FIITJEE *Solutions to IITJEE–2005 Mains Paper*

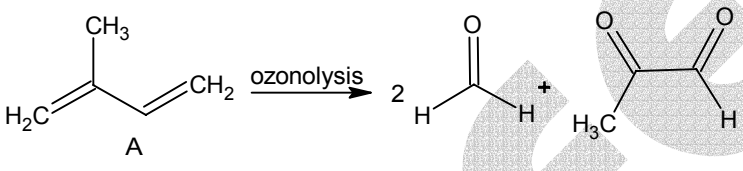
Chemistry

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.

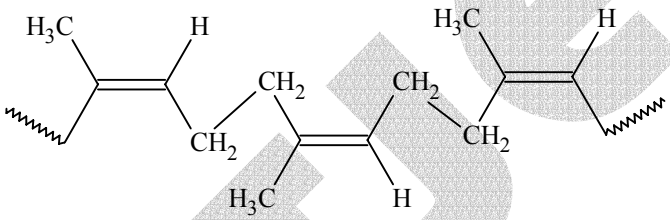
Q.1. Monomer A of a polymer on ozonolysis yields two moles of HCHO and one mole of CH_3COCHO.
a) Deduce the structure of A.
b) Write the structure of "all cis" – form of polymer of compound A.

Solution1. (a)



A

(b)



"all cis" form of polymer of A

Q.2. Fill in the blanks

a) $^{235}U_{92} + {}_0n^1 \longrightarrow {}^{137}A_{52} + {}^{97}B_{40} + ...$

b) $^{82}Se_{34} \longrightarrow 2\ {}_{-1}e^{o} + ...$

Solution 2. (a) $^{235}U_{92} + {}_0n^1 \rightarrow {}^{137}A_{52} + {}^{97}B_{40} + 2\ {}_0n^1$

(b) $^{82}Se_{34} \rightarrow 2\ {}_{-1}e^{0} + {}^{82}Kr_{36}$

Q.3. a) Calculate the amount of Calcium oxide required when it reacts with 852 gm of P_4O_{10}.
b) Write the structure of P_4O_{10}.

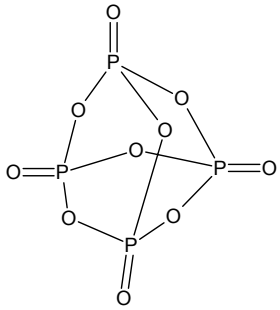
Solution 3. a) $6CaO + P_4O_{10} \rightarrow 2Ca_3(PO_4)_2$

Moles of $P_4O_{10} = \dfrac{852}{284} = 3$

Moles of CaO = 3 × 6 = 18

Wt. of CaO = 18 × 56 = 1008 gm.

(b)



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.

Solution4. 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.

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

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

Diameter = $2r_1 = 2(0.414\ r_2) = 2 \times 0.414 \times \frac{400}{2\sqrt{2}}$ = 117.1 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 6.023×10^{14} / cm^2 and surface area is 1000 cm^2, find out the no. of surface sites occupied per molecule of N_2.

Solution 5. $P_{N_2} = 0.001$ atm , T = 298 K, V = 2.46 cm^2

By ideal gas, PV = nRT

$$n_{N_2} = \frac{PV}{RT} = \frac{0.001 \times 2.46 \times 10^{-3}}{0.0821 \times 298} = 1.0 \times 10^{-7}$$

Now molecules of $N_2 = 6.023 \times 10^{23} \times 1 \times 10^{-7} = 6.023 \times 10^{16}$

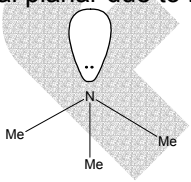
Now total surface sites available = $6.023 \times 10^{14} \times 1000 = 6.023 \times 10^{17}$

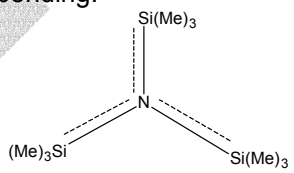
$\therefore$ Surface site used to adsorb $N_2 = \frac{20}{100} \times 6.023 \times 10^{17} = 12.04 \times 10^{16}$

$\therefore$ Sites occupied per molecule of $N_2 = \frac{12.04 \times 10^{16}}{6.02 \times 10^{16}} = 2$

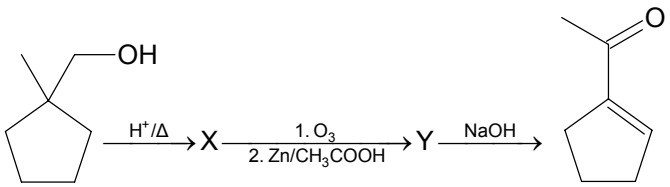
Q.6. Predict whether the following molecules are iso structural or not. Justify your answer.
(i) NMe_3 (ii) $N(SiMe_3)_3$

Solution 6. $N(Me)_3$ & $N(SiMe_3)_3$ are not isostructural. $N(Me)_3$ is trigonal pyramidal while $N(SiMe_3)_3$ is trigonal planar due to back bonding.



