

Solutions to IITJEE-2005 Mains Paper

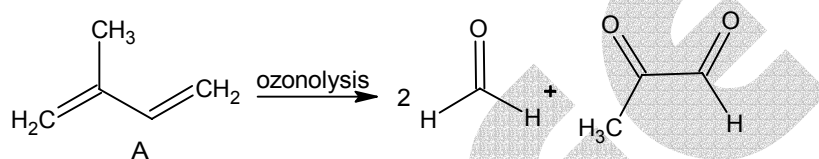
Chemistry

Time: 2 hours

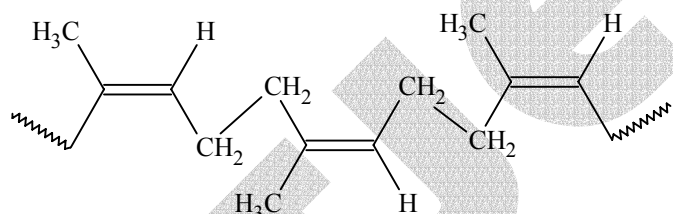
Note: Question number 1 to 8 carries **2 marks** each, 9 to 16 carries **4 marks** each and 17 to 18 carries **6 marks** each.

- Q.1.** Monomer A of a polymer on ozonolysis yields two moles of HCHO and one mole of CH₃COCHO.
 a) Deduce the structure of A.
 b) Write the structure of "all cis" – form of polymer of compound A.

Solution1. (a)



(b)



"all cis" form of polymer of A

Q.2. Fill in the blanks

- a) $^{235}_{92}\text{U} + {}^1_0\text{n} \longrightarrow {}^{137}_{52}\text{A} + {}^{97}_{40}\text{B} + \dots$
 b) $^{82}_{34}\text{Se} \longrightarrow 2 {}^0_{-1}\text{e} + \dots$

- Solution 2.** (a) $^{235}_{92}\text{U} + {}^1_0\text{n} \longrightarrow {}^{137}_{52}\text{A} + {}^{97}_{40}\text{B} + 2 {}^1_0\text{n}$
 (b) $^{82}_{34}\text{Se} \longrightarrow 2 {}^0_{-1}\text{e} + {}^{82}_{36}\text{Kr}$

- Q.3.** a) Calculate the amount of Calcium oxide required when it reacts with 852 gm of P₄O₁₀.
 b) Write the structure of P₄O₁₀.

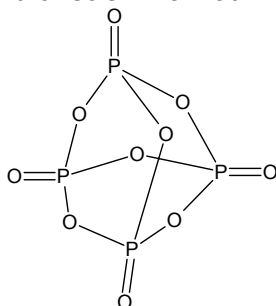
Solution 3. a) $6\text{CaO} + \text{P}_4\text{O}_{10} \rightarrow 2\text{Ca}_3(\text{PO}_4)_2$

$$\text{Moles of P}_4\text{O}_{10} = \frac{852}{284} = 3$$

$$\text{Moles of CaO} = 3 \times 6 = 18$$

$$\text{Wt. of CaO} = 18 \times 56 = 1008 \text{ gm.}$$

(b)



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- Q.4.** An element crystallizes in fcc lattice having edge length 400 pm. Calculate the maximum diameter of atom which can be placed in interstitial site without distorting the structure.

Solution 4. In FCC, interstitial sites will be octahedral voids & tetrahedral voids.

For octahedral voids

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

For tetrahedral voids

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

Where r_1 = radius of atom in interstitial sites

r_2 = radius of atom arranged in FCC.

$$\text{i.e. } 4r_2 = \sqrt{2} a,$$

For maximum diameter of atom in interstitial site, octahedral voids will be considered.

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

- Q.5.** 20% surface sites have adsorbed N_2 . On heating N_2 gas evolved from sites and were collected at 0.001 atm and 298 K in a container of volume is 2.46 cm^3 . Density of surface sites is $6.023 \times 10^{14} / \text{cm}^2$ and surface area is 1000 cm^2 , find out the no. of surface sites occupied per molecule of N_2 .

