Electrochemistry - Part 1

Objectives

After going through this lesson, the learners will be able to understand the following:

- Describe an electrochemical cell and differentiate between galvanic and electrolytic cell.
- Comprehend the production of electricity and the spontaneous chemical reaction.
- Construct a galvanic or voltaic cell and write the chemical equation for the redox half reactions taking place at the anode and the cathode.

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Introduction

The study of electricity produced from energy released in spontaneous chemical reactions and the use of this energy for non-spontaneous chemical reactions to occur is called Electrochemistry. Refining of a large number of metals, fluorine, chlorine and sodium hydroxide etc. is primarily done by electrochemical methods. The sources of electrical energy produced by conversion of chemical energy used in various instruments and devices are fuel cells and batteries. The study of electrochemistry is significant in the present times as the energy produced is efficient, pollution free and thus eco friendly. The transmissions of sensory signals through cells to the brain and vice versa and communication between the cells have electrochemical origin. Electrochemistry is therefore, a very vast and interdisciplinary subject.

Electrochemical Cell

Daniel cell (Fig 1) converts the chemical energy liberated during the redox reaction to electrical energy and has an electrical potential equal to 1.1 V when concentration of Zn^{2+} and Cu^{2+} ions is unity (1 mol dm^{-3}). Such a device is called a galvanic or a voltaic cell.

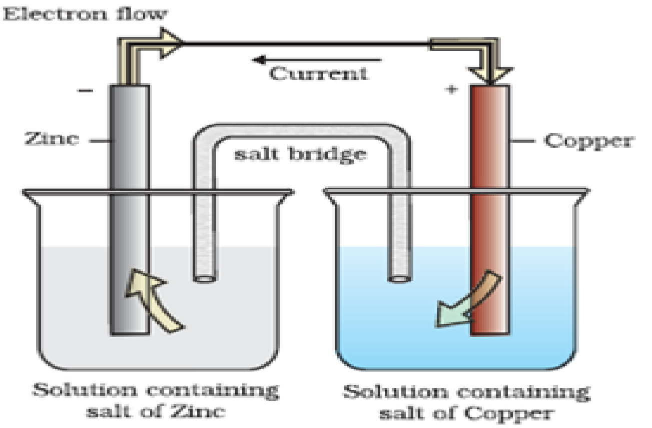
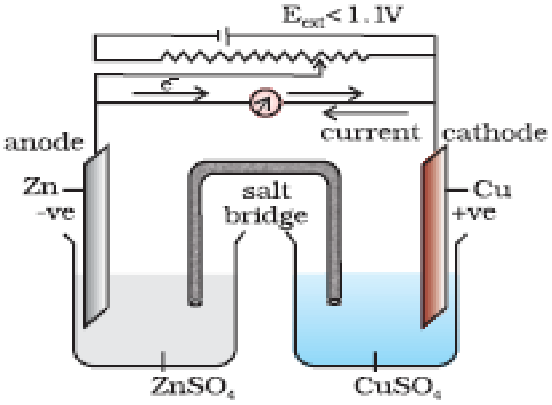


Fig. 1: Daniell cell having electrodes of zinc and copper dipping in the solutions of their respective salts.

The redox reaction of the Daniel cell is:

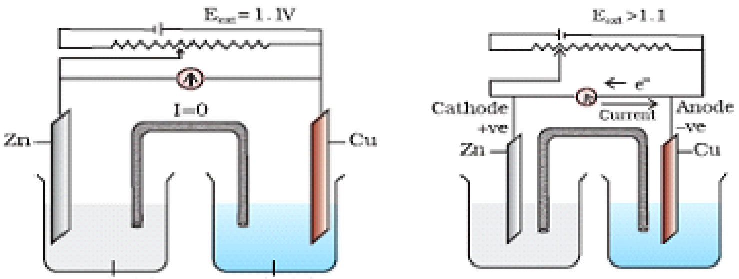
$$\mathbf{Zn\,(s) + Cu^{2+}\,(aq) \rightarrow Zn^{2+}(aq) + Cu\,(s)}$$

If an external opposite potential is applied and increased slowly [Fig. 2a], we find that the reaction continues to take place till the opposing voltage reaches the value 1.1 V [Fig. 2b], when the reaction stops altogether and no current flows through the cell. Any further increase in the external potential again starts the reaction but in the opposite direction [Fig.2c]. It now functions as an electrolytic cell, a device for using electrical energy to carry non-spontaneous chemical reactions.



