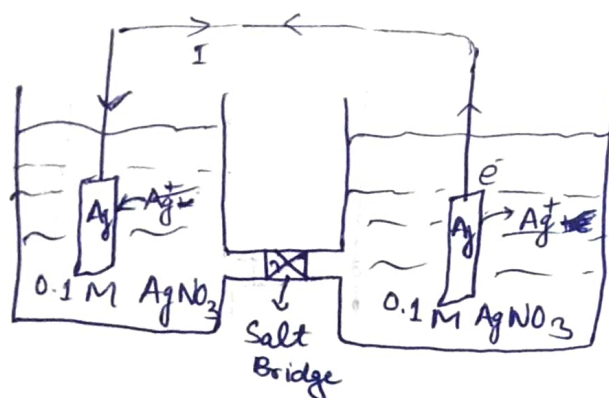


①



~~96.5 C~~ have

when 1 C charge is passed, then  $\frac{1}{96485} \text{ mol}$   
 of  $\text{e}^-$  is passed  
 (coulomb)

so, when 96.5 C is passed, the moles of  
 $\text{e}^- = \frac{96.5}{96485}$

moles from stoichiometry  $[\text{Ag}^+ + \text{e}^- \rightarrow \text{Ag}]$

moles of  $\text{e}^-$  passed = moles of Ag deposited

$\therefore$  moles of Ag deposited at left compartment =  $\frac{96.5}{96485}$

mass of Ag deposited =  $107.86 \times \frac{96.5}{96485}$

mass of Ag deposited  $\approx 0.1078 \text{ g}$

Ans

① Comment: Maximum amount of Ag that could be deposited from 0.1 M  $\text{AgNO}_3$  solution (25 mL)



$$0.1\text{M}, 25\text{ mL } \text{AgNO}_3 \text{ sol}^n \Rightarrow 0.1 \times 107.86 \times \frac{25}{1000} \text{ g Ag}$$

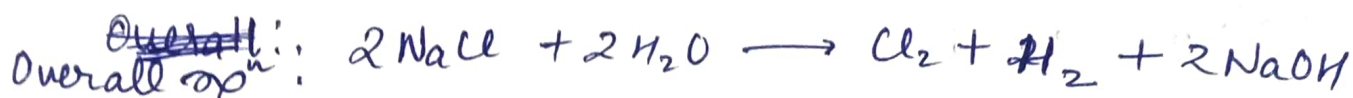
$$\text{Max}^m \text{ Ag that could deposit} = \underline{0.26965 \text{ g Ag}}$$

$$\text{Ag actually deposited} = 0.1078 \text{ g}$$

which is consistent, since Actual Ag deposited can not be higher than max<sup>m</sup> (without any unwanted stripping)  
or etc.



## Chlor Alkali Process



For each mole of  $\text{Cl}_2 / \text{H}_2$  evolved,  
 $2 \text{mol e}^-$  is transferred

Therefore  $\frac{\text{moles}}{\text{s}}$  of  $\text{Cl}_2 / \text{H}_2$  evolved  $= \frac{I}{nF}$

$$= \frac{20 \text{ (A)}}{2 \times 96485 \text{ C/mol (mol/eqv)}}$$

$$= 1.036 \times 10^{-4} \frac{\text{moles}}{\text{s}} \text{ of } \text{Cl}_2 / \text{H}_2$$

Bonus:

$$1.036 \times 10^{-4} \text{ mol/s of Cl}_2$$

$$= 1.036 \times 35.45 \times 2 = 7.348 \times 10^{-3} \text{ g/s of Cl}_2$$

$$\therefore \text{mass rate of } \text{Cl}_2 = \underline{7.348 \times 10^{-3} \text{ g/s}}$$

Now,

$$\begin{aligned} & 1.036 \times 10^{-4} \frac{\text{mol}}{\text{s}} \text{ of } \text{H}_2 \\ &= 1.036 \times 10^{-4} \times 2 \text{ g/s of } \text{H}_2 \end{aligned}$$

$$\therefore \text{mass rate of } \text{H}_2 = 2.072 \times 10^{-4} \text{ g/s}$$