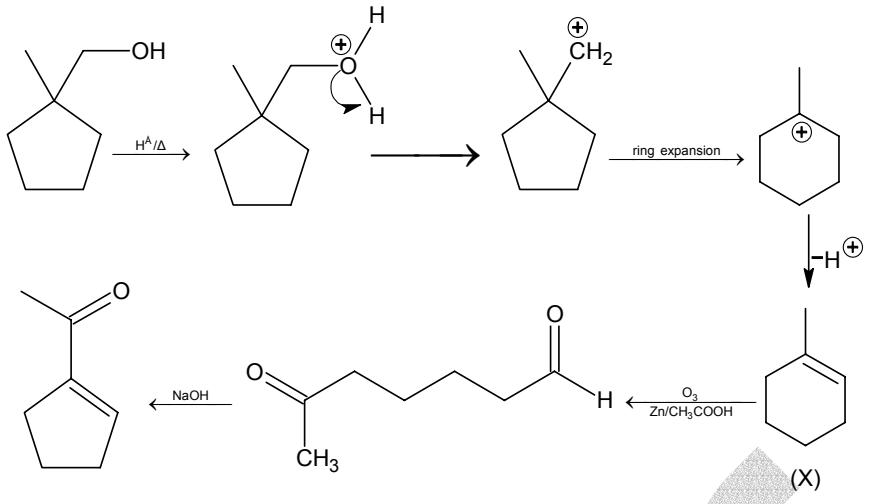


Q.7.



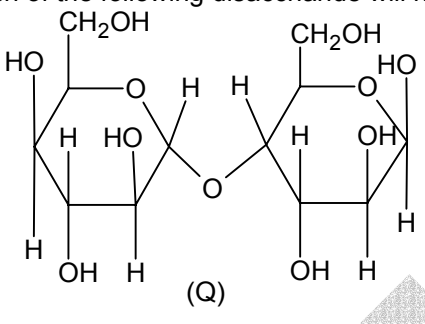
Identify X and Y.

Solution 7.

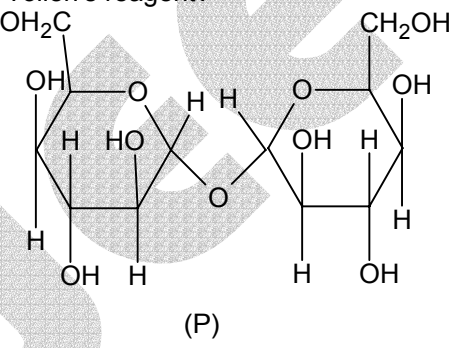


Q.8. Which of the following disaccharide will not reduce Tollen's reagent?

a)



b)



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

$$2AgBr + \underset{\substack{\text{Hydroquinone}\\(\text{developer})}}{C_6H_4(OH)_2} \longrightarrow \underset{\substack{(\text{black silver}\\\text{particles})}}{2Ag} + 2HBr + \underset{\text{quinone}}{C_6H_4O_2}$$

$$\underset{\substack{(\text{sensitive,}\\\text{unexposed}\\\text{emulsion})}}{AgBr} + \underset{\text{Hypo solution}}{2Na_2S_2O_3} \longrightarrow Na_3\left[Ag(S_2O_3)_2\right] + NaBr$$

b) $$Na_2S_2O_3 + 2H^+ \longrightarrow 2Na^+ + H_2SO_3 + \underset{\text{colloidal sulphur}}{S\downarrow}$$

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

Identify A and B.
a) Write IUPAC name of A and B.
b) Find out spin only magnetic moment of B.