When $E_{ext} < 1.1$ V
(i) Electrons flow from Zn rod to Cu rod hence current flows from Cu to Zn.
(ii) Zn dissolves at anode and copper deposits at cathode.

Fig. 2a



When $E_{ext} = 1.1V$
(i) No flow of electrons or current.
(ii) No chemical reaction.

Fig.2b

When $E_{ext} > 1.1V$
(i) Electrons flow from Cu to Zn and current flows from Zn to Cu.
(ii) Zinc is deposited at the zinc electrode and copper dissolves at copper electrode.

Fig. 2c

Fig 2: Functioning of Daniel cell when external voltage E_{ext} opposing the cell potential is applied

Both types of cells are quite important and therefore a study some of the salient features is discussed in this module.

Galvanic Cell or Voltaic Cell

A galvanic cell is also referred to as a voltaic cell. The common household battery is an example of a galvanic cell. The flow of electrons from one chemical reaction to another occurs through an outside circuit resulting in the passage of *current*. Current is measured in amperes (A) and is a measure of the number of electrons that flow past a certain point in the circuit at any given moment.

A galvanic cell is an electrochemical cell that converts the chemical energy of a spontaneous redox reaction into electrical energy. In this device the Gibbs energy of the spontaneous redox reaction is converted into electrical work which may be used for running motor or other electrical gadgets like heater, fan, geyser, etc.

Daniell cell discussed earlier is one such cell in which the following redox reaction occurs.

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

This reaction is a combination of two half reactions whose addition gives the overall cell reaction:

1. $Cu^{2+} \ + \ 2e^{-} \rightarrow Cu\,(s)$ (reduction half reaction)
2. $Zn(s) \rightarrow Zn^{2+} \ + \ 2e^{-}$ (oxidation half reaction)

These reactions occur in two different portions of the Daniell cell. The reduction half reaction occurs on the copper electrode while the oxidation half reaction occurs on the Zinc electrode.

These two portions of the cell are also called half-cells or redox couples. The copper electrode may be called the reduction half-cell and the zinc electrode, the oxidation half-cell.

Innumerable galvanic cells can be constructed on the pattern of Daniell cells by taking combinations of different half-cells. Each half cell consists of a metallic electrode dipped into an electrolyte. The two half-cells are connected by a metallic wire through a voltmeter and a switch externally. The electrolytes of the two half-cells are connected internally through a salt bridge as shown in Fig.1. The salt bridge allows movement of ions from one solution to the other and also helps maintain electrical neutrality of the solutions in the two half cells. Sometimes, both the electrodes dip in the same electrolyte solution and in such cases a salt bridge is not required.

At each electrode-electrolyte interface there is a tendency of metal ions from the solution to deposit on the metal electrode trying to make it positively charged. At the same time, metal atoms of the electrode have a tendency to go into the solution as ions and leave behind the electrons at the electrode trying to make it negatively charged. At equilibrium, there is a separation of charges and depending on the tendencies of the two opposing reactions, the electrode may be positively or negatively charged with respect to the solution. A potential difference develops between the electrode and the electrolyte which is called electrode potential. Electrode potential is expressed in units of volts (V), which is the potential energy per unit charge. Current is the movement of the electrons and is expressed in units of amperes, or amps (A). **When the concentrations of all the species involved in a half-cell is unity then the electrode potential is known as standard electrode potential**. According to IUPAC convention, standard reduction potentials are called as **standard electrode potential**s. In a galvanic cell, the half-cell in which oxidation takes place is called anode and it has a negative potential with respect to the solution. The other half-cell in which reduction takes place is called cathode and it has a positive potential with respect to the solution. Thus, there exists a potential difference between the two electrodes and as soon as the switch is in the on position the electrons flow from negative electrode to positive electrode. The direction of the flow of current is opposite to that of electron flow. Electrical potential is analogous to gravitational potential. Just as water flows from a position of higher gravitational potential to a position of lower gravitational potential, electrons flow from higher electric potential to lower electrical potential.

Electromotive Force (EMF)

The potential difference between the two electrodes of a galvanic cell is called the cell potential and is measured in volts. The cell potential is the difference between the electrode potentials (reduction potentials) of the cathode and anode. It is called the cell electromotive force (EMF) of the cell when no current is drawn through the cell. It is an accepted convention that while representing the galvanic cell, the anode is denoted on the left and the cathode on the right.