Volume rate  $\rightarrow$

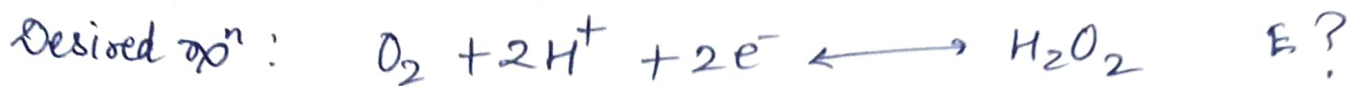
considering  $\text{Cl}_2$  and  $\text{H}_2$  as ideal gases

1 Mol of  $\text{Cl}_2/\text{H}_2$  will occupy 22.4 L

$$\begin{aligned} \therefore \text{volume rate of } \text{Cl}_2 &= 1.036 \times 10^{-4} \times 22.4 \\ &= 23.2064 \times 10^{-4} \frac{\text{L}}{\text{s}} \end{aligned}$$

$$\begin{aligned} \& \text{ vol}^{\text{m}} \text{ rate of } \text{H}_2 &= 1.036 \times 10^{-4} \times 22.4 \\ &= 23.2064 \times 10^{-4} \frac{\text{L}}{\text{s}} \end{aligned}$$

③



Since both Half cell reactions ~~have~~ does not have same number of  $\text{e}^-$  transferred. Therefore we must ~~go to~~ solve it the Gibbs free Energy Approach.

$$\text{for Rx}^n 1: \quad \Delta G_1 = -4FE_1$$

$$\text{for Rx}^n 2: \quad \Delta G_2 = -2FE_2$$

for Desired rx<sup>n</sup>,

$$\Delta G = \Delta G_1 - \Delta G_2$$

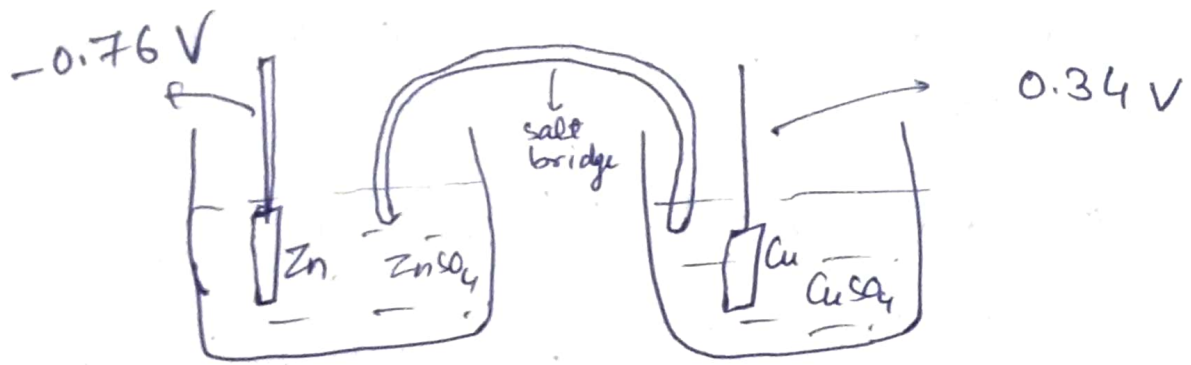
$$\Delta G = -2FE$$

$$\therefore -2FE = -4FE_1 - (-2FE_2)$$

$$\boxed{E = 2E_1 - E_2}$$



④



① No current will pass if salt bridge is removed.

Therefore measured potential = 0 V

② when positive end of Multimeter is connected to  $\text{Cu}_{\text{rod}}$  (+ve electrode) and negative end of Multimeter is connected to  $\text{Zn}_{\text{rod}}$  (-ve electrode) Then potential  $\approx 1.1 \text{ V}$   $\left[ E = 0.34 - (-0.76) = 1.1 \text{ V} \right]$

when wires of multimeter is connected opposite (+ve end with Zn rod and -ve end with Cu rod) the measured potential will be  $-1.1 \text{ V}$  (Negative of cell potential)

③

$$\Delta G = -nF(\text{EMF})$$

Charging is non spontaneous process,  $\therefore \Delta G > 0$

$$\therefore \text{EMF during charging} = -1.1 \text{ V}$$

During Discharging  $\Delta G < 0$ , (spontaneous)

$$\therefore \text{EMF during discharging} = +1.1 \text{ V}$$

(d) when positive end of multimeter is connected to Copper end.

