

Example 10

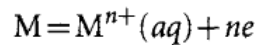
Determine the corrosion rate of carbon steel in salt solution from the following laboratory data. Consider the corrosion rate by a)mpy , b)mdd. C) Calculate the current density in $\mu\text{A}/\text{cm}^2$

ΔW (g)	0.0153	0.0290	0.0409	0.055	0.0685
T (h)	48	96	144	192	240

Given: $K=3.45 \times 10^6$, ρ for carbon steel= $7.86 \text{ gm}/\text{cm}^3$, area = 24.96 cm^2 , $n=2$ and atomic mass = $55.8 \text{ g}/\text{mole}$.

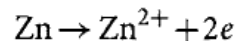
Double layer theory

When a metal is immersed in an electrolyte, a dynamic equilibrium is established across the interface with a potential difference between the metal and electrolyte. The atoms of the metal, M, ionize producing aquo-ions, $M^{n+}(\text{aq})$, and electrons, ne , according to:



Where M represents metal atoms. The metal is left with a negative charge and its positively charged metal ions, $M^{n+}(\text{aq})$, in the electrolyte are attracted back towards the metal surface. Thus, a potential difference and dynamic equilibrium between the metal and the solution is established. The atoms of the metal continue to ionize until the displacement of electrical charges produced balances the tendency of the metallic atoms to ionize into the electrolyte.

Consider, for example, a piece of zinc metal in water. Zinc dissolves producing positively charged zinc ions (cations):



The zinc ions in the solution remain very close to the metal surface. The zinc metal becomes negatively charged as the positive ions leave its surface. The excess electrons on the zinc surface orient themselves opposite to a layer of zinc ions of equal and opposite charge on the water side of the zinc/water interface. Such a process leads to the formation of an electrical double layer of about 1 nm (10^{-7} cm) thickness along the metal/solution interface (Fig. 2.9). Figure 2.9A shows the metal/solution interface at the moment of immersion and the formation of double layer is shown in Figs 2.9B and C. The double layer shown in Figs 2.9B and C is formed as a result of attraction between the negative ions (anions) and positive ions (cations) on one hand, and repulsion between similarly charged ion, anions or cations on the other hand.

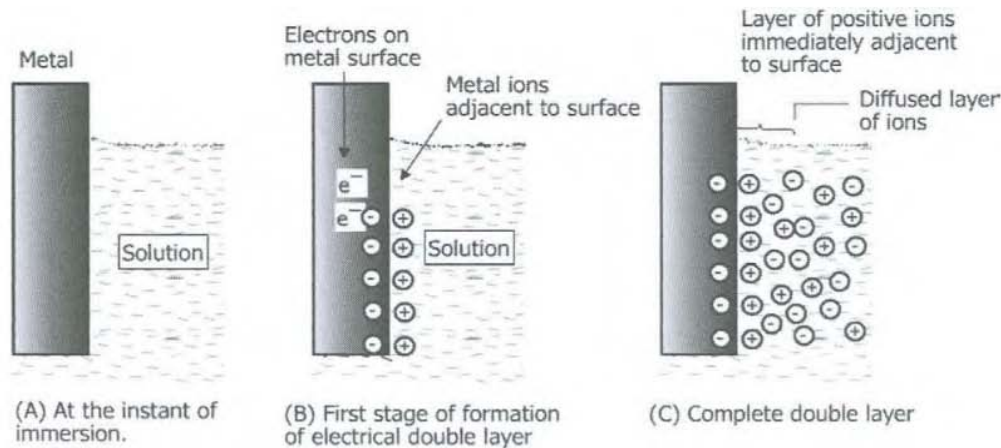
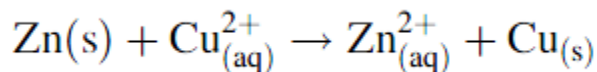


Figure 2.9 Representation of electrical double layer at a metal/solution interface

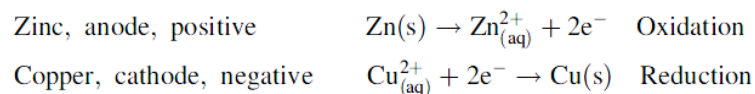
As a result of the above interactions, cations diffuse amongst the anions until an equilibrium is established between the metal and solution, and between the bulk of the solution and the layer adjacent to the metal surface. The plane passing through the ions absorbed on the metal surface is called the *Inner Helmholtz plane*, whereas the plane passing through the center of solvated cation is called the *Outer Helmholtz plane*, which also marks the beginning of a diffuse layer when an excess of charges is neutralized (Fig. 2.9C).

