

Electrochemistry

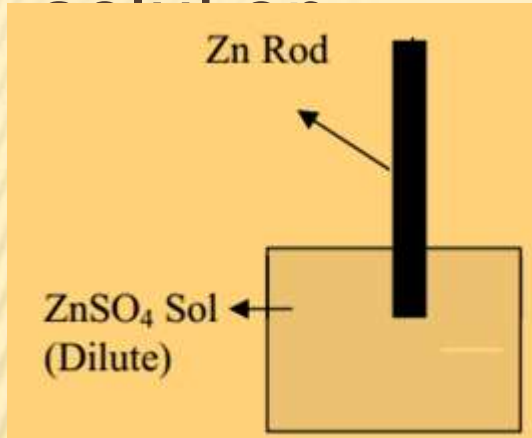
Part 2

Dr.S.E.Bhandarkar

**INDICATOR AND
REFERENCE ELECTRODES**

HALF CELL

✘ When a Metal Rod dipped in its salt



Oxidation reaction is as below (Anode)



Reduction reaction is as below (Cathode)



Nernst Equation



$$E = E^0 - \frac{2.303 RT}{\eta F} \text{Log}_{10} \frac{[\text{M}]^m [\text{N}]^n}{[\text{A}]^a [\text{B}]^b}$$

$$\text{at } 25^{\circ}\text{C } R=8.313 \text{ J}, F=96500 \text{ v}, t=(25 + 273)^{\circ}\text{K}$$

$$E = E^0 - \frac{0.0591}{\eta} \text{Log}_{10} \frac{[\text{M}]^m [\text{N}]^n}{[\text{A}]^a [\text{B}]^b}$$

CONSTRUCTION AND WORKING

We will Discuss Construction and working of

1. Indicator Electrodes

A) Hydrogen Electrode

B) Quinhydrone Electrode

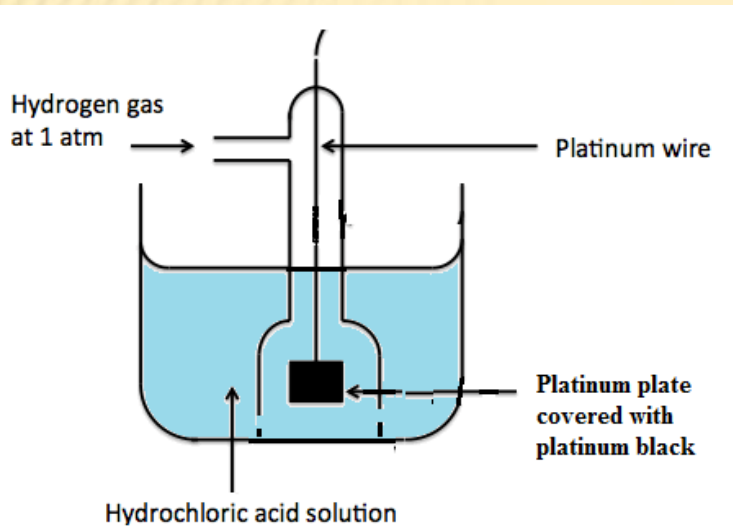
C) Glass Electrode

2. Reference Electrode

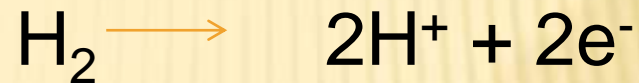
Calomel Electrode

INDICATOR ELECTRODES

A. HYDROGEN ELECTRODE



Oxidation Reaction is as below



Nernst equation :

$$E = E^0 - 0.0591 / n \text{ Log}_{10} \frac{[\text{M}]^m [\text{N}]^n}{[\text{A}]^a [\text{B}]^b}$$

$$E_{\text{ox}} = E_{\text{ox}}^0 - 0.0591/2 \log [\text{H}^+]^2 / [\text{H}_2]$$

