Chapter 5

Electrochemistry and Metallic Corrosion

Electrochemistry, the area of chemistry concerned with the interconversion of chemical and electrical energy, is enormously important in modern science and technology not only because of batteries but also because it makes possible the manufacture of essential industrial chemicals and materials.

5.1. Galvanic Cells

In a galvanic cell, if you immerse a strip of zinc metal in an aqueous solution of copper sulfate, you find that a dark colored solid deposits on the surface of the zinc and that the blue color characteristic of the Cu^{+2} ion slowly disappears from the solution

Figure (5.1) the redox reaction of zinc metal with aqueous Cu^{+2} ions

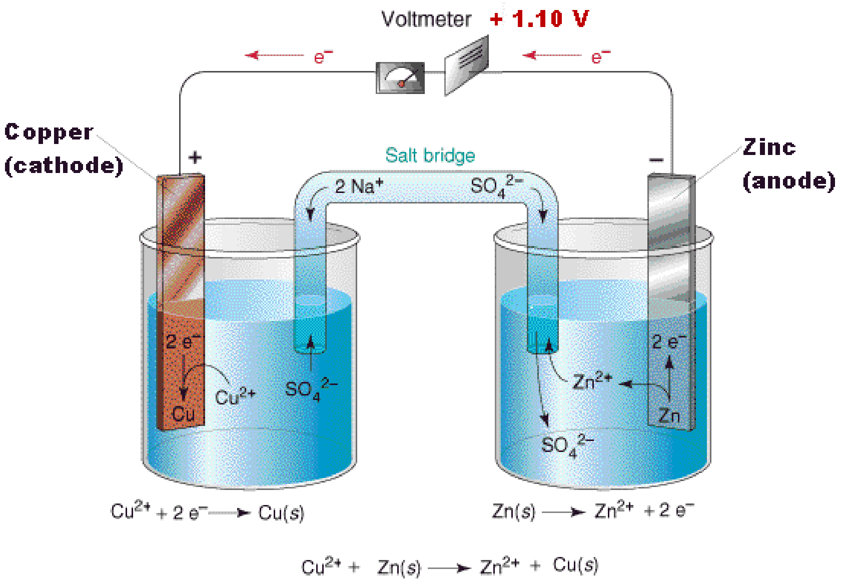
Figure (5.1). Chemical analysis shows that the dark colored deposit consists of tiny particles of copper metal and that the solution now contains zinc ions. Therefore, the reaction is

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

This is redox reaction in which Zn is oxidized to Zn^{2+} and Cu^{2+} is reduced to Cu. Recall that an **oxidation is a loss of electrons (increase in oxidation number)** and **reduction is a gain of electrons (a decrease in oxidation number).** We can represent the oxidation and reduction aspects of the reaction by separating the overall process into half-reactions, one representing the oxidation reaction and the other representing the reduction:

Oxidation half-reaction $Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$

Reduction half -reaction $Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$



Figure(5.2): A Daniell cell, an example of a galvanic cell

We say that **Cu^{2+} is the oxidizing agent because, in gaining electrons from Zn, it causes the oxidation of Zn to Zn^{2+}.** Similarly, we say that **Zn is the reducing agent because, in losing electrons to Cu^{+2}, it causes the reduction of Cu^{2+} to Cu.**

The apparatus shown in Figure (5.2) is a type of galvanic cell called a Daniell cell, the English chemistry who first constructed it in 1836. It consists of two separate half-cells, a beaker containing a strip of zinc that dips into an aqueous solution of zinc sulfate and a second beaker containing a strip of copper that dips into aqueous copper sulfate **the strips of zinc and copper are called electrodes** and are connected by an electrically conducting wire. In addition, the two solutions are connected by **a salt bridge, a U- shaped tube that contains a gel permeated with solutions of an inert electrolyte, such as Na_2SO_4.** The ions of the inert electrolyte do not react with the other ions in the solutions, and they are not oxidized or reduced at the electrodes.

The reaction that occurs in the Daniell cell is the same one that occurs when Zn reacts directly with Cu^{2+}, but now, because the Zn metal and Cu^{2+} ions are in separate compartments, the electrons are transferred from Zn to Cu^{2+} through the wire. Consequently, the oxidation and reduction half- reactions occur at separate electrodes and an electric current flow through the wire. Electrons are not transferred through the solution because of the metal wire is a much better conductor of electrons than is water.

