

2nd Half

2. (a) What is ionic mobility? Mention its relation with velocity of the ions.
- (b) Write down the Debye-Hückel-Onsager equation with proper description of the terms involved and based on the equation draw a graph (Λ) vs. \sqrt{c} . What can be inferred from the slope?
- (c) HCl solution has much higher molar conductivity than KCl solution at same concentration - explain. Further predict with appropriate reason if such difference between H⁺ and K⁺ will be significant in non-aqueous solvent.
- (d) Draw a representative titration curve of KCl and AgNO₃ and explain the nature.
- (e) Find out E_{cell}^0 where the overall reaction is given by:



The standard reduction potential (E^o) values of Co²⁺/Co and Fe²⁺/Fe are -0.28V and -0.45V, respectively. Construct a galvanic cell where reaction will occur spontaneously and calculate the equilibrium constant for the cell reaction.

$$[(1+1)+(2+2)+(2+1)+3+(2+1+1)]$$

(a) Ionic mobility \rightarrow speed at which ions move through the electrolyte (molten or aq soln) under the influence of external applied electric field between 2 electrodes.

- no. of ions/m \propto ionic speed

$$(resistivity \leftarrow \text{viscosity}) M = \frac{\text{Ionic Speed}}{\text{Potential Gradient}}$$

$$(b) \text{ Slope} = \frac{82.4}{(DT)^{1/2} n} + \frac{8.20 \times 10^5}{(DT)^{5/2} A} \times (-1)$$

Electrophoretic effect term Asymmetric effect term.

Slope \rightarrow tells about the magnitude of interionic attractive forces in soln.

-ve slope \rightarrow indicates $\uparrow \uparrow$ with dilution.

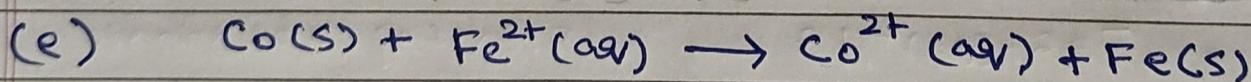
(c) $H^+ > K^+ \rightarrow$ Debye Proton Jump.

In non aq medium \rightarrow no hydronium formation

Conductivity due to movement of H^+ & not e^- unlike in aq medium

Proton jump mech not feasible

\hookrightarrow Diff in conductivity not that significant.

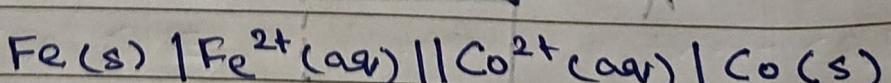


$$\text{Given} - E^\circ_{Co^{2+}/Co} = -0.28V \quad E^\circ_{Fe^{2+}/Fe} = -0.45V$$

$$E^\circ_{\text{cell}} = E^\circ_{Co/Co^{2+}} + E^\circ_{Fe^{2+}/Fe}$$

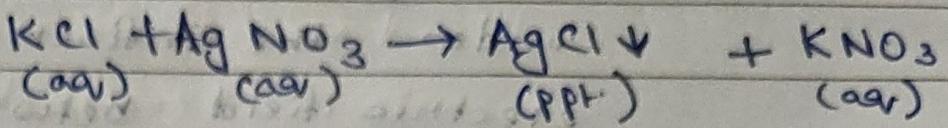
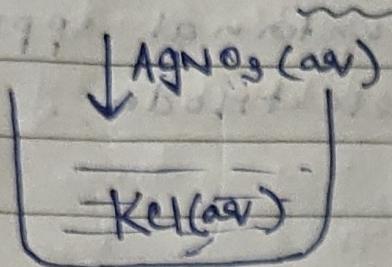
$$= +0.28 - 0.45 = -0.17V$$

