

Chapter-18. Electromotive force

Q1.

Sol: (i) $\text{Ag} / \text{Ag}^+ (10^{-5} \text{ M}), E_{\text{Ag}^+/\text{Ag}}^0 = 0.80 \text{ V}$



$$E_{\text{Ag}^+/\text{Ag}} = E_{\text{Ag}^+/\text{Ag}}^0 - \frac{2.303 RT}{nF} \log Q$$

$$E_{\text{Ag}^+/\text{Ag}} = 0.80 \text{ V} - \frac{0.0592}{1} \log \frac{1}{[\text{Ag}^+]}$$

$$E_{\text{Ag}^+/\text{Ag}} = 0.80 \text{ V} - 0.0592 \log(10^{-5}) = 0.80 \text{ V} - 5 \times 0.0592 = 0.30 \text{ V} \quad \text{Ans}$$

(ii) $\text{Cu} / \text{Cu}^{2+} (0.2 \text{ M}), E_{\text{Cu}^{2+}/\text{Cu}}^0 = 0.34 \text{ V}$

$$E_{\text{Cu}^{2+}/\text{Cu}} = E_{\text{Cu}^{2+}/\text{Cu}}^0 - \frac{2.303 RT}{nF} \log Q$$

$$= 0.34 \text{ V} - \frac{0.0592}{2} \log \frac{1}{[\text{Cu}^{2+}]} = 0.34 \text{ V} - \frac{0.0592}{2} \times \log 5$$

$$= 0.34 \text{ V} - \frac{0.0592}{2} \times 0.699 = 0.32 \text{ V} \quad \text{Ans}$$

Q2.

Sol: (i) $(\text{Pt}) \text{H}_2 / \text{HCl} (1 \text{ M})$ and $\text{Pt}(\text{Cl}_2) / \text{HCl} (1 \text{ M})$

(1 atm)

1 atm

$$E_{2\text{H}^+/\text{H}_2}^0 = 0$$

$$E_{\text{Cl}_2/2\text{Cl}^-}^0 = 1.36 \text{ V}$$

Since $E_{\text{Cl}_2/2\text{Cl}^-}^0 > E_{2\text{H}^+/\text{H}_2}^0$

So Cl_2/Cl^- electrode behaves as cathode, so that the cell has +ve emf.

Cell reaction: $\text{Cl}_2 + \text{H}_2 \longrightarrow 2\text{HCl}$

Cell notation: $\text{Pt} / \text{H}_2, \text{H}^+ \parallel \text{Cl}_2, \text{Cl}^- / \text{Pt}$

(ii) $\text{Cu} / \text{Cu}^{2+} (1 \text{ M}) \& \text{Cl}^- / \text{Cl}_2 (\text{Pt})$

1 M 1 atm

$$E_{\text{Cu}^{2+}/\text{Cu}}^0 = 0.34 \text{ V} \quad \& \quad E_{\text{Cl}_2/\text{Cl}^-}^0 = 1.36 \text{ V}$$

Since $E_{\text{Cl}_2/\text{Cl}^-}^0 > E_{\text{Cu}^{2+}/\text{Cu}}^0$

So Cl_2/Cl^- behaves as cathode & hence Cl_2 get reduced.

Cell reaction: $\text{Cl}_2 + \text{Cu} \longrightarrow \text{Cu}^{2+} + 2\text{Cl}^-$

Cell notation: $\text{Cu} / \text{Cu}^{2+} \parallel \text{Cl}_2, \text{Cl}^- / \text{Pt}$

Q3. Fluorine is the strongest oxidising agent possible so it is not possible for F^- too oxidised by any other elements listed in the electrochemistry series.

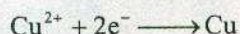
Q4.



Initially 0.1M

Finally $0.1 - 0.1 \times \frac{90}{100} \quad 0.09 \quad 0.09$

$0.1 - 0.09$



$\mathcal{E}_{\text{Cu}^{2+}/\text{Cu}} = \mathcal{E}_{\text{Cu}^{2+}/\text{Cu}}^0 - \frac{0.0592}{2} \log \frac{1}{[\text{Cu}^{2+}]}$

$\mathcal{E}_{\text{Cu}^{2+}/\text{Cu}} = +0.34\text{V} - \frac{0.0592}{2} \log \frac{1}{0.09} = +0.34\text{V} - 0.031\text{V} = 0.31\text{V} \quad \text{Ans}$

Q5. $1\text{N CuSO}_4 = 1 \times 2 \text{ M CuSO}_4$



Initially excess 2N

At eq^b 2 - X

$\mathcal{E}_{\text{Fe}^{2+}/\text{Fe}}^0 = -0.44$

$\mathcal{E}_{\text{Cu}^{2+}/\text{Cu}}^0 = 0.34\text{V}$

At eq^b, $E_{\text{cell}} = 0$ and $Q = K_{\text{eq}}^b$

So from $E_{\text{cell}} = E_{\text{cell}}^0 - \frac{0.0592}{2} \log Q$

At eq^b, $0 = E_{\text{cell}}^0 - \frac{0.0592}{2} \log k_{\text{eq}^b}$

$\mathcal{E}_{\text{cell}}^0 = + \frac{0.0592}{2} \log \frac{[\text{Fe}^{2+}]}{[\text{CuSO}_4]}$

$0.78 = \frac{+0.0592}{2} \log \frac{x}{2-x} \Rightarrow \frac{x}{2-x} = \text{antilog}(+26.35)$

$\Rightarrow X = 2.24 \times 10^{26} (2 - x)$

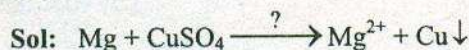
If $2 - x = y \Rightarrow x = 2 - y$

$(2 - y) = 2.2456 \times 10^{26} y$

$y = \frac{2}{2.2456 \times 10^{26}} = 8.906 \times 10^{-27} \quad \text{Ans}$

\therefore So concⁿ of CaSO_4 at eq^b = $2 - x = y = 8.906 \times 10^{-27} \text{M} \quad \text{Ans}$

Q6.



$\mathcal{E}_{\text{Mg}/\text{Mg}^{2+}}^0 = 2.36\text{V} \Rightarrow \mathcal{E}_{\text{Mg}^{2+}/\text{Mg}}^0 = -2.36\text{V}$

$\mathcal{E}_{\text{Cu}/\text{Cu}^{2+}}^0 = -0.34\text{V}$

$$\mathcal{E}_{\text{Cu}^{2+}/\text{Cu}}^0 > \mathcal{E}_{\text{Mg}^{2+}/\text{Mg}}^0 \quad \text{So Cu}^{2+} \text{ can be reduced by Mg.}$$

Q7.

