

Reference Electrodes

The reaction potential is measured with reference to a standard half-cell or electrode. The hydrogen half-cell provides the basic standard, but in practice is awkward to use. For this reason, several other reference half-cells have been developed. Some of these reference cells are listed in the following table along with their potential with respect to the hydrogen half-cell and location of use.

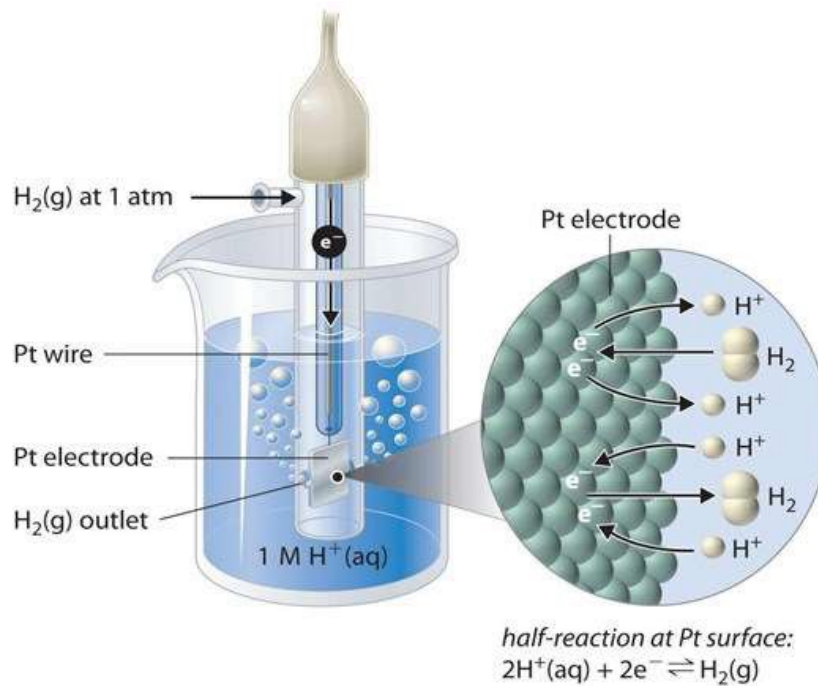
Half-Cell	Potential Ref. SHE (v)	Environment
Copper : Copper Sulfate	+0.3160	Soil
Tenth Normal Calomel	+0.3337	Laboratory
Normal Calomel	+0.2800	Laboratory
Saturated Calomel	+0.2415	Laboratory
Silver : Silver Chloride (0.1M KCl)	+0.2880	Seawater
Silver : Silver Chloride (Seawater)	+0.2222	Seawater
Silver : Silver Chloride (3.8M KCl)	+0.1990	Seawater
Hydrogen	0	Laboratory
Zinc	-0.7600	Seawater

1- Hydrogen Electrode (SHE)

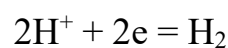
The hydrogen electrode is used as a reference for electrode potential measurements. Theoretically, it is the most important electrode for use in aqueous solutions. The reversible hydrogen electrode in a solution of hydrogen ions at unit activity exhibits a potential, which is assumed to be zero at all temperatures.

The electrode consists of a platinum wire immersed in a solution (Fig. below) 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 the platinum surface.

Unfortunately, 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 Second, if a current is withdrawn from the electrode, the electrode acts as an anode because of the ionization of gas molecules. Also, the electrode is fragile and delicate to handle.



The electrode potential for hydrogen E_{H_2} can be determined as follows:



$$E_{\text{H}^+/\text{H}_2} = E^{\circ}_{\text{H}^+/\text{H}_2} + 2.303 \frac{RT}{nF} \log \frac{[\text{H}^+]^2}{[\text{H}_2]}$$

where H^+ is activity of hydrogen ions, and H_2 is hydrogen partial pressure.

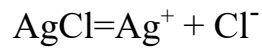
At one atmosphere pressure (H_2), $\text{H}^+ = 1$, and $E^{\circ}_{\text{H}^+/\text{H}_2} = 0$ by definition.