for Spontⁿ \rightarrow

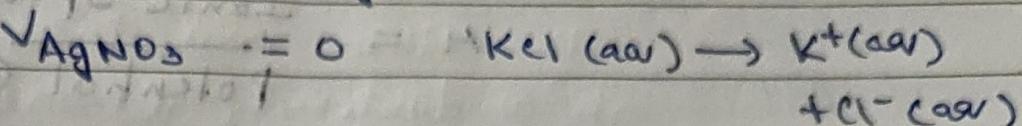


$$K_{\text{eq}} = \frac{[Fe^{2+}(aq)]}{[Co^{2+}(aq)]}$$

KCl vs AgNO₃

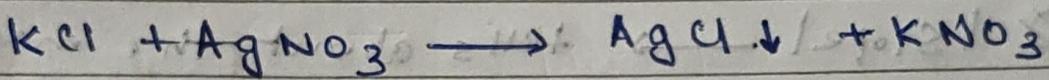


Before starting titration —



AgNO₃ is added dropwise ($0 < \sqrt{\text{AgNO}_3} < \text{eq. pt}$) —

AgCl is a SS and thus precipitates out. AgCl does not dissociate & thus it has no contribution in the conductance of the soln.



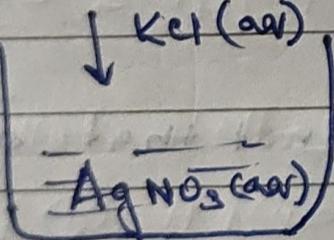
In overall soln $\text{Cl}^-(\text{aq})$ is being replaced by $\text{NO}_3^-(\text{aq}) \Rightarrow [\text{Cl}^-] \downarrow \& [\text{NO}_3^-] \uparrow$

But $\lambda_{\text{Cl}^-} \approx \lambda_{\text{NO}_3^-} \Rightarrow \Lambda_{\text{soln}} = \text{const.}$ till eq. pt.

After end point —

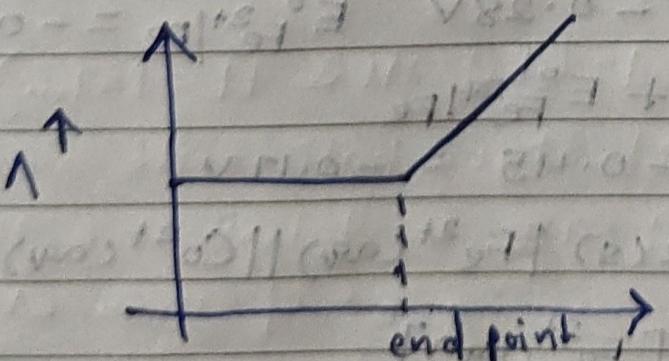
$[\text{KNO}_3] = \text{const}$ since all of KCl has reacted but $[\text{AgNO}_3] \uparrow \Rightarrow [\text{Ag}^+] \& [\text{NO}_3^-] \uparrow$ in soln
 $\Rightarrow \Lambda_{\text{soln}} \uparrow \text{sharply}$.

AgNO₃ vs KCl



$[\text{Ag}^+] \downarrow \text{and } [\text{K}^+] \uparrow$
 but $\lambda_{\text{Ag}^+} \approx \lambda_{\text{K}^+} \Rightarrow \Lambda_{\text{soln}} \text{ const}$ till eq. pt.
 After eq. pt —

$[\text{K}^+] \& [\text{Cl}^-] \uparrow$ in soln $\Rightarrow \Lambda_{\text{soln}} \uparrow \text{sharply}$



$\sqrt{\text{AgNO}_3}$ "OR"
 $\sqrt{\text{KCl}}$ →
 (as per titration given)

OR

(b) How does Kohlrausch's law of independent migration of ions help in determining the molar conductivity at infinite dilution of a weak electrolyte.

(c) Compare the ionic mobilities of the following anions in aqueous solution: OH^- , Cl^- , Br^- and I^- .

(d) Describe the conductometric titration between AgNO_3 and KCl solution.

(e) Write down the electrode reaction and the Nernst equation for the following electrode:
 $\text{Ag}-\text{AgCl(s)}|\text{Cl}^-$.

(f) Consider the following reaction in an electrochemical cell operating at 25°C : $\text{A} + \text{B}^+ \rightarrow \text{A}^+ + \text{B}$ where the concentration of the A^+ and B^+ are 0.8 M and 0.4 M respectively. The standard cell potential is 0.01 V . Calculate the free energy change and configure the cell (considering $2.303\text{RT/F} = 0.059 \text{ V}$).