For Hydrogen Electrode $E_{\text{ox}}^0 = 0$

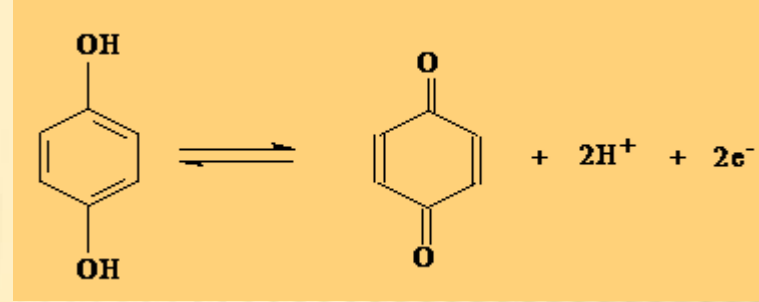
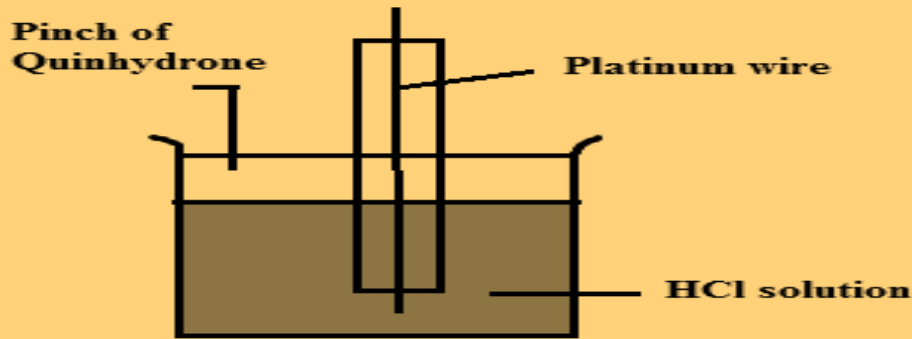
$$E_{\text{ox}} = - 0.0591/2 \log [\text{H}^+]^2$$

$$E_{\text{ox}} = -0.0591 \log [\text{H}^+]$$

$$E_{\text{ox}} = 0.0591 \text{ pH}$$

B. QUINHYDRONE ELECTRODE

Quinhydrone = Quinone + Hydroquinone



Oxidation Reaction

Nernst equation
$$E = E^0 - 0.0591 / n \text{ Log}_{10} \frac{[\text{M}]^m [\text{N}]^n}{[\text{A}]^a [\text{B}]^b}$$

$$E_{\text{ox}} = E_{\text{ox}}^0 - 0.0591/2 \log [\text{Q}][\text{H}^+]^2 / [\text{H}_2\text{Q}]$$

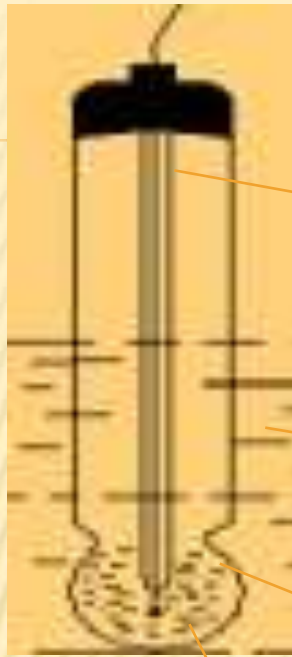
$$E_{\text{ox}} = E_{\text{ox}}^0 - 0.0591/2 \log [\text{H}^+]^2$$

$$E_{\text{ox}} = E_{\text{ox}}^0 - 0.0591 \log [\text{H}^+]$$

$$E_{\text{ox}} = E_{\text{ox}}^0 + 0.0591 \text{ pH}$$

$$E_{\text{ox}} = -0.69 + 0.0591 \text{ pH}$$

C. GLASS ELECTRODE



Platinum wire

HCl solution

1N HCl solution

Semipermeable membrane



Oxidation Reaction

Nernst equation :

$$E = E^0 - 0.0591 / \eta \text{ Log}_{10} \frac{[\text{M}]^m [\text{N}]^n}{[\text{A}]^a [\text{B}]^b}$$

