

REFERENCE ELECTRODE

The Electrode of standard potential with which we can compare the potential is called the Reference Electrode.

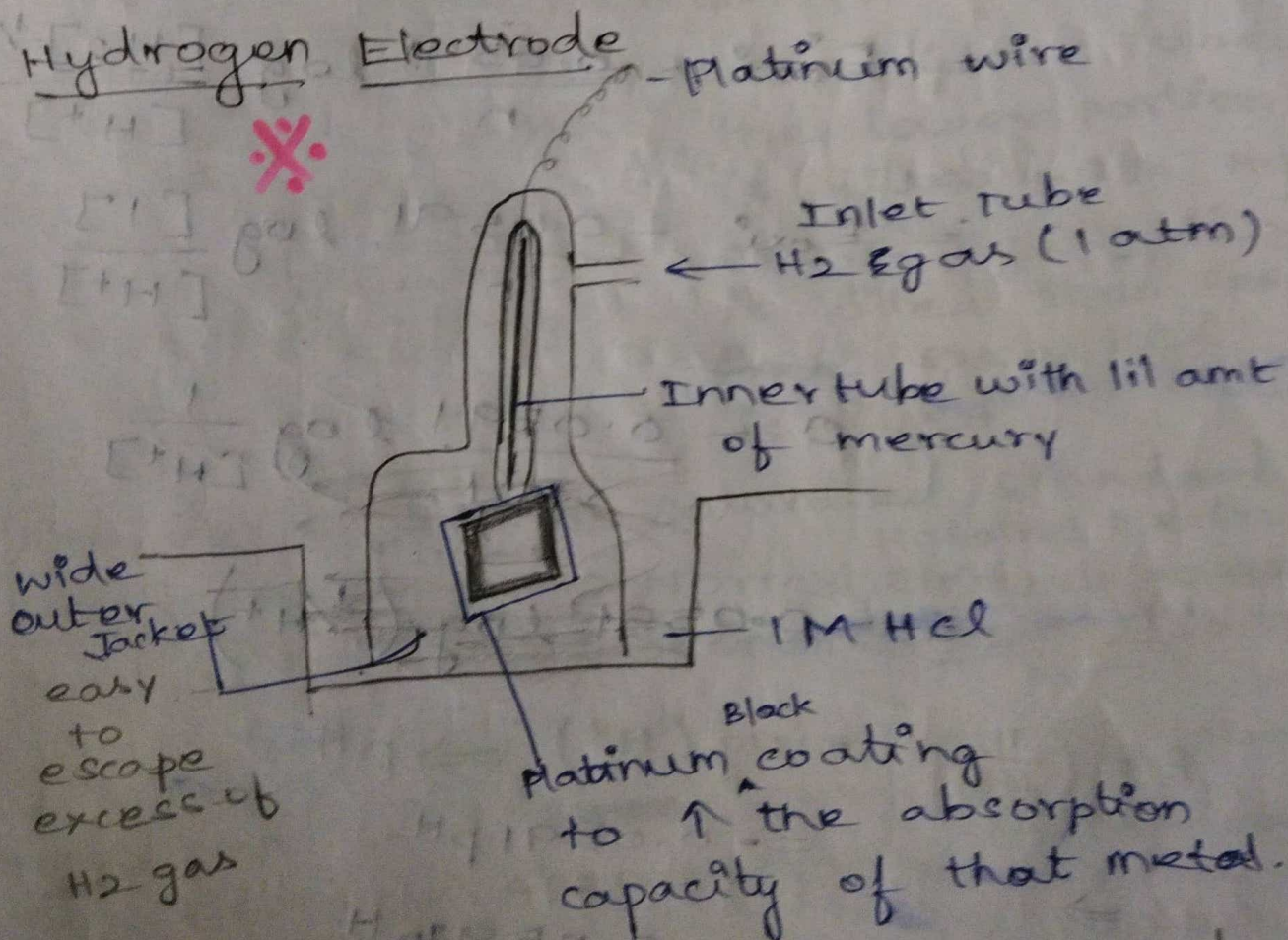
Primary Reference Electrode

