Electrochemical Cells

Consider the redox reaction

$$Zn(s) + Cu^{2+}_{(aq)} \rightarrow Zn^{2+}_{(aq)} + Cu_{(s)}$$

Zinc transfers two electrons to cupric ion. Thus zinc is the reducing agent. Cupric ion is the oxidizing agent. By separating the zinc (reducing agent) and the cupric ion (oxidizing agent) physically, the transfer of electrons can occur through an external conducting medium and as a result electricity is generated due to the progress of the redox reaction. An electrochemical cell is an experimental apparatus for generating electricity by using a redox reaction. The Daniel cell for the system shown in Figure.

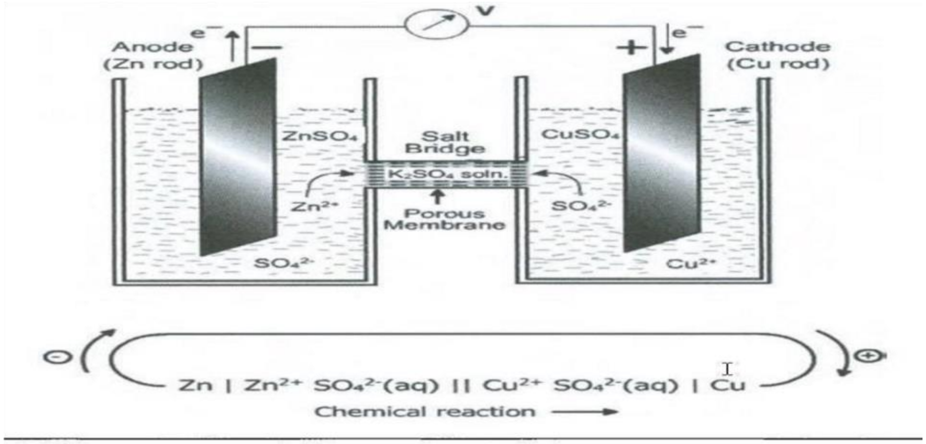
Zinc, anode, positive	$Zn(s) \rightarrow Zn^{2+}_{(aq)} + 2e^-$	Oxidation
Copper, cathode, negative	$Cu^{2+}_{(aq)} + 2e^- \rightarrow Cu(s)$	Reduction

A salt bridge enables the movement of ions from one container to another and acts a conducting medium and completes the circuit. During the redox reaction electrons flow from the zinc anode through the wire and voltmeter to the copper cathode. In solution cations Zn+2 , Cu+2 and K+ move toward the copper cathode and anions SO_4^{2} ; Cl move toward the zinc anode.

In the electrochemical cell an electric current flows from the zinc anode to the copper cathode. The difference in electrical potential between the anode and cathode is measured by the voltmeter, and is known as the cellk voltage. The cell voltage is also known as the cell potential or electromotive force (emf). The cell voltage also depends on the concentration of the ions. Electrochemical cells are represented as cell diagrams. For the ***Daniel cell***, assuming the solutions are 1.0M, we may write:

$$Zn(s)|\,Zn^{2+}(1M)||Cu^{2+}(1M)|Cu(s)$$

The single vertical line denotes a boundary between solid electrode and solution, and the double vertical lines signify the salt bridge. By convention the anode is on the left and the cathode is on the right of the salt bridge.



Daniel cell

Standard Electrode Potentials

The measured voltage of the Daniel cell is 1.10V. This is the overall voltage of the cell consisting of two half-reactions, namely the oxidation of zinc and the reduction of cupric ion. The individual potentials of the half-reactions cannot be measured. The potentials of the halfreactions can be obtained relative to a standard. The standard is a hydrogen electrode. This consists of a platinum electrode immersed in 1M HCl with hydrogen gas bubbling through at 1 atmosphere pressure. The reaction is:

$$2\mathrm{H}^+(1\,M) + 2\mathrm{e}^- \rightarrow \mathrm{H}_2(1\,\mathrm{atm})E^\circ = 0\,\mathrm{V}$$

and the potential of this is zero. The hydrogen electrode is known as standard hydrogen electrode (SHE) with a reduction potential of 0. Now we connect the zinc electrode system to a standard hydrogen electrode system with a salt bridge, as shown in Figure 1.3. The cell diagram is as follows:

$$\mathrm{Zn}_{(s)}||\mathrm{Zn}^{2+}(1\mathrm{M})\,||\,\mathrm{H}^+(1\mathrm{M})\,||\,\mathrm{H}_2(1\,\mathrm{atm})|\mathrm{Pt}_{(s)}$$