The electrode at which oxidation takes place called the anode (zinc strip in this example), and **the electrode at which a reduction takes place is called cathode** (the copper strip). The anode and cathode half-reactions must add to give the overall cell reaction:

Anode (oxidation) half – reaction: $Zn_{(s)} \rightarrow Zn^{2+}_{(aq)} + 2\,e^{-}$

Cathode (reduction) half- reaction: $Cu^{2+}_{(aq)} + 2e^{--} \rightarrow Cu_{(s)}$

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

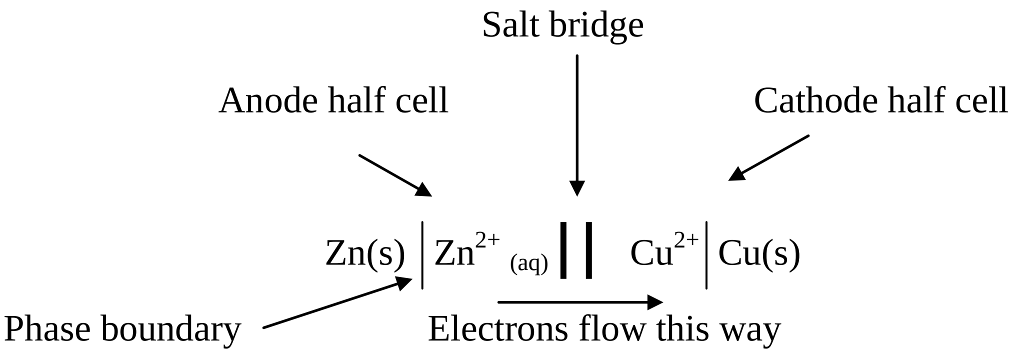
The salt bridge is necessary to complete the electrical circuit. Without it, the solution in the anode compartment would become positively charged as Zn^{2+} ions appeared in it, and the solution in the cathode compartment would become negatively charged as Cu^{2+} ions were removed from it. Because of the charge imbalance, the electrode reactions would quickly come to a halt and electron flow through the wire would cease.

Anode

- Is where oxidation occurs
- Is where electrons are produced
- Is what anions migrate toward
- Has a negative sign

Cathode

- Is where reduction occurs
- Is where electrons are consumed
- Is what cations migrate toward
- Has a positive sign



For the cell shown in Figure (5.2) Na^+ ions move out of the salt bridge into the cathode compartment and Zn^{2+} ions moves into the salt bridge from the anode compartment.

5.2. Cell Potentials

Let's return to the Daniell cell in Figure (5.2) to find an electrical measure of the tendency for a cell reaction to occur. Electrons move through the external circuit from the zinc anode to the copper cathode , **the force that pushes the negativity charged electrons away from anode (- electrode) and pulls them toward the cathode (+ electrode) is an electrical potential called the electromotive force (emf), also known as the cell potential (E) or the cell voltage.**

$$\mathbf{E = E_{cathode} - E_{anode}}$$

The SI unit of electrical potential is volt (V), and the potential of a galvanic cell is defined as a positive quantity. The relation between volt and SI units of energy (Joule, J), and electric charge (Coulomb, C) is given by the equation

$$1J = 1C \times 1V$$

Where $1W = 1J/sec = (1C \times 1V)/sec = 1A \times 1V$

If both electrodes are in their standard states **" solution at 1M concentration, gases at a partial pressure of 1 atm, solids and liquids in pure form, at 25 C" the cell potential called standard cell potential.**

$$Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s) \qquad E^0 = 1.10\ V$$

For example, E^0 is the cell potential measured at 25 C for a cell that has pure Zn and Cu metal electrodes and 1M concentrations of Zn^{2+} and Cu^{2+}

5.3. Standard Electrode Potential

Consider, for example, a cell in which H_2 gas is oxidized to H^+ ions at the anode and Cu^{2+} ions are reduced to copper metal at the cathode.

Anode (oxidation) $H_2(g) \rightarrow 2H^+(aq) + 2e^-$

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

Overall cell reaction $H_2(g) + Cu^{2+}_{(aq)} \rightarrow 2H^+_{(aq)} + Cu(s)$

The standard potential for this cell, 0.37 V at 25 C, measures the sum of the reaction tendencies of the oxidation and reduction half- reactions:

It's not possible to measure the potential of a single electrode; we can measure only a potential difference by placing a voltmeter between two electrodes.