Hydrogen Electrode

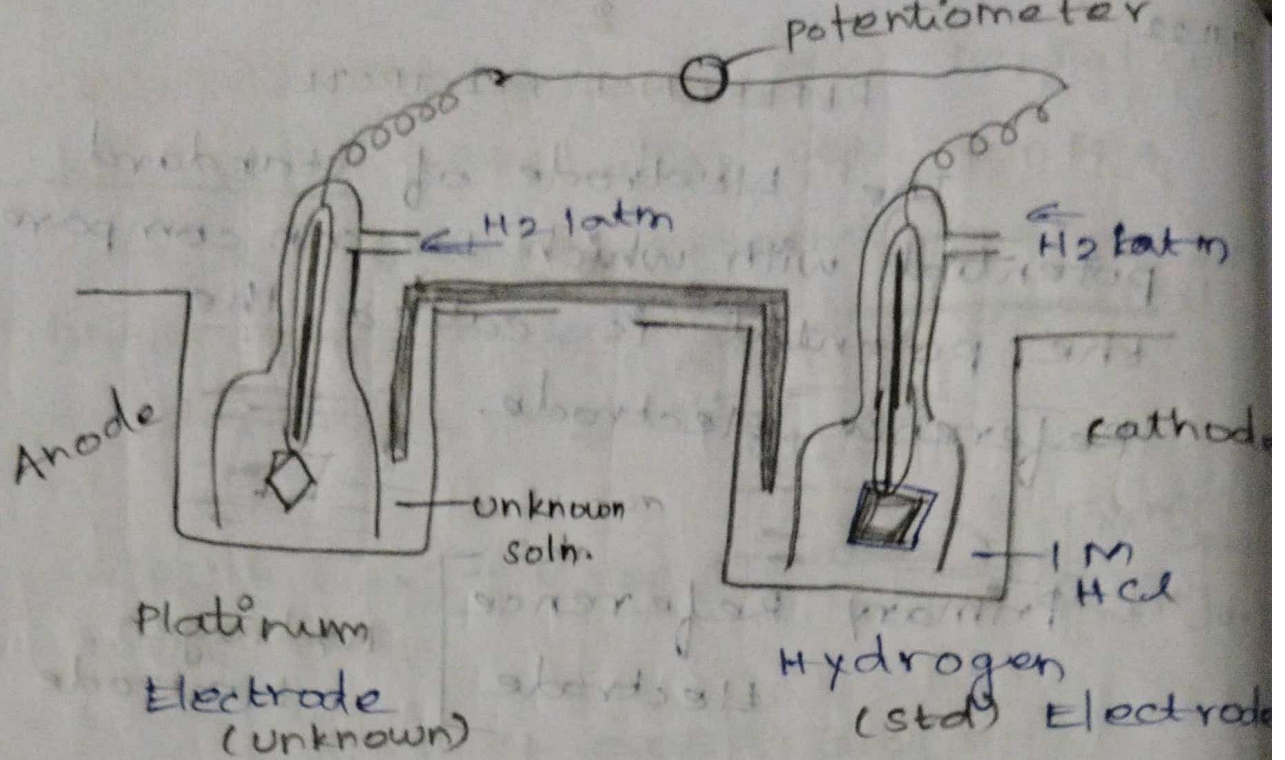
Secondary Reference Electrode

Calomel Electrode.

Hydrogen Electrode



Using this Hydrogen Electrode we can find the pH value of unknown soln.