Sol: (i) $\text{Mg} + \text{Cl}_2(1 \text{ atm}) \rightleftharpoons \text{Mg}^{2+}(10^{-2}\text{M}) + 2\text{Cl}^-(2 \times 10^{-2}\text{M})$ ($2e^-$ is transferred)

$$\mathcal{E}_{\text{Mg}^{2+}/\text{Mg}}^0 = -2.36\text{V} \quad \& \quad \mathcal{E}_{\text{Cl}_2/\text{ZCl}^-}^0 = 1.36\text{V}$$

$$\begin{aligned} \mathcal{E}_{\text{Cell}}^0 &= \mathcal{E}_{\text{Cell}}^0 - \frac{0.0592}{2} \log[\text{Cl}^-]^2[\text{Mg}^{2+}] \\ &= 3.72\text{V} - \frac{0.0592}{2} \log\{(2 \times 10^{-2})^2 \times 10^{-2}\} = 3.72\text{V} - \frac{0.0592}{2} \log(4 \times 10^{-6}) \\ &= 3.72 - \frac{0.0592}{2} (-6 + \log 4) = 3.72\text{V} + 0.16\text{V} = 3.88\text{V} \quad \text{Ans} \end{aligned}$$

(ii) $\text{Zn} + \text{Fe}^{2+}(10^{-3}\text{M}) \rightleftharpoons \text{Zn}^{2+}(10^{-4}\text{M}) + \text{Fe}$

$$\mathcal{E}_{\text{Zn}^{2+}/\text{Zn}}^0 = -0.76\text{V} \quad \& \quad \mathcal{E}_{\text{Fe}^{2+}/\text{Fe}}^0 = -0.44\text{V}$$

$$\mathcal{E}_{\text{Cell}}^0 = -\mathcal{E}_{\text{Zn}^{2+}/\text{Zn}}^0 + \mathcal{E}_{\text{Fe}^{2+}/\text{Fe}}^0 = 0.76\text{V} + (-0.44\text{V}) = 0.32\text{V}$$

$$\begin{aligned} \mathcal{E}_{\text{Cell}} &= \mathcal{E}_{\text{Cell}}^0 - \frac{2.303}{nF} \log \frac{[\text{Zn}^{2+}]}{[\text{Fe}^{2+}]} \\ &= 0.32\text{V} - \frac{0.0592}{2} \log \frac{10^{-4}}{10^{-3}} \times 10^{-1} = 0.32\text{V} - \frac{0.0592}{2} \times (-1) = 0.3496\text{V} \quad \text{Ans} \end{aligned}$$

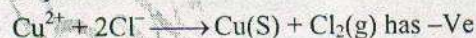
Q8.

Sol: $\text{Zn(s)} + \text{Pb}^{2+}(1\text{M}) \longrightarrow \text{Zn}^{2+}(1\text{M}) + \text{Pb(s)}, \mathcal{E}_{\text{Cell}}^0 = 0.66\text{V}$

$$\begin{aligned} \mathcal{E}_{\text{cell}} &= \mathcal{E}_{\text{cell}}^0 - \frac{0.0592}{2} \log \frac{[\text{Zn}^{2+}]}{[\text{Pb}^{2+}]} \\ &= 0.66 - \frac{0.0592}{2} \log \frac{0.1}{0.1} = 0.66\text{V} \quad \text{Ans} \end{aligned}$$

Q9.

Sol: In electrolytic cell that reaction will occur which has -ve emf. Since the reacⁿ



Emf, So this reacⁿ can be made to occur in electrolytic cell.

Ans (C)

Q10.

Sol: Since $E_{\text{Cell}} = +\text{ve}$, so reaction will proceed in forward direction but only to a extent at which it attain eq^b and so Ni^{2+} remain in some amount. **Ans (C)**

Q11.

Sol: (a) Since X can displace Ag^+ from its salt, so it has more reducing power than Ag, so Oxidation Potential of X will be higher than that of Ag.

$$\mathcal{E}_{\text{Ag}/\text{A}^{2+}}^0 < \mathcal{E}_{\text{X}/\text{X}^{2+}}^0 \quad \therefore \mathcal{E}_{\text{X}^{2+}/\text{X}}^0 < \mathcal{E}_{\text{Ag}^+/\text{Ag}}^0$$

$$\varepsilon^0_{X^{2+}/X} < 0.8 \text{ V} \text{ --- (1)}$$

Also since X can't displace Cu^{2+} from its salt so it has less reducing power than Cu, so less oxidation potential & so high reduction potential.

$$\begin{aligned} \varepsilon^0_{X^{2+}/X} &> \varepsilon^0_{\text{Cu}^{2+}/\text{Cu}} \\ &> 0.34 \text{ V} \text{ --- (2)} \end{aligned}$$

$$\therefore (1) \& (2) \quad 0.34 \text{ V} < \varepsilon^0_{X^{2+}/X} < 0.8 \text{ V} \quad \text{Ans}$$

(b) Since X can't displace Zn^{2+} or Fe^{2+}

$$\text{So } \varepsilon^0_{X^{2+}/X} > \varepsilon^0_{\text{Zn}^{2+}/\text{Zn}} > \varepsilon^0_{\text{Fe}^{2+}/\text{Fe}}$$

$$\varepsilon^0_{X^{2+}/X} > -0.76 \text{ V} \& > -0.44 \text{ V}$$

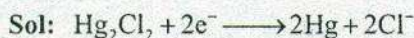
$\therefore \varepsilon^0_{X^{2+}/X}$ Should be greater than -0.44 V for only of Zn^{2+} or Fe^{2+} not to displace

Also X can reduced H^+ to H_2 , So it has high reducing power than H_2

\therefore reduction potential will be less.

$$\therefore \varepsilon_{X^{2+}/X} < 0 \Rightarrow \therefore -0.44 \text{ V} < E_{X^{2+}/X} \quad \text{Ans}$$

Q12.



$$0.1 \text{ N} = 0.1 \text{ M}$$

$$\varepsilon_{\text{Hg}_2^{2+}/\text{Hg}, \text{Cl}^-} = \varepsilon^0_{\text{Hg}_2^{2+}/\text{Hg}} - \frac{2.303 \text{ RT}}{n\text{F}} \log Q$$

For the above reaction; $Q = [\text{Cl}^-]^2 = (0.1)^2 = 10^{-2}$

$$\varepsilon^0_{\text{Hg}_2^{2+}/\text{Hg}, \text{Cl}^-} = 0.28 \text{ V}$$

$$\begin{aligned} \therefore \varepsilon_{\text{Hg}_2^{2+}/\text{Hg}, \text{Cl}^-} &= 0.28 \text{ V} - \frac{0.0592}{2} \log 10^{-2} = 0.28 \text{ V} - \frac{0.0592}{2} \times (-2) \\ &= 0.28 + 0.0592 = 0.339 \text{ V} \quad \text{Ans} \end{aligned}$$

Q13.

Sol: In concentration cell, we know that reaction tends to occur in the direction such that the conc.ⁿ in both half cell becomes equal.

So in half cell with lower H^+ conc.ⁿ it forms & in half cell with higher H^+ conc.ⁿ, it consume.

$$\therefore [\text{H}^+] = 10^{-8} \text{ M} \quad \& \quad [\text{H}^+]_2 = 0.025 \text{ M}$$

Act as anode

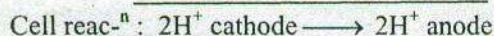
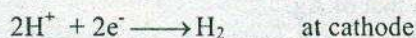
Act as cathode

So H^+ get formed

So H^+ get consumed

Cell Notation: $\text{Pt} / \text{H}_2, \text{H}^+ (10^{-8} \text{ M}) // \text{H}^+ (0.025 \text{ M}) \text{H}_2 / \text{Pt}$

Cell reac.ⁿ



$$\begin{aligned}\therefore \mathcal{E}_{\text{cell}} &= \mathcal{E}_{\text{cell}}^0 - \frac{0.0592}{1} \log \frac{[\text{H}^+]_{\text{anode}}}{[\text{H}^+]_{\text{cathode}}} \\ \mathcal{E}_{\text{cell}} &= 0 - \frac{0.0592}{1} \log \frac{10^{-8}}{0.025} = -\frac{0.0592}{1} \left(\log \frac{10^{-5}}{25} \right) \\ &= -\frac{0.0592}{1} (-5 - \log 25) = -0.0592 (-6.398) = 0.379 \text{ volt} \quad \text{Ans}\end{aligned}$$

Q14.