Solution 10. $$Fe^{3+} + \underset{(\text{excess})}{SCN^-} \xrightarrow{\text{aqueous}} \underset{(A)(\text{blood red})}{\left[Fe(SCN)(H_2O)_5\right]^{2+}}$$

$$\underset{(A)(\text{blood red})}{\left[Fe(SCN)(H_2O)_5\right]^{2+}} + \underset{(\text{excess})}{6F^-} \longrightarrow \underset{(B)(\text{colourless})}{[FeF_6]^{3-}} + SCN^- + 5H_2O$$

a) Pentaaquathiocyanato iron (III) ion
hexafluro ferrate (III)

b) Magnetic moment $= \sqrt{n(n+2)} = \sqrt{35}$ = 5.92 B.M., where n = number of unpaired electrons

Q.11. $2X_{(g)} \longrightarrow 3Y_{(g)} + 2Z_{(g)}$

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.

Solution 11. $2X_{(g)} \longrightarrow 3Y_{(g)} + 2Z_{(g)}$

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

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

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

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

d)

	2X	⟶	3Y	+	2Z
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/2π units.

Solution 12. a) $mvr = \dfrac{nh}{2\pi}$ $\quad r = a_o = 0.529 \text{ Å}$

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

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

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

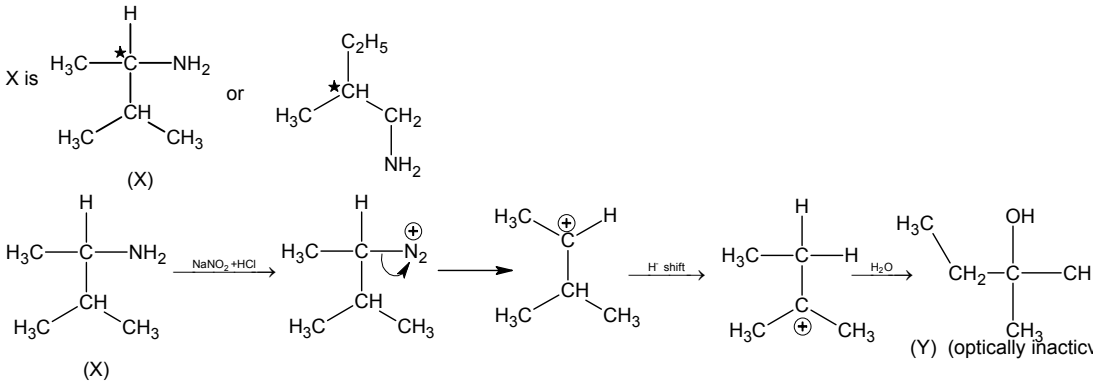
Orbital angular momentum $= \sqrt{\ell(\ell+1)}\,\dfrac{h}{2\pi}$

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

Q.13. $\underset{(X)}{C_5H_{13}N} \xrightarrow[-N_2]{NaNO_2,HCl} Y$ (Tertiary alcohol + other products)

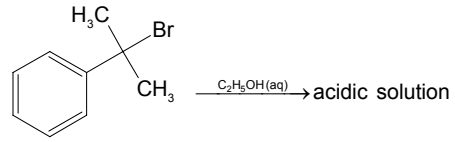
(Optically active)
Find X and Y. Is Y optically active? Write the intermediate steps.

Solution13.

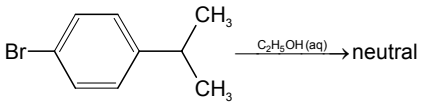


Q.14. Give reasons:

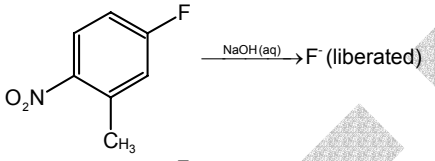
a) i)



ii)



b) i)



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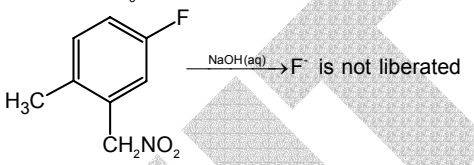
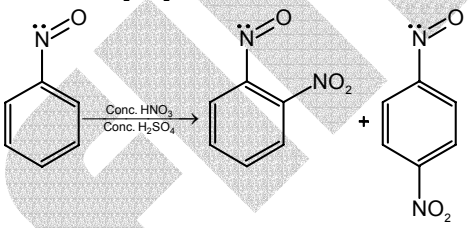


c) i)