Solution 5. $P_{\text{N}_2} = 0.001 \text{ atm}$, $T = 298 \text{ K}$, $V = 2.46 \text{ cm}^3$

By ideal gas, $PV = nRT$

$$n_{\text{N}_2} = \frac{PV}{RT} = \frac{0.001 \times 2.46 \times 10^{-3}}{0.0821 \times 298} = 1.0 \times 10^{-7}$$

$$\text{Now molecules of } \text{N}_2 = 6.023 \times 10^{23} \times 1 \times 10^{-7} = 6.023 \times 10^{16}$$

$$\text{Now total surface sites available} = 6.023 \times 10^{14} \times 1000 = 6.023 \times 10^{17}$$

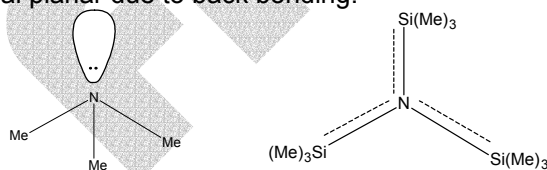
$$\therefore \text{Surface site used to adsorb } \text{N}_2 = \frac{20}{100} \times 6.023 \times 10^{17} = 12.04 \times 10^{16}$$

$$\therefore \text{Sites occupied per molecule of } \text{N}_2 = \frac{12.04 \times 10^{16}}{6.02 \times 10^{16}} = 2$$

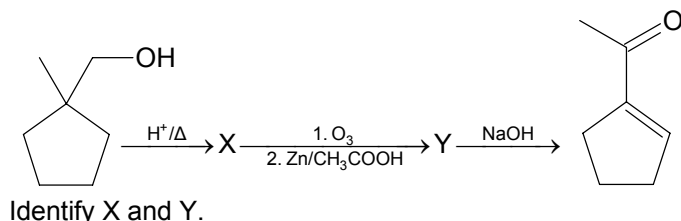
- Q.6.** Predict whether the following molecules are iso structural or not. Justify your answer.

(i) NMe_3 (ii) $\text{N}(\text{SiMe}_3)_3$

Solution 6. $\text{N}(\text{Me})_3$ & $\text{N}(\text{SiMe}_3)_3$ are not isostructural. $\text{N}(\text{Me})_3$ is trigonal pyramidal while $\text{N}(\text{SiMe}_3)_3$ is trigonal planar due to back bonding.