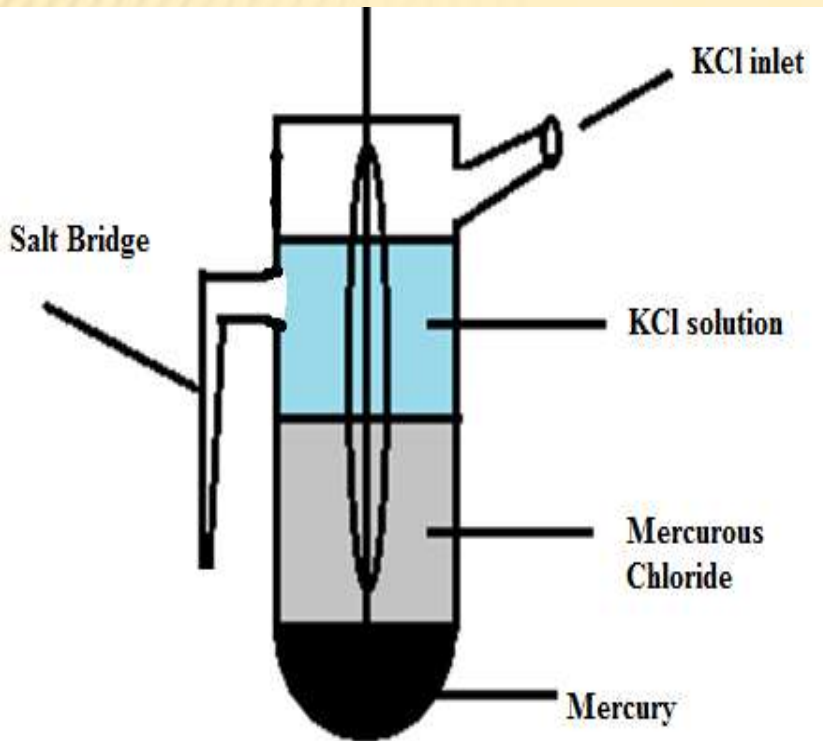
$$E_{\text{ox}} = E_{\text{ox}}^0 - 0.0591/2 \log [\text{H}^+]^2$$

$$E_{\text{ox}} = E_{\text{ox}}^0 - 0.0591/2 \log [\text{H}^+]^2$$

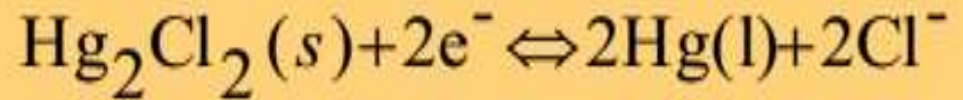
$$E_{\text{ox}} = E_{\text{ox}}^0 - 0.0591 \log [\text{H}^+]$$

$$E_{\text{ox}} = E_{\text{ox}}^0 + 0.0591 \text{ pH}$$

REFERENCE ELECTRODE CALOMEL ELECTRODE



Net Cell Reaction is



$$E = E^0 - \frac{2.303RT}{nF} \log [\text{Cl}^-]^2$$

$$E = E^0 - \frac{2.303RT}{F} \log [\text{Cl}^-], \text{ where } n=2$$

$$E = E^0 - 0.0591 \log [\text{Cl}^-] \text{ at } 298\text{K}$$

$E_{\text{oxidation Calomel}}$

Saturated KCl : -0.24V

1N KCl Solution : -0.28V

IMPORTANT POINTS

- × $E_{\text{cell}} = E_{\text{oxidation LHS}} + E_{\text{reduction RHS}}$
- × $E_{\text{Reduction RHS}} = -E_{\text{oxidation RHS}}$
- × Thus
- × $E_{\text{cell}} = E_{\text{oxidation LHS}} - E_{\text{oxidation RHS}}$

Electrode whose oxidation potential is higher is always placed on LHS

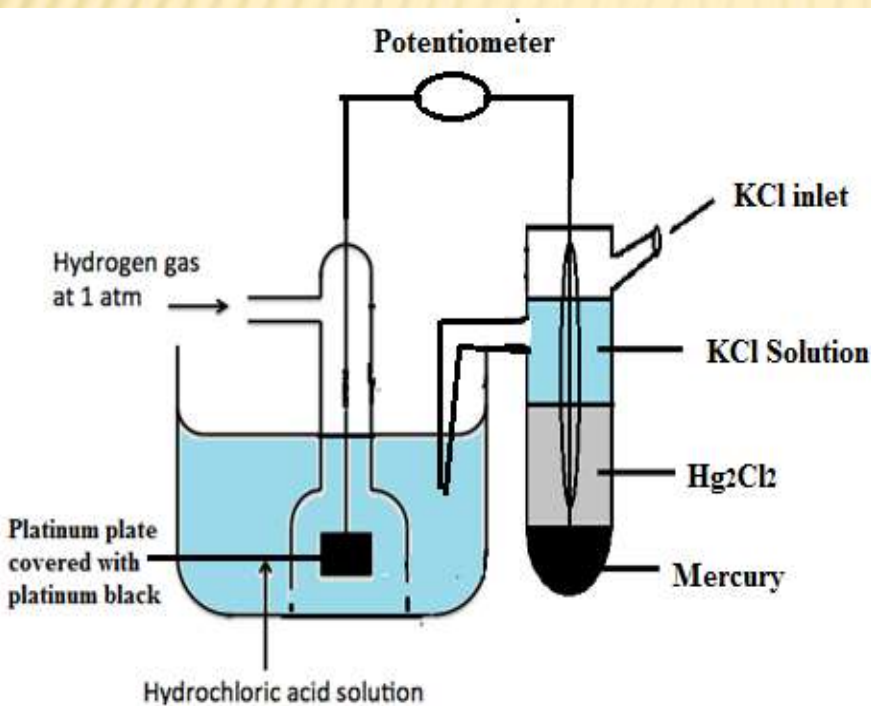
DETERMINATION OF pH USING HYDROGEN ELECTRODE

