

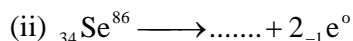
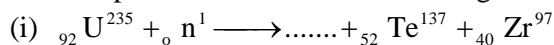


SOLUTIONS TO IIT–JEE 2005, (MAINS)

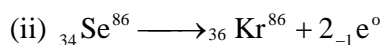
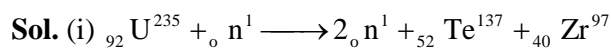
MEMORY BASED QUESTIONS

CHEMISTRY

1. Complete and balance the following reactions.

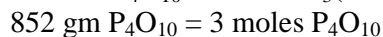
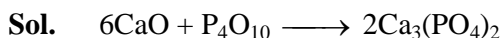


[2]



2. How many grams of CaO are required to neutralize 852 gm of P_4O_{10} ? Draw structure of P_4O_{10} molecule.

[2]

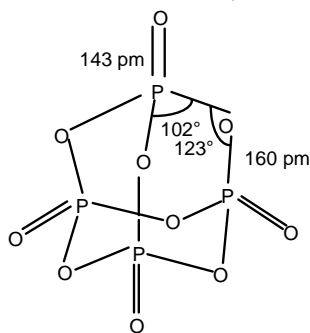


Since 1 mole of P_4O_{10} neutralizes 6 moles of CaO

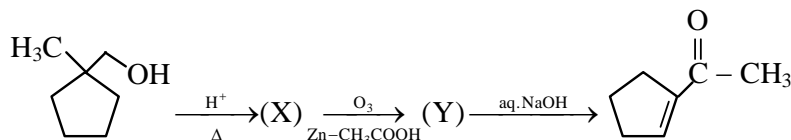
Therefore, 3 moles of P_4O_{10} will neutralize $6 \times 3 = 18$ moles of CaO

\therefore Weight of CaO required = $18 \times 56 = 1008$ gm

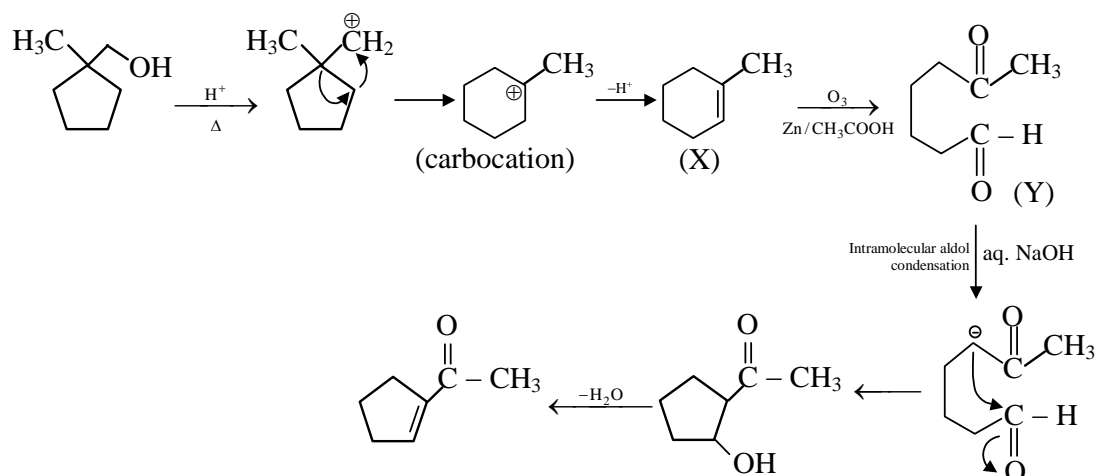
Structure of P_4O_{10} :



3. Identify (X) and (Y) in the following reaction sequence.



[2]

Sol.

4. Find the velocity (in ms^{-1}) of electron in first Bohr's orbit of radius a_0 . Also find the de Broglie's wavelength (in m). Find the orbital angular momentum of 2p orbital of hydrogen atom in units of $\hbar/2\pi$.