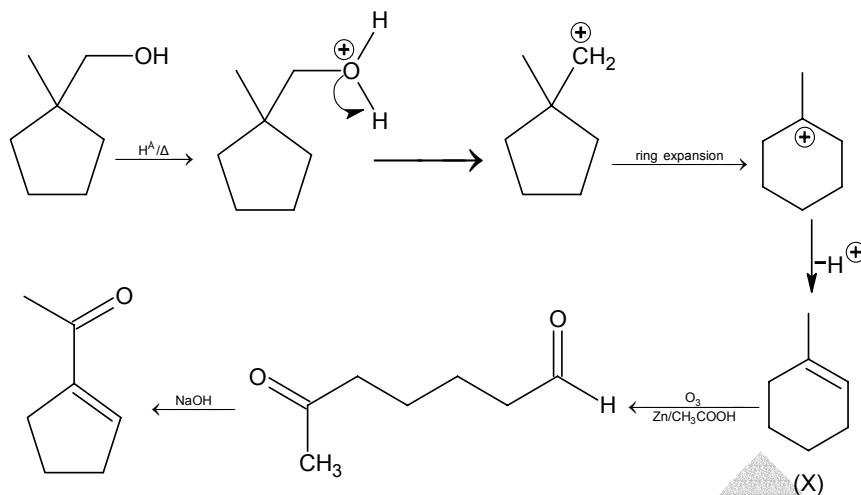


- Q.7.**

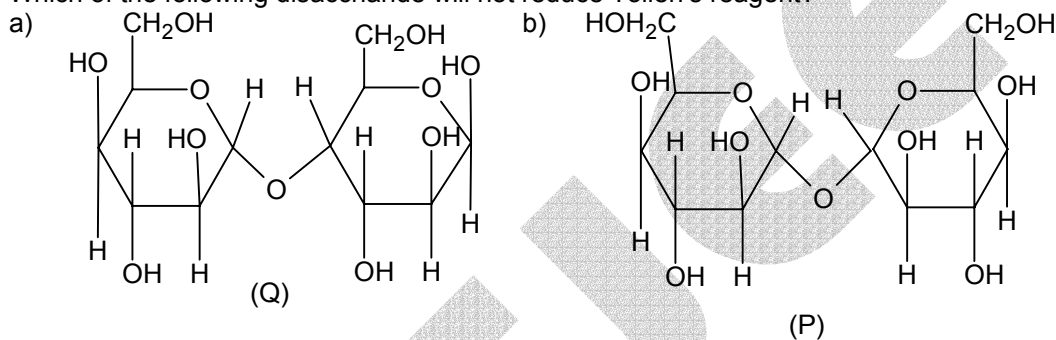


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Solution 7.



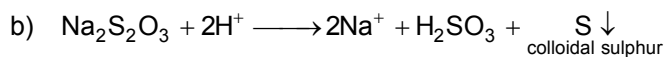
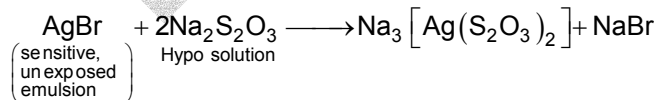
Q.8. Which of the following disaccharide will not reduce Tollen's reagent?



Solution 8. In structure (P) both the rings are present in acetyl form therefore it will not hydrolyse in solution that why Fehling solution cannot react with this. In structure (Q) one ring present in the form of hemiacetal. This will hydrolyse in solution and it can reduce Fehling solution.

Q.9. Write balanced chemical equation for developing a black and white photographic film. Also give reason why the solution of sodium thiosulphate on acidification turns milky white and give balance equation of this reaction.

Solution 9. a) Reactions used in developing the photographic film

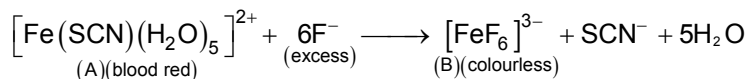


Q.10. $\text{Fe}^{3+} \xrightarrow{\text{SCN}^- (\text{excess})} \text{blood red (A)} \xrightarrow{\text{F}^- (\text{excess})} \text{colourless (B)}$

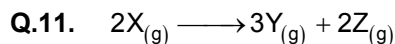
Identify A and B.

- Write IUPAC name of A and B.
- Find out spin only magnetic moment of B.

Solution 10. $\text{Fe}^{3+} + \text{SCN}^- \xrightarrow[\text{(excess)}]{\text{aqueous}} [\text{Fe}(\text{SCN})(\text{H}_2\text{O})_5]^{2+}$
(A)(blood red)



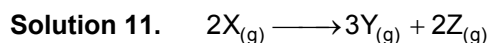
- a) Pentaaquathiocyanato iron (III) ion
hexafluoro ferrate (III)
- b) Magnetic moment = $\sqrt{n(n+2)} = \sqrt{35} = 5.92$ B.M., where n = number of unpaired electrons



Time (in Min)	0	100	200
Partial pressure of X (in mm of Hg)	800	400	200

Assuming ideal gas condition. Calculate

- a) Order of reaction
b) Rate constant.
c) Time taken for 75% completion of reaction.
d) Total pressure when $P_x = 700$ mm.

