EMF of the cell is intensive property → Non additive

But Gibbs energy extensive property → additive.

Ques. $E^\circ_{Au^+/Au} = 1.69\,V$; $E^\circ_{Au^{3+}/Au} = 1.40\,V$

$E^\circ_{Au^{+3}/Au^+} = ?$

Target

Sol:- $Au^{+3} + 2e^- \longrightarrow Au^+$; $E^\circ_3 = ?$ — ③ ΔG_3

$Au^+ + e^- \longrightarrow Au$; $E^\circ_1 = 1.69\,V$ — ① ΔG_1

$Au \longrightarrow Au^+ + e^-$; $E^\circ_1 = -1.69\,V$

$Au^{+3} + 3e^- \longrightarrow Au$; $E^\circ_2 = 1.40\,V$ — ② ΔG_2

Eqn ① + ② = ③

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

$$\{\Delta G = -nFE\}$$

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

$$-F(n_3 E_3^\circ) = -F(n_1 E_1^\circ + n_2 E_2^\circ)$$

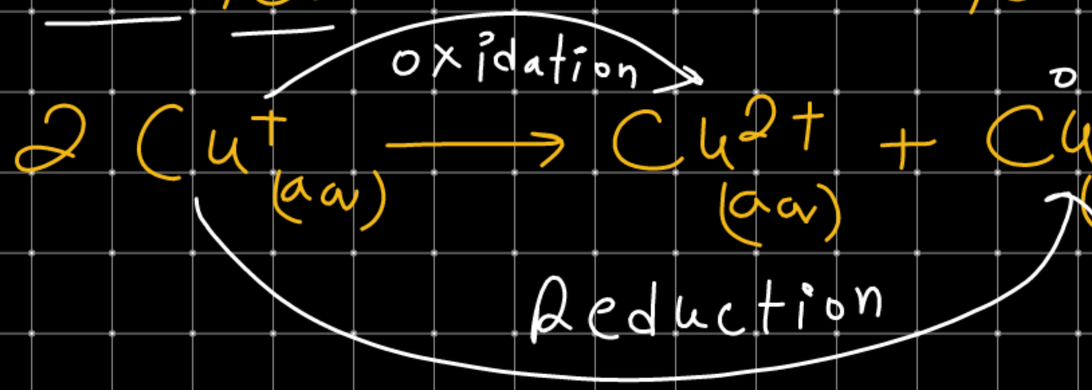
$$n_3 = 2, \quad n_1 = 1, n_2 = 3$$

$$2E_3^\circ = 1 \times (-1.69) + 3 \times 1.40$$

$$2E_3^\circ = -1.69 + 4.20$$

$$2E_3^\circ = 2.51\,V \Rightarrow \boxed{E_3^\circ = \frac{2.51}{2} = 1.25\,V}$$

(8) Ques.2. $E^\circ_{Cu^{2+}/Cu^+} = 0.15\,V$; $E^\circ_{Cu^+/Cu} = 0.52\,V$



Sol.

$$E^\circ_{cell} = E^\circ_{Cu^+/Cu^{2+}} + E^\circ_{Cu^+/Cu}$$

$$= -0.15\,V + 0.52\,V$$

$$E^\circ_{cell} = 0.37\,V$$

Concentration Cell :-

When two similar electrode but having different Concentration of electrolytic soln are Conected/ Combined, then Concentration cell formed.

$$E^{\circ}_{cell} = 0$$

Representation :-

$$M_{(s)} \mid M^{+n}_{(aq)(C_1)} \,||\, M^{+n}_{(aq)(C_2)} \mid M_{(s)}$$

Anode :- $M_{(s)} \longrightarrow M^{+n}_{(aq)(C_1)} + ne$

Cathode :- $M^{+n}_{(C_2)} + ne^- \longrightarrow M_{(s)}$

Cell rxn :- $M_{(s)} + M^{+n}_{(C_2)} \longrightarrow M^{+n}_{(C_1)} + M_{(s)}$

$E^\circ_{cell} = E^\circ_{M/M^{+n}} + E^\circ_{M^{+n}/M}$

$= (x) + (-x)$

$E^\circ_{cell} = 0$

$$E_{cell} = E^{\circ}_{cell} - \frac{0.059}{n} \log \frac{[P]^m}{[R]^n}$$

$$E_{cell} = 0 - \frac{0.059}{n} \log \left(\frac{c_1}{c_2}\right)$$

Ex :- Concentration Cell of H_2-electrode.

$$H_{2(g)}\,(P_1) \mid H^+_{(aq)}\,(c_1) \;\|\; H^+_{(aq)}\,(c_2) \mid H_{2(g)}\,(P_2)$$

Cell rxn :- $$H_{2\,(P_1)} + 2H^+_{(c_2)} \longrightarrow 2H^+_{(c_1)} + H_{2\,(P_2)}$$

$$E_{cell} = 0 - \frac{0.059}{2} \log \frac{[H^+]_{C_1}^2 \cdot (P_{H_2})_{P_2}}{[H^+]_{(C_2)}^2 \cdot (P_{H_2})_{P_1}}$$

$$\boxed{E_{cell} = -\frac{0.059}{2} \log \left(\frac{C_1^2 \cdot P_2}{C_2^2 \cdot P_1} \right)}$$