Sol: Let the concⁿ of Cu^{2+} is x for the cell reaction to occur.



$$Q = \frac{[\text{Cu}^{2+}]}{[\text{Zn}^{2+}]} = \frac{x}{1} \quad \text{For } \text{Cu}^{2+} + 2\text{e}^- \rightarrow \text{Cu}; \quad Q = \frac{1}{(\text{Cu}^{2+})} = \frac{1}{x}$$

For cell reaction to occur

$$\mathcal{E}_{\text{cell}} > 0$$

$$\mathcal{E}_{\text{Zn}^{2+}/\text{Zn}}^0 - \mathcal{E}_{\text{Cu}^{2+}/\text{Cu}}^0 > 0 \Rightarrow \mathcal{E}_{\text{Cu}^{2+}/\text{Cu}}^0 < \mathcal{E}_{\text{Zn}^{2+}/\text{Zn}}^0$$

$$\mathcal{E}_{\text{Cu}^{2+}/\text{Cu}}^0 - \frac{2.303RT}{nF} \log Q < -0.76$$

$$0.34 - \frac{0.0592}{2} \log \frac{1}{x} < -0.76$$

$$\frac{0.0592}{2} \log \frac{1}{x} > 1.1 \Rightarrow \log \frac{1}{x} > 37.162$$

$$x < 10^{-37.162} = 6.2 \times 10^{-38} \text{ M} \quad \text{Ans}$$

Q15.

Sol: In electrochemical cell / galvanic cell

+ve electrode is cathode & -ve electrode is anode.

\therefore Concⁿ in anode half cell = 10^{-6} M

$$\mathcal{E}_{\text{Cell}} = 0.118 \text{ V} = \frac{-0.0592}{1} \log \frac{[\text{H}^+]_{\text{anode}}}{[\text{H}^+]_{\text{cathode}}}$$

$$\Rightarrow 0.118 \text{ V} = \frac{-0.0592}{1} \log \frac{10^{-6}}{[\text{H}^+]_{\text{cathode}}}$$

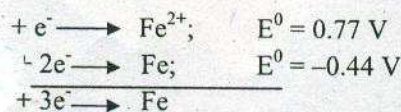
$$\Rightarrow -2 = \log \frac{10^{-6}}{[\text{H}^+]_{\text{cathode}}} \Rightarrow \frac{10^{-6}}{[\text{H}^+]_{\text{cath}}} = 10^{-2}$$

$$[\text{H}^+]_{\text{cathode}} = \frac{10^{-6}}{10^{-2}} = 10^{-4} \text{ M} \quad \text{Ans}$$

Q16.

Sol: For $\text{Fe}^{2+} + \text{Zn} \longrightarrow \text{Zn}^{2+} + \text{Fe}$

$$\mathcal{E}_{\text{Cell}} = \mathcal{E}_{\text{Fe}^{2+}/\text{Fe}}^0 - \mathcal{E}_{\text{Zn}^{2+}/\text{Zn}}^0 = -0.41 - (-0.76) = 0.35 \text{ V} \quad \text{Ans}$$



$$\Delta G_3 = \Delta G_1 + \Delta G_2$$

$$-n_3 F E_3 = -n_1 F E_1 - n_2 F E_2$$

$$3E_3 = 1 \cdot E_1 + 2 \cdot E_2$$

$$E_3 = \frac{E_1 + 2E_2}{3} = \frac{0.77 + 2(-0.44)}{3} = -0.04 \text{ V} \quad \text{Ans}$$

Q18.

Sol:

Reducing oxidising



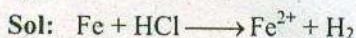
$$E_{\text{cell}}^0 = E_{\text{Hg}_2^{2+}/\text{Hg}}^0 - E_{\text{Hg}^{2+}/\text{Hg}}^0 = 0.92 - 0.788 = 0.132 \text{ V}$$

$$\therefore E_{\text{cell}}^0 = \frac{0.0592}{1} \log K_{\text{eq}}^{-b}$$

$$\frac{0.132}{0.0592} = \log K_{\text{eq}}^{-b}$$

$$K_{\text{eq-b}} = 10^{2.23} = 1.71 \times 10^2 \quad \text{Ans}$$

Q19.



$$E_{\text{cell}} = E_{\text{H}^+/\text{H}_2}^0 - E_{\text{Fe}^{2+}/\text{Fe}}^0 = 0 - (-0.44) = 0.44 \text{ V}$$

Since E_{cell} is +ve, so the reaction can happen

Q20.



Let at concⁿ x M of Cr^{3+} , $E_{\text{cell}} = 0$

$$\therefore E_{\text{cell}} = E_{\text{cell}}^0 - \frac{0.0592}{6} \log \frac{[\text{Zn}^{2+}]^3}{[\text{Cr}^{3+}]^2}$$

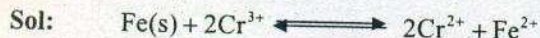
$$0 = (E_{\text{Cr}^{3+}/\text{Cr}}^0 - E_{\text{Zn}^{2+}/\text{Zn}}^0) - \frac{0.0592}{6} \log \frac{1^3}{x^2}$$

$$= \{-0.74 - (-0.76)\} + \frac{0.0592}{6} \log x^2$$

$$\Rightarrow -0.02 = \frac{0.0592}{6} \times 2 \log x$$

$$\log x = \frac{-0.06}{0.0592} = -1 \Rightarrow x = 10^{-1} = 0.1 \text{ M} \quad \text{Ans}$$

Q21.



Initially excess 1 0 0

At eq^b 1-2x 2x x

At eq^b, $\varepsilon_{\text{cell}} = 0$, $Q = k_{\text{eq}}^{-b}$

$$\varepsilon_{\text{Cell}}^0 - \frac{2.303RT}{nF} \log k_{\text{eq}}^{-b} = 0$$

$$\left(\varepsilon_{\text{Cr}^{3+}/\text{Cr}^{2+}}^0 - \varepsilon_{\text{Fe}^{2+}/\text{Fe}}^0 \right) - \frac{0.0592}{2} \log \frac{[\text{Cr}^{2+}]^2 [\text{Fe}^{2+}]}{[\text{Cr}^{3+}]^2} = 0$$

$$\Rightarrow (-0.407 + 0.44) - \frac{0.0592}{2} \log \frac{(2x)^2 x}{(1-2x)^2} = 0$$

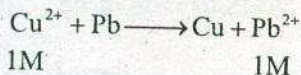
$$\Rightarrow \frac{-0.033 \times 2}{0.0592} = \log \frac{4x^3}{(1-2x)^2}$$

$$\frac{4x^3}{(1-2x)^2} = 10^{-1.1148} = 0.07676$$

Solving we get $x = 0.42 \text{ M}$ **Ans**

Q22.