Zinc is the anode,

Email (rusul.ahmed.hashim@uomus.edu.iq)

$$Zn_{(s)} \rightarrow Zn^{2+}_{(aq)} + 2e^{-} \qquad \text{oxidation} \qquad E^{\circ}_{zn/Zn^{2+}} = 0.76\ \text{V}$$

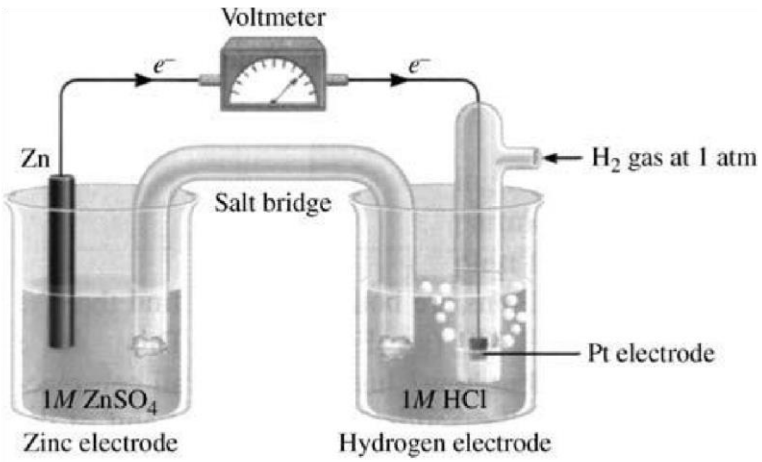


Figure 1.3 An electrochemical cell consisting of zinc and hydrogen electrodes

At the Pt electrode

$$2H^{+}_{(aq)} + 2e^{-} \rightarrow H_{2(g)} \qquad \text{reduction} \qquad E^{\circ}_{H^{+}/H_2} = 0.0\ \text{V}$$

When $Zn^{2+} = 1\,M, H^{+} = 1\,M, H_{2(g)}$ at 1 atm (i.e., standard state conditions) the emf of the cell = 0.76 V at 25°C.

$$E^{\circ}_{cell} = E^{\circ}_{ox} + E^{\circ}_{red}$$
$$E^{\circ}_{cell} = E^{\circ}_{zn/zn^{2+}} + E^{\circ}_{H^{+}/H_2}$$
$$0.76 = E^{\circ}_{zn/zn^{2+}} + 0$$

The standard oxidation potential of zinc = 0.76 V. The overall reaction is the sum of oxidation and reduction potentials (see Figure 1.3). The standard electrode potential can be obtained by connecting a hydrogen electrode system to a copper electrode system through a Ubridge and a voltmeter, as shown in Figure 1.4. In this system copper is the cathode since reduction occurs.

$$Cu^{2+}_{(aq)} + 2e^- \rightarrow Cu(s)$$

For this system the cell diagram may be written as:

$$Pt_{(s)}\,|H_2(1\,atm)\,|\,H^+(1M)\,||\,Cu^{2+}(1M)\,|\,Cu(s)$$

The half-cell reactions are:

Anode (oxidation)	$H_2(1\,atm) \rightarrow 2H^+(1\,M) + 2e^-$	$E^\circ_{H_2/H^+}$
Cathode (reduction)	$Cu^{2+}(1\,M) + 2e^- \rightarrow Cu(s)$	$E^\circ_{Cu^{2+}/Cu}$
Overall	$H_2(1\,atm) + Cu^{2+}(1\,M) \rightarrow 2H^+(1\,M) + Cu(s)$	E°_{cell}

The potential under standard conditions is 0.34 V at 25°C.

$$E^\circ_{cell} = E^\circ_{H_2/H^+} + E^\circ_{Cu^{2+}/Cu}$$

$$0.34\,V = 0 + E^\circ_{Cu^{2+}/Cu}$$

Email (rusul.ahmed.hashim@uomus.edu.iq)

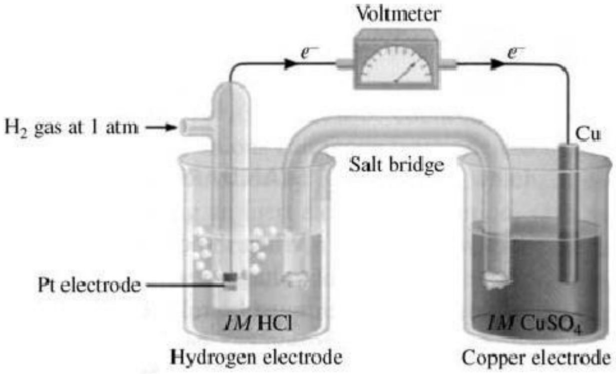


Figure 1.4 *An electrochemical cell consisting of copper and hydrogen electrodes*

Thus, the standard reduction potential of copper $E^\circ_{Cu^{2+}/Cu}$ is 0.34 V. Hence, the standard oxidation potential, $E^\circ_{Cu^{2+}/Cu} = -0.34$ V.