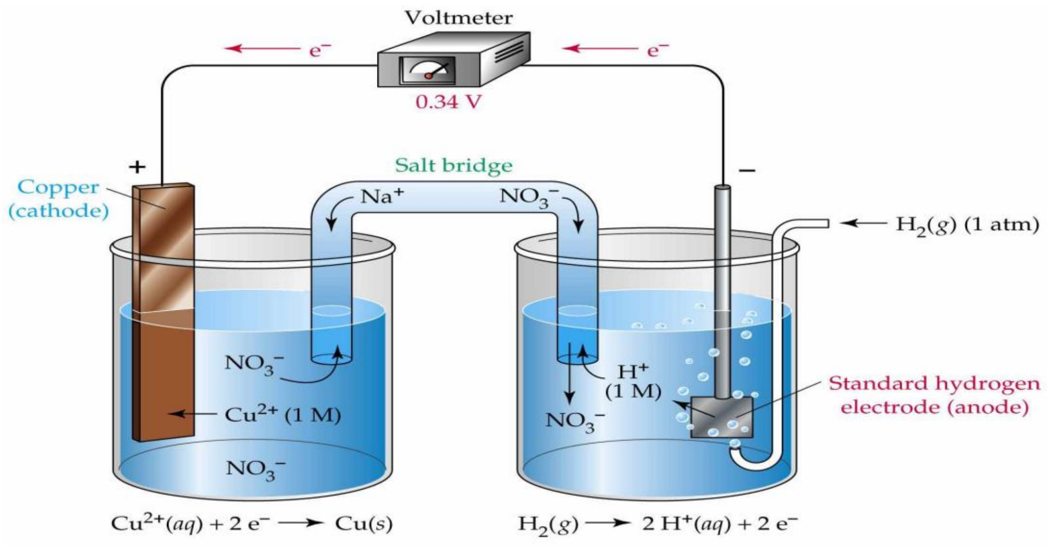


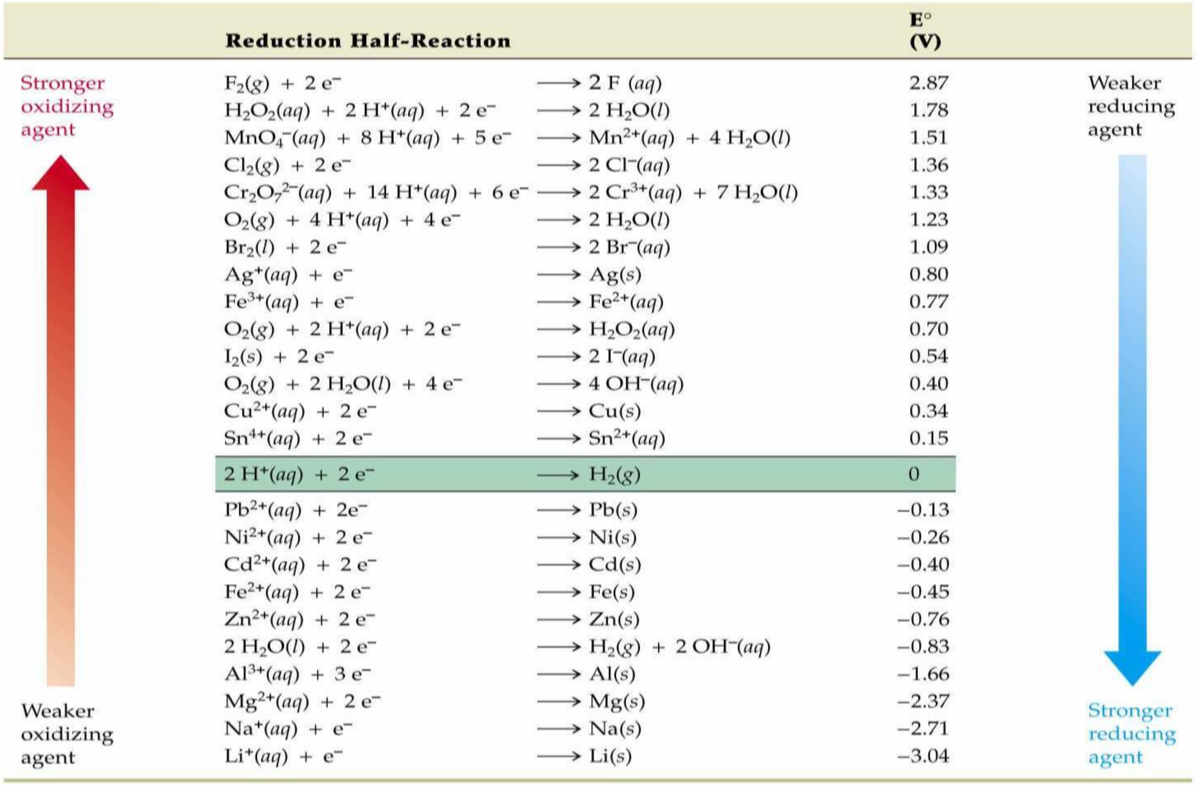
Figure (5.3): Standard hydrogen electrode