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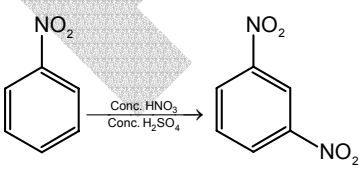
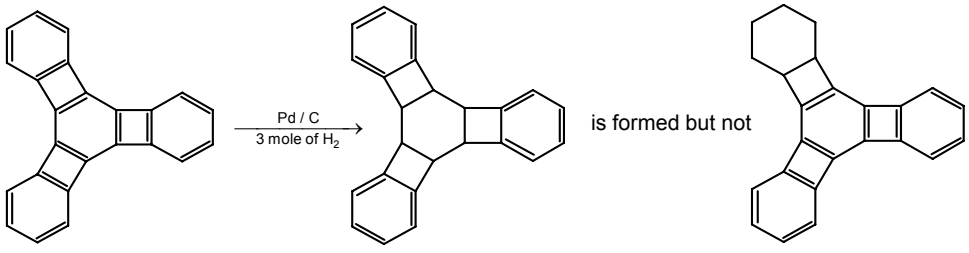
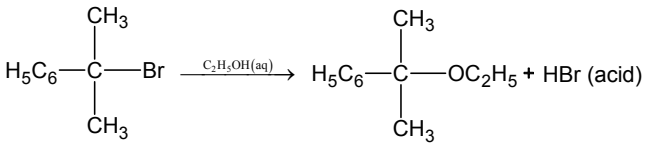


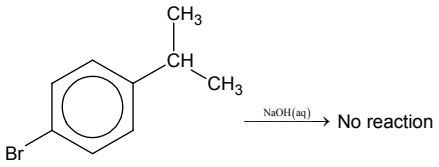
d)



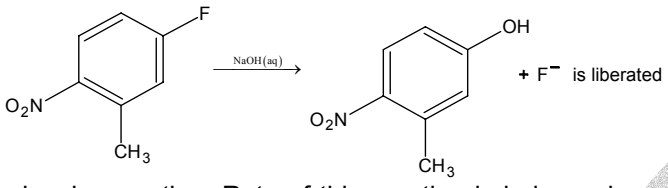
Solution14.(a) (i)



(ii)

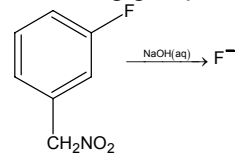


(b) (i)



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

(ii)



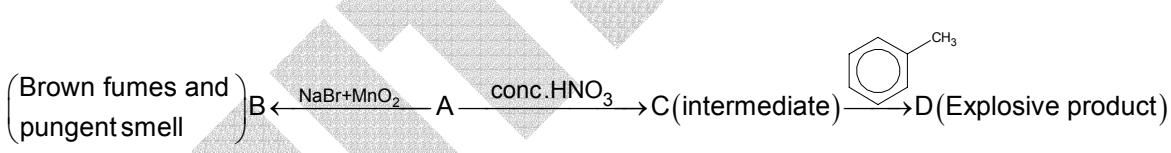
Bimolecular mechanism is not possible is this case.

(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..



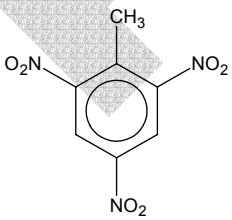
Find A, B, C and D. Also write equations A to B and A to C.

Solution15. (A) H_2SO_4

(B) Br_2

(C) $NO_2^{\oplus}$

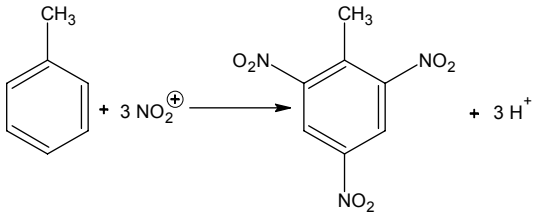
(D)



Reactions involved are:

$$\underset{(A)}{2H_2SO_4} + 2NaBr + MnO_2 \longrightarrow \underset{(B)(\text{Brown fumes})}{Br_2} + Na_2SO_4 + MnSO_4 + 2H_2O$$

$$\underset{(A)}{H_2SO_4} + HNO_3 \longrightarrow HSO_4^- + \underset{(C)}{NO_2^{\oplus}} + H_2O$$



(D) (Explosive)

Q.16. (B) $\xleftarrow{\text{Moist air}}$ MCl_4 $\xrightarrow{Zn}$ (A)

white fumes having pungent smell — (M = transitionelement colourless) — (purple color)