A galvanic cell is generally represented by putting a vertical line between metal and electrolyte solution and putting a double vertical line between the two electrolytes connected by a salt bridge. Under this convention the emf of the cell is positive and is given by the potential of the half-cell on the right hand side minus the potential of the half-cell on the left hand side i.e. $E_{cell} = E_{right} - E_{left}$

This is illustrated by the following example:

Half-cell reactions:

Cathode (reduction): $2Ag^{+}(aq) + 2e^{-} \rightarrow 2Ag(s)$ (Eq. 1)

Anode (oxidation): $Cu(s) \rightarrow Cu^{2+}(aq) + 2e^{-}$ (Eq. 2)

CellReaction: $Cu(s) + 2Ag^{+}(aq) \rightarrow Cu^{2+}(aq) + 2Ag(s)$ (Eq. 3)

The overall reaction (Eq. 3) is the sum of the half reactions (Eq.1) and (Eq.2) in the cell and the silver electrode acts as a cathode and copper electrode acts as an anode. The cell can be represented as: $Cu(s)|Cu^{2+}(aq)||Ag^{+}(aq)|Ag(s)$

$$E_{cell} = E_{right} - E_{left} = E_{Ag^{+}/Ag} - E_{Cu^{2+}/Cu}$$

Measurement of Electrode Potential using a SHE as the Reference Electrode:

The potential of an individual half-cell cannot be measured but only the difference between the two half-cell potentials that gives the emf of the cell can be measured. If the potential of one electrode (half-cell) is known then that of the other can be determined with respect to this.

According to convention, a half-cell called standard hydrogen electrode (Fig.3) represented by $Pt(s)|H_2(g)|H^{+}(aq)$, is assigned a zero potential at all temperatures corresponding to the reaction: $H^{+}(aq) + e^{+} \rightarrow ½ H_2(g)$

A hydrogen electrode is the standard reference electrode for measuring electrode potentials. The standard hydrogen electrode consists of a platinum electrode coated with platinum black. The electrode is dipped in an acidic solution and pure hydrogen gas is bubbled through it. The electrode surface in contact with the solution is actually a layer of hydrogen adsorbed onto the surface of the platinum. The concentration of both the reduced and oxidized forms of hydrogen is maintained at unity (Fig. 3). This implies that the pressure of hydrogen gas is one bar and the concentration of hydrogen ion in the solution is one molar.

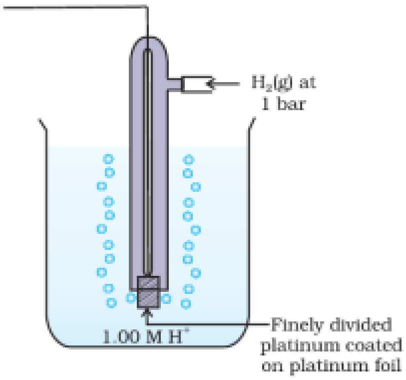


Fig 3. Standard Hydrogen electrode

At 298 K the emf of the cell, standard hydrogen electrode, the second half-cell constructed by taking standard hydrogen electrode as anode (reference half-cell) and the other half-cell as cathode, gives the reduction potential of the other half-cell. If the concentrations of the oxidized and the reduced forms of the species in the right hand half-cell are unity, then the cell potential is equal to standard electrode potential, E^o_R of the given half-cell.

$E^o = E^o_R - E^o_L = E^o_R - 0 = E^o_R$ (As E^o_L for standard hydrogen electrode is zero)

The measured emf of the cell: $Pt(s)|H_2(g, 1\ bar)|H^+(aq, 1\ M)||Cu^{2+}(aq, 1\ M)|Cu$

is 0.34 V and it is also the value for the standard electrode potential of the half-cell corresponding to the reaction :

$$Cu^{2+}(aq,\ 1M) + 2e^- \rightarrow Cu\,(s)$$

Similarly, the measured emf of the cell:

$Pt(s)|H_2(g, 1\ bar)|H^+(aq, 1\ M)||Zn^{2+}(aq, 1M)|Zn$

is -0.76 V corresponding to the standard electrode potential of the half-cell reaction:

$$Zn^{2+}(aq,\ 1\ M) + 2e^- \rightarrow Zn\,(s)$$

The positive value of the standard electrode potential in the first case indicates that Cu^{2+} ions get reduced more easily than H^+ ions. The reverse process cannot occur, that is, hydrogen ions cannot oxidise Cu (or alternatively, hydrogen gas can reduce copper ion) under the standard conditions described above. Thus, Cu does not dissolve in HCl. In nitric acid it is oxidised by nitrate ion and not by hydrogen ion. The negative value of the standard electrode potential in the second case indicates that hydrogen ions can oxidise zinc (or zinc can reduce hydrogen ions).