Sol: $\varepsilon_{\text{Cell}} = \varepsilon_{\text{Cell}}^0 - \frac{0.0592}{n} \log Q$



If the concⁿ is 0.001 M then $Q = \frac{[\text{Pb}^{2+}]}{[\text{Cu}^{2+}]} \Rightarrow Q = \frac{0.001}{0.001} = 1$

$$\therefore \varepsilon_{\text{Cell}} = \varepsilon_{\text{Cell}}^0 - \frac{0.0592}{2} \log 1$$

$$\therefore \varepsilon_{\text{Cell}} = \varepsilon_{\text{Cell}}^0$$

So Emf doesn't change by any amount.

Q23.

Sol: At PH = 10

$$[\text{H}^+] = 10^{-10} \text{ M}$$

$$\begin{aligned} \varepsilon_{\text{H}^+/\text{H}_2} &= \varepsilon_{\text{H}^+/\text{H}_2}^0 - \frac{0.0592}{1} \log \frac{1}{[\text{H}^+]} = 0 + \frac{0.0592}{1} \log [\text{H}^+] \\ &= +0.0592 \log 10^{-10} = -0.592 \text{ V} \quad \text{Ans} \end{aligned}$$

Q24.



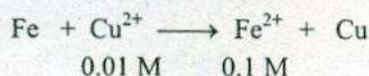
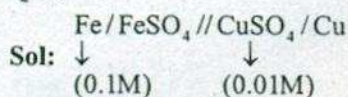
$$\frac{\text{oxidised form}}{\text{Reduced form}} = \frac{[\text{Fe}(\text{CN})_6]^{3-}}{[\text{Fe}(\text{CN})_6]^{4-}} = x(\text{say})$$

$$\varepsilon = \varepsilon^0 - \frac{0.0592}{1} \log \frac{[\text{Fe}(\text{CN})_6]^{4-}}{[\text{Fe}(\text{CN})_6]^{3-}}$$

$$0.28 \text{ V} = 0.36 \text{ V} - \frac{0.0592}{1} \log \frac{1}{x} \Rightarrow \frac{-0.08 \times 1}{0.0592} = \log x$$

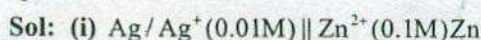
$$x = 10^{\frac{-8}{5.92}} = 0.0445 \quad \text{Ans}$$

Q25.



$$\begin{aligned} \varepsilon_{\text{Cell}} &= \varepsilon^0_{\text{Cell}} - \frac{0.0592}{2} \log \frac{[\text{Fe}^{2+}]}{[\text{Cu}^{2+}]} \\ &= \left(\varepsilon^0_{\text{Cu}^{2+}/\text{Cu}} - \varepsilon^0_{\text{Fe}^{2+}/\text{Fe}} \right) - \frac{0.0592}{2} \log \frac{0.1}{0.01} \\ &= (0.34 + 0.44) - \frac{0.0592}{2} \times 1 = 0.78 + 0.03 = 0.75 \text{ V} \quad \text{Ans} \end{aligned}$$

Q26.



$$\varepsilon_{\text{Cell}} = \varepsilon^0_{\text{Cell}} - \frac{0.0592}{A} \log Q$$



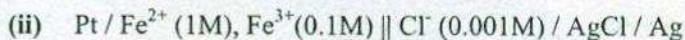
$$Q = \frac{[\text{Ag}^+]^2}{[\text{Zn}^{2+}]} = \frac{[0.01]^2}{0.01} = 10^{-3}$$

$$\therefore \varepsilon_{\text{Cell}} = \varepsilon^0_{\text{Cell}} - \frac{0.0592}{2} \log 10^{-3} = \varepsilon^0_{\text{Cell}} + \frac{0.0592 \times 3}{2}$$

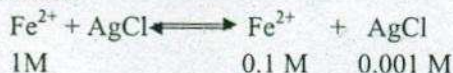
$$= \left(E^0_{\text{Zn}^{2+}/\text{Zn}} - E^0_{\text{Ag}^+/\text{Ag}} \right) + 0.0592 \times 1.5$$

$$= (-0.76 - 0.80) \text{ V} + 0.0888 \text{ V} = (-1.56 + 0.0888) \text{ V} = -1.4712 \text{ V} \quad \text{Ans}$$

Since $\varepsilon_{\text{cell}} < 0$, so the reaction is not spontaneous



Cell reaction



$$Q = \frac{[\text{Fe}^{3+}][\text{Cl}^-]}{[\text{Fe}^{2+}]} = \frac{0.1 \times 0.001}{\times 1} = 10^{-4}$$

$$\begin{aligned}\varepsilon_{\text{Cell}} &= \varepsilon^0_{\text{Cell}} - \frac{0.0592}{1} \log Q \\ &= (0.22 - 0.77) - \frac{0.0592}{1} \log 10^{-4} \\ &= -0.55 + 4 \times 0.0592 \\ &= -0.3132 \text{ V}\end{aligned}$$

Since $\varepsilon_{\text{Cell}} < 0$, so the reaction is not spontaneous

(iii) $\text{Zn} / \text{ZnO}_2^{2-} (0.1\text{M}), \text{OH}^- (1\text{M}) \parallel \text{HgO} / \text{Hg}$



$$Q = \frac{[\text{ZnO}_2^{2-}]}{[\text{OH}^-]^2} = \frac{0.1}{1^2} = 0.1$$

$$\begin{aligned}\varepsilon_{\text{Cell}} &= \varepsilon^0_{\text{Cell}} - \frac{0.0592}{2} \log Q \\ &= \left(\varepsilon^0_{\text{HgO/Hg}} - \varepsilon^0_{\text{Zn/O}_2/\text{Zn}} \right) - \frac{0.0592}{2} \log 10^{-1} \\ &= (0.85 - (0.76)) - \frac{0.0592}{2} \times (-1) = 1.61 + 0.03 = 1.63 = +\text{Ve}\end{aligned}$$

So the reaction is spontaneous. The value of E_{Cell} is diff.ⁿ because I have used $\text{Zn}^{2+} / \text{Zn}$ in place of $\text{ZnO}_2^{2-} / \text{Zn}$ & $\text{Hg}^{2+} / \text{Hg}$ in place of HgO / Hg .

Q27.



Initially 0.5 0 0

At eq- 0.5-0.5x 0.5x 0.5x

$$K_a = \frac{(0.5x)(0.5x)}{0.5-0.5x} = \frac{0.5x^2}{1-x} = 1.77 \times 10^{-4}$$

$$x^2 = \frac{1.77}{0.5} \times 10^{-4} \Rightarrow x^2 = \frac{1.77}{0.5} \times 10^{-4}$$

So conc.ⁿ of H^+ in anode compartment containing $\text{HCOOH} = (1.88 \times 10^{-2} \text{M}) \times 0.5 = 0.94 \times 10^{-2} \text{M}$

Similarly



Initially 1M 0 0

At eq-^b 1-x x x

$$K_a = \frac{x^2}{1-x} \approx x^2 \Rightarrow x = \sqrt{K_a} = \sqrt{18} \times 10^{-3}$$

$$x = 4.2426 \times 10^{-3} \text{M}$$

So $[\text{H}^+]$ in cathodic compartment = $4.2426 \times 10^{-2} \text{M}$,

$$\begin{aligned}\mathcal{E}_{\text{Cell}} &= \mathcal{E}_{\text{Cell}}^0 - \frac{0.0592}{1} \log \frac{[\text{H}^+]_{\text{anode}}}{[\text{H}^+]_{\text{cathode}}} \\ &= 0 - \frac{0.0592}{1} \log \frac{0.84 \times 10^{-2}}{4.243 \times 10^{-3}} \\ &= -0.0592 \times (+0.3458) = -0.0243 \text{ volt} \quad \text{Ans}\end{aligned}$$

Q28.