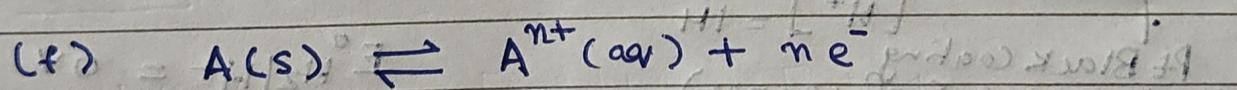
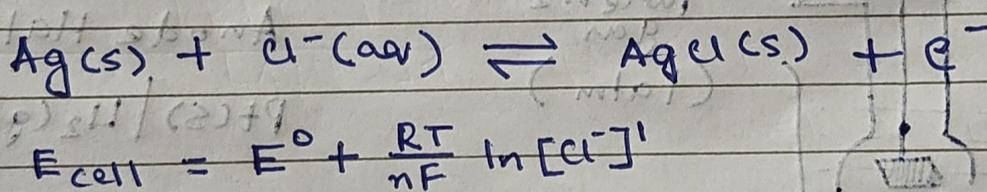
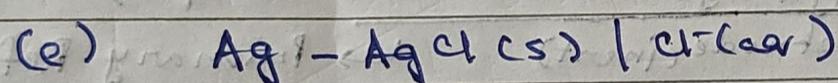
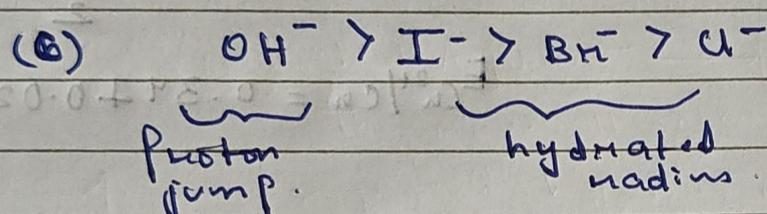
OR

(f) Show that every ten-fold decrease in the activity of cation produces a decrease of $(0.0592/n)$ volt of the potential, where n is the number of electron(s) associated with process.

(b) Kohlrausch's law of independent migration of ions states that the molar conductivity of an electrolyte is the sum of the contributions of its individual ions. This law is valid for limiting molar conductivity which is at infinite dilution.

Thus, for WE, the Λ_m^o can be calculated with the help of known Λ_m^o of SE's and their constituent ions.

$$\Lambda_m^\circ (\text{CH}_3\text{COOH}) = \Lambda_m^\circ (\text{CH}_3\text{COONa}) + \Lambda_m^\circ (\text{HCl}) - \Lambda_m^\circ (\text{NaCl})$$



$$E_A|A^{nt} = E^0_{A|A^{nt}} - \frac{0.0592}{n} \log_{10} [A^{nt}(\text{ca})]$$

$$\text{When } [A^{n+}(\text{aq})]^\circ = \frac{1}{10} [A^{n+}(\text{aq})]$$

$$\log_{10} [\text{A}^n(\text{aq})]^t = \log_{10} [\text{A}^n(\text{aq})] - \log_{10} t$$

$$E_{\text{final}} = E_{\text{initial}} + 0.0592 \text{ eV}$$

$$E_A^{\circ} | R^+ = E_A^{\circ} | A^{nt} - \frac{0.0592}{n} \log_{10} [A_{(aq)}^{nt}] - \frac{0.0592}{n}$$