Therefore,

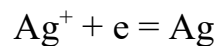
$$E_{\text{H}^+/\text{H}_2} = 0.059 \log [\text{H}^+]^1$$

2- Silver-Silver Chloride Electrode (SSCE)

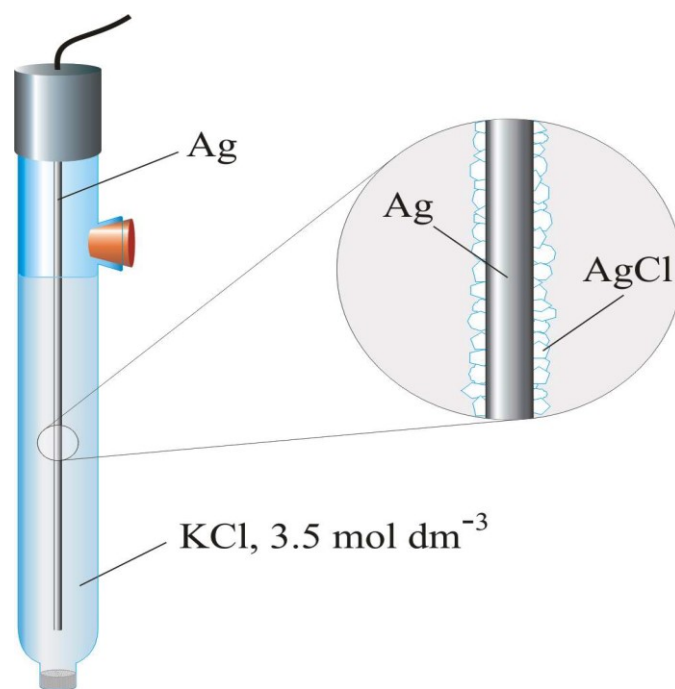
This electrode is composed of a silver wire coated with silver chloride and immersed in a solution of chloride ions. The chloride equilibrium is given by:



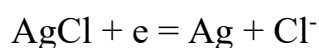
The metallic silver reaches equilibrium with silver ions according to the following reaction:



The overall electrode reaction is, therefore, given by:



The electrode potential, $E_{\text{AgCl}/\text{Ag}}^{\circ}$, is given by:



$$E_{\text{AgCl}/\text{Ag}} = E_{\text{AgCl}/\text{Ag}}^{\circ} + 2.303 \frac{RT}{nF} \log \frac{[\text{AgCl}]}{[\text{Ag}] * [\text{Cl}]}$$

$$[Ag]=1 \quad \text{and} \quad [AgCl]=1$$

Therefore,

$$E_{AgCl/Ag} = E_{AgCl/Ag}^{\circ} - \frac{2.303RT}{F} \log[Cl]$$

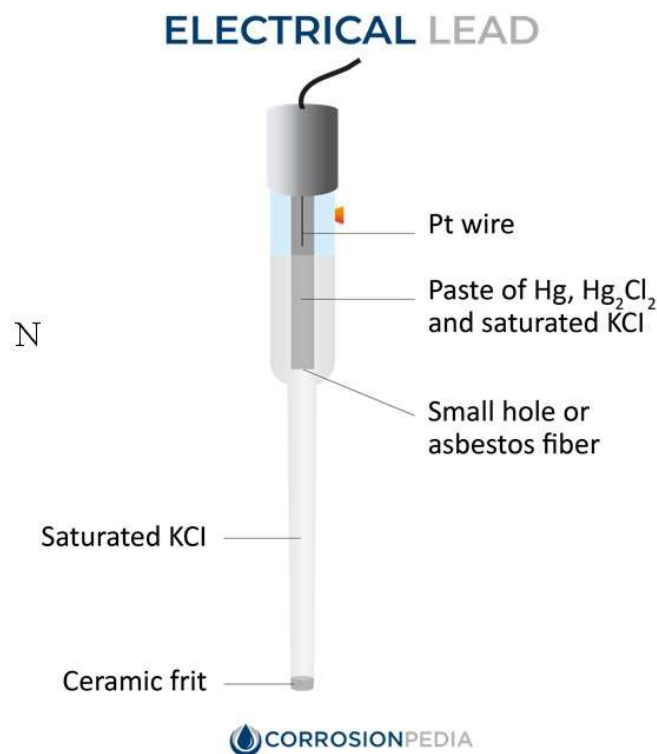
Or at 25 °C

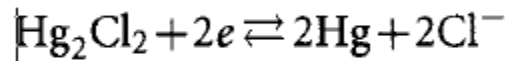
$$E_{AgCl/Ag} = E_{AgCl/Ag}^{\circ} - 0.0592 \log[Cl]$$

$$E_{AgCl/Ag} = 0.25 - 0.0592 \log[Cl]$$

3- The Calomel Electrode (SCE)