Sol: $(\text{Pt}/\text{H}_2)\text{H}^+(\text{C} = \text{unknown}) \parallel \text{KCl sol}^{\text{n}} / \text{Hg}_2\text{Cl}_2 / \text{Hg}; E = 0.4783$

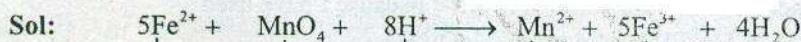


$$\begin{aligned}\mathcal{E}_{\text{Cell}} &= \mathcal{E}_{\text{Cell}}^0 - \frac{0.0592}{2} \log \frac{[\text{H}^+][\text{Cl}^-]^2}{1} \\ &= \left(\mathcal{E}_{\text{Hg}_2\text{Cl}_2/\text{Hg}/\text{KCl}}^0 - \mathcal{E}_{\text{H}^+/\text{H}_2}^0 \right) - \frac{0.0592}{2} \log [\text{H}^+]^2 (\text{I})^2\end{aligned}$$

If we use standard calomel electrode then KCl conc.ⁿ should be 1 M.

$$\begin{aligned}0.4783 &= (0.2420 - 0) - \frac{0.0592}{2} \times 2 \log [\text{H}^+] \\ \frac{0.2363}{0.0592} &= -\log [\text{H}^+] \Rightarrow \text{PH} = 3.99 \quad \text{Ans}\end{aligned}$$

Q29.



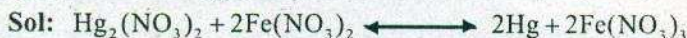
Given $\begin{matrix} \downarrow & \downarrow & \downarrow & \downarrow & \downarrow \\ 0.1 \text{ M} & 1 \times 10^{-2} \text{ M} & 1 \times 10^{-3} \text{ M} & 1 \times 10^{-4} \text{ M} & 1 \text{ M} \end{matrix}$

$$Q = \frac{[\text{Mn}^{2+}][\text{Fe}^{3+}]^5}{[\text{Fe}^{2+}]^5[\text{MnO}_4^-][\text{H}^+]^8} = \frac{10^{-4} \times 1^5}{(10^{-3})^5 (10^{-2}) (10^{-3})^8} = \frac{10^{-4}}{10^{-5} \times 10^{-2} \times 10^{-24}} = 10^{20+7} = 10^{27}$$

$$\mathcal{E}_{\text{Cell}} = \mathcal{E}_{\text{Cell}}^0 - \frac{2.303RT}{nF} \log Q$$

$$\begin{aligned}\mathcal{E}_{\text{Cell}} &= \left(\mathcal{E}_{\text{MnO}_4^-, \text{Mn}^{2+}}^0 - \mathcal{E}_{\text{Fe}^{3+}/\text{Fe}^{2+}}^0 \right) - \frac{0.0592}{5} \log 10^{27} \\ &= (1.51 - 0.771) - \frac{0.0592}{5} \times 27 = 0.739 - 0.31968 = 0.419 \text{ V} \quad \text{Ans}\end{aligned}$$

Q30.



$$\mathcal{E}_{\text{Hg}_2^{2+}, \text{Hg}}^0 = 0.79 \text{ V}, \mathcal{E}_{\text{Fe}^{3+}, \text{Fe}^{2+}}^0 = 0.77 \text{ volt}$$

$$\text{At eq}^b \quad \mathcal{E}_{\text{Cell}} = 0 \Rightarrow \mathcal{E}_{\text{Cell}}^0 = \frac{0.0592}{n} \log K_{\text{eq}}^b$$

$$(0.79 - 0.77) = \frac{0.0592}{2} \log k_{\text{eq}}^b$$

$$\frac{0.04}{0.0592} = \log K_{eq} \Rightarrow K_{eq} = 10^{\frac{+0.04}{0.0592}} = 4.78$$

Ans

Q31.



Initially (0.1M from KBr)

At eq^b -S S 0.1 + S

$$\therefore K_{sp} = [\text{Ag}^+][\text{Br}^-] = S(0.1 + S) = 6 \times 10^{-13}$$

$$\Rightarrow S \times 0.1 = 6 \times 10^{-13} \Rightarrow S = 6 \times 10^{-12}$$

$$\therefore [\text{Ag}^+] = 6 \times 10^{-12} \text{ M}$$

$$Q = \frac{1}{[\text{Ag}^+]} = \frac{1}{(6 \times 10^{-12})}$$

$$\therefore \varepsilon_{\text{Ag}^+/\text{Ag}} = \varepsilon_{\text{Ag}^+/\text{Ag}}^0 - \frac{0.0592}{1} \log \frac{1}{[\text{Ag}^+]}$$

$$= 0.80 + \frac{0.0592}{1} \log(6 \times 10^{-12}) = 0.80 + 0.0592(-12 + \log 6)$$

$$= 0.80 - 0.664 = 0.14 \text{ V} \quad \text{Ans}$$

Q32.

Sol: pH = 3.5, $[\text{H}^+] = 10^{-3.5} \text{ M}$

pH = 10.5, $[\text{H}^+] = 10^{-10.5} \text{ M}$

For concentration cell; $Q = \frac{[\text{H}^+]_{\text{anode}}}{[\text{H}^+]_{\text{cathode}}} = \frac{10^{-10.5}}{10^{-3.5}}$

$$\varepsilon_{\text{Cell}}^0 = 0$$

$$\varepsilon_{\text{Cell}} = \frac{-0.0592}{1} \log \frac{10^{-10.5}}{10^{-3.5}} = -0.0592 \log(10^{-7}) = -0.0592 \times (-7)$$

$$\varepsilon_{\text{Cell}} = 0.4244 \text{ V} \quad \text{Ans}$$

Q33.

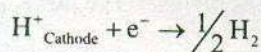
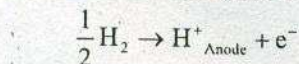
Sol: $[\text{H}^+]$ in one cell = 1M

$[\text{OH}^-]$ in another half cell = 1M

$[\text{H}^+][\text{OH}^-] = 10^{-14}$

$[\text{H}^+] \cdot 1 = 10^{-14} \Rightarrow [\text{H}^+] = 10^{-14} \text{ M}$

In concentration cell, half cell with less $[\text{H}^+]$ act as anode.



$$Q = \frac{[H^+]_{\text{anode}}}{[H^+]_{\text{cathode}}} = \frac{10^{-14}}{1}$$

$$\therefore \varepsilon_{\text{Cell}} = \frac{-0.0592}{1} \log 10^{-14} = 14 \times 0.0592 = 0.83 \text{ V} \quad \text{Ans}$$

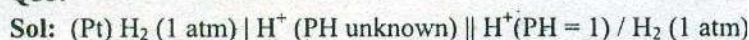
1M NH_3 has lower OH^- concⁿ because it is a weaker base. So $[\text{H}^+]$ will be higher
So, $\log [\text{H}^+]$ will be higher & hence $-0.0592 \log [\text{H}^+]$ will be lower

Q34.



$$\varepsilon_{\text{Cell}} = \varepsilon_{\text{Cu}^+/\text{Cu}} - \varepsilon_{\text{Cu}^{2+}/\text{Cu}} = 0.52 - 0.34 = 0.18 \text{ V} \quad \text{Ans}$$

Q35.