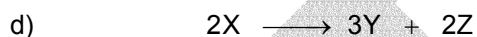


- a) By the given data, we can observe that $t_{1/2}$ of the X is constant i.e. 100 min. therefore order of reaction is one.

b) Rate constant $K = \frac{0.693}{t_{1/2}}$

$$= \frac{0.693}{100} = 6.93 \times 10^{-3} \text{ min}^{-1}$$

- c) Time taken for 75% completion of reaction = $2 t_{1/2}$



Initial pressure 800 0 0

At any time $800 - x$ $3/2 x$ x

Given $800 - x = 700$ mm

$x = 100$ mm

Total pressure = $700 + 150 + 100 = 950$ mm

- Q.12.** a) Calculate velocity of electron in first Bohr orbit of hydrogen atom (Given $r = a_0$).
b) Find de-Broglie wavelength of the electron in first Bohr orbit.
c) Find the orbital angular momentum of 2p orbital in terms of $h/2\pi$ units.

Solution 12. a) $mvr = \frac{nh}{2\pi}$ $r = a_0 = 0.529 \text{ \AA}$

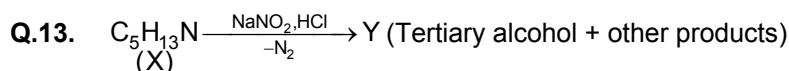
$$v = \frac{nh}{2\pi mr} = 2.18 \times 10^6 \text{ m/sec } (n = 1)$$

b) $\lambda = \frac{h}{mv} = \frac{6.63 \times 10^{-34}}{9.1 \times 10^{-31} \times 2.18 \times 10^6} = 0.33 \times 10^{-9} \text{ m} = 3.3 \text{ \AA}$

- c) For 2 p value of $\ell = 1$

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

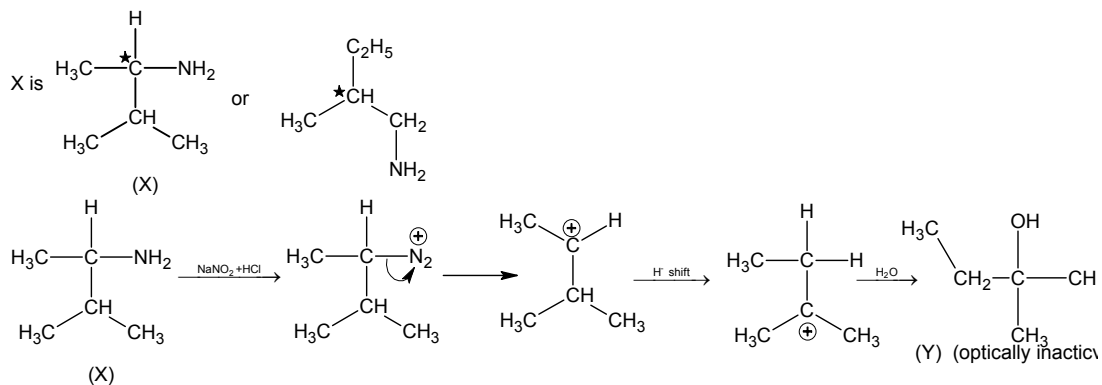
$$= \sqrt{2} \frac{h}{2\pi}$$



(Optically active)

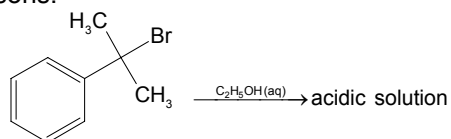
Find X and Y. Is Y optically active? Write the intermediate steps.

Solution 13.