Electrochemical Cells

Consider the redox reaction

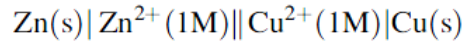


Zinc transfers two electrons to cupric ion. Thus zinc is the reducing agent. Cupric ion is the oxidizing agent. By separating the zinc (reducing agent) and the cupric ion (oxidizing agent) physically, the transfer of electrons can occur through an external conducting medium and as a result electricity 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.

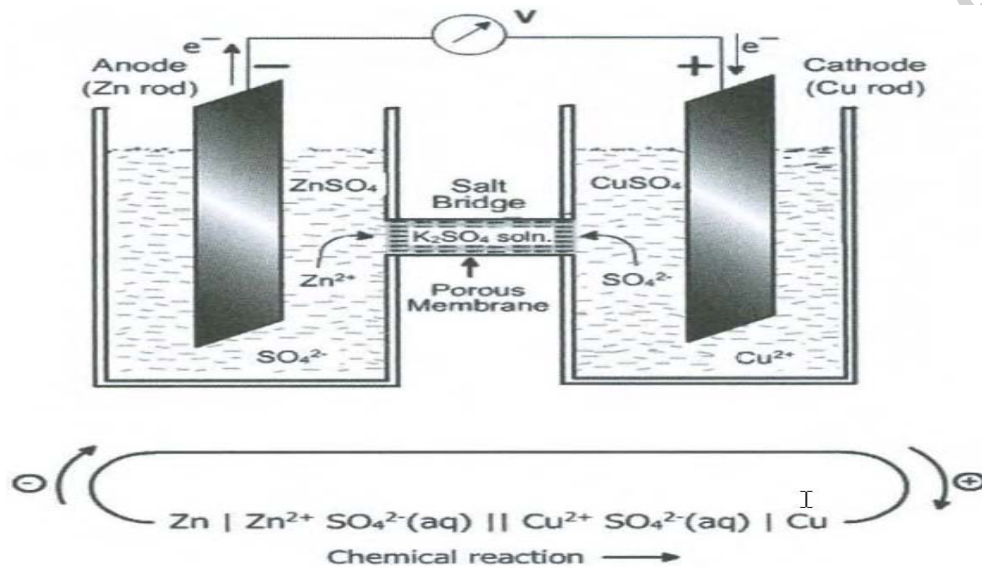


A salt bridge enables the movement of ions from one container to another and acts a conducting medium and completes the circuit. During the redox reaction electrons flow from the zinc anode through the wire and voltmeter to the copper cathode. In solution cations Zn^{2+} , Cu^{2+} and K^+ move toward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



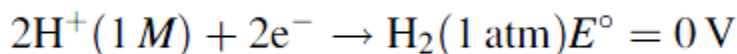
The single vertical line denotes a boundary between solid electrode and solution, and the double vertical lines signify the salt bridge. By convention the anode is on the left and the cathode is on the right of the salt bridge.



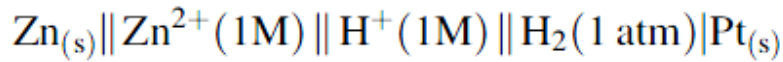
Daniel cell

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 half-reactions 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:



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:



Zinc is the anode,

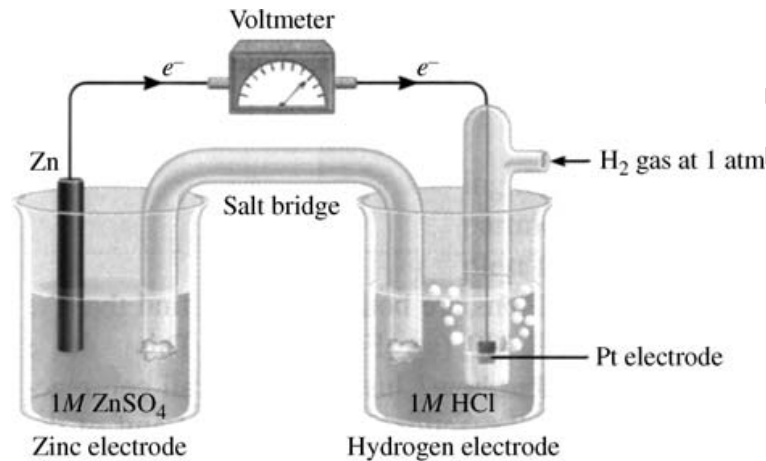
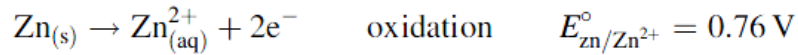
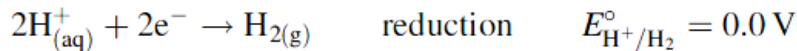