[2]

Sol. For hydrogen atom: $Z = 1$, $n = 1$

$$v = 2.18 \times 10^6 \times \frac{Z}{n} \text{ms}^{-1}$$

$$v = 2.18 \times 10^6 \text{ms}^{-1}$$

de Broglie's wavelength,

$$\lambda = \frac{h}{mv} = \frac{6.626 \times 10^{-34}}{9.1 \times 10^{-31} \times 2.18 \times 10^6} = 3.34 \times 10^{-10} \text{m}$$

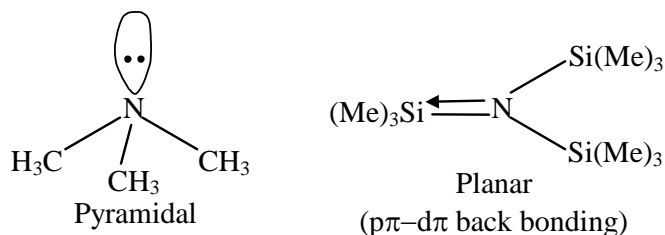
$$\text{Orbital angular momentum} = \sqrt{l(l+1)} \frac{h}{2\pi}$$

For 2p orbital: $l = 1$

$$= \sqrt{2} \frac{h}{2\pi}$$

5. Write the structures of $(\text{CH}_3)_3\text{N}$ and $(\text{Me}_3\text{Si})_3\text{N}$. Are they isostructural? Justify your answer.

[2]

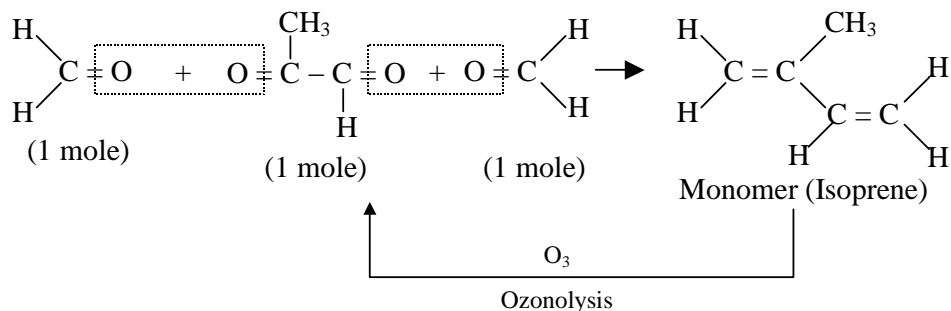
Sol.

These are not isostructural because silicon uses its vacant d-orbitals for back bonding with lone pair electrons of central N atom so it is planar in shape while other has pyramidal shape.

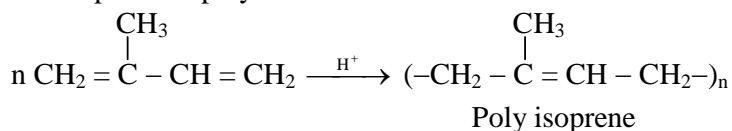
6. A monomer of a polymer on ozonolysis gives two moles of CH_2O and one mole of CH_3COCHO . Write the structure of monomer and write 'all-cis' configuration of polymer chain.

[2]

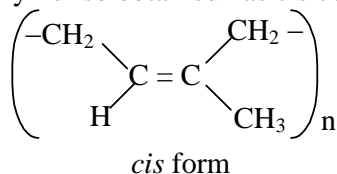
Sol.



So the possible polymer.



The polymer so obtained has cis configuration all through



7. In face centred cubic (fcc) crystal lattice, edge length is 400 pm. Find the diameter of greatest sphere which can be fit into the interstitial void without distortion of lattice.