In anode half cell, let the concⁿ of H^+ = x M

$$\therefore \text{pH} = -\log [\text{H}^+] = -\log x$$

In cathode half cell, pH = 1 $\Rightarrow [\text{H}^+] = 10^{-1} \text{ M}$

$$\varepsilon_{\text{Cell}} = 0.16 \text{ V}$$

For concentration cell, $\varepsilon_{\text{Cell}}^0 = 0$

$$\varepsilon_{\text{Cell}} = \frac{-0.0592}{1} \log \frac{[\text{H}^+]_{\text{anode}}}{[\text{H}^+]_{\text{cathode}}}$$

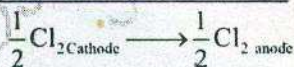
$$0.16 \text{ V} = \frac{-0.0592}{1} \log \frac{x}{10^{-1}} \Rightarrow 0.16 = -0.0592 \log 10x$$

$$\frac{0.16}{0.0592} = -(\log 10 + \log x) \Rightarrow 2.7 = -1 - \log x \Rightarrow -\log x = \text{pH} = 3.7 \quad \text{Ans}$$

Q36.

Sol: It is the case of concentration cell of chlorine.

So, cell notation : Pt/2Cl⁻, Cl₂(P = 0.9 atm) || Cl₂ (0.1 atm), 2Cl⁻ / Pt



$$Q = \frac{(P_{\text{Cl}_2 \text{ anode}})^{1/2}}{(P_{\text{Cl}_2 \text{ cathode}})^{1/2}} = \left(\frac{0.9}{0.1} \right)^{1/2} = 9^{1/2}$$

$$\therefore \varepsilon_{\text{Cell}} = 0 - \frac{0.0593}{1} \log (9)^{1/2} = \frac{-0.0592}{2} \log (9) = -0.0282 \text{ V}$$

So $\varepsilon_{\text{Cell}}$ is negative, so the reaction written will non spontaneous.

Q37.

Sol: pH in cathode = 3 $\Rightarrow [H^+]_{\text{cathode}} = 10^{-3}M$

Let pH in anode = x $\Rightarrow [H^+]_{\text{anode}} = 10^{-x}M$

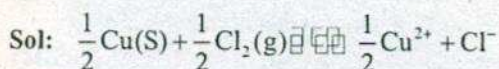
$$\mathcal{E}^0_{\text{Cell}} = 272 \text{ mv} = 0.272 \text{ V}$$

$$\therefore \mathcal{E}_{\text{Cell}} = \frac{-0.0592}{1} \log \frac{[H^+]_{\text{anode}}}{[H^+]_{\text{cathode}}}$$

$$0.272 = -0.0592 \log \frac{10^{-x}}{10^{-3}} = -0.0592 \log 10^{-(x-3)}$$

$$0.272 = 0.0592 (x - 3) \Rightarrow x - 3 = \frac{0.272}{0.0592} = 4.59 \Rightarrow x = 7.59 \quad \text{Ans}$$

Q38.



$$\mathcal{E}^0_{\text{Cl}_2/\text{Cl}^-} = +1.36 \text{ V}, \mathcal{E}^0_{\text{Cu}^{2+}/\text{Cu}} = 0.34 \text{ V}$$

$$\therefore \mathcal{E}^0_{\text{Cell}} = \mathcal{E}^0_{\text{Cl}_2/\text{Cl}^-} - \mathcal{E}^0_{\text{Cu}^{2+}/\text{Cu}} = 1.36 - 0.34 = 1.02 \quad \text{Ans}$$

$$\Delta G^0 = -nF \mathcal{E}^0_{\text{Cell}} = -1 \times 96500 \times 1.02 = -98430 \text{ J} \quad \text{Ans}$$

$$\mathcal{E}^0_{\text{Cell}} = \frac{0.0592}{1} \log K_{\text{eq-b}}$$

$$1.02 = 0.0592 \log K_{\text{eq-b}}$$

$$\log K_{\text{eq-b}} = \frac{1.02}{0.0592} = 17.23$$

$$K_{\text{eq-b}} = 1.97 \times 10^{17} \quad \text{Ans}$$

Q39.

Sol: $\mathcal{E}_{\text{F}_2/\text{F}^-} = 2.75 \text{ V}$ & $\mathcal{E}^0_{\text{F}_2/\text{F}^-} = 2.87 \text{ V}$



Let the pressure of F_2 gas is P atm.

$$\therefore \mathcal{E}_{\text{F}_2/\text{F}^-} = \mathcal{E}^0_{\text{F}_2/\text{F}^-} - \frac{0.0592}{1} \log \frac{[\text{F}^-]}{(\text{P}_{\text{F}_2})^{1/2}}$$

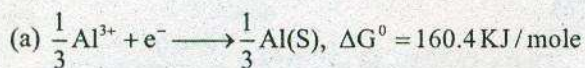
$$2.75 = 2.87 - \frac{0.0592}{1} \log \frac{0.38}{(\text{P})^{1/2}} \Rightarrow 2.03 = \log \frac{0.38}{(\text{P})^{1/2}}$$

$$\frac{0.38}{(\text{P})^{1/2}} = 106.421 \Rightarrow \text{P}^{1/2} = \frac{0.38}{106.42}$$

$$\text{P}^{1/2} = 3.57 \times 10^{-3}; \quad \text{P} = 1.275 \times 10^{-5} \text{ atm} \quad \text{Ans}$$

Q40.

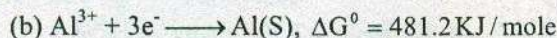
Sol: $\varepsilon^0 = -1.662 \text{ V}$



$$\Delta G^0 = -nF \varepsilon^0$$

$$160.4 \times 10^3 = -1 \times 96500 \times E^0$$

$$\varepsilon^0 = \frac{-1.604 \times 10^5}{96500} = -1.662 \text{ V}$$



$$\Delta G^0 = -nF \varepsilon^0$$

$$481.2 \times 10^3 = -3 \times 96500 \times E^0$$

$$\varepsilon^0 = \frac{-4.812 \times 10^5}{3 \times 96500} = -1.662 \text{ V} \quad \text{Ans}$$

So in both (a) & (b), E^0 are same

Q41.

Sol: No, because without salt bridge ions accumulate at electrode & so reaction stops.

Q42.

Sol: No, not at all, size doesn't affect the voltage. It affect the current at which cell work only

Q43.