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 which acts as a salt bridge to the other half of the cell





$$E^\circ = 0.241 \text{ V}$$

The electrode potential can be written as:

$$E_{\text{calomel}} = E^\circ + \frac{2.303RT}{2F} \log \frac{1}{[\text{Cl}^-]}$$

Or at 25 C

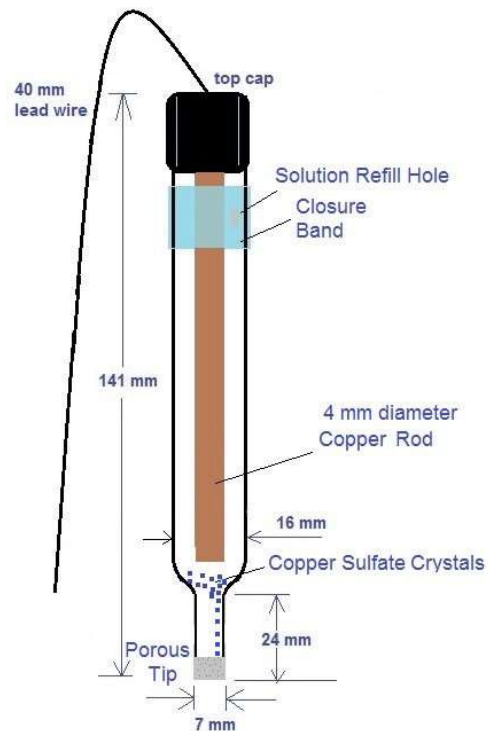
$$E_{\text{calomel}} = E^\circ - 0.0592 \log [\text{Cl}^-]$$

The value of E° for the half cell reaction of calomel electrode is 0.241 V. Thus, the electrode potential becomes:

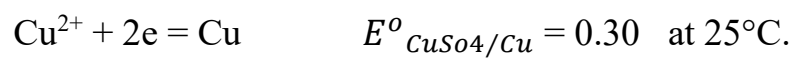
$$E_{\text{calomel}} = 0.241 - 0.0592 \log [\text{Cl}^-]$$

4- Copper-Copper Sulfate Electrode (SCCE)

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 a 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, fig below.



The reaction of the Cu-CuSO₄ half cell is



and the electrode potential;

$$E_{\text{Cu}^{2+}/\text{Cu}} = E^{\circ}_{\text{Cu}^{2+}/\text{Cu}} + 0.0592 \log [\text{Cu}]$$

5- Pb/PbCl $E^{\circ} = -0.33 \text{ V}$

6- Zn/ZnCl₂ $E^{\circ} = -0.76 \text{ V}$

Convert from reference electrode

$$E_{\text{SHE}} = E_{\text{m}} + E^{\circ}_{\text{Ref.}}$$

Example1:

A potential of metal A is -0.17 Standard hydrogen electrode (SHE), determine its potential verses Saturated calomel electrode (SCE), Pb/PbCl₂, Cu/CuSO₄, Zn/ZnCl₂, Ag/AgCl.

Solution.:

$$E_{\text{SHE}} = E_m + E^{\circ}_{\text{Ref.}}$$

$$-0.17 = E + 0.24$$

$$E = -0.41 \text{ V (SCE)}$$

So that:

$$E_m = -0.17 + 0.33 = 0.16 \text{ V (Pb/PbCl}_2\text{)}$$

$$E = -0.17 - 0.3 = -0.47 \text{ V (Cu/CuSO}_4\text{)}$$

$$E = -0.17 + 0.76 = 0.59 \text{ V (Zn/ZnCl}_2\text{)}$$

$$E = -0.17 - 0.25 = -0.42 \text{ V (Ag/AgCl)}$$

Example 2:

The potential of metal B is (-0.68 SCE), determine its potential verses Ag/AgCl, Pb/PbCl₂, Zn/ZnCl₂.

Solution

First of all, convert the potential to SHE

$$E_{\text{SHE}} = E_m + E_{\text{Ref.}}$$

$$E_{\text{SHE}} = -0.68 + 0.24$$

$$= -0.44 \text{ V SHE}$$

$$- 0.44 = E_m + 0.25$$

$$E = - 0.69 \text{ V (Ag/AgCl)}$$

$$- 0.44 = E_m + (- 0.33)$$

$$E = - 0.44 + 0.33 = - 0.11 \text{ V (Pb/PbCl}_2\text{)}$$

$$- 0.44 = E_m + (- 0.76)$$

$$E = 0.32 \text{ V (Zn/ZnCl}_2\text{)}$$