[2]

Sol. In fcc lattice the largest void present is octahedral void. If the radius of void sphere is R and of lattice sphere is r . Then

$$\therefore r = \frac{\sqrt{2} \times 400}{4} = 141.42 \text{ pm}$$

Applying condition for octahedral void

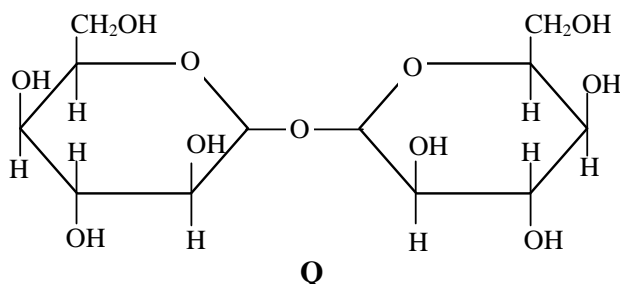
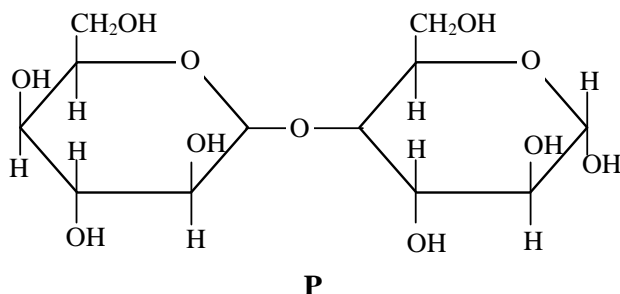
$$2(r + R) = \text{edge length, } a$$

$$\therefore 2R = a - 2r$$

$$= 400 - 2 \times 141.42$$

$$\therefore \text{Diameter of greatest sphere} = 117.16 \text{ pm}$$

8.

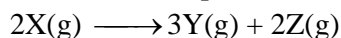


Which of the following will reduce Tollen's reagent. Explain

[2]

Sol. In these two disaccharides structures, (P) will be reducing sugar since both monosaccharide units are not linked through their reducing centers in it while in structure (Q) both the monosaccharide units are linked through their reducing centers i.e. aldehydic and ketonic groups.

9. At constant temperature and volume X decomposes as



P_x is the partial pressure of X.

Observation No.	Time (in minute)	P_x (in mm of Hg)
1	0	800
2	100	400
3	200	200

What is the order of reaction with respect to X ?

- Find the rate constant.
- Find the time for 75% completion of the reaction.
- Find total pressure when pressure of X is 700 mm of Hg.

[4]

Sol. Applying integrated rate law of first order kinetics

$$\begin{aligned}
 k_1 &= \frac{2.303}{t} \log \left(\frac{P_o}{P_t} \right) \\
 &= \frac{2.303}{100} \log \left(\frac{800}{400} \right) \\
 &= \frac{2.303}{100} \log 2 = 6.932 \times 10^{-3} \text{ min}^{-1}
 \end{aligned}$$

$$k_2 = \frac{2.303}{t} \log \left(\frac{P_o}{P_t} \right)$$

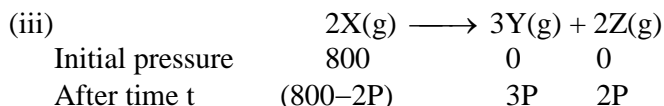
$$= \frac{2.303}{200} \log \left(\frac{800}{200} \right) = 6.932 \times 10^{-3} \text{ min}^{-1}$$

In the two observations the values of rate constant remain same. Therefore it must be following the first order kinetics. Hence order of reaction with respect to X is one.

(i) Rate constant, $k = 6.932 \times 10^{-3} \text{ min}^{-1}$

$$(ii) 6.932 \times 10^{-3} = \frac{2.303}{t} \log \left(\frac{100}{25} \right)$$

$$\therefore t_{75\%} = 200 \text{ min.}$$



When the pressure of X is 700 mm of Hg then

$$800 - 2P = 700$$

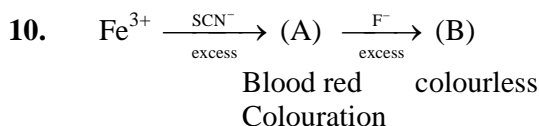
$$2P = 100$$

$$P = 50 \text{ mm of Hg}$$

$$\text{Total pressure} = 800 - 2P + 3P + 2P$$

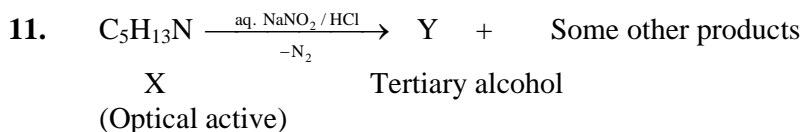
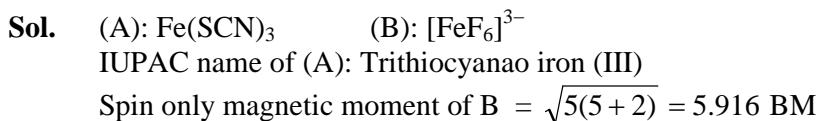
$$= 800 + 3P$$