Figure 1.3 An electrochemical cell consisting of zinc and hydrogen electrodes

At the Pt electrode



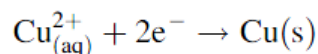
When $\text{Zn}^{2+} = 1 \text{ M}$, $\text{H}^+ = 1 \text{ M}$, $\text{H}_2(\text{g})$ at 1 atm (i.e., standard state conditions) the emf of the cell = 0.76 V at 25°C.

$$E_{\text{cell}}^{\circ} = E_{\text{ox}}^{\circ} + E_{\text{red}}^{\circ}$$

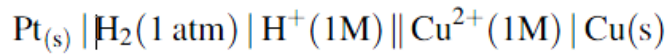
$$E_{\text{cell}}^{\circ} = E_{\text{zn}/\text{zn}^{2+}}^{\circ} + E_{\text{H}^+/\text{H}_2}^{\circ}$$

$$0.76 = E_{\text{zn}/\text{zn}^{2+}}^{\circ} + 0$$

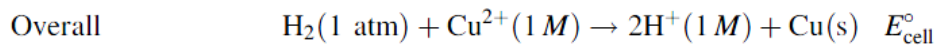
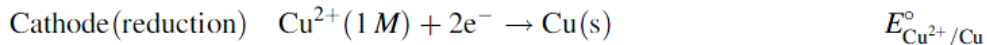
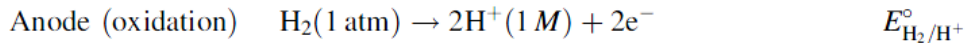
The standard oxidation potential of zinc = 0.76 V. The overall reaction is the sum of oxidation and reduction potentials (see Figure 1.3). The standard electrode potential can be obtained by connecting a hydrogen electrode system to a copper electrode system through a U-bridge and a voltmeter, as shown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



For this system the cell diagram may be written as:



The half-cell reactions are:



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

$$E_{\text{cell}}^\circ = E_{\text{H}_2/\text{H}^+}^\circ + E_{\text{Cu}^{2+}/\text{Cu}}^\circ$$

$$0.34 \text{ V} = 0 + E_{\text{Cu}^{2+}/\text{Cu}}^\circ$$

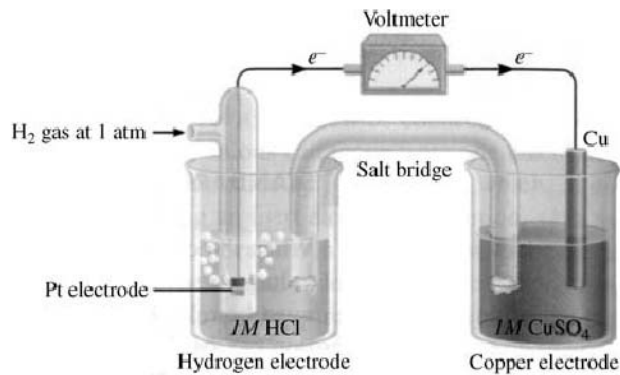
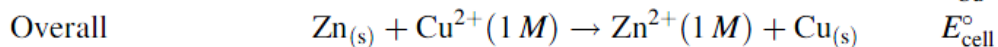
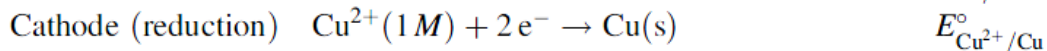
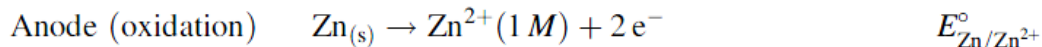


Figure 1.4 An electrochemical cell consisting of copper and hydrogen electrodes

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

Now we consider the Daniel cell:



The emf of the cell

$$E_{\text{cell}}^\circ = E_{\text{Zn}/\text{Zn}^{2+}}^\circ + E_{\text{Cu}^{2+}/\text{Cu}}^\circ$$

$$= 0.76 \text{ V} + 0.34 \text{ V} = 1.10 \text{ V}$$

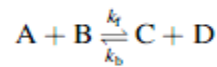
Thermodynamics:

The science of energy changes, has been widely applied to corrosion studies for many years, it determine whether or not corrosion is theoretically possible.

The driving force for chemical reactions has been expressed in thermodynamic treatments as the balance between the effect of energy (enthalpy) and the effect of probability is called entropy.

Thermodynamics deals with energy and its changes in reactions. Reactions are viewed in terms of changes in free energy. According to the first law of thermodynamics energy can be neither created nor destroyed. The second law states that the free energy is released from the system to surroundings in all spontaneous changes. Corrosion reactions are spontaneous and are governed by the laws of thermodynamics.