Electrode whose oxidation potential is higher is always placed on LHS

SOP of Hydrogen Electrode > SOP of Calomel Electrode

0.00V -0.24V

LHS RHS



$$E_{\text{cell}} = E_{\text{oxidation LHS}} - E_{\text{oxidation RHS}}$$

$$E_{\text{cell}} = E_{\text{oxidation LHS}} - E_{\text{oxidation RHS}}$$

$$\begin{aligned} E_{\text{cell}} &= E_{\text{oxidation H}_2} - E_{\text{oxidation CE}} \\ &= 0.0591\text{pH} - (-0.24) \\ &= 0.0591\text{pH} + 0.24 \end{aligned}$$

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

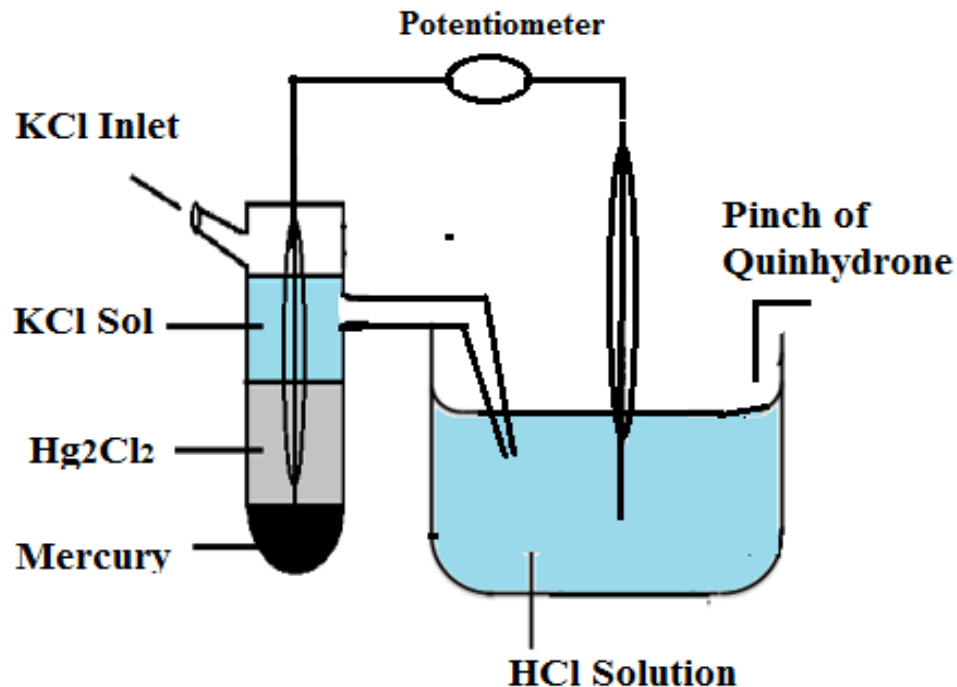
$$\text{pH} = (E_{\text{cell}} - 0.24) / 0.0591$$

$$-\log_{10} [\text{H}^+] = (E_{\text{cell}} - 0.24) / 0.0591$$

DETERMINATION OF pH USING QUINHYDRONE ELECTRODE

Electrode whose oxidation potential is higher is always placed on LHS
SOP of Calomel Electrode > SOP of Hydrogen Electrode

$$\begin{array}{ccc} -0.69V & > & -0.24V \\ \text{LHS} & & \text{RHS} \end{array}$$