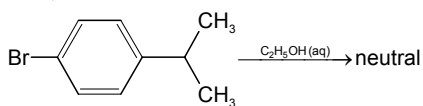


Q.14. Give reasons:

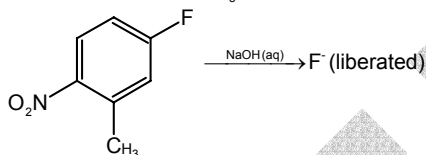
a) i)



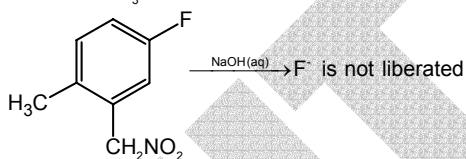
ii)



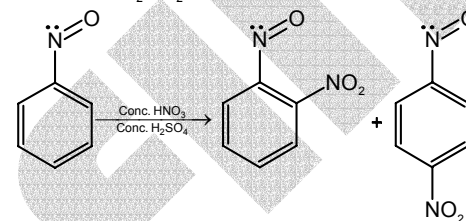
b) i)



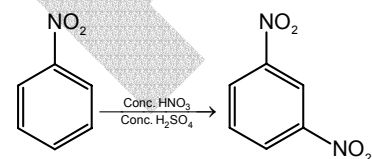
ii)



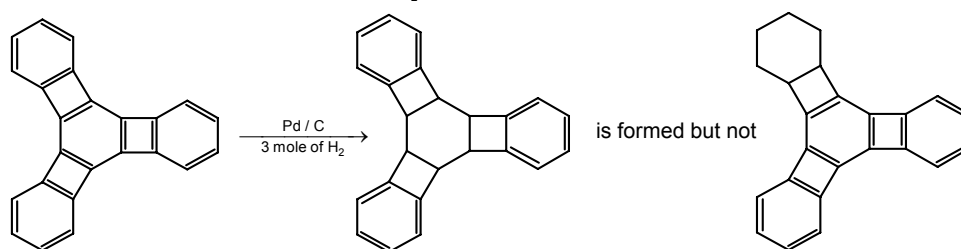
c) i)



ii)

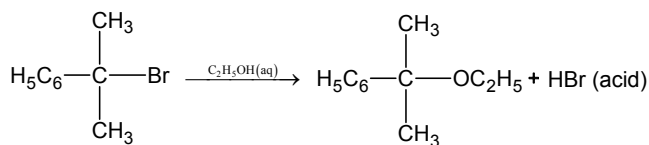


d)

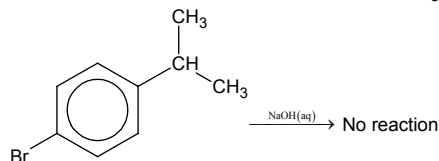


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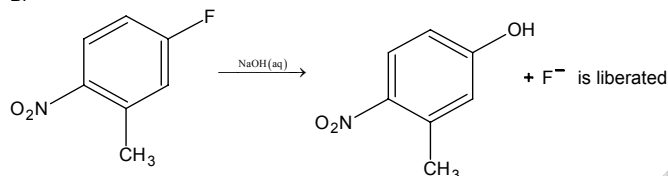
Solution 14.(a) (i)



(ii)

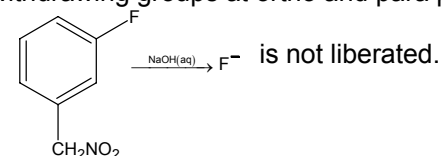


(b) (i)



This is a bimolecular reaction. Rate of this reaction is being enhanced by presence of electron withdrawing groups at ortho and para positions.

(ii)



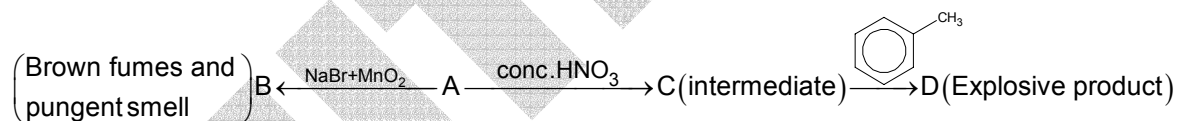
Bimolecular mechanism is not possible in this case.

(c) (i) Due to presence of lone pair on nitrogen atom NO group is electron donating and ortho, para directing.

(ii) NO_2 group is electron withdrawing and meta directing.

(d) Due to reduction of central ring, three four membered antiaromatic rings become stable while on reduction of terminal ring only one antiaromatic ring can be stabilized.