$$E_{\text{cell}} = E_{\text{oxi}}^{\circ} - \frac{0.0591}{n} \log \left(\frac{P}{R} \right)$$

$$E_{\text{cell}} = E_{\text{oxi}}^{\circ} - \frac{0.0591}{n} \log \frac{[H_2]^{1/2}}{[H^+]}$$

$$E_{\text{cell}} = E_{\text{oxi}}^{\circ} - \frac{0.0591}{n} \log \frac{[1]}{[H^+]}$$

$$E_{\text{cell}} = 0 - \frac{0.0591}{n} \log \frac{1}{[H^+]}$$

$$E_{\text{cell}} = -0.0591 \log \left(\frac{1}{[H^+]} \right)$$

$$\log \left(\frac{1}{[H^+]} \right) = -\log (H^+) \Rightarrow pH$$

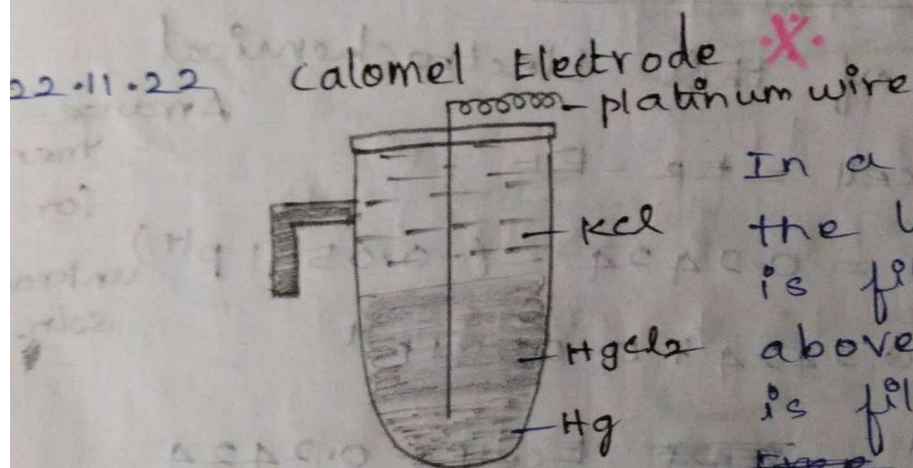
$$= -0.0591 pH$$

\Rightarrow

$$E_{\text{cell}} = -0.0591 pH$$

Limitations of Hydrogen Electrode.

- * We have to pass only H_2 gas 1 atm pressure
- * We have to maintain ^(HCl) soln at 1M only for whole process
- * Platinum foil easily gets affected ^{corroded} if the soln has any impurities

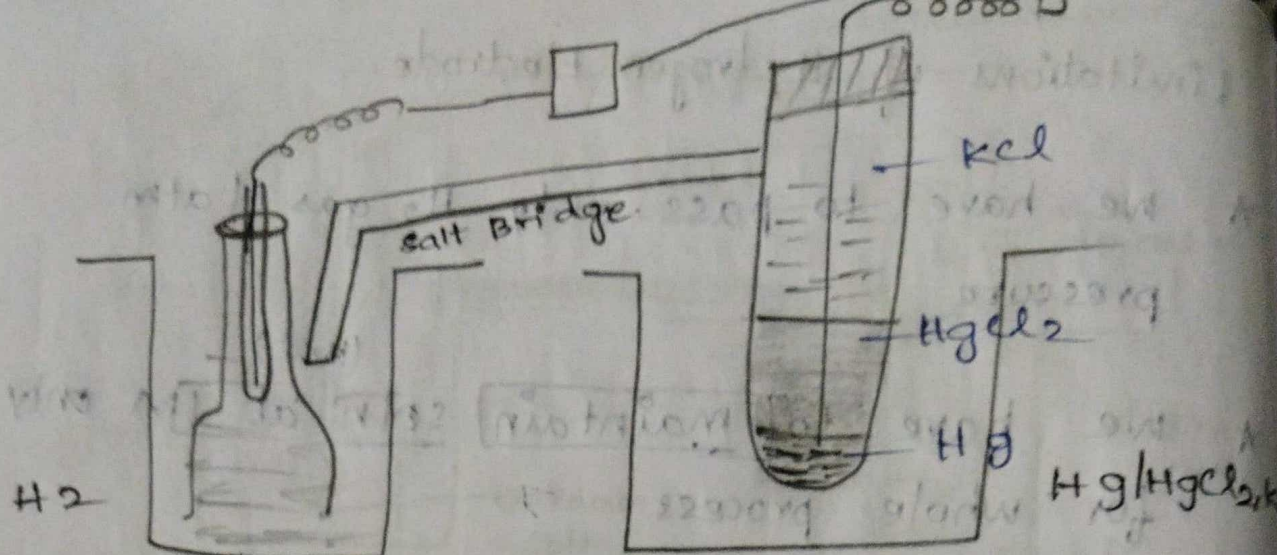


In a Glass Tube the lower portion is filled with Hg above Hg, $HgCl_2$ is filled then remain ~~free~~ space KCl is filled