$$E_{\text{Agent}} = \frac{0.0592}{n} \quad (\text{Proved})$$

2nd Half

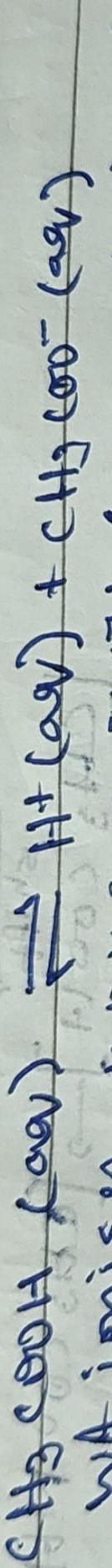
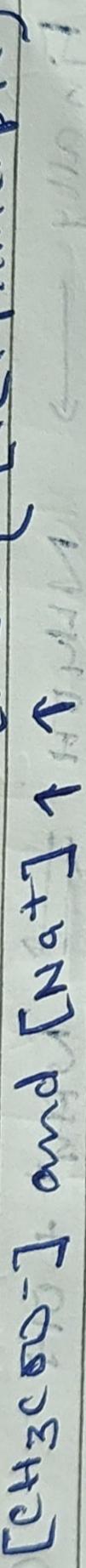
Answer all questions

5. (a) Draw conductometric titration curve of weak acid and strong base. Label all the axes and explain the nature of the graph.
- (b) What is Kohlrausch's law of independent ion migration? Explain why it should be applicable to weak electrolyte at infinite dilution.
- (c) Arrange in increasing order of ion conductivity and explain the trend: Cl⁻, OH⁻, Br⁻, F⁻. [~]
- (d) Explain Standard hydrogen electrode with electrode design and half-cell reaction.
- (e) $E_{\text{cu}^{2+}/\text{Cu}}^0 = +0.34 \text{ V}$ (SHE), Find out reduction potential of the electrode when Cu²⁺ concentration is 2.5 M.

[4+(2+2) + 3+3+2]

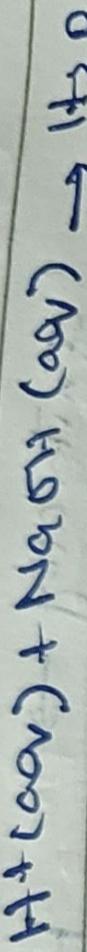
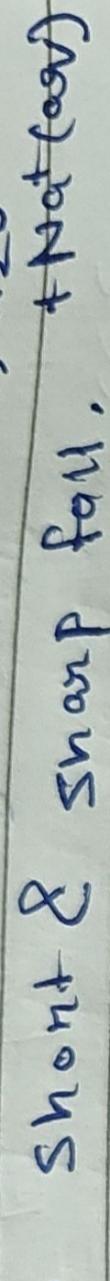
Rapidly at first.
 $\text{CH}_3\text{COOH} \rightarrow \text{CH}_3\text{COO}^- + \text{H}^+$
 $\text{AgNO}_3 \text{ eq. } \text{Pt} \rightarrow [\text{OH}^-] \uparrow$

Shows that
 $\text{CH}_3\text{COOH} \rightarrow \text{CH}_3\text{COO}^- + \text{H}^+$



WA ionisation more on $[\text{H}^+]$ \downarrow (L.C. principle)

Now further add of NaOH eq. Pt \downarrow



short & sharp fall.