Sol: $\text{Mg} / \text{Mg}^{2+} \parallel \text{Fe}^{3+} / \text{Fe}^{2+}$

$$I = 150 \text{ mA}$$

$$t = 20 \text{ min} = 20 \times 60 \text{ sec}$$

$$Q = I \cdot t = 150 \times 10^{-3} \times 1.2 \times 10^3 = 180 \text{ coulombs}$$

$$W = Z \cdot Q = \frac{\text{gm eq. wt.}}{96500} \cdot Q = \frac{12}{96500} \times 15 \times 12 = 0.0224 \text{ g} \quad \text{Ans}$$

Q44.

Sol: (i) $\text{Cd}^{2+} + 2e^- \longrightarrow \text{Cd(s)}, E^0 = -0.403 \text{ V}$

(ii) $\text{CdS(s)} + 2e^- \longrightarrow \text{Cd(s)} + \text{S}^{2-}(\text{aq}), E^0 = -1.21 \text{ V}$

(iii) $\text{Cd(s)} + \text{S}^{2-}(\text{aq}) \longrightarrow \text{CdS(s)} + 2e^-, E^0 = 1.21 \text{ V}$

(i) - (ii) $\text{Cd}^{2+} + \text{S}^{2-} \longrightarrow \text{CdS}, E^0 = -0.403 + 1.21 = 0.807$

$\Rightarrow \text{CdS} \longrightarrow \text{Cd}^{2+} + \text{S}^{2-}, E^0 = -0.807 \text{ V}$

$$\Delta G^0 = -nF \varepsilon^0 = -2 \times 96500 \times 0.807 = 155.8 \text{ KJ/mole}$$

$$\varepsilon^0 = \frac{0.0592}{2} \log K_{sp} \Rightarrow \frac{-0.807 \times 2}{0.0592} = \log K_{sp}$$

$$K_{sp} = 10^{-27.26} = 4.99 \times 10^{-28} \quad \text{Ans}$$

Q45.

Sol: $\text{Cd(s)} + 2\text{H}^+(\text{aq}) \longrightarrow \text{Cd}^{2+}(\text{aq}) + \text{H}_2(\text{g})$

$$\varepsilon_{\text{Cd}^{2+}/\text{Cd}}^0 = -0.40 \text{ V} \quad \& \quad \varepsilon_{\text{H}^+/\text{H}_2}^0 = 0.0 \text{ V}$$

$$W_{\text{max}} = \Delta G = -nF \varepsilon_{\text{Cell}}$$

$$\varepsilon_{\text{Cell}} = \varepsilon_{\text{Cell}}^0 - \frac{0.0592}{2} \log Q$$

$$= \left(E_{\text{H}^+/\text{H}_2}^0 - E_{\text{Cd}^{2+}/\text{Cd}}^0 \right) - \frac{0.0592}{2} \log \frac{0.780}{2 \times 0.780}$$

$$= (0 - (-0.40)) - \frac{0.0592}{2} \log \left(\frac{1}{2} \right)$$

$$= 0.40 + 8.9 \times 10^{-3} = 0.409$$

$$\therefore \text{Work done} = -2 \times 96500 \times 0.409 = -78919.724 \text{ J} = -78.9197 \text{ KJ} \quad \text{Ans}$$

-Ve work implies that work is done by cell.

Q46.

Sol: For concentration cell, $\varepsilon_{\text{Cell}}^0 = 0$

$$\text{For } \varepsilon_{\text{Cell}} = \frac{-0.0592}{2} \log Q$$

For $\varepsilon_{\text{cell}}$ to be + Ve, log Q should be -Ve

\therefore Q should be less than 1.

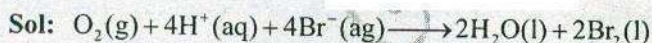
$$\Rightarrow Q = \frac{0.04}{1.0}$$

Cr^{3+} with less concentration will be in right direction of the reaction & Cr^{3+} with higher concⁿ will be on the left side.



\therefore Cr^{3+} with less concⁿ act as anode so the dilute solⁿ side will be the anodic side.

Q47.



$$Q = \frac{1}{[\text{H}^+]^4 [\text{Br}^-]^4}$$

At pH = 3.6; $[\text{H}^+] = 10^{-3.6} = 2.51 \times 10^{-4} \text{ M}$.

\therefore For [Br⁻] standard solⁿ = 1M

$$Q = \frac{1}{(2.51 \times 10^{-4})^4 \times 1} = \frac{1}{39.61 \times 10^{-16}}$$

$$\varepsilon_{\text{cell}}^0 = \varepsilon_{\text{O}_2, 4\text{H}^+/\text{H}_2\text{O}}^0 - \varepsilon_{\text{Br}_2/\text{Br}^-}^0 = 1.23 - 1.07 = 0.16$$

$$\varepsilon_{\text{cell}} = \varepsilon_{\text{cell}}^0 - \frac{0.0592}{4} \log \frac{1}{39.61 \times 10^{-16}} = 0.16 - \frac{0.0592}{4} (16 \log 39.61)$$

$$\varepsilon_{\text{cell}}^0 = 0.16 - \frac{0.0592}{4} \times 14.40 = 0.16 - 0.213$$

= -0.053 V, (-ve), so the reaction is not spontaneous.

Q48.

Sol: $\varepsilon_{\text{cell}} = 0.45$ with standard hydrogen electrode as anode



Initially AgSCN 0.1 M

At eq^b S S 0.1 + S

$$\therefore K_{\text{sp}} = S(0.1 + S)$$

$$\therefore \varepsilon_{\text{Cell}} = \varepsilon_{\text{Ag}^+/\text{Ag}}^0 - \varepsilon_{\text{H}^+/\text{H}_2}^0$$

$$0.45 = \varepsilon_{\text{Ag}^+/\text{Ag}}^0 - \frac{0.0592}{1} \log \frac{1}{[\text{Ag}^+]} - 0$$

$$0.45 = 0.80 + \frac{0.0592}{1} \log (\text{Ag}^+)$$

$$\frac{-0.35}{0.0592} = \log [\text{Ag}^+]$$

$$[\text{Ag}^+] = 10^{-5.9} = 1.124 \times 10^{-6} \therefore S = [\text{Ag}^+] = 1.124 \times 10^{-6}$$

$$\therefore K_{\text{sp}} = s(0.1 + s) \approx 0.1 \cdot s = 1.124 \times 10^{-7} \quad \text{Ans}$$

Q49.

$$\text{Sol: } \varepsilon_{\text{Cell}} = \frac{+0.0592}{10} \log K_{\text{eq}^b}$$

$$(1.51 + 0.49) = \frac{0.0592}{10} \log K_{\text{eq}^b} \Rightarrow \frac{20}{0.0592} = \log K_{\text{eq}^b}$$

$$\Rightarrow \log K_{\text{eq}^b} = 337.8 \quad K_{\text{eq}^b} = 10^{338} \quad \text{Ans}$$

Objective Problems

Q1. Ans - (b) In galvanic cell, Anode is -ve electrode, Cathode is +ve electrode.
because from anode e^- is leaving and there must be -vely charge, so that it can charge e^- s.

Q2. Ans - (a)

Q3. Ans - (b) Cu is oxidising & so e^- is loosing & that e^- is taken Ag^+ & it get reduced.