Measured potential during charging =  $1.1 + \epsilon$

It will show slightly higher potential during charging due to internal losses. ( $1.1 + \text{losses}$  say:  $1.14 \text{ V}$ )

Measured potential during discharging =  $1.1 - \epsilon$

It will show slightly lower potential during discharging ( $1.1 - \text{losses}$  say:  $1.07 \text{ V}$ )

(e) when positive end of multimeter is connected to Zinc end.

measured potential during charging =  $-1.1 - \epsilon$

measured potential during discharging =  $-1.1 + \epsilon$

NOTE: To avoid Confusion, think of the scenario when the ~~wire~~ <sup>positive end of wire</sup> is connected to Cu rod.

Eg:  $+1.14 \text{ V}$  ( $1.1 + \epsilon$ ) in part (d) will be equal to  $-1.14 \text{ V}$  ( $-1.1 - \epsilon$ ) in part (e) during charging.

Similarly:  $+1.07 \text{ V}$  ( $1.1 - \epsilon$ ) in part (d) during discharging is equivalent to  $-1.07 \text{ V}$  ( $-1.1 + \epsilon$ ) in part (e).

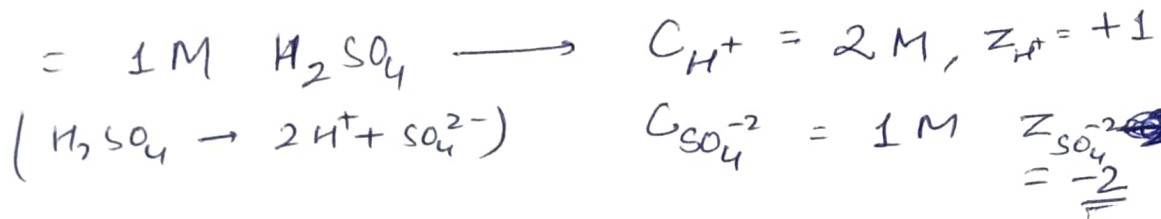


5

debye length

$$\lambda = \sqrt{\frac{\epsilon RT}{F^2 \sum z_i^2 c_i}}$$

aqueous sol<sup>n</sup> of 1M H<sub>2</sub>SO<sub>4</sub> and 0.1 mM H<sub>2</sub>SO<sub>4</sub>



for 0.1 mM H<sub>2</sub>SO<sub>4</sub> → C<sub>H<sup>+</sup></sub> = 0.2 mM, z<sub>H<sup>+</sup></sub> = +1  
 C<sub>SO<sub>4</sub><sup>2-</sup></sub> = 0.1 mM, z<sub>SO<sub>4</sub><sup>2-</sup></sub> = -2

given permittivity,  $\epsilon = 6.933 \times 10^{-10}$  F/m, T = 298 K

$$\lambda = \sqrt{\frac{6.933 \times 10^{-10} \left(\frac{F}{m}\right) \times 8.314 \left(\frac{J}{mol \cdot K}\right) \times 298 (K)}{(96485)^2 \left(\frac{C}{mol}\right)^2 \times \left[ (+1)^2 \times 2 \times 1000 \left(\frac{mol}{m^3}\right) + (-2)^2 \times 1 \times 1000 \left(\frac{mol}{m^3}\right) + (+1)^2 \times 0.2 \times 10^{-3} \times 1000 \frac{mol}{m^3} + (-2)^2 \times 0.1 \times 10^{-3} \times 1000 \frac{mol}{m^3} \right]}$$

$$= \sqrt{\frac{17177.006 \times 10^{-10}}{(96485)^2 \times 6000.6}}$$

$$= 1.753 \times 10^{-10} \text{ m}$$

$$\lambda = 1.753 \text{ \AA}$$

$$\lambda \propto \frac{1}{\sqrt{\sum z_i^2 c_i}}$$

$$\therefore \lambda_{0.1\text{mM}} / \lambda_{1\text{M}} = \sqrt{\frac{(+1)^2 \times 2 \times 1000 + (-2)^2 \times 1 \times 1000}{(+1)^2 \times 0.2 \times 10^{-3} \times 1000 + (-2)^2 \times 0.1 \times 10^{-3} \times 1000}}$$

$$\frac{\lambda_{0.1\text{mM}}}{\lambda_{1\text{M}}} = 100$$

⑥

$$i = i_0 \left[ \exp\left(\frac{\alpha_a F \eta_s}{RT}\right) - \exp\left(-\frac{\alpha_c F \eta_s}{RT}\right) \right]$$