$$= 800 + 3 \times 50 = 950 \text{ mm of Hg}$$



What are (A) and (B)? Give IUPAC name of (A). Find the spin only magnetic moment of (B).

[4]

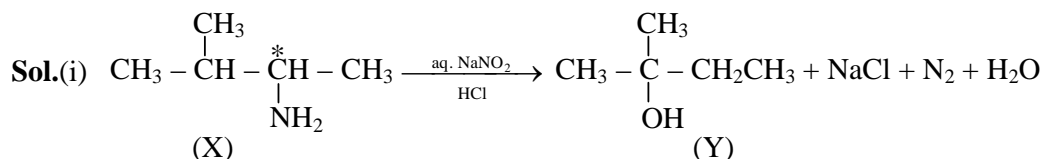


(i) Identify (X) and (Y).

(ii) Is (Y) optically active?

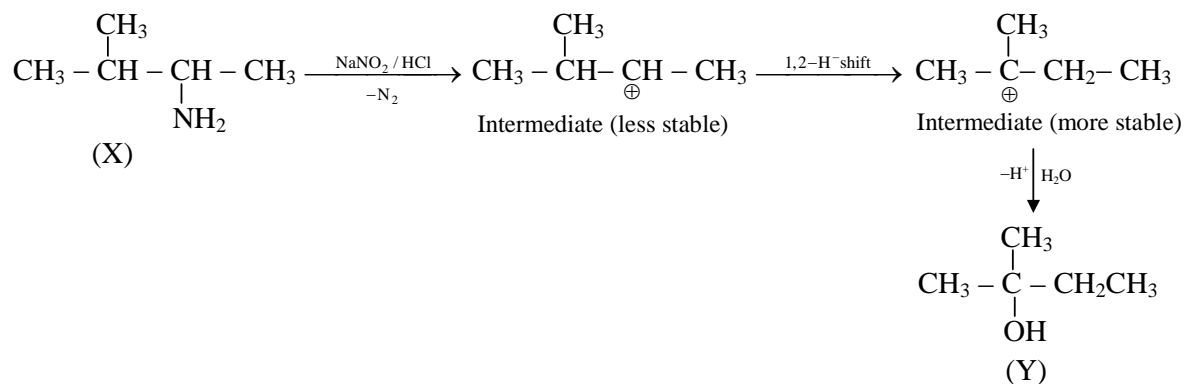
(iii) Give structure(s) of intermediate(s) if any in the formation from (X) to (Y).

[4]



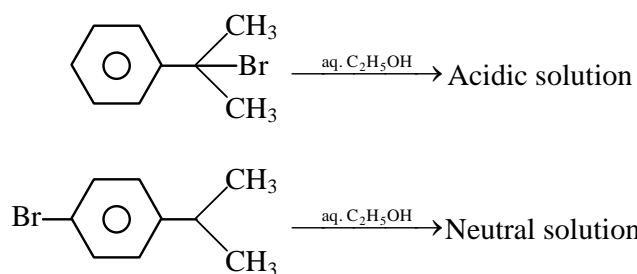
(ii) No

(iii)