The chemists have chosen a reference half-cell called **Standard hydrogen electrode (S.H.E), shown in Figure (5. 3) it consists of a platinum electrode in contact with H_2 gas and aqueous H^+ ions at standard- state condition [1 atm H_2(g), 1 M $H^+_{(aq)}$, 25 C], is assigned an arbitrary potential of exactly 0 V.**

$$\underset{\underset{0.34\ V}{\uparrow}}{E^0_{Cell}} = \underset{\underset{0V}{\uparrow}}{E^0_{H2\rightarrow H+}} + \underset{\underset{0.34\ V}{\uparrow}}{E^0_{Cu2+\rightarrow Cu}} = 0.34\ V$$

We can determine standard potentials for other half-cells simply by constructing galvanic cells in which each half-cell of interest is paired up with S.H.E. From experiments of the sort just described, hundreds of half –cell potentials have been determined. A short list is represented in Table (5.1), the list half-cell potentials are **standard electrode potentials "electrode potential at standard condition"**

Table (5.1): Standard reduction potential at 25 C



	Reduction Half-Reaction		E° (V)	
Stronger oxidizing agent	$F_2(g) + 2e^-$	$\longrightarrow 2\ F\ (aq)$	2.87	Weaker reducing agent
	$H_2O_2(aq) + 2H^+(aq) + 2e^-$	$\longrightarrow 2H_2O(l)$	1.78	
	$MnO_4^-(aq) + 8H^+(aq) + 5e^-$	$\longrightarrow Mn^{2+}(aq) + 4H_2O(l)$	1.51	
	$Cl_2(g) + 2e^-$	$\longrightarrow 2Cl^-(aq)$	1.36	
	$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^-$	$\longrightarrow 2Cr^{3+}(aq) + 7H_2O(l)$	1.33	
	$O_2(g) + 4H^+(aq) + 4e^-$	$\longrightarrow 2H_2O(l)$	1.23	
	$Br_2(l) + 2e^-$	$\longrightarrow 2Br^-(aq)$	1.09	
	$Ag^+(aq) + e^-$	$\longrightarrow Ag(s)$	0.80	
	$Fe^{3+}(aq) + e^-$	$\longrightarrow Fe^{2+}(aq)$	0.77	
	$O_2(g) + 2H^+(aq) + 2e^-$	$\longrightarrow H_2O_2(aq)$	0.70	
	$I_2(s) + 2e^-$	$\longrightarrow 2I^-(aq)$	0.54	
	$O_2(g) + 2H_2O(l) + 4e^-$	$\longrightarrow 4OH^-(aq)$	0.40	
	$Cu^{2+}(aq) + 2e^-$	$\longrightarrow Cu(s)$	0.34	
	$Sn^{4+}(aq) + 2e^-$	$\longrightarrow Sn^{2+}(aq)$	0.15	
	$2H^+(aq) + 2e^-$	$\longrightarrow H_2(g)$	0	
	$Pb^{2+}(aq) + 2e^-$	$\longrightarrow Pb(s)$	−0.13	
	$Ni^{2+}(aq) + 2e^-$	$\longrightarrow Ni(s)$	−0.26	
	$Cd^{2+}(aq) + 2e^-$	$\longrightarrow Cd(s)$	−0.40	
	$Fe^{2+}(aq) + 2e^-$	$\longrightarrow Fe(s)$	−0.45	
	$Zn^{2+}(aq) + 2e^-$	$\longrightarrow Zn(s)$	−0.76	
	$2H_2O(l) + 2e^-$	$\longrightarrow H_2(g) + 2OH^-(aq)$	−0.83	
	$Al^{3+}(aq) + 3e^-$	$\longrightarrow Al(s)$	−1.66	
	$Mg^{2+}(aq) + 2e^-$	$\longrightarrow Mg(s)$	−2.37	
	$Na^+(aq) + e^-$	$\longrightarrow Na(s)$	−2.71	
Weaker oxidizing agent	$Li^+(aq) + e^-$	$\longrightarrow Li(s)$	−3.04	Stronger reducing agent