Ques. Calculate E_{cell} of following -

(i) $Cu_{(s)} | Cu^{2+}_{(0.01M)} || Cu^{2+}_{(0.1M)} | Cu_{(s)}$

(ii) $Pt, H_{2(g)} | H^+_{(pH=5)} || HCl_{(pH=3)} | H_{2(g)}$, Pt

$pH = 5$

$[H^+]_1 = 10^{-5}$

$pH = 3$

$[H^+]_2 = 10^{-3}$

Sol. (i) $Cu_{(s)} + Cu^{2+}_{(0.1M)} \longrightarrow Cu^{2+}_{(0.01M)} + Cu_{(s)}$

$$E_{Cell} = 0 - \frac{0.06}{2} \log \frac{(10^{-2})}{(10^{-1})}$$

$$E_{cell} = -0.03 \log (10^{-1})$$

$$\boxed{E_{cell} = 0.03\,V}$$

(ii) $H_2(g) + 2H^+(10^{-3}) \longrightarrow 2H^+(10^{-5}) + H_2(g)$

$$E_{cell} = -\frac{0.06}{2} \log \frac{[H^+]_1^2}{[H^+]_2^2} \Rightarrow E_{cell} = -0.03 \log \frac{10^{-5} \times 10^{-5}}{10^{-3} \times 10^{-3}}$$

$$E_{Cell} = -0.03 \log(10^{-4})$$

$$= +0.03 \times 4$$

$$\boxed{E_{Cell} = 0.12\ V}$$

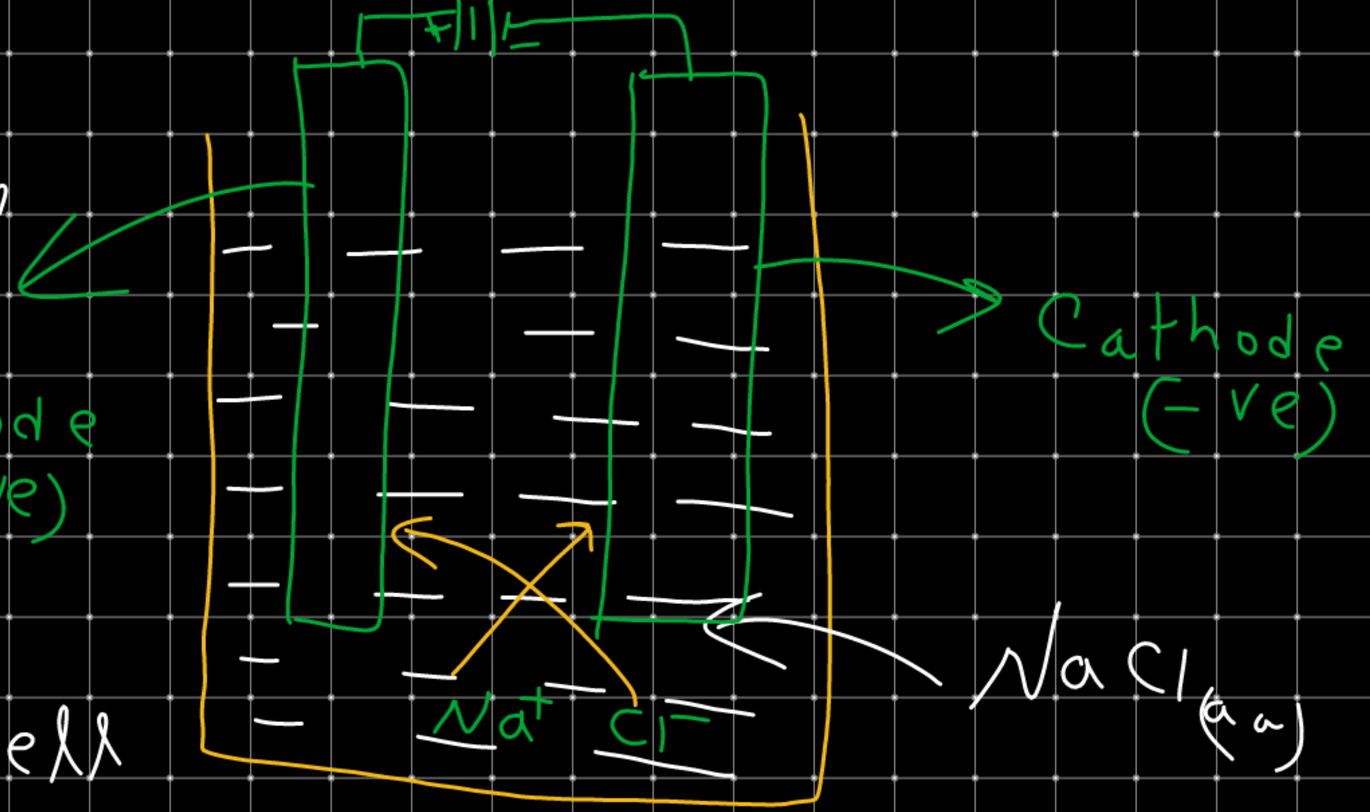
Electrolysis

The phenomenon of Chemical decomposition of Aqous or molten state of electrolytic soln by passing electrical Current.

The device in which

in phenomenon occur k/a

electrolytic cell



In electrolytic cell

non-spontaneous redox occur while in galvanic cell spontaneous redox rexn occur

These are two aspect of electrolysis –

(1) Qualitative aspect :- To measure nature of product formed at electrode.

(2) Quantitative aspect :- To measure amount of product formed at electrode.

① Qualitative aspect :-

Product formed at electrode depend on -

(1) Nature of electrolyte

(2) Nature of electrode

(1) Inner electrode / Non attackble

ex :- Pt, graphite, Hg

(2) Reactive electrode / Attackble electrode

ex :- all active metals (Cu, Zn, Mg)

(3) Concentration of electrolytic soln

Ex :- $NaCl_{(molten)}$, $NaCl_{(aq)}$, $NaCl_{(dil)}$

Indentification of Product :-