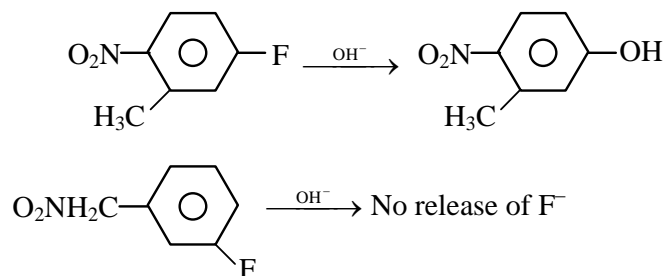


12. Give reasons

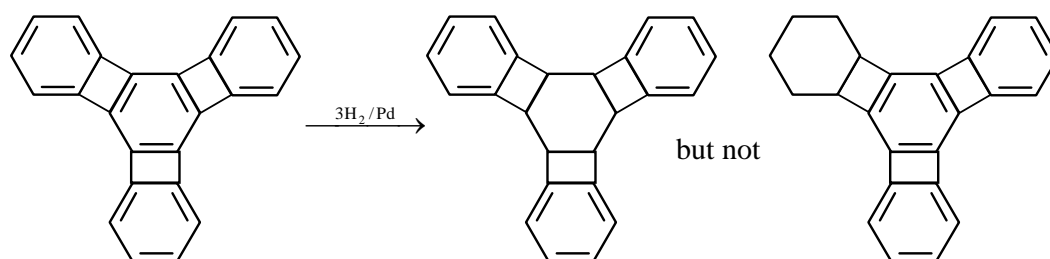
(a)



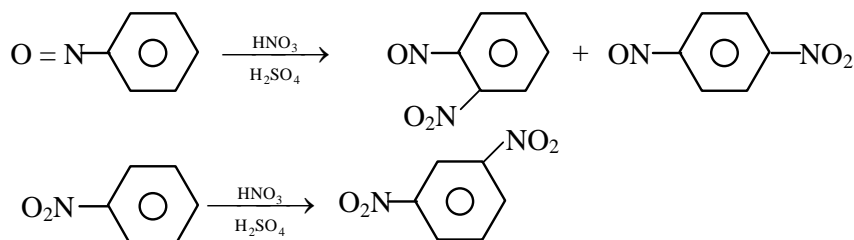
(b)



(c)

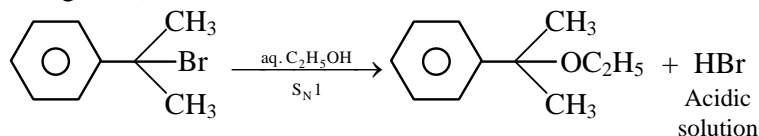


(d)



[4]

Sol. (a) $\text{PhC}(\text{CH}_3)_2\text{Br}$ is 3° halide so it undergoes nucleophilic substitution reaction easily according to $\text{S}_{\text{N}}1$ mechanism as follow



While $\text{Br}-\text{C}_6\text{H}_4-\text{CH}(\text{CH}_3)_2$ is an aryl halide and does not undergo nucleophilic substitution reaction because Br is bonded to sp^2 hybridized carbon atom of benzene ring.

(b) Given compound is activated aryl halide hence it undergoes aromatic nucleophilic substitution reaction by $\text{S}_{\text{N}}\text{AR}$ mechanism due to presence of very strong electron withdrawing group ($-\text{NO}_2$) at para position and electron releasing group ($-\text{CH}_3$) at meta position of fluorine atom.

While $\text{O}_2\text{NCH}_2-\text{C}_6\text{H}_3(\text{F})$ is not reactive towards aromatic nucleophilic substitution reaction as the ring is not highly deactivated because $-\text{NO}_2$ group is not directly attached to the benzene ring.

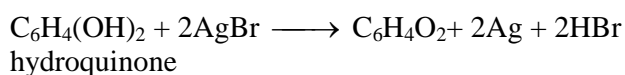
(c) Hydrogenation takes place on the surface of catalyst through adsorption desorption steps. The three benzene rings attached to the central benzene ring are not in the same plane during adsorption. Only central benzene ring will directly be adsorbed on the surface of Pd where hydrogenation will occur.

(d) $-\text{NO}$ group is activating and ortho, para directing group while $-\text{NO}_2$ group is deactivating and meta directing.