low amount of H^+ present due to partial ionisation
gets neutralised \uparrow

when few drops added \uparrow the H^+

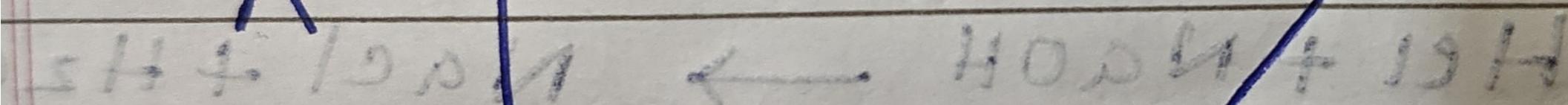
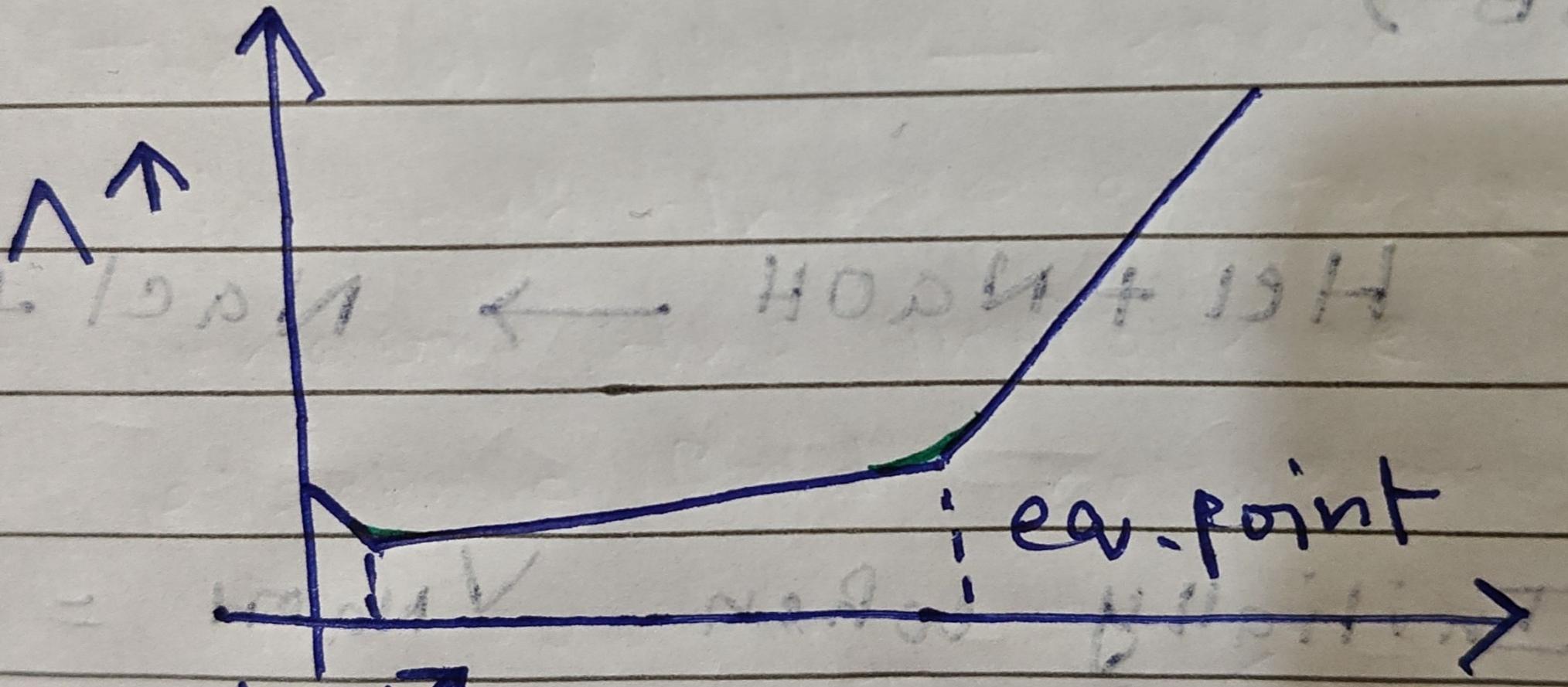
AcOH is wa

Inhibition & variation since

$\text{CH}_3\text{COONa} + \text{H}_2\text{O} \rightarrow \text{CH}_3\text{COOH} + \text{NaOH}$

$\text{CH}_3\text{COONa} + \text{H}_2\text{O} \rightarrow \text{CH}_3\text{COOH} + \text{NaOH}$

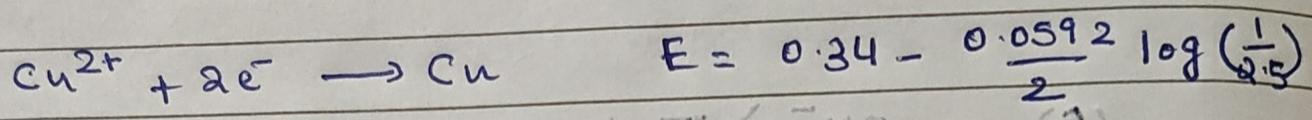
(BZ + A)