$$E_{\text{cell}} = E_{\text{oxidation LHS}} - E_{\text{oxidation RHS}}$$

$$E_{\text{cell}} = E_{\text{oxidation LHS}} - E_{\text{oxidation RHS}}$$

$$\begin{aligned} E_{\text{cell}} &= E_{\text{oxidation CE}} - E_{\text{oxidation QE}} \\ &= (-0.24) - (-0.69 + 0.0591 \text{pH}) \\ &= 0.45 - 0.0591 \text{pH} \end{aligned}$$

$$-0.0591 \text{pH} = E_{\text{cell}} - 0.45$$

$$0.0591 \text{pH} = 0.45 - E_{\text{cell}}$$

$$\text{pH} = (0.45 - E_{\text{cell}}) / 0.0591$$

$$-\log_{10} [\text{H}^+] = (0.45 - E_{\text{cell}}) / 0.0591$$

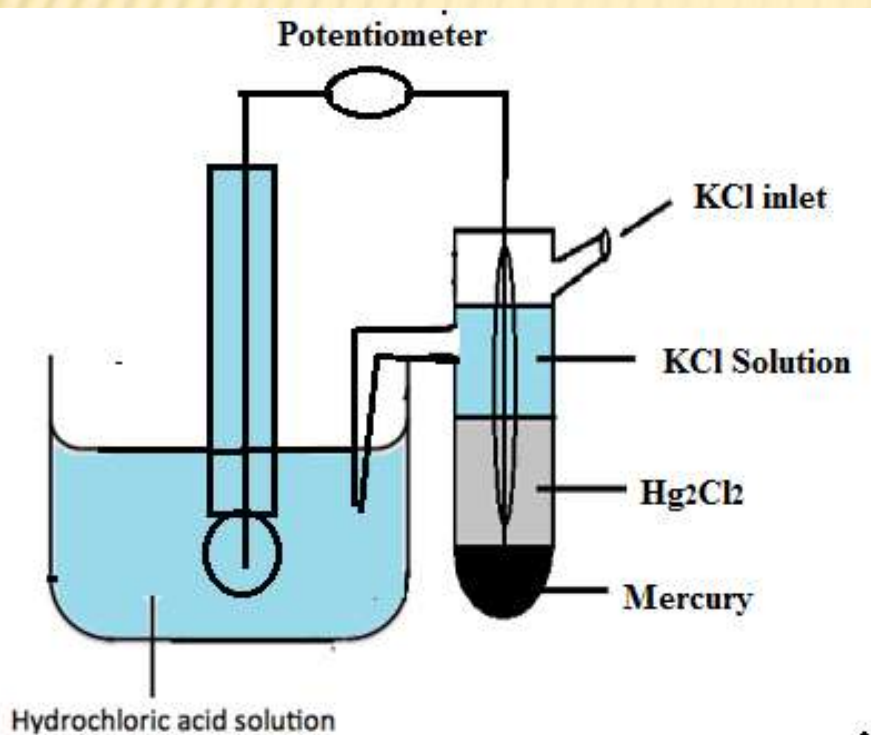
DETERMINATION OF PH USING GLASS ELECTRODE

Electrode whose oxidation potential is higher is always placed on LHS

SOP of Glass Electrode > SOP of Calomel Electrode

LHS

RHS



$$E_{\text{cell}} = E_{\text{oxidation LHS}} - E_{\text{oxidation RHS}}$$

$$E_{\text{cell}} = E_{\text{oxidation LHS}} - E_{\text{oxidation RHS}}$$

$$\begin{aligned} E_{\text{cell}} &= E_{\text{oxidation GE}} - E_{\text{oxidation CE}} \\ &= E^0_{\text{oxidation GE}} + 0.0591\text{pH} - (-0.24) \\ &= E^0_{\text{oxidation GE}} + 0.0591\text{pH} + 0.24 \end{aligned}$$

$$0.0591\text{pH} = E_{\text{cell}} - E^0_{\text{oxidation GE}} - 0.24$$

$$\text{pH} = (E_{\text{cell}} - E^0_{\text{oxidation GE}} - 0.24) / 0.0591$$

$$-\log_{10} [\text{H}^+] = (E_{\text{cell}} - E^0_{\text{oxidation GE}} - 0.24) / 0.0591$$

THANK YOU