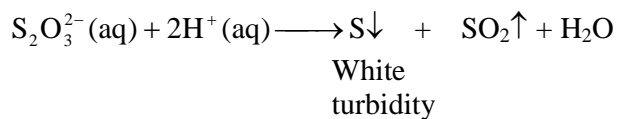
13. Write the chemical reaction involved in developing of a black and white photographic film. An aqueous $\text{Na}_2\text{S}_2\text{O}_3$ solution is acidified to give a milky white turbidity. Identify the product and write the balanced half chemical reaction for it.

[4]

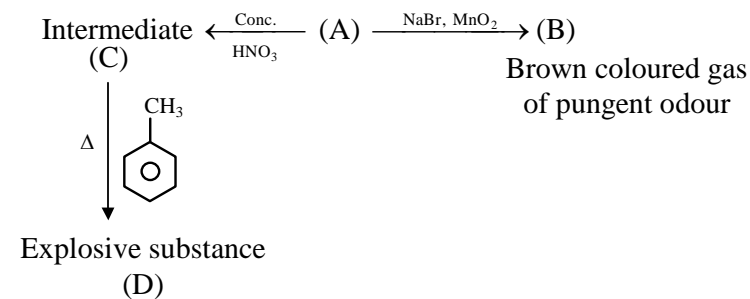
Sol. Chemical reaction involved in developing of a black and white photographic film is as follows



Aqueous solution of $\text{Na}_2\text{S}_2\text{O}_3$ on acidification gives milky white turbidity of colloidal sulphur.

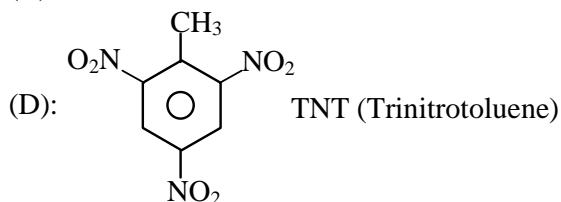


14.

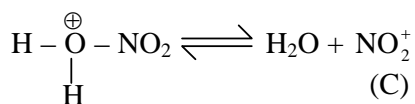
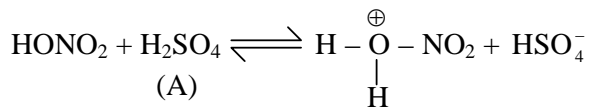
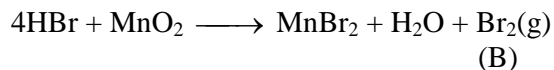
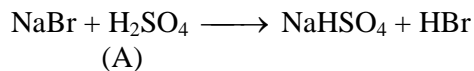


Identify (A), (B), (C) and (D). Give the reaction for (A) \longrightarrow (B) and (A) \longrightarrow (C)

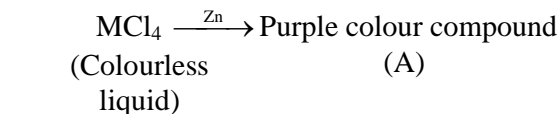
[4]

Sol. (A): conc. H_2SO_4 (B): Br_2 (C): NO_2^+ 

Reactions involved are:



15.



M = Transition metal

↓ Moist air

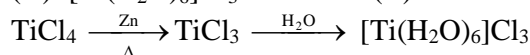
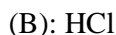
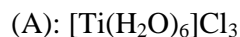
(B)

White fumes

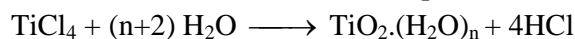
Identify (A), (B) and MCl_4 . Also explain colour difference between MCl_4 and (A).

[4]

Sol.

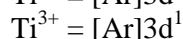
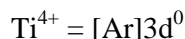


Purple (A)



(B)

(white fumes)



TiCl_4 is colourless as it has an empty d subshell and hence d–d transition is impossible. Whereas Ti^{3+} is coloured due to d–d transitions. Ti^{3+} absorbs greenish yellow component of white light during excitation of electrons, hence its aqueous solution appears as purple. It is because purple is the complimentary colour of greenish yellow in white light.

16.

