08/04/21

Potential ✓

Cell ✓

Measurement of potential ✓

↳ w.r.t Reference ✓ 1° SHE

2° SCE

Ag | AgCl

EMF - series (Hydrogen scale) ✓

SHE

$$H_2 \longrightarrow 2H^+ + 2e^-$$

$$2H^+ + 2e^- \longrightarrow H_2\uparrow$$

} n = 0

Reversible electrode.

Nernst eqn

$$2H^+ + 2e^- \longrightarrow H_2\uparrow$$

$$E_{elec} = E^\circ_{elec} - 2.303 \frac{RT}{nF} \log \frac{1}{[H^+]}$$

$$= 0 \; 2.303 RT/F \log [H^+]$$

Limitations - HCl - Poison to 'Pt'

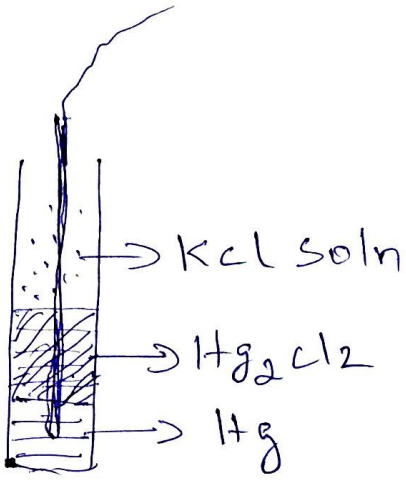
- Unit concentration (1M HCl) challenging.

Secondary Ref (2^0)

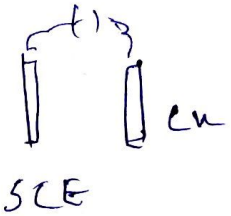
Saturated Calomel Electrode (SCE)

$Hg_2Cl_2 \Rightarrow Hg^+ \; Cl^- \; Hg^+ \; Cl^-$

Mercurous chloride Paste



As Anode



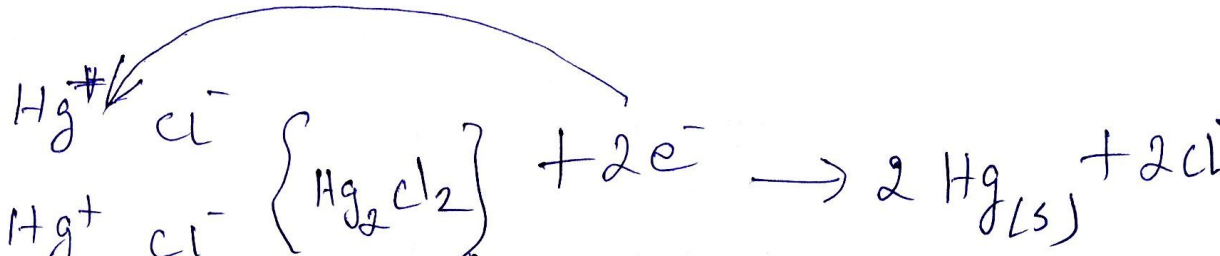
$2\,Hg \longrightarrow 2Hg^+ + 2e^-$

$2Hg^+ + 2Cl^- \rightarrow Hg_2Cl_2$

$2Hg + 2Cl^- \longrightarrow Hg_2Cl_2 + 2e^-$ ⟶ Net

$[Cl^-]$ - goes down

As cathode.



The concentration of Cl^- ↑

In both the cases.

Reversible w.r.t $[Cl^-]$

Nernst eqn

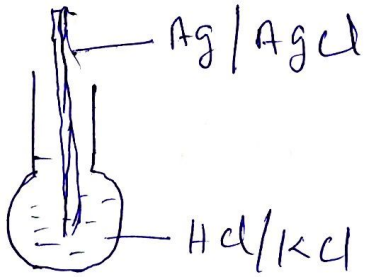
$$Hg_2Cl_2 + 2e^- \longrightarrow 2Hg + 2Cl^-$$

$$E_{ele} = E^\circ_{ele} - \frac{2.303\,RT}{nF} \log \frac{[Cl^-]^2[Hg]^2}{[Hg_2Cl_2]}$$

$$E_{ele} = 0.2422 - \frac{2.303\,RT}{2F} \log [Cl^-]$$

E°_{elec}	V	KCl
	0.2422	Saturated
	0.2810	1 M
	0.3335	0.1 M

Ag/AgCl



As Anode

$$Ag_{(s)} \longrightarrow Ag^{+} + e^{-}$$

$$Ag^{+} + Cl^{-} \longrightarrow AgCl$$

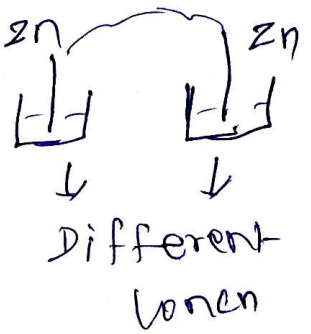
$$Ag + Cl^{-} \longrightarrow AgCl + e^{-}$$