⑦ linear approximation  
 $e^x = 1 + x$

$$i = i_0 \left[ 1 + \frac{\alpha_a F \eta_s}{RT} - \left( 1 - \frac{\alpha_c F \eta_s}{RT} \right) \right]$$

$$i = \frac{i_0 (\alpha_a + \alpha_c) F \eta_s}{RT}$$

⑧ Tafel relation,

Anodic :  $i = i_a = i_0 \exp\left(\frac{\alpha_a F \eta_s}{RT}\right)$

Cathodic  $i = -i_c = -i_0 \exp\left(-\frac{\alpha_c F \eta_s}{RT}\right)$

⑥  $\alpha_a = 0.6$  ,  $\alpha_c = 0.4$

Tafel slope  $\underset{\text{(Anodic)}}{b_a} = \frac{2.303 RT}{\alpha_a F}$   
 $= 0.09856 \frac{V}{\text{dec}}$   
 $= 98.56 \frac{mV}{\text{decade}}$

Tafel Slope (Cathodic)  $b_c = \frac{-2.303 RT}{\alpha_c F}$

⊗

$$= \frac{-2.303 \times 8.314 \times 298}{0.4 \times 96485}$$

$$= -147.84 \frac{mV}{\text{decade}}$$

$$\eta_s < \frac{ba}{3}$$

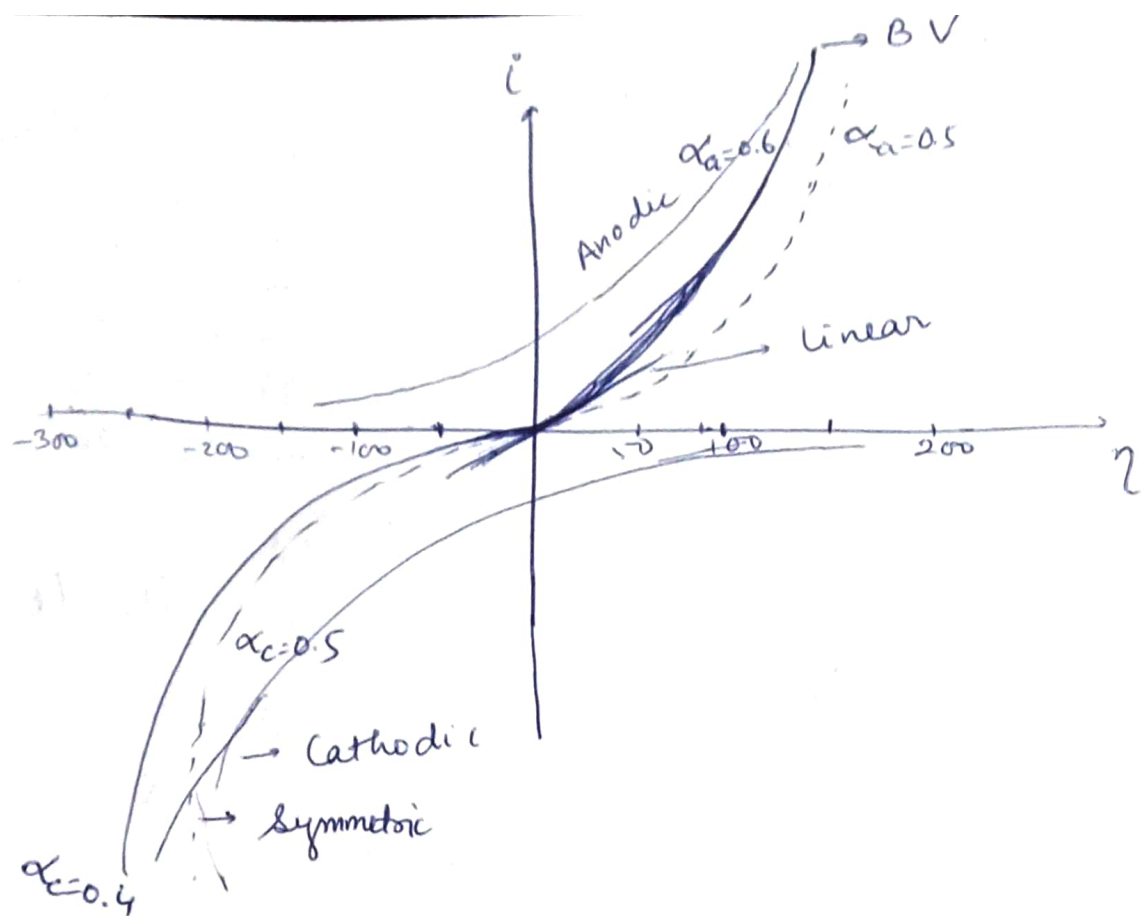
Linear approximation is good

$$\eta_s > \frac{ba}{2}$$

Tafel Approximation is good.

---

(c)



$$-2b_c < \eta_s < 2b_a$$

$$-295.68 < \eta_s < 197.12$$

(d)

$$i_0 = 5 \text{ mA/cm}^2$$

$$i = 7.5 \text{ mA/cm}^2$$

$$\eta_s$$

Linear:  $i = i_0 (\alpha_a + \alpha_c) \frac{F \eta_s}{RT}$