20% of surface sites are occupied by N_2 molecules. The density of surface site is $6.023 \times 10^{14} \text{ cm}^{-2}$ and total surface area is 1000 cm^2 . The catalyst is heated to 300 K while N_2 is completely desorbed into a pressure of 0.001 atm and volume 2.46 cm^3 . Find the number of active sites occupied by each N_2 molecule.

[4]

Sol.

Number of surface sites occupied by N_2 molecules = 20%Density of surface sites = $6.023 \times 10^{14} \text{ cm}^{-2}$ Total surface area = 1000 cm^2 Total number of surface sites = Density \times Total surface area

$$= 6.023 \times 10^{14} \times 1000$$

$$= 6.023 \times 10^{17}$$

$$\text{Sites occupied by nitrogen molecule} = \frac{20}{100} \times 6.023 \times 10^{17} = 1.2046 \times 10^{17}$$

$$\text{Number of nitrogen molecule} = \frac{PV}{RT} \times N_{\text{Av}}$$

We have: $T = 300 \text{ K}$, $P = 0.001 \text{ atm}$, $V = 2.46 \text{ cm}^3$

$$= \frac{0.001 \times 2.46 \times 10^{-3}}{0.0821 \times 300} \times 6.023 \times 10^{23} = 6.016 \times 10^{16}$$

Therefore, number of sites occupied by each nitrogen molecule

$$= \frac{\text{Sites occupied by } N_2 \text{ molecules}}{\text{Number of } N_2 \text{ molecules}} = \frac{1.2046 \times 10^{17}}{6.016 \times 10^{16}} \approx 2$$

17. For the reaction,
 $Ag^+(aq) + Cl^-(aq) \rightleftharpoons AgCl(s);$

Given:

Species	ΔG° (kJ/mol)
$Ag^+(aq)$	+77
$Cl^-(aq)$	-129
$AgCl(s)$	-109

Write the cell representation of above reaction and calculate E° at 298 K.

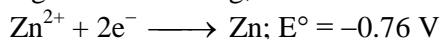
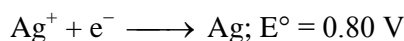
Calculate the $\log_{10} K_{sp}(AgCl)$ at 298 K.

If 6.539×10^{-2} g of metallic zinc is added to 100 ml saturated solution of $AgCl$, find the

value of $\log_{10} \frac{[Zn^{2+}]}{[Ag^+]^2}$.

How many moles of Ag will be precipitated in the above reaction.

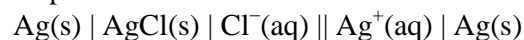
Given that



(It was given that Atomic mass of $Zn = 65.39$)

[6]

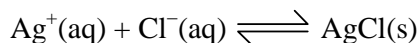
Sol. Cell representation of the reaction is



$$\begin{aligned} \Delta G_R^\circ &= \Delta G_{AgCl}^\circ - (\Delta G_{Ag^+}^\circ + \Delta G_{Cl^-}^\circ) \\ &= -109 - 77 - (-129) \\ &= -57 \text{ kJ mol}^{-1} \end{aligned}$$

$$E_{cell}^\circ = -\frac{\Delta G_R^\circ}{nF} = \frac{57 \times 10^3}{1 \times 96500} = 0.59 \text{ V}$$

The cell reaction is



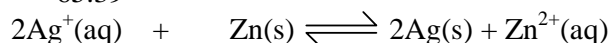
$$\Delta G_R^\circ = 2.303 RT \log_{10} K_{sp}(AgCl)$$

$$\log_{10} K_{sp}(AgCl) = -\frac{57 \times 10^3}{2.303 \times 8.314 \times 298} = -9.989 \approx -10$$

$$\therefore K_{sp}(AgCl) = 10^{-10} \text{ M}^2$$

$$[Ag^+]_{sat} = \sqrt{K_{sp}(AgCl)} = 10^{-5} \text{ M}$$

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



Applying Nernst equation for the above reaction,

$$E = E^\circ - \frac{0.059}{2} \log_{10} \frac{[Zn^{2+}]}{[Ag^+]^2}$$

At equilibrium, $E_{cell} = 0$; $E_{cell}^\circ = 1.56 \text{ V}$

$$0 = 1.56 - \frac{0.059}{2} \log_{10} \frac{[\text{Zn}^{2+}]}{[\text{Ag}^+]^2}$$

$$\log_{10} \frac{[\text{Zn}^{2+}]}{[\text{Ag}^+]^2} = \frac{1.56 \times 2}{0.059} = 52.88$$