As Cathode

$$AgCl + e^{-} \longrightarrow Ag_{(s)} + Cl^{-}$$

Electrode is reversible w.r.t Cl^{-}

$$E_{ele} = E^{0}_{ele} - \frac{2.303\,RT}{1F} \log [Cl^{-}]$$

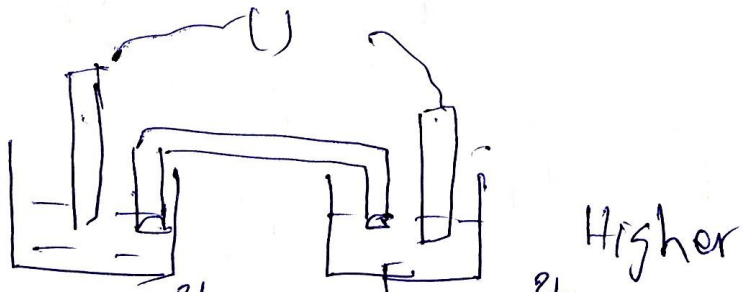


Concentration cell

↙ Electrolyte Concn

↘ Electrode Concn

Electrolyte



Anode

$$Zn \longrightarrow Zn^{2+}_{(C_1)} + 2e^{-}$$

Cathode

$$Zn^{2+}_{(C_2)} + 2e^- \longrightarrow Zn(s)$$

Net reaction $Zn^{2+}_{C_2} \longrightarrow Zn^{2+}_{C_1}$

The ions moves/transfers from ~~left to~~ Right to left

Nernst eqn

$$E_{cell} = E^\circ_{cell} - \frac{2.303\,RT}{nF} \log \frac{C_1}{C_2}$$

$$E^\circ_{cell} = E^\circ_C - E^\circ_A = E^\circ_{Zn^{2+}/Zn} - E^\circ_{Zn^{2+}/Zn}$$

$$= -0.76 - (-0.76) = 0$$

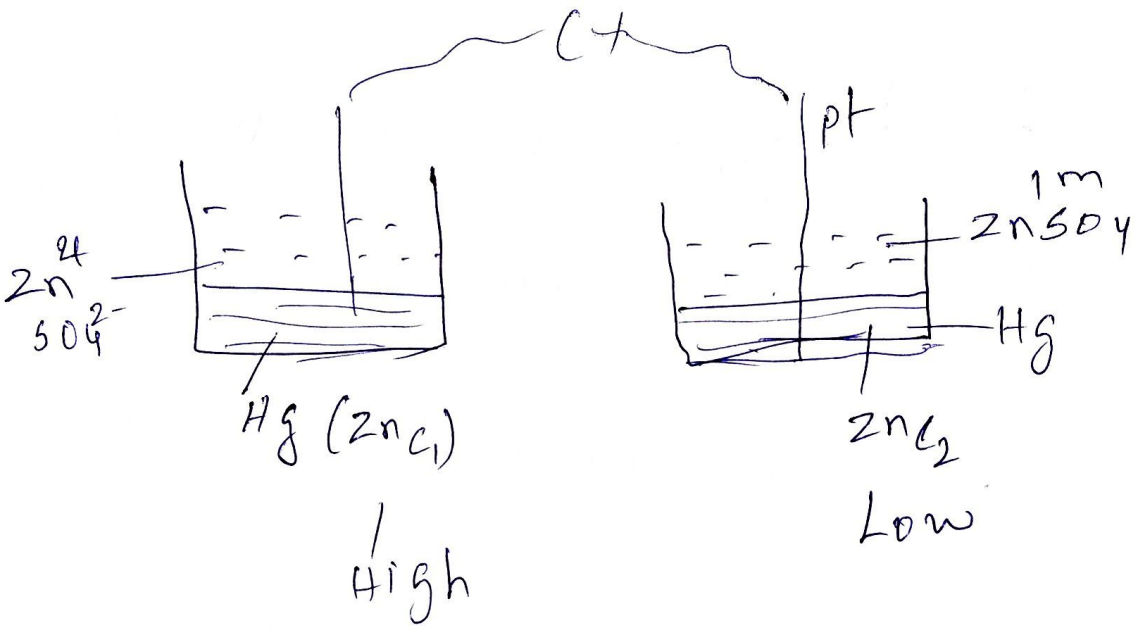
$$E_{cell} = \frac{2.303}{2F} RT \log \frac{C_2}{C_1}$$

Higher concn

lower concn.

Electrode Concn

EMF ~~arises~~ arises - Difference in Concn of two Electrodes



Anode $Hg\text{-}Zn_{C_1} \longrightarrow Zn^{2+} + 2e^-$

Cathode $Zn^{2+} + 2e^- \longrightarrow Zn_{C_2}\text{-}Hg$

Net

$$Hg\text{-}Zn_{C_1} \longrightarrow Hg\text{-}Zn_{C_2}$$

Zn - Tranfers from Left to Right

$$E_{cell} = E^0_{cell} - \frac{2.303\,RT}{nF} RT \log \frac{C_2}{C_1} \Rightarrow = \frac{2.303\,RT}{2F} \log \frac{C_1}{C_2}$$