Consider the reaction:



where k_f is the forward reaction rate constant and k_b the rate constant for the backward reaction. From the point of view of transition state theory, A and B react to form an activated complex (A...B), which leads to the products C and D, depending upon energetically favourable conditions. The energy profile of the reaction is represented in Figure 1.1.

Entropy : the idea of entropy has been expressed as thermodynamic probability and is defined as the number of ways in which microscopic particles can be distributed among states accessible to them. The thermodynamic probability is an extensive quantity and is not mathematical probability that ranges between 0 and 1.

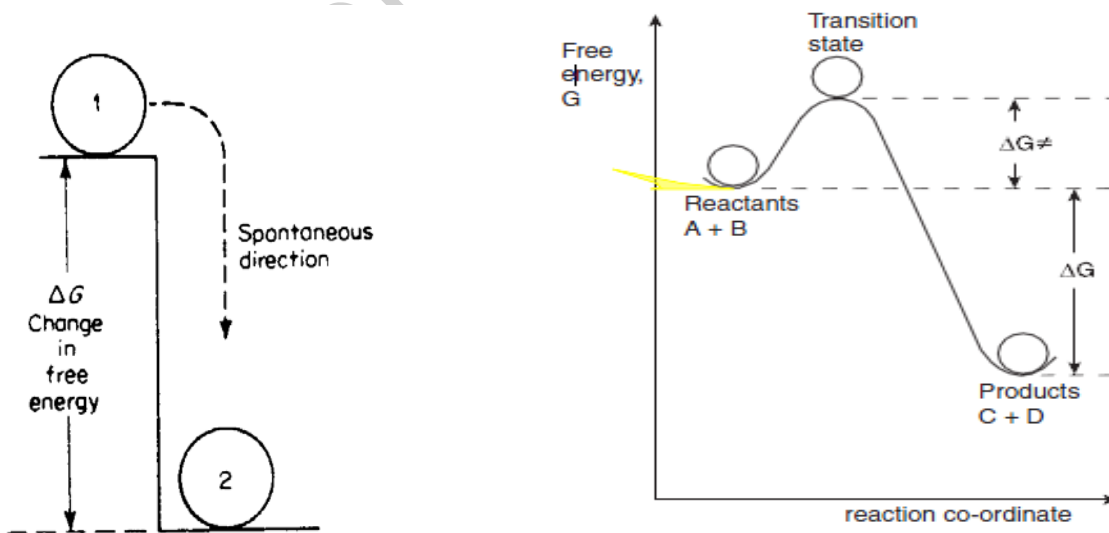


Figure 1.1 Energy profile of a reaction

Consideration is spontaneous, and the transition state with the complex (A...B) reaches lower energy by giving C and D.

$$\text{Rate of forward reaction} = k_f [A] [B]$$

$$\text{Rate of reverse reaction} = k_b [C] [D]$$

At equilibrium we have $k_f [A] [B] = k_b [C] [D]$

$$K = \frac{k_f}{k_b} = \frac{[C] [D]}{[A] [B]}$$

When $k_f > k_b$ we have a large value for K and the forward reaction is predominant and the reverse reaction is negligible. On the other hand when $k_f < k_b$ the reverse reaction is favoured and the value of K is very small.

From thermodynamics we have the relationship between free energy and equilibrium constant for a reaction:

$$\Delta G^\circ = -RT \ln K$$

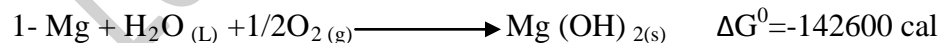
$$\Delta G^\circ = -2.303 RT \log K$$

Free Energy

The change in free energy ΔG is a direct measure of the work capacity or maximum electric energy available from a system. If the change in free energy accompanying the transition of a system from one state to another is negative, this indicates a loss in free energy and also the spontaneous reaction direction of the system. That is, if no external forces act on the system, the system will tend to transform to its lowest energy state. If the change in free energy is positive, this indicates that the transition represents an increase in energy, and this requires that additional energy be added to the system. These principle are illustrated in the figure by a mechanical analogy. The transition from position (1) to position(2) is the spontaneous direction for this particular system (represents a decrease in free energy)

Free Energy Change

The tendency for any chemical reaction to go, including the reaction of a metal with its environment, is measured by Gibbs free energy change (ΔG). The more negative the value of ΔG , the greater is the tendency for the reaction to go. For example:-



The reaction tendency of (2) is less than that of (1)

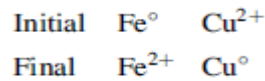


The free energy is positive, indicating that the reaction has no tendency to go at all, and gold correspondingly, does not corrode in aqueous media to form Au(OH)₃.