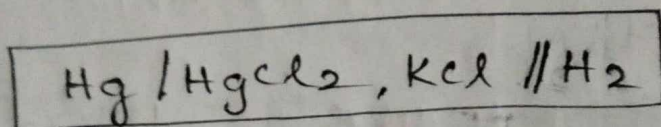
-0.2422
 [standard KCl \rightarrow saturated, standard calomel Electrode
 $1.0\ N\ KCl \rightarrow$ Normal Electrode $= 0.2800$
 $0.1\ N\ KCl \rightarrow$ Decinormal Electrode $= 0.3338$

Based on KCl ~~changes~~ Normality \downarrow Electropotential value developed voltage $-0.2424V$ Electrode potential

of Electrode changes/Varies



Here calomel Electrode acts as standard Electrode



To find pH of this Electrochemical Arrangement for

$$E_{\text{cell}} = E_R - E_L$$

calomel (standard) H_2

$$= 0.2424 - (-0.0591 \text{ pH})$$

unknown soln.

$$E_{\text{cell}} = 0.2424 + 0.0591 \text{ pH}$$

$$0.0591 \text{ pH} = \cancel{0.24} E_{\text{cell}} - 0.2424$$

$$\text{pH} = \frac{E_{\text{cell}} - 0.2424}{0.0591}$$

construction

Glass Tube \rightarrow \downarrow Hg \rightarrow HgCl₂ \rightarrow \uparrow KCl \rightarrow

\rightarrow Saltbridge (for Electrode pot) \rightarrow

Based on KCl - N - Electrode pot

varies.

working

connected to H_2 Electrode connected with saltbridge, coupled with potentiometer to find Electrode potential

and pH of unknown soln.

Advantages

- ★ simple construction
- ★ Entirely closed one.

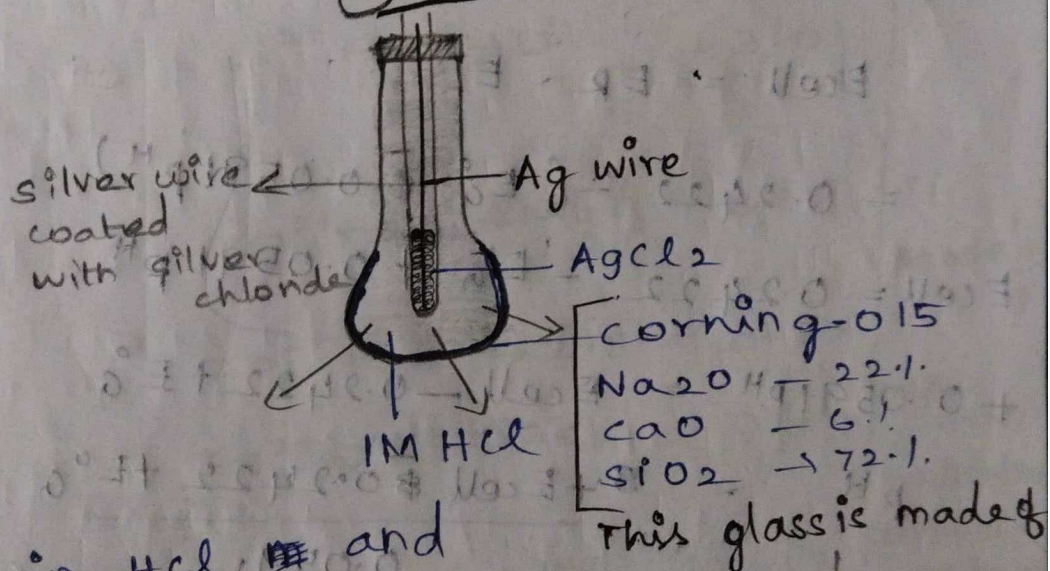
23.11.22

2.