5.4. Electrode Potential: the Nernst Equation

Electrode potentials **"potential difference between the metal and its ions in the solution"**, depend on temperature and on the composition of the reaction mixture, represented by Nernst equation

$$E = E^0 + [RT/nF] \ln [M^{n+}] \quad \text{or} \quad E = E^0 + [2.303\ RT/nF] \log [M^{n+}]$$

$$E = E^0 + [0.0592/n] \log [M^{n+}] \text{ …….at 25C}$$

Where

E …………Electrode potential, Volt

E^0………...Standard electrode potential, Volt

n………….Number of electron gained or lost

R………... Universal gas constant, 8.31 volt. Coulomb/ mol.K

T……….. Temperature, K

F……… Faraday's constant, 96500 coulomb

$[M^{n+}]$…….Solution concentration by molar

Example (1): - Calculate the electrode potential and the electromotive force of the following cell; Zn/Zn^{2+} (0.1 M) // Cu^{2+}(0.1M) /Cu, E^0_{Zn} =-0.76 V, E^0_{Cu}=+0.34 V.

Solution:-

Oxidation **$Zn \rightarrow Zn^{2+} + 2e$ (Anode)**

Reduction **$Cu^{2+} + 2e \rightarrow Cu$ (Cathode)**

$$E\,Zn_{(anode)} = E^O + \tfrac{0.059}{n}\log[M^{n+}] = (-0.76) + \tfrac{0.059}{2}\log[0.1]$$

$$E\,Cu_{(cathode)} = E^O + \tfrac{0.059}{n}\log[M^{n+}] = (+0.34) + \tfrac{0.059}{2}\log[0.1]$$

$$\text{e.m.f.} = E_{cathode} - E_{anode} = (+0.31) - (-0.79) = 1.1 \text{ V}$$

Example (2): Calculate the e.m.f (electro motive force) of the following cell:

$Zn / Zn^{2+} (0.01M) // Zn^{2+} (0.1M)/ Zn$ where $E^o_{zn} = -0.76V$

Solution:

Oxidation: $Zn \qquad\qquad Zn^{2+} + 2e$ (Anode)

Reduction: $Zn^{2+} + 2e \qquad\qquad Zn$ (Cathode)

$$E\,Zn_{(anode)} = E^O + \frac{0.059}{n}\log[M^{n+}] = (-0.76) + \frac{0.059}{2}\log[0.01] = -0.82\,volt$$

$$E\,Zn_{(cathode)} = E^O + \frac{0.059}{n}\log[M^{n+}] = (-0.76) + \frac{0.059}{2}\log[0.1] = -0.79\,volt$$

e.m.f. = $E_{cathode} - E_{anode} = (-0.79) - (-0.82) = +0.03$ V

5.5. Corrosion

Corrosion is the breaking down or destruction of a material especially a metal, through chemical reactions. The most common form of corrosion is rusting, which occurs when iron combines with oxygen and water. To prevent corrosion, we first have to understand how it occurs and different types of corrosion.

5.5. 1. Corrosion prevention

Corrosion Control Corrosion can be controlled by the following ways:

- Proper material selection; materials are selected to have the least corrosion rates in the given medium like stainless steels.
- Improving the design of some equipment; like avoiding sharp bends, galvanic couple
- Coating to protect the outer surface by; metallic coating like chromium, inorganic coating like phosphate, Organic coating like rubber ,water soluble coatings, high solid coating , powder coatings and PVC and polyurethane
- Alteration the environment; lowering the temperature, decreasing the velocity, and altering pH
- Adding the inhibitors; are substances add by small concentration like amines interrupting the chemical reaction that causes corrosion. Major use for corrosion inhibitors are petroleum refining, oil and gas exploration, chemical production and water treatment facilities.
- Cathodic protection:
    - Sacrificial anode: - Sacrificial Anodes are highly active metals that are used to prevent a less active material surface from corroding. sacrificial anodes are generally made of zinc, Aluminum, Magnesium

- Impressed current: - These consist of anodes connected to a DC power source; the negative terminal of current source is connected to the metal while the positive terminal is attached to an auxiliary anode. This method is often used to protect buried pipelines and ship hulls