REFERENCE ELECTRODES
CHAPTER 4

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Reference Electrodes :-

1)Hydrogen Electrode :

The hydrogen electrode is used as a reference for electrode potential measurements . Theoretically , it is the most important electrode for use in aqueous solutions.

The reversible hydrogen electrode in a solution of hydrogen ions at unit activity exhibits a potential, which is assumed to be zero at all temperatures .The electrode consists of a platinum wire immersed in a solution containing hydrogen ions and saturated with hydrogen gas . Platinum is immersed completely in aqueous arsenic free hydrochloric acid, and hydrogen gas free from oxygen and carbon monoxide is bubbled to platinum surface.

Slowly the air is displaced by hydrogen and the reversible potential is achieved. Unfortunate, this electrode has some drawbacks . First the reversibility of hydrogen electrode cannot be maintained in oxidizing media. Second if a current is withdrawn from the electrode the electrode acts an anode ,because of the ionization of gas molecules.

$$(H_2 \longrightarrow 2H + 2e^-) \; E^o = 0.00 \; V$$
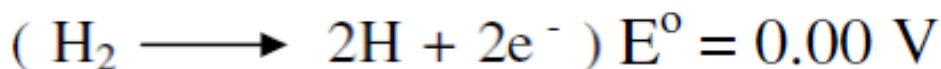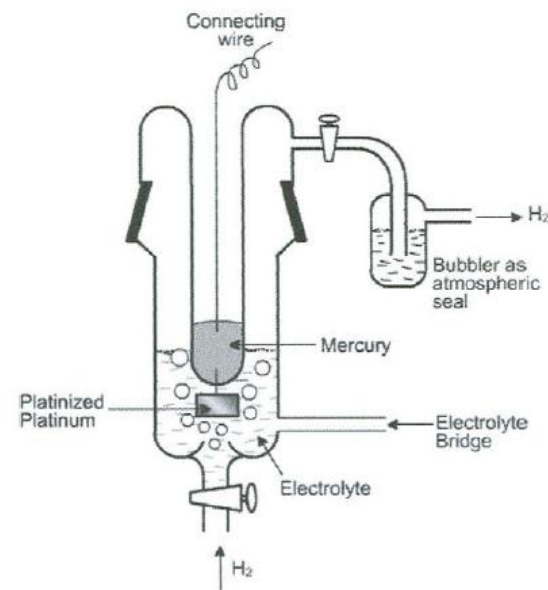
2) Silver – Silver chloride Electrode :

This electrode is composed of a silver chloride and immersed in a solution of chloride ions .The chloride equilibrium is given by : $AgCl \rightleftarrows Ag^+ + Cl^-$

Two other reactions involve a dynamic equilibrium between deposition and dissolution of silver together with solubility equilibrium between silver chloride and its ions .The metallic silver reaches equilibrium with silver ions according to the following reaction : $Ag^+ + e \rightleftarrows Ag$
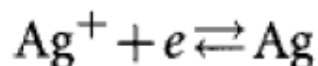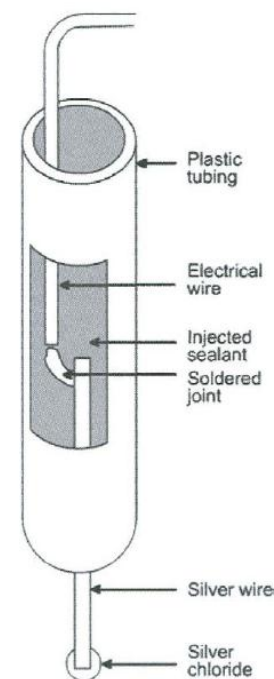
The overall electrode reaction is therefore given by :

$$AgCl + e \rightleftarrows Ag + Cl^- \quad (E^\circ_{AgCl/Ag} = 0.024\,V)$$

The following are the values of $E_{Ag/AgCl}$ for different HCl concentrations:

Concentration (M)	Electrode potential (volts)
0.1	0.28
0.01	0.34
0.001	0.40

- Plastic tubing
- Electrical wire
- Injected sealant
- Soldered joint
- Silver wire
- Silver chloride

3) Copper – Copper Sulfate Electrode :

This is a reference electrode which is easy , robust and stable . It is used mainly in Cathodic protection measurements , such as the measurement of pipe – to – soil potential .It has lower accuracy than other electrodes used for laboratory work .It consists of copper metal placed in a solution containing copper sulfate and copper sulfate crystals placed in a non-conducting holder with a porous plug .The equation for the copper-copper sulfate electrode potential is given by :

$$E^\circ_{Cu-CuSO_4} = 0.316 + 0.0009(25°C)\,\text{volts}$$

The reaction of the Cu-CuSO$_4$ half cell is $Cu^{2+} + 2e \rightleftarrows Cu$

A saturated solution of 1.47 mole Cu-CuSO$_4$ at 25 C is used .

$a_{(Cu^{2+})} = \text{Molarity(M)x Activity coefficient } \gamma$.

$a_{(Cu^{2+})} = 1.47\text{x}0.037$ (γ is found from table of activity coefficients) .