Since the equilibrium constant K_c for the reaction,

$2\text{Ag}^+(\text{aq}) + \text{Zn}(\text{s}) \rightleftharpoons 2\text{Ag}(\text{s}) + \text{Zn}^{2+}(\text{aq})$ is very high i.e. $10^{52.88}$, so the reaction will almost go to completion. Therefore, the moles of Ag precipitated is 10^{-5} .

18. (i) $\mu_{\text{obs}} = \sum_i \mu_i x_i$

where μ_i is the dipole moment of a stable conformer of the molecule, $\text{Z} - \text{CH}_2 - \text{CH}_2 - \text{Z}$ and x_i is the mole fraction of the stable conformer

Given: $\mu_{\text{obs}} = 1.0 \text{ D}$ and $x(\text{Anti}) = 0.82$

Draw all the stable conformers of $\text{Z} - \text{CH}_2 - \text{CH}_2 - \text{Z}$ and calculate the value of $\mu(\text{Gauche})$.

(ii) Draw the stable conformer of

$\text{Y} - \text{CHD} - \text{CHD} - \text{Y}$ (mesoform)

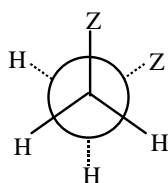
When $\text{Y} = \text{CH}_3$ (rotation about $\text{C}_2 - \text{C}_3$)

$\text{Y} = \text{OH}$ (rotation about $\text{C}_1 - \text{C}_2$)

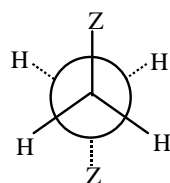
in Newmann projection.

[6]

Sol.(i) The compound $\text{Z} - \text{CH}_2 - \text{CH}_2 - \text{Z}$ will have just two stable conformers i.e. Gauche and anti forms.



(Gauche form)



(Anti form)

Mole fraction of anti conformer of $\text{Z} - \text{CH}_2 - \text{CH}_2 - \text{Z}$, $x(\text{Anti}) = 0.82$

Therefore, mole fraction of Gauche form, $x(\text{Gauche}) = 1 - 0.82 = 0.18$

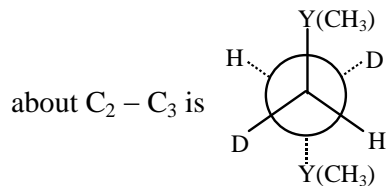
The antiform of $\text{Z} - \text{CH}_2 - \text{CH}_2 - \text{Z}$ will have zero dipole moment as its individual bond dipole moments will be cancelled out by one another.

$$\mu_{\text{obs}} = \mu(\text{Gauche}) \cdot x(\text{Gauche}) + \mu(\text{Anti}) \cdot x(\text{Anti})$$

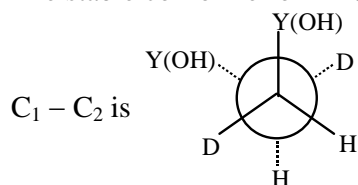
$$1 = \mu(\text{Gauche}) \times 0.18 + 0 \times 0.82$$

$$\mu(\text{Gauche}) = \frac{1}{0.18} = 5.56 \text{ D}$$

- (ii) The stable conformer of $\text{Y-CHD} - \text{CHD} - \text{Y}$ (mesoform) when $\text{Y} = \text{CH}_3$ and rotated



The stable conformer of $\text{Y-CHD} - \text{CHD} - \text{Y}$ (mesoform) when $\text{Y} = \text{OH}$ and rotated about



Note: All these questions of IIT-JEE (Mains) 2005 are based on the memory of the select BANSAL students who appeared in the examination. BANSAL CLASSES does not take any responsibility for any sort of discrepancy whatsoever.