Q.15..

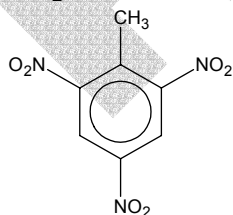


Find A, B, C and D. Also write equations A to B and A to C.

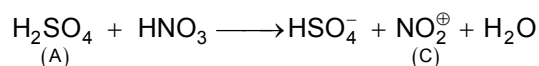
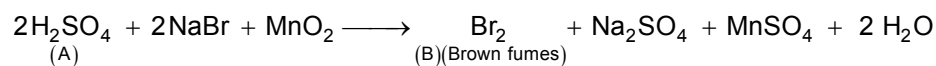
Solution 15.

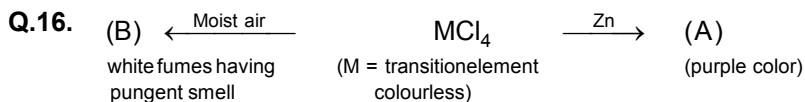
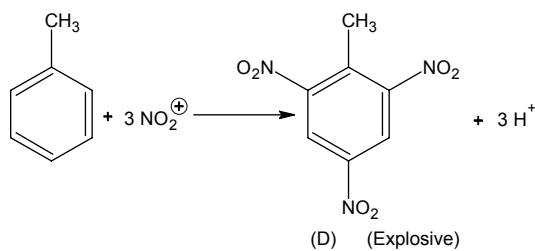
(A) H_2SO_4 (B) Br_2 (C) NO_2^\oplus

(D)



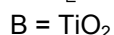
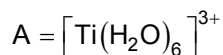
Reactions involved are:





Identify the metal M and hence MCl_4 . Explain the difference in colours of MCl_4 and A.

Solution 16. M = Ti



Ti(+IV) ion contains no d-electrons, while d – d transition of single electron of Ti(+III) will cause colour change.

Q.17. $\mu_{\text{obs}} = \sum \mu_i x_i$

Where μ_i is the dipole moment of stable conformer and x_i is the mole fraction of that conformer.

a) Write stable conformer for Z — CH_2 — CH_2 — Z in Newman's projection.

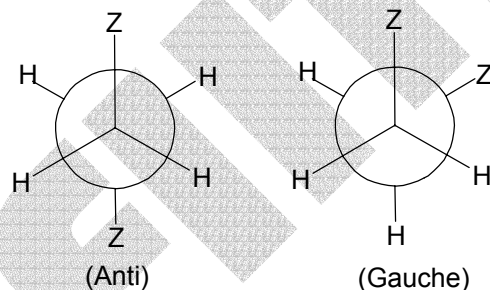
If $\mu_{\text{solution}} = 1.0 \text{ D}$ and mole fraction of anti form = 0.82, find μ_{Gauche} .

b) Write most stable meso conformer of



If (i) Y = CH_3 about C_2 — C_3 rotation and (ii) Y = OH about C_1 — C_2 rotation.

Solution 17.a)



Mole fraction of anti form = 0.82

Mole fraction of Gauche form = 0.18

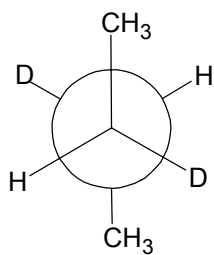
$$\mu_{\text{obs}} = 1$$

$$1 = \mu_{(\text{anti})} \times 0.82 + \mu_{(\text{Gauche})} \times 0.18$$

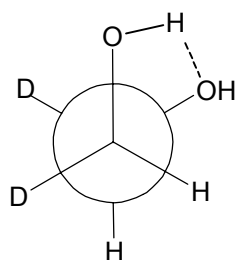
$$\mu_{(\text{anti})} = 0$$

$$\therefore 1 = \mu_{(\text{Gauche})} \times 0.18$$

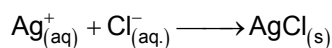
$$\mu_{\text{Gauche}} = \frac{1}{0.18} = 5.55 \text{ D}$$

b)
i)

ii)



