^\circ = 0.77\ V$

$$\text{moles of Zn added} = \frac{6.539 \times 10^{-2}}{65.39} = 10^{-3} \text{ moles}$$

(1) + (2): $2\ Ag^+\ (aq) + Zn(s) \rightleftharpoons Zn^{2+}\ (aq) + 2Ag(s)\ E^\circ = 1.57\ V$

(from $\Delta G^\circ = \Delta G_1^\circ, + \Delta G_2^\circ$)

$2\ Ag^+(aq) + Zn(s) \rightleftharpoons Zn^{2+}\ (aq) + 2Ag(s) \qquad E^\circ = 1.57V$

10^{-6} moles 10^{-3} moles.

$n = 2$

at equilibrium $E_{cell} = 0$

$$E^\circ_{Cell} = \frac{0.059}{n} \log \frac{[zn^{2+}]}{[Ag^+]^2}$$

$$\log \frac{[Zn^{2+}]}{[Ag^+]^2} = \frac{1.57 \times 2}{0.0591} = 52.8.$$