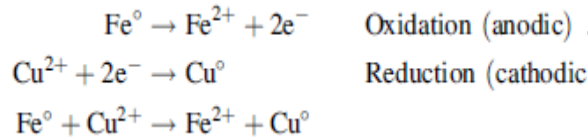
The driving force for chemical reaction depends not only on the chemical formula of species involved but also on the activities of the reactants and products. Free energy is a thermodynamic property that has been assigned to express the resultant enthalpy of a substance and its inherent probability. At constant temperature, free energy can be expressed as:

Nernst equation

Consider the system in which metallic iron is immersed in a solution of copper sulfate. In course of time metallic copper begins to appear. This process is known as a cementation reaction. The species present initially and after a lapse of time are as follows:



Then, we may write the reactions occurring as:



The equilibrium constant K and the free energy change in the overall cementation reaction may be written as:

$$\Delta G = \Delta G^\circ + RT \ln \frac{[\text{Fe}^{2+}][\text{Cu}^o]}{[\text{Fe}^o][\text{Cu}^{2+}]}$$

Since the corrosion of iron in copper sulfate solution involves an oxidation and reduction reactions with exchange of electrons, the reaction must involve an electrochemical potential difference, related to the equilibrium constant. This relationship may be written as:

$$\Delta G = -nFE$$

and is known as the Faraday's law. Here F (the Faraday) = 96 494 coulombs, E is the potential difference, n, the number of electrons transferred. Under standard state conditions,

$$\Delta G^\circ = -nFE^\circ$$

Neglecting solids we may write, for the reaction of iron in copper sulfate solution

$$-nFE = -nFE^\circ + RT \ln \frac{[\text{Fe}^{2+}]}{[\text{Cu}^{2+}]}$$

Division by $-nF$ leads to:

$$E = E^\circ - \frac{RT}{nF} \ln \frac{[\text{Fe}^{2+}]}{[\text{Cu}^{2+}]}$$

In general terms:

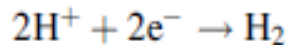
$$E = E^\circ - \frac{RT}{nF} \ln \frac{[\text{Products}]}{[\text{Reactants}]}$$

Converting to log and $T = 298$, and inserting numerical F ; R values:

$$E = E^\circ - \frac{0.059}{n} \log \frac{[\text{Products}]}{[\text{Reactants}]}$$

This equation is known as the ***Nernst equation***, and is extensively used in electrochemical measurements. Under equilibrium conditions $E = E^\circ$ and the experimentally obtained values of E° are tabulated in the literature. E° values can be used to determine whether a reaction will occur or not.

Having established the criterion for the reaction, such as oxidation of a metal, in terms of the oxidation potential value and its sign and magnitude, it is useful to learn as to how these potentials are experimentally determined. The oxidation potentials are obtained by measuring against a standard hydrogen electrode, consisting of a platinum electrode immersed in 1 M HCl with hydrogen gas at 1 atmosphere pressure passing through it. The standard hydrogen electrode is assigned a value of 0.0 for the reaction



and the measured potential of the metal in question, say copper or zinc, is obtained with respect to the standard hydrogen electrode.

This is "Nernst equation" which expresses the emf of the cell in term of activity of product and reactant.

*The activity of dissolved substance is equal to its concentration in moles per thousand grams (molality) of water multiplied by correction factor (γ) called activity coefficient.

$$\gamma = f(T, C)$$

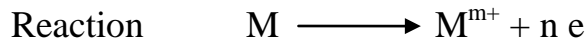
*If the substance is a gas its activity is equal to its fugacity

*The activity of pure substance (Solid) = 1

*The activity of water = 1 [concentration throughout the reaction is constant]

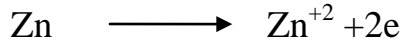
Example 1 :-

Metal / Metal ion half cells



$$\text{Nernst equation} \quad E_{\text{M}/\text{M}^{m+}} = E_{\text{M}/\text{M}^{m+}}^0 + \frac{R T}{n F} \ln a_{\text{M}^{m+}}$$