Now we consider the Daniel cell:

Anode (oxidation)	$Zn_{(s)} \rightarrow Zn^{2+}(1\,M) + 2\,e^-$	$E^\circ_{Zn/Zn^{2+}}$
Cathode (reduction)	$Cu^{2+}(1\,M) + 2\,e^- \rightarrow Cu(s)$	$E^\circ_{Cu^{2+}/Cu}$
Overall	$Zn_{(s)} + Cu^{2+}(1\,M) \rightarrow Zn^{2+}(1\,M) + Cu_{(s)}$	E°_{cell}

The emf of the cell

$$\begin{aligned} E^\circ_{cell} &= E^\circ_{Zn/Zn^{2+}} + E^\circ_{Cu^{2+}/Cu} \\ &= 0.76\,V + 0.34\,V = 1.10\,V \end{aligned}$$

Reference Electrodes

1- <u>Hydrogen Electrode</u>:

Email (rusul.ahmed.hashim@uomus.edu.iq)

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. 2.10) containing hydrogen ions and saturated with hydrogen gas. Platinum is immersed completely in aqueousarsenic 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.

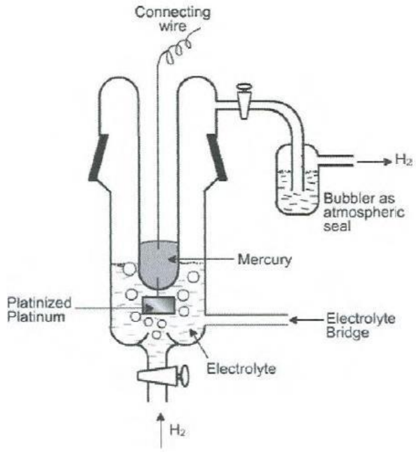


Fig 2-10

2- Silver-Silver Chloride Electrode

This electrode is composed of a silver wire coated with silver chloride and immersed in a solution of chloride ions (Fig. 2.12). The chloride equilibrium is given by:

$$AgCl \rightleftarrows Ag^{+} + Cl^{-}$$

E^o= 0.25 V

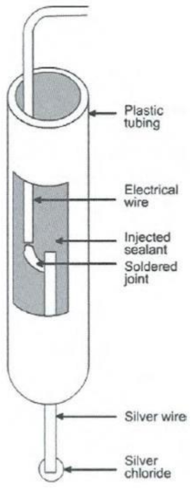


Figure 2.12 Silver-Silver chloride reference electrode

Email (rusul.ahmed.hashim@uomus.edu.iq)

3- 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 which acts as a salt bridge to the other half of the
cell (Fig. 2.13).

$$\mathrm{Hg}^{+} + e = \mathrm{Hg}$$

The overall equilibrium is expressed by:

$$\mathrm{Hg_2Cl_2} + 2e \rightleftarrows 2\mathrm{Hg} + 2\mathrm{Cl}^{-} \qquad \mathbf{E = 0.241\ V}$$

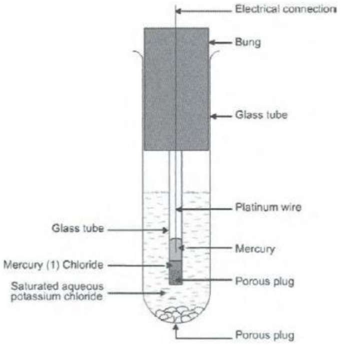


Figure 2.13 A saturated calomel reference electrode

4- 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 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. 2.14).

$E^{o}= 0.3$ V

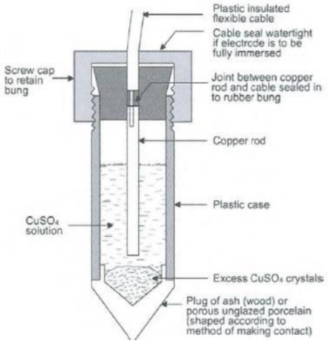


Figure 2.14 Reference copper-copper sulfate electrode

5- Pb /PbCl $E^{o}= -0.33$ V

6- $Zn/ZnCl_2$ $E^{o}= -0.76$ V

Convert from reference electrode

ESHE = Em + ESt.

Example1:

A potential of metal A is -0.17 SHE, determine its potential verses SCE, $Pb/PbCl_2$, $Cu/CuSO_4$, $Zn/ZnCl_2$, Ag/AgCl.