common ion effect

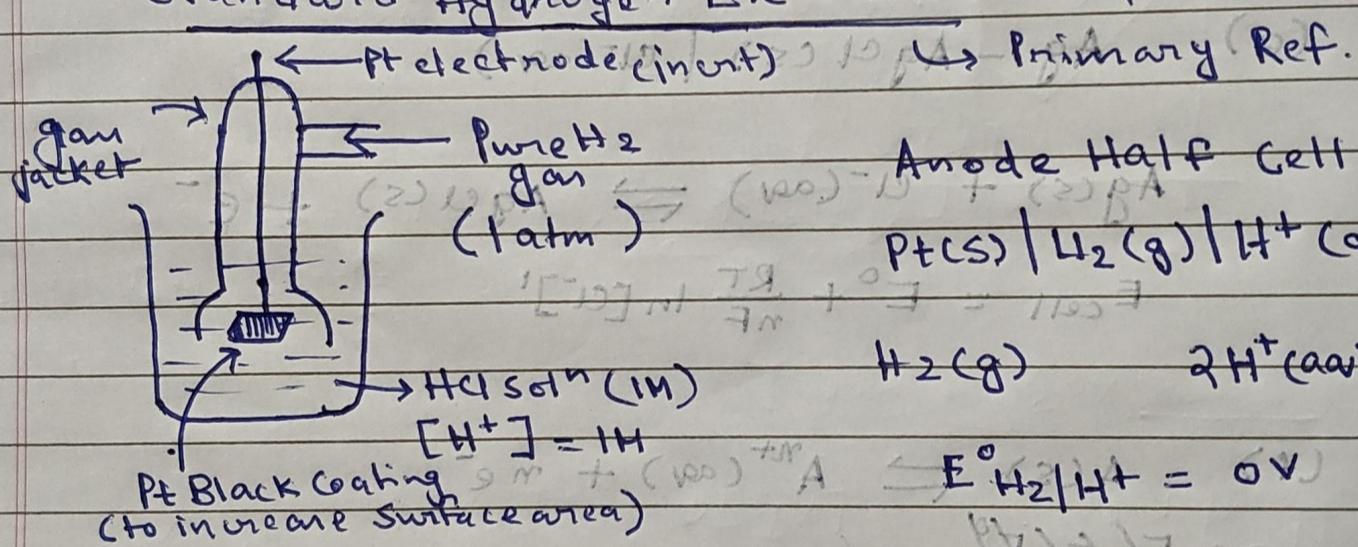
(b) Kohlrausch's law applies to WE (d)
 at ∞ dilution since at that point
 - the dissociation is complete and
 each ion contributes independently to
 the overall conductivity regardless of
 the other ions present. This is because
 at ∞ dilution interactions between ions are
 negligible and thus each ion can migrate freely.

$$(c) E^\circ_{Cu^{2+}/Cu} = 0.34 \text{ V} \quad [Cu^{2+}] = 2.5 \text{ M}$$

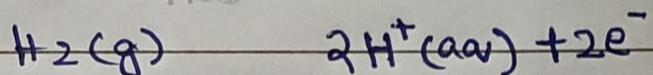
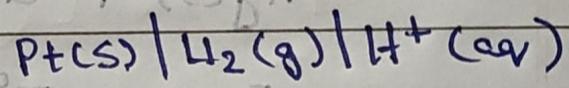


$$E_{Cu^{2+}/Cu} = 0.34 + 0.0296 \log(2.5)$$

Standard Hydrogen Electrode (SHE)

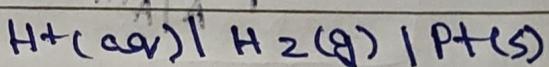


Anode Half Cell :-



$$E^\circ_{H_2/H^+} = 0 \text{ V}$$

The SHE is a reference electrode whose electrode potential = $E^\circ_{H_2/H^+} = 0 \text{ V}$



has been defined to be $E^\circ_{H_2/H^+} = 0 \text{ V}$ at standard condn ($[H^+] = 1 \text{ M}$ & $PP = 1 \text{ atm}$) at 25°C
 - thus the potentials of other half cells are compared to that of SHE to determine their SRP
 SHE is imp for determining E° of other electrochemical half cells and understanding relative acid and base strength of different substances.