Q.18. a) Calculate ΔG_r^0 of the following reaction



Given

$$\Delta G_f^0 (\text{AgCl}) \quad -109 \text{ kJ/mole}$$

$$\Delta G_f^0 (\text{Cl}^-) \quad -129 \text{ kJ/mole}$$

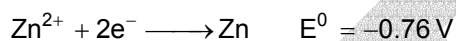
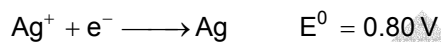
$$\Delta G_f^0 (\text{Ag}^+) \quad 77 \text{ kJ/mole}$$

Represent the above reaction in form of a cell.

Calculate E° of the cell. Find $\log_{10} K_{\text{sp}}$ of AgCl.

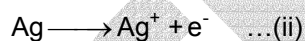
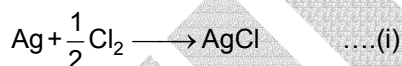
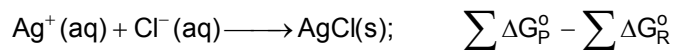
b) 6.539×10^{-2} g of metallic Zn (amu = 65.39) was added to 100 ml of saturated solution of AgCl.

Calculate $\log_{10} \frac{[\text{Zn}^{2+}]}{[\text{Ag}^+]^2}$. Given that



Also find how many moles of Ag will be formed?

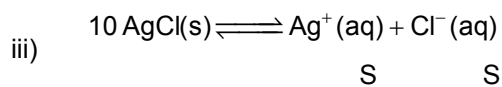
Solution 18. Cell reactions are

hence cell representation is $\text{Ag} | \text{Ag}^+ | \text{AgCl} | \text{Cl}^- | \text{Cl}_2, \text{Pt}$ 

$$\begin{aligned} \text{i) } \Delta G^\circ &= -109 - (-129 + 77) \\ &= -109 + 129 - 77 \\ &= 20 - 77 = -57 = -1 \times F \times E^\circ \\ -57 &= -1 \times 96500 \times E^\circ \\ \Rightarrow E^\circ &= \frac{57000}{96500} = 0.59 \text{ Volts} \end{aligned}$$

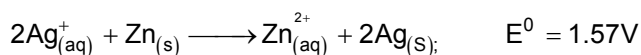
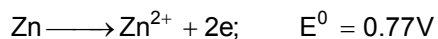
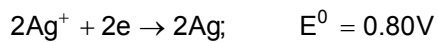
$$\begin{aligned} \text{ii) } -57 &= -2.303 RT \log K_0 \\ \log K_0 &= \frac{57 \times 1000}{2.303 \times 8.314 \times 298} \\ \log K_0 &= 9.98 \approx 10 \\ K_0 &= 10^{10} \end{aligned}$$

$$\begin{aligned}\therefore K_{sp} &= 1/K_0 \\ \therefore K_{sp} &= 10^{-10} \\ \therefore \log K_{sp} &= -10\end{aligned}$$



$$\begin{aligned}10^{-10} &= S^2 \\ \therefore S &= 10^{-5} \text{ m / L}\end{aligned}$$

b) When $\frac{65.39 \times 10^{-2}}{65.39} = 10^{-3}$ moles of Zn has been added,



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

$$\log_{10} K_{(\text{eq})} = 52.8$$

Therefore, this reaction will move in forward direction completely. Hence moles of Ag formed will be 10^{-6}

At equilibrium, ($E_{\text{cell}} = 0$)

$$E_{\text{Cell}}^0 = \frac{+0.0591}{2} \log_{10} \frac{[\text{Zn}^{2+}]}{[\text{Ag}^+]^2}$$

$$\therefore \frac{1.56 \times 2}{0.0591} = \log \frac{[\text{Zn}^{2+}]}{[\text{Ag}^{2+}]^2} = 52.8$$