Sol.:

ESHE = Em + ERef.
-0.17 = E + 0.24 E= -0.41 V (SCE) So that:
E= -0.17 + 0.33= 0.16 V ($Pb/PbCl_2$)
E= - 0.17 – 0.3= - 0.47 V ($Cu/CuSO_4$)
E= -0.17 + 0.76 = 0.59 V ($Zn/ZnCl_2$)
E= - 0.17 – 0.25 = - 0.42 V (Ag/AgCl)

Example 2:

The potential of metal B is (-0.68 SCE), determine its potential verses Ag/AgCl, $Pb/PbCl_2$,

Email (rusul.ahmed.hashim@uomus.edu.iq)

$Zn/ZnCl_2$.
First of all, convert the potential to SHE

$E_{SHE} = E_m + E_{Ref.}$
$E_{SHE} = -0.68 + 0.24$
$= -0.44$ V SHE
$-0.44 = E_m + 0.25$
E = - 0.19 V (Ag/AgCl)
$-0.44 = E_m + (-0.33)$
E= - 0.44 + 0.33 = - 0.11 V ($Pb/PbCl_2$)
$-0.44 = E_m + (-0.76)$
E= 0.32 V ($Zn/ZnCl_2$)

H.W.

No.	Reference Electrode	Metal A	Metal B	Metal C
1	$Pb/PbCl_2$	0.721	0.13	0.62
2	$Zn/ZnCl_2$			
3	Ag/AgCl			
4	SCE			

Polarization

Email (rusul.ahmed.hashim@uomus.edu.iq)

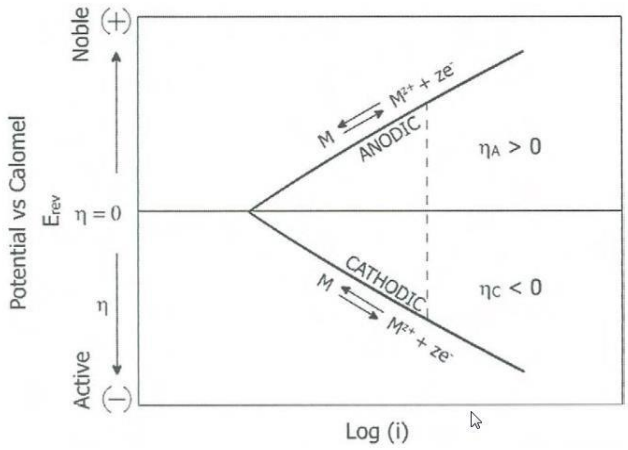


Figure 3.6 Polarization diagram (reversible electrode)

Activation polarization

Activation polarization is caused by a slow electrode reaction step , the reaction at the electrode requires an activation energy in order to proceed , the most important example is the hydrogen ion reduction reaction at a cathode:

$2H^+ + e^- \rightarrow H_2$

For this reaction, the polarization is called hydrogen over-potential

Over-potential is defined as the polarization (potential change) of an equilibrium electrode that results from current flow across the electrode-solution interface.

Hydrogen ion reduction is done by the following steps:

1-adsorption of hydrogen ion from solution to metal electrode

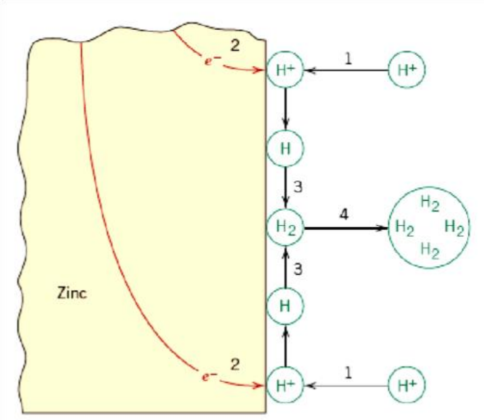
2-electron transfer from zinc to form hydrogen atom

3-cobining of two hydrogen atoms to form a molecule of hydrogen

$$2H \rightarrow H_2$$

4-the coalescence of many hydrogen molecules to form a bubble

Email (rusul.ahmed.hashim@uomus.edu.iq)



Factors affecting activation polarization

1-**current density**: where activation polarization increases with current density

2- **Materials**: Activation polarization varies with one metal to another because of the specific effect of current density.

3- **Surface Roughness**: Activation polarization is high on a smooth surface compared to a shiny surface.

4- **Temperature**: Increased temperatures decrease polarization as less activation energy would be needed and the exchange current density would be increased.

5- **Pressure**: Hydrogen over-voltage increases rapidly with decreasing pressure.

6- **pH**: Over-voltage increase initially and decreases with increased pH value.

7- **Agitation**: It has no effect on activation polarization, because it is a charge transfer process involving electrons and not a mass transfer.

Adsorption of Ions: The hydrogen overvoltage is decreased by adsorption of anions and increased by adsorption of cations.

Email (rusul.ahmed.hashim@uomus.edu.iq)