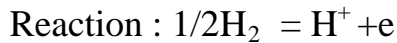
i.e



$$E_{\text{Zn}/\text{Zn}^{+2}} = E_{\text{Zn}/\text{Zn}^{+2}}^0 + \frac{59}{n} \log a_{\text{Zn}^{+2}}$$

$$E_{\text{Zn}/\text{Zn}^{+2}} = -763 + \frac{59}{2} \log a_{\text{Zn}^{+2}}$$

Example 2 :- Hydrogen electrode



$$E_{\text{H}_2/\text{H}^+} = E_{\text{H}_2/\text{H}^+}^0 + 59 \log \frac{a_{\text{H}^+}}{P_{\text{H}_2}^{1/2}}$$

$$= 0 + 59 \log a_{\text{H}^+} - \frac{59}{2} \log P_{\text{H}_2}$$

$$E_{\text{H}_2/\text{H}^+} = -59 \text{ pH} - 29.5 \log P_{\text{H}_2}$$

Example 3 :- Oxygen Electrode



$$E_{\text{OH}^-/\text{O}_2} = E_{\text{OH}^-/\text{O}_2}^0 + 59 \log \frac{P_{\text{O}_2}^{1/4}}{a_{\text{OH}^-}}$$

$$E_{\text{OH}^-/\text{O}_2} = E_{\text{OH}^-/\text{O}_2}^0 + \frac{59}{4} \log P_{\text{O}_2} - 59 \log a_{\text{OH}^-}$$

$$= +401 + \frac{59}{4} \log P_{\text{O}_2} - 59 \log a_{\text{OH}^-}$$

Since $(a_{\text{OH}^-}) (a_{\text{H}^+}) = 10^{-14}$

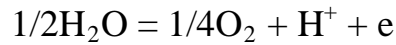
$$E_{\text{OH}^-/\text{O}_2} = E_{\text{OH}^-/\text{O}_2}^0 + 15 \log P_{\text{O}_2} - 59 \log \frac{10^{-14}}{a_{\text{H}^+}}$$

$$= 1229 - 59 \text{ pH} + 15 \log P_{\text{O}_2}$$

This expression can be written as:-

$$E = 1229 + 59 \log P_{O_2}^{1/4} a_{H^+}$$

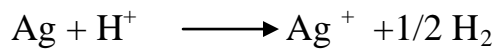
Which corresponds to the reaction:



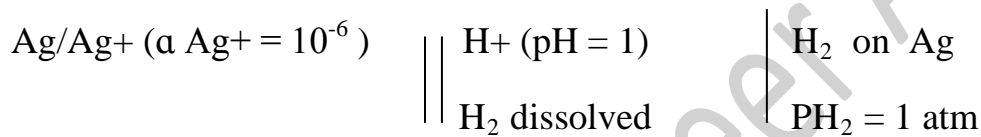
With $E_{OH^-/O_2}^0 = +1229$ mv (SHE)

Example 4:-

Determine the thermodynamic tendency for silver to corrode in a deaerated acid solution of pH = 1.0 Assume $a_{Ag^+} = 10^{-6}$ and $P_{H_2} = 1$ atm . [$E_{Ag^+/Ag}^0 = 799$ mv]



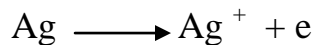
Cell representation and calculation:-



LHE

RHE

At LHE



$$\begin{aligned} E_{Ag/Ag^+} &= E_{Ag^+/Ag}^0 + \frac{59}{1} \log 10^{-6} \\ &= 799 + 59 \log 10^{-6} \\ &= 445 \text{ mv} \end{aligned}$$

At RHE



$$\begin{aligned} E_{H_2/H^+} &= E_{H_2/H^+}^0 + \frac{59}{1} \log \frac{a_{H^+}}{(P_{H_2})^{1/2}} \\ &= 0 + 59 \log a_{H^+} \\ &= -59 \text{ pH} = -59 \text{ mv} \end{aligned}$$

$$E_{\text{cell}} = E_{\text{RHE}} - E_{\text{LHE}}$$

$$E_{\text{cath}} - E_{\text{anod}} \\ = -59 - 445 = -504 \text{ mv}$$

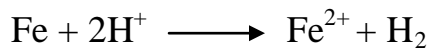
$$\Delta G = -nF E_{\text{cell}}$$

$$\Delta G = + \quad \text{silver will not corrode}$$

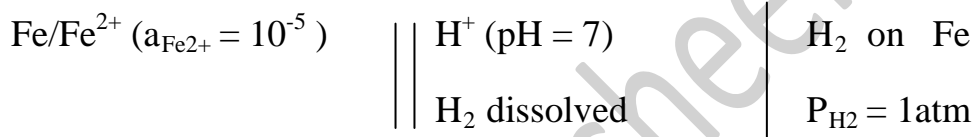
Example 5 :-

Determine the tendency for iron to corrode in deaerated water. Assume $a_{\text{Fe}^{2+}} = 10^{-5}$, $\text{pH} = 7$, and $P_{\text{H}_2} = 1 \text{ atm}$ ($E_{\text{Fe}^0/\text{Fe}^{2+}}^0 = -440 \text{ mv}$)