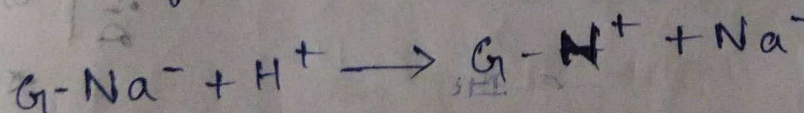
Glass Electrode (

Also known as Glass Electrode

Internal Reference Electrode
Ions selective electrode



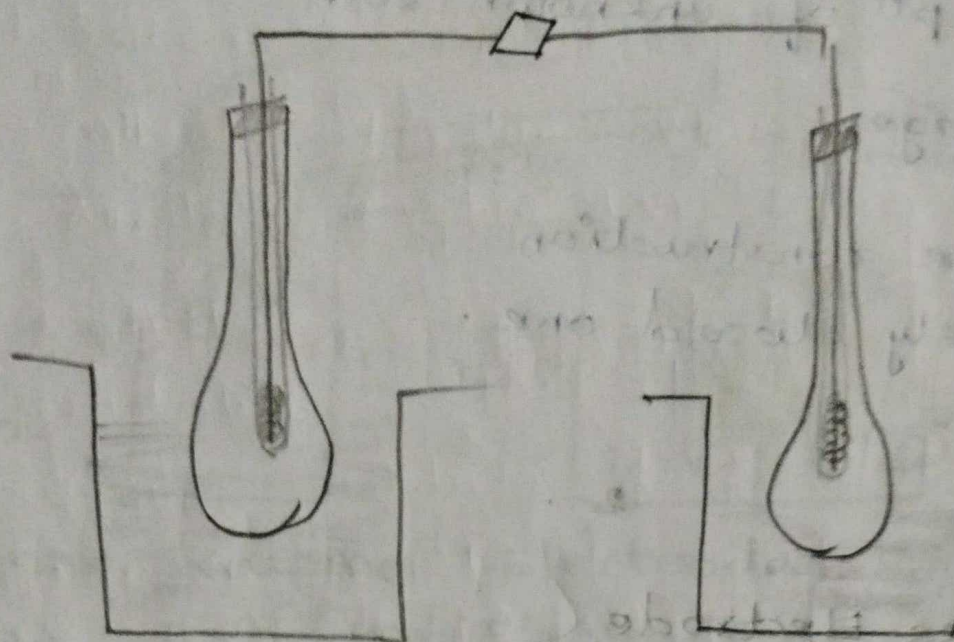
H⁺ ions in HCl and Na₂O in glass reacts and form



Ag, AgCl, HCl || Glass

$$E_{\text{glass electrode}} = E_{\text{Ag}}^{\circ} - \frac{0.0591}{n} \log [H^+]$$

$$E_G = E_G^{\circ} - 0.0591 \text{ pH} \quad \text{pH} = -\log [H^+]$$



Glass Electrode

calomel

$$E_G = E_G^\circ - 0.0591 \text{ pH}$$

$$E_{\text{cell}} = E_R - E_L$$

$$= 0.2422 - (E_G^\circ - 0.0591 \text{ pH})$$

$$E_{\text{cell}} = 0.2422 - E_G^\circ + 0.0591 \text{ pH}$$

$$+ 0.0591 \text{ pH} = E_{\text{cell}} - 0.2422 + E_G^\circ$$

$$\text{pH} = \frac{E_{\text{cell}} - 0.2422 + E_G^\circ}{0.0591}$$

~~$$\text{pH} = \frac{0.2422 - E_{\text{cell}} - E_G^\circ}{0.0591}$$~~

Advantages

- * coloured turbid solution
- * Accurate value
- * ↑ Resistivity, good Electrical conductivity
- * construction easy
- * should not poison easily

Disadvantages

- * standard/specified potentiometer only can be used.
- * A soln that contain 0-10 only can be measured above 10 x