Q4. Ans - (b) $\varepsilon_{\text{H}^+/\text{H}_2}^0 = 0$

$$\varepsilon_{\text{Ag}^+/\text{Ag}}^0 = 0.80$$

Reducing potential of Ag > Red. Potential of H_2 ; so Ag has more oxidising power than H_2 , So H_2 can't oxidise silver in standard case.

$$\text{Q5. Ans - (a) } \varepsilon_{\text{H}^+/\text{H}_2} = \varepsilon_{\text{H}^+/\text{H}_2}^0 - \frac{0.0592}{1} \log \frac{1}{\text{H}^+}$$

$$-0.118 = 0 + 0.0592 \log[H^+]$$

$$\log[H^+] = \frac{-0.118}{0.0592} = -2$$

$$[H^+] = 10^{-2} \text{ M}$$

Q6. Ans - (b) $\therefore \mathcal{E}_{\text{cell}} = \mathcal{E}_{\text{H}^+/\text{H}_2}^0 - \mathcal{E}_{\text{Zn}^{2+}/\text{Zn}}^0 = 0 - (-0.76) = 0.76 \text{ V}$

Q7. Ans - (a) Reducing power $\propto \frac{1}{\text{Reduction potential}}$

Q8. Ans - (b) $\mathcal{E}_{\text{cell}}^0 = \mathcal{E}_{\text{Fe}^{2+}/\text{Fe}}^0 - \mathcal{E}_{\text{Zn}^{2+}/\text{Zn}}^0$
 $= -0.41 - (-0.76) = 0.76 - 0.41 = 0.35 \text{ V}$

Q9. Ans - (a) Since the largest gap is betⁿ II & III

Q10. Ans - (d) Again the largest gap is in between I < IV

Q11. Ans - (b) Again for the same reason.

Q12. Ans - (c)

$$(n_1 + n_2) \cdot F \cdot \mathcal{E} = n_1 F \mathcal{E}_1 + n_2 F \mathcal{E}_2$$

$$3 \cdot \mathcal{E} = 1 \mathcal{E}_1 + 2 \mathcal{E}_2$$

$$\mathcal{E} = \frac{\mathcal{E}_1 + 2 \mathcal{E}_2}{3} = \frac{0.77 + 2(-0.44)}{3} = -0.0367 = -0.04$$

Q13. Ans - (a) $\mathcal{E}_{\text{cell}} = \mathcal{E}_{\text{Cl}_2/\text{Cl}^-}^0 - \mathcal{E}_{\text{Mg}^{2+}/\text{Mg}}^0$
 $= 1.36 - (-2.36) = 1.36 + 2.36 = 3.72 \text{ V}$ Ans

Q14. Ans - (b) $\mathcal{E}_{\text{cell}}^0 = \mathcal{E}_{\text{Mg}^{2+}/\text{Mg}}^0 - \mathcal{E}_{\text{Zn}^{2+}/\text{Zn}}^0$

all are in standard condition, so it has same $\mathcal{E}_{\text{cell}}^0$.

Q15. Ans - (a) because \mathcal{E}^0 is an intensive property

Q16. Ans - (c) Since ΔG , is an extensive property $\therefore \Delta G_2 = 2\Delta G_1$

Q17. Ans - (d) $\mathcal{E}_{\text{cell}}^0 = \frac{0.00592}{n} \log K_{\text{eq}}$

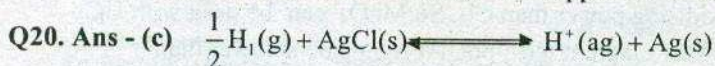
For $\mathcal{E}_{\text{cell}}^0 > 0$, K_{eq} should be greater than 1.

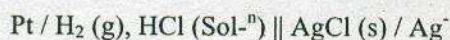
Q18. Ans - (b) $\mathcal{E}_{\text{cell}}^0 < 0$, so at standard condition it is not possible for reaction to happen.

Q19. Ans - (b) Max^m emf will be obtained if

$$\begin{aligned} \text{Emf} &= \frac{-0.0592}{1} \log \frac{[H^+]_{\text{anode}}}{[H^+]_{\text{cathode}}} \\ &= \frac{-0.0592}{1} \log [H^+]_{\text{anode}} \quad \therefore [H^+]_{\text{cathode}} = 1 \text{ M gives} \end{aligned}$$

$[H^+]_{\text{anode}}$ is the least which will happen in 0.1 M CH_3COOH .





Q21. Ans - (a, d) $\epsilon_{\text{cell}} = \epsilon_{\text{cell}}^0 - \frac{0.0592}{2} \log \frac{[\text{T}_i^+]^2}{[\text{Cu}^+]}$

To increase ϵ_{cell} , $\log \frac{(\pi_1^+)^2}{[\text{Cu}^{2+}]}$ should decrease. So $[\text{T}_i^+]$ should decrease & $[\text{Cu}^{2+}]$ should increase.

Q22. Ans - (b) $\Delta \epsilon_{\text{cell}} = \frac{-0.0592}{2} \left\{ \log [\text{Zn}^{2+}] - \log \frac{[\text{Zn}^{2+}]}{10} \right\}$

$\epsilon_i - \epsilon_f = \frac{-0.0592}{2} \log \frac{[\text{Zn}^{2+}]}{[\text{Zn}^{2+}]} \times 10 = -\frac{(0.0592)}{2} \times 1$

$\therefore \epsilon$ will decrease by -0.03 V

Q23. Ans - (b) At $\text{pH} = 10$, $[\text{H}^+] = 10^{-10} \text{ M}$

$\epsilon_{\text{H}^+/\text{H}_2} = -\frac{0.0592}{1} \log \frac{1}{[\text{H}^+]} = -0.592 \text{ V}$

Q24. Ans - (d) $\epsilon_i - \epsilon_f = \frac{-0.0592}{1} \left\{ \log [\text{H}^+]_i - \log [\text{H}^+]_f \right\}$

$= \frac{-0.0592}{1} (\log 1 - \log 10^{-7}) = \frac{-0.0592}{1} \times -\log 10^{-7} = \frac{-0.0592}{1} \times 7 = -0.41 \text{ V Ans}$

Q25. Ans - (a) In Na^+ & H^+ , H^+ will reduce first because it has higher reduction potential than that of Na^+ . In SO_4^{2-} & OH^- , OH^- will oxidise first because it has lower reduction potential than that of SO_4^{2-} . So at cathode H_2 will produce & at anode O_2 will be produced.

Q26. Ans - (c) Let the reduction potential of Cu^+ / Cu is ϵ than

$1.\epsilon + 1 \times 0.153 = (1+1) \times 0.337$ by $\{n_1\epsilon_1 + n_2\epsilon_2 = (n_1 + n_2)\epsilon_3\}$

$\epsilon = 0.674 - 0.153 = 0.521 \text{ V Ans}$

Q27. Ans - (b)

Q28. Ans - (b) Temp. coefficient = $5 \times 10^{-5} \text{ V/K}$

$\left. \frac{\partial E}{\partial T} \right|_p = 5 \times 10^{-5} = +ve$

So when the cell work its gets discharge & so E decreases.

Since $\left. \frac{\partial E}{\partial T} \right|_p = +ve$

So if E decrease, then T will also decrease

Q29. Ans - (a) Since Reduction potential of MnO_4^- is larger than that of Cl_2 ; So MnO_4^- can reduce easily. So it has higher oxidising power than Cl_2 . So MnO_4^- can be used with HCl .

Q30. Ans - (c) According to the rule in latimer diagram red- n pot. At right side is lower than Reduction potential.