Cell reaction



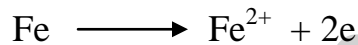
Cell representation and calculation:-



LHE

RHE

At LHE



$$E_{\text{Fe}/\text{Fe}^{2+}} = E_{\text{Fe}/\text{Fe}^{2+}}^0 + \frac{59}{2} \log a_{\text{Fe}^{2+}} \\ = -440 + \frac{59}{2} \log 10^{-5} \\ = -558 \text{ mv (SHE)}$$

At RHE

$$E_{\text{H}_2/\text{H}^+} = 0 + \frac{59}{1} \log a_{\text{H}^+} \\ = -59 \text{ pH} = -59 (7) = -413 \text{ mv (SHE)}$$

$$E_{\text{cell}} = E_{\text{cath}} - E_{\text{anod}} = -413 - (-558) = +175 \text{ mv}$$

$$\Delta G \text{ (negative)} \quad \text{iron will corrode}$$

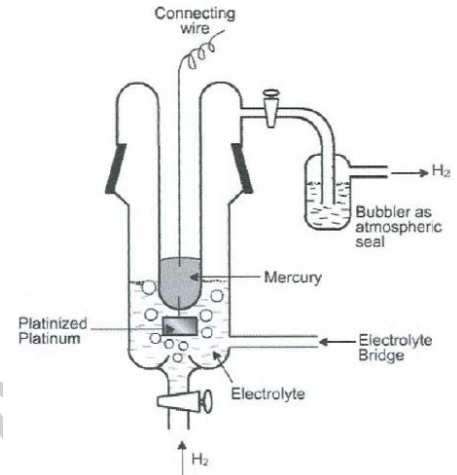
Reference Electrodes

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.

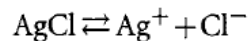
The electrode consists of a platinum wire immersed in a solution (Fig. 2.10) containing hydrogen ions and saturated with hydrogen gas. Platinum is immersed completely in aqueous arsenic free hydrochloric acid, and hydrogen gas free from oxygen and carbon monoxide is bubbled to the platinum surface.

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.



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:



$$E^0 = 0.25 \text{ V}$$

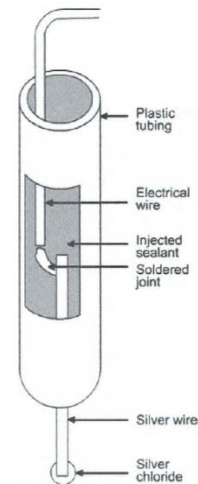
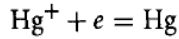


Figure 2.12 Silver-Silver chloride reference electrode

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).



The overall equilibrium is expressed by:

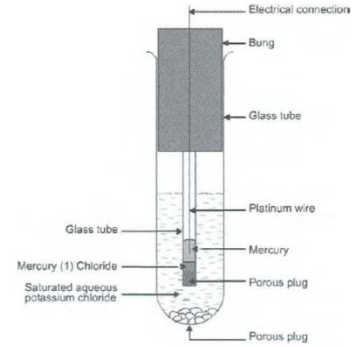
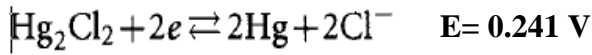


Figure 2.13 A saturated calomel reference electrode

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).

$$E^0 = 0.3 \text{ V}$$

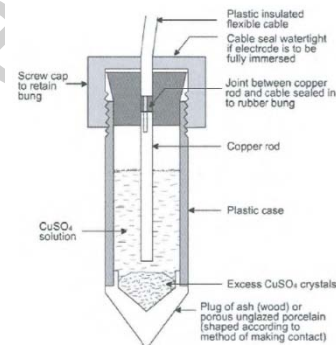


Figure 2.14 Reference copper-copper sulfate electrode



Convert from reference electrode

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

Example1:

A potential of metal A is -0.17 SHE, determine its potential verses SCE, Pb/PbCl₂, Cu/CuSO₄, Zn/ZnCl₂, Ag/AgCl.

Sol.:

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

$$-0.17 = E + 0.24$$

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

So that:

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

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

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

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

Example 2:

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

First of all, convert the potential to SHE

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

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

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

$$-0.44 = E_m + 0.25$$

$$E = -0.19 \text{ V (Ag/AgCl)}$$

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

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

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

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

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

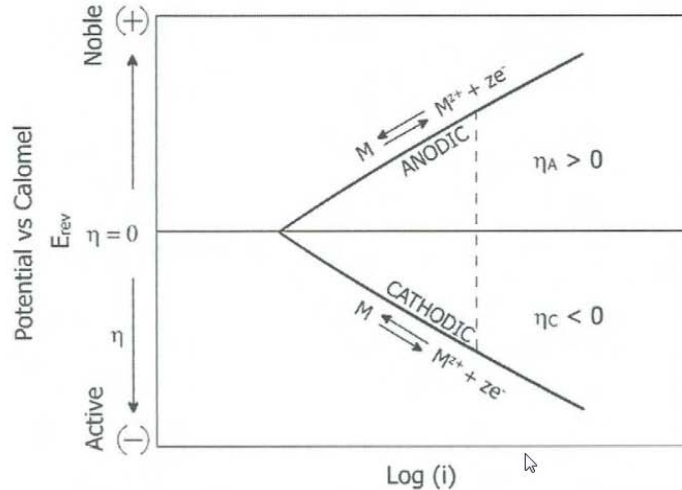
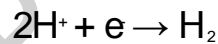


Figure 3.6 Polarization diagram (reversible electrode)

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:

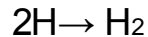


For this reaction, the polarization is called hydrogen over-potential

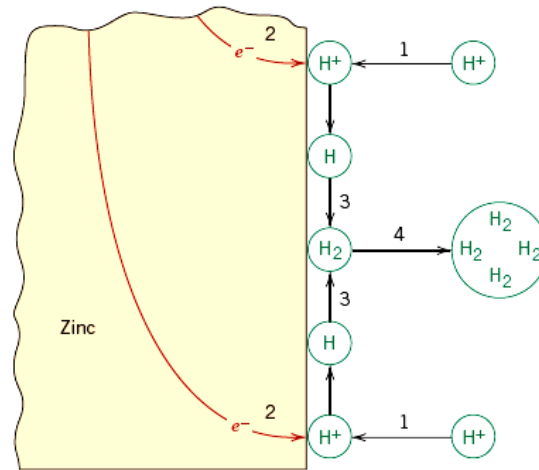
Over-potential is defined as the polarization (potential change) of an equilibrium electrode that results from current flow across the electrode-solution interface.

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-combining of two hydrogen atoms to form a molecule of hydrogen



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

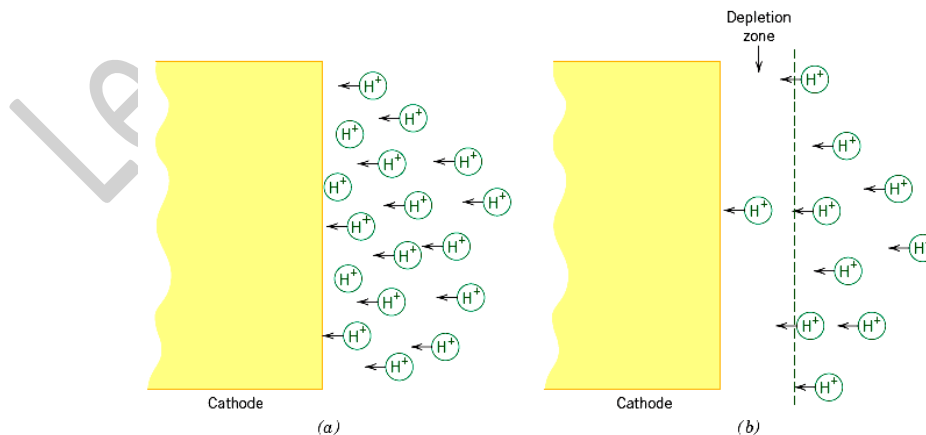


Factors affecting activation polarization

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

Concentration polarization

Consider the hydrogen evolution reaction at low reduction rate the distribution of hydrogen ions in the solution adjacent to the electrode surface is relatively uniform, while at high reduction rate the region adjacent to the electrode surface will become depleted of hydrogen



Effect of various factors on concentration polarization

- 1-Agitation. By agitation, the thickness of the diffusion layer is decreased, and the rate of diffusion of ions increases. There is no build up of any concentration gradient between the corroding surface and bulk electrolyte. The end result is a decrease in concentration polarization and an increase in the rate of corrosion. As the rate of agitation is increased the corrosion potential shifts in the noble direction because of a decrease in cathodic overpotential caused by concentration polarization.
- 2-Temperature. As the temperature rises, the thickness of diffusion layer is decreased and the corrosion current is increased.
- 3-Velocity. The higher the velocity, the less is concentration polarization. At a sufficiently high velocity, concentration polarization becomes zero because the ionic flux is now sufficient to maintain the surface concentration of ions at the electrode/electrolyte surface equal to the bulk concentration

Combined polarization

Both activation and concentration polarization usually occur at an electrode, at low reaction rates activation usually controls, whereas at higher concentration becomes controlling .the total polarization of an electrode is the sum of them as below>

$$\eta_t = \eta_c + \eta_a$$

