Ques. Cal. reduction potential of following.

(i) $Pt, H_2 (2\ atm) | HCl (0.02\ M)$

(ii) $Pt, Cl_2 (10\ atm) | Cl^- (10^{-3}\ M)$ $E^\circ_{Cl_2/Cl^-} = 1.69\ V$

Sol. (i) $2H^+ (2\times10^{-2}\ M) + 2e^- \longrightarrow H_{2(g)} (2\ atm)$ $\boxed{n=2}$

$$E_{H^+/H_2} = 0 - \frac{0.0591}{2} \log \frac{P_{H_2}}{[H^+]^2}$$

$$E_{R.P.} = -\frac{\cancel{0.06}^{\,0.03}}{\cancel{2}} \log \frac{2}{(2\times10^{-2})^2}$$

$$E_{R.P.} = -0.03 \log \frac{\cancel{2}}{\cancel{4}\times10^{-4}}$$

$$E_{R.P.} = -0.03 \log \left(\frac{10^4}{2}\right)$$

$$= -0.03\left[\log(10^4) - \log 2\right]$$

$$= -0.03\left[4\times1 - 0.30\right]$$

$$= -0.03 \times 3.70\ V \Rightarrow \boxed{E_{R.P.} = -0.11\ V}$$

Q.2. At what pH of HCl soln, of H_2 electrode reduction potential is -0.188 V

Sol.

$$E_{RP} = -0.0591 \times pH$$

$$+0.188 = +0.0591 \times pH$$

$$pH = \frac{0.188}{0.0591} = 3.1$$

Q.3 In H_2 electrode pH of HCl Soln Change from 2 to 4, Cal Change in reduction potential

Sol.

$$E_{R.P_1} = -0.0591 \times pH_1 \quad -(1)$$

$$E_{R.P_2} = -0.0591 \times pH_2 \quad -(2)$$

$$E_{R.P_2} - E_{R.P_1} = 0.0591(pH_1 - pH_2)$$

$$\Delta E_{R.P} = 0.0591 \times (2-4)$$

$$= -0.1182$$

Reduction Potential decreases ↓ when pH ↑

Q.4 A soln of $ZnSO_4$ in which Zn rod is dipped, is diluted to 10 times then reduction potential of Zn electrode will be -

(a) ↑ by 30 mV

(b) ↑ by 60 mV

(c) ↓ by 30 mV ✓

(d) ↓ by 60 mV

$$Zn^{2+}_{(aq)} + 2e^- \longrightarrow Zn_{(s)}$$

$$\left\{ C = \frac{n}{V} \qquad V \uparrow \; C \downarrow \right\}$$

initially

$$E_{RP} = E^\circ_{RP} - \frac{0.059}{2} \log\left(\frac{1}{[Zn^{2+}]}\right) \quad (1)$$

Now 10 times diluted

$$E'_{RP} = E^\circ_{RP} - \frac{0.059}{2} \log\left(\frac{1}{\left[\frac{Zn^{2+}}{10}\right]}\right)$$

$$E'_{Rp} = E^\circ_{Rp} - \frac{0.059}{2} \log\left(10 \times \frac{1}{[Zn^{2+}]}\right)$$

m× n

$$E'_{Rp} = E^\circ_{Rp} - \frac{0.059}{2}\left[\log\left(\frac{1}{[Zn^{2+}]}\right) + \log(10)\right]$$

$$E'_{Rp} = E^\circ_{Rp} - \frac{0.059}{2}\log\left(\frac{1}{[Zn^{2+}]}\right) - \frac{0.059}{2}\cdot\log(10)$$

0.03

from eq (1)

$$E'_{Rp} = E_{Rp} - 0.03 \times 1 \Rightarrow E_{Rp} = E^\circ_{Rp} - 3\times10^{-2}\times10^{-1}\times10$$

$$\boxed{E_{Rp} = E^\circ_{Rp} - 30\,mV}$$

divalent metal ion (Charge +2)

monvalent metal ion (— " — +1)

Brahmastra :

For divalent metal ion

(1) For each and every 10 times dilution reduction potential decreases by 30 mV

(2) For monvalent metal ion

— " —— 10 times dilution reduction potential decreases by 60 mV

Q. Cal EMF of Cell in following.

(1) $Cr_{(s)} | Cr^{+3} (0.01m) || Fe^{2+} (0.1m) | Fe_{(s)}$

Given $E^\circ_{Cr^{+3}/Cr} = -0.75V$, $E^\circ_{Fe^{+2}/Fe} = 0.45V$

Sol- $E^\circ_{cell} = E^\circ_{Cr/Cr^{+3}} + E^\circ_{Fe^{2+}/Fe}$

$= 0.75 + 0.45$

$E^\circ_{cell} = 1.20V$

Note:

$Zn_{(s)} \longrightarrow Zn^{2+}$; $E^\circ = +1.20\,V$; $\Delta G = 60\,kj$

$\times 2$

$2Zn_{(s)} \longrightarrow 2Zn^{2+}$; $E^\circ = ? = 1.20\,V$

$\Delta G = 2 \times 60 = 120\,kj$

(1) Electrode potential is intensive property while gibbs energy is extensive property.

(2) intensive properties are non-addive in nature, while extensive properties are additive.

$$2Cr_{(s)} + 3Fe^{2+}_{(aq)} \longrightarrow 2Cr^{+3}_{(aq)} + 3Fe_{(s)}$$

$$E_{cell} = E^{\circ}_{cell} - \frac{0.06}{6} \log \frac{[Cr^{+3}]^2}{[Fe^{2+}]^3}$$

$$E_{cell} = 1.20 - 0.01 \log \frac{\cancel{10^{-2}} \times 10^{-2}}{\cancel{10^{-1}} \times \cancel{10^{-1}} \times \cancel{10^{-1}}}$$

$$= 1.20 - 0.01 \log (10^{-1})$$

$$= 1.20 + 0.01 \times 1$$

$$\boxed{E_{cell} = 1.21\ V}$$