So $a_{Cu^{2+}} = 0.051$

And the electrode potential is :

$$E_{Cu^{2+}/Cu} = E_{Cu^{2+}/Cu} + \frac{0.0592}{2} \log a_{(Cu^{2+})}$$

Where

$a_{(Cu^{2+})} =$ activity of copper which is unity ,

$E^o_{Cu} = 0.34$ V at 25^oC.
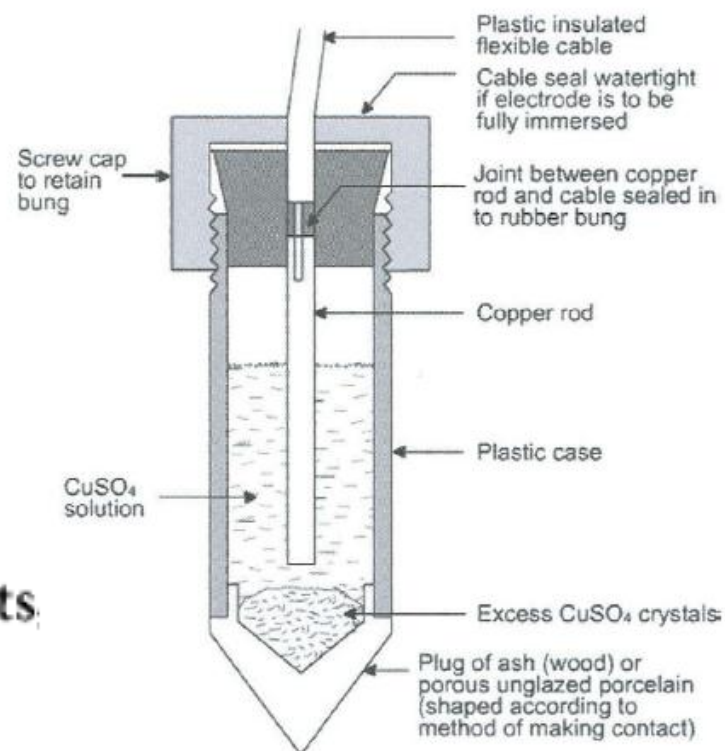
Substituting in the above eq. we obtain

$$E_{Cu^{2+}/Cu} = 0.34 + \frac{0.0592}{2} \log(0.051)$$

$$E_{Cu^{2+}/Cu} = 0.30 \text{ volts}$$

So

$$E_{Cu^{2+}/Cu} = 0.316 + 0.009 \ (T^oC) \text{ volts}$$

Plastic insulated flexible cable

Cable seal watertight if electrode is to be fully immersed

Screw cap to retain bung

Joint between copper rod and cable sealed in to rubber bung

Copper rod

Plastic case

CuSO₄ solution

Excess CuSO₄ crystals

Plug of ash (wood) or porous unglazed porcelain (shaped according to method of making contact)
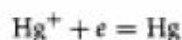
4) The calomel Electrode :-

It is the most commonly used reference electrode. It has a constant and reproducible potential. The electrode basically consists of a platinum wire dipped into pure mercury which rests in a paste of mercurous chloride and mercury. The paste is in contact with a solution of potassium chloride.

Mercurous chloride is slightly soluble, and it is in equilibrium with mercurous ions according to:

$$Hg^+ + e = Hg$$

The overall equilibrium is expressed by:
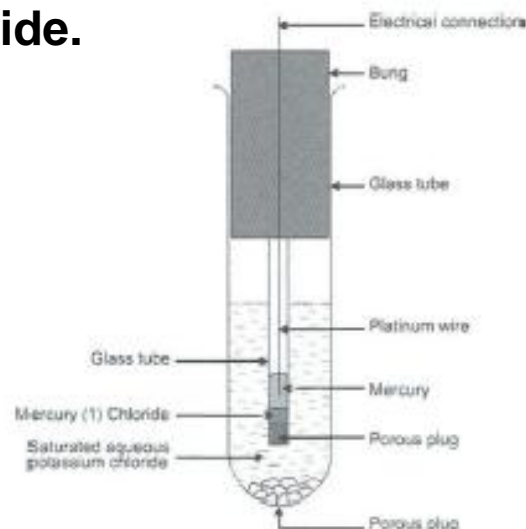
$$Hg_2Cl_2 + 2e \rightleftharpoons 2Hg + 2Cl^-$$

The mercurous chloride and mercury are at unit activity. Therefore, the electrode potential can be written as:

$$E_{Calomel} = E° + \frac{RT}{2F} \ln\left(\frac{1}{a_{Cl^-}}\right)$$

or

$$E_{Calomel} = E° - \frac{0.0592}{2} \log a_{Cl^-}$$

The value of $E°$ for the half cell reaction of calomel electrode is 0.267 V. Thus, the electrode potential becomes:

$$E_{Calomel} = 0.267 - \frac{0.0592}{2} \log\left(a_{Cl^-}\right)$$

Electrode Potentials of Calomel Electrode

(Standard hydrogen electrode taken as reference)

Electrode	Potential (volts)
$Hg/Hg_2Cl_2/KCl$ (Sat.)	0.2444
$Hg/Hg_2Cl_2/KCl$ (1.0 N)	0.289
$Hg/Hg_2Cl_2/KCl$ (0.1 N)/Salt Bridge	0.3356