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

Solution 16. M = Ti

$$A = \left[Ti(H_2O)_6\right]^{3+}$$

$B = TiO_2$

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

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

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

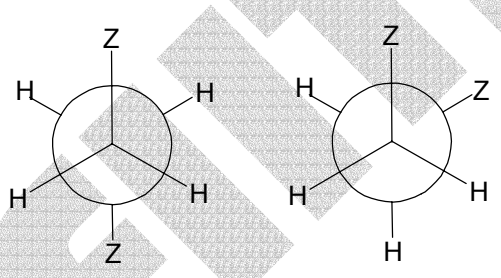
a) Write stable conformer for $Z — CH_2 — CH_2 — Z$ in Newman's projection.
If $\mu_{solution}$ = 1.0 D and mole fraction of anti form = 0.82, find μ_{Gouche}.

b) Write most stable meso conformer of

CHDY
|
CHDY

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

Solution17.a)



(Anti) (Gauche)

Mole fraction of anti form = 0.82

Mole fraction of Gauche form = 0.18

$\mu_{ob.} = 1$

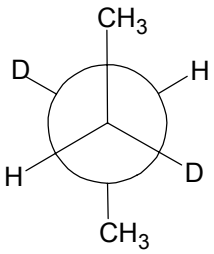
$1 = \mu_{(anti)} \times 0.82 + \mu_{(Gauce)} \times 0.18$

$\mu_{(anti)} = 0$

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

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

b) i)



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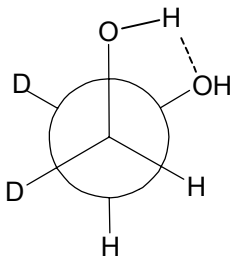

Q.18. a) Calculate ΔG_r^0 of the following reaction

$$Ag^+_{(aq)} + Cl^-_{(aq.)} \longrightarrow AgCl_{(s)}$$

Given

$\Delta G_f^0\,(AgCl)$ $\quad -109\,KJ/mole$

$\Delta G_f^0\,(Cl^-)$ $\quad$ - 129 kJ/mole

$\Delta G_f^0\,(Ag^+)$ $\quad$ 77 kJ/mole

Represent the above reaction in form of a cell.

Calculate E° of the cell. Find $\log_{10}K_{sp}$ 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 $\log_{10}\dfrac{\left[Zn^{2+}\right]}{\left[Ag^+\right]^2}$. Given that

$Ag^+ + e^- \longrightarrow Ag \qquad E^0 = 0.80\,V$

$Zn^{2+} + 2e^- \longrightarrow Zn \qquad E^0 = -0.76\,V$

Also find how many moles of Ag will be formed?

Solution18. Cell reactions are

$$Ag + \frac{1}{2}Cl_2 \longrightarrow AgCl \qquad ....(i)$$

$$Ag \longrightarrow Ag^+ + e^- \qquad ...(ii)$$

$$\frac{1}{2}Cl_2 + e \longrightarrow Cl^- \qquad ...(iii)$$

$$Ag^+ + Cl^- \longrightarrow AgCl \qquad ...(i - ii - iii)$$

hence cell representation is $Ag\,|\,Ag^+\,|\,AgCl\,|\,Cl^-\,|\,Cl_2, Pt$

$$Ag^+(aq) + Cl^-(aq) \longrightarrow AgCl(s); \qquad \sum \Delta G_P^o - \sum \Delta G_R^o$$

i) $\Delta G^o = -109 - (-129 + 77)$

$= -109+129 - 77$

$= 20 - 77 = -57 = -1 \times F \times E^o$

$-57 = -1 \times 96500 \times E^o$

$\Rightarrow E^o = \dfrac{57000}{96500} = 0.59$ Volts

ii) $-57 = -2.303\,RT \log K_0$

$\log K_0 = \dfrac{57 \times 1000}{2.303 \times 8.314 \times 298}$

$\log K_0 = 9.98 \approx 10$

$K_0 = 10^{10}$

$\therefore K_{sp} = 1/K_0$
$\therefore K_{sp} = 10^{-10}$
$\therefore \log K_{sp} = -10$

iii) $10\,AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq)$

S S

$10^{-10} = S^2$
$\therefore S = 10^{-5}$ m / L

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

$2Ag^+ + 2e \rightarrow 2Ag; \quad E^0 = 0.80V$

$Zn \longrightarrow Zn^{2+} + 2e; \quad E^0 = 0.77V$

$2Ag^+_{(aq)} + Zn_{(s)} \longrightarrow Zn^{2+}_{(aq)} + 2Ag_{(S);} \quad E^0 = 1.57V$

10^{-6} mole 10^{-3} moles
$\log_{10} K_{(eq)} = 52.8$

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

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

$$E^0_{Cell} = \frac{+0.0591}{2} \log_{10} \frac{\left[Zn^{2+}\right]}{\left[Ag^+\right]^2}$$

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

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