$$\eta_s = \frac{7.5}{5} \times \frac{0.314 \times 298}{96485}$$

$$= 0.0385 \text{ V} = 38.5 \text{ mV}$$

Tafel: Anodic:

$$i = i_0 \exp\left(\frac{0.6 F}{RT} \eta_s\right)$$

$$= 17.35 \text{ mV}$$

Cathodic:  $-i = -i_0 \exp\left(\frac{-0.4 F}{RT} \eta_s\right) \Rightarrow \eta_s = 26.02 \text{ mV}$



Using Full Butler Volmer

⑦

$$7.5 = 5 \left( \exp\left(\frac{0.6F}{RT} \eta_s\right) - \exp\left(-\frac{0.4F}{RT} \eta_s\right) \right)$$

$$1.5 = \exp(23.36 \eta_s) - \exp(-15.57 \eta_s)$$

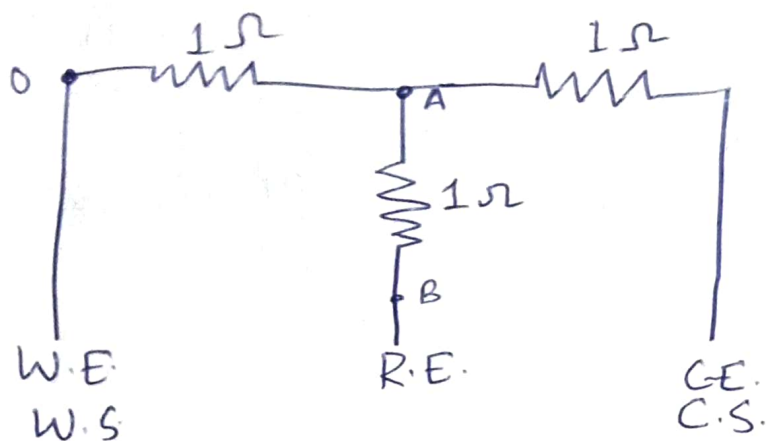
solving,

$$\eta_s = \underline{31.92 \text{ mV}}$$

close to Linear approximation

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⑦



$$I = 1 \text{ A}$$

Since Reference electrode has very high resistance, therefore practically no current will flow through  $1\Omega$  resistor connected in RE (b/w point A & B)

Therefore potential measured b/w WE & RE will be actually measured b/w points O and A.

$$\begin{aligned}\text{Therefore potential measured} &= 1 \text{ A} \times 1\Omega \\ &= 1 \text{ V}\end{aligned}$$