Sometimes metals like platinum or gold are used as inert electrodes. They do not participate in the reaction but provide their surface for oxidation or reduction reactions and for the conduction of electrons. For example, Pt is used in the following half-cells:

Hydrogen electrode: Pt(s)|H_2(g)|H^+(aq)   With half-cell reaction: $H^+ (aq) + e^- \rightarrow ½H_2$(g)

Bromine electrode: Pt(s)|Br_2(aq)|Br^-(aq)   With half-cell reaction: ½ $Br_2(aq) + e^- \rightarrow Br^-$ (aq)

Table 1 The standard electrode potentials at 298 K

Ions are present as aqueous species and H_2O as liquid; gases and solids are shown by g and s.

Reaction (Oxidised form + ne^-	$\rightarrow$ Reduced form)	$E^\ominus$/V
$F_2(g) + 2e^-$	$\rightarrow 2F^-$	2.87
$Co^{3+} + e^-$	$\rightarrow Co^{2+}$	1.81
$H_2O_2 + 2H^+ + 2e^-$	$\rightarrow 2H_2O$	1.78
$MnO_4^- + 8H^+ + 5e^-$	$\rightarrow Mn^{2+} + 4H_2O$	1.51
$Au^{3+} + 3e^-$	$\rightarrow Au(s)$	1.40
$Cl_2(g) + 2e^-$	$\rightarrow 2Cl^-$	1.36
$Cr_2O_7^{2-} + 14H^+ + 6e^-$	$\rightarrow 2Cr^{3+} + 7H_2O$	1.33
$O_2(g) + 4H^+ + 4e^-$	$\rightarrow 2H_2O$	1.23
$MnO_2(s) + 4H^+ + 2e^-$	$\rightarrow Mn^{2+} + 2H_2O$	1.23
$Br_2 + 2e^-$	$\rightarrow 2Br^-$	1.09
$NO_3^- + 4H^+ + 3e^-$	$\rightarrow NO(g) + 2H_2O$	0.97
$2Hg^{2+} + 2e^-$	$\rightarrow Hg_2^{2+}$	0.92
$Ag^+ + e^-$	$\rightarrow Ag(s)$	0.80
$Fe^{3+} + e^-$	$\rightarrow Fe^{2+}$	0.77
$O_2(g) + 2H^+ + 2e^-$	$\rightarrow H_2O_2$	0.68
$I_2 + 2e^-$	$\rightarrow 2I^-$	0.54
$Cu^+ + e^-$	$\rightarrow Cu(s)$	0.52
$Cu^{2+} + 2e^-$	$\rightarrow Cu(s)$	0.34
$AgCl(s) + e^-$	$\rightarrow Ag(s) + Cl^-$	0.22
$AgBr(s) + e^-$	$\rightarrow Ag(s) + Br^-$	0.10
$2H^+ + 2e^-$	$\rightarrow H_2(g)$	0.00
$Pb^{2+} + 2e^-$	$\rightarrow Pb(s)$	-0.13
$Sn^{2+} + 2e^-$	$\rightarrow Sn(s)$	-0.14
$Ni^{2+} + 2e^-$	$\rightarrow Ni(s)$	-0.25
$Fe^{2+} + 2e^-$	$\rightarrow Fe(s)$	-0.44
$Cr^{3+} + 3e^-$	$\rightarrow Cr(s)$	-0.74
$Zn^{2+} + 2e^-$	$\rightarrow Zn(s)$	-0.76
$2H_2O + 2e^-$	$\rightarrow H_2(g) + 2OH^-(aq)$	-0.83
$Al^{3+} + 3e^-$	$\rightarrow Al(s)$	-1.66
$Mg^{2+} + 2e^-$	$\rightarrow Mg(s)$	-2.36
$Na^+ + e^-$	$\rightarrow Na(s)$	-2.71
$Ca^{2+} + 2e^-$	$\rightarrow Ca(s)$	-2.87
$K^+ + e^-$	$\rightarrow K(s)$	-2.93
$Li^+ + e^-$	$\rightarrow Li(s)$	-3.05

Increasing strength of oxidising agent

Increasing strength of reducing agent

1. A negative $E^\ominus$ means that the redox couple is a stronger reducing agent than the H^+/H_2 couple.
2. A positive $E^\ominus$ means that the redox couple is a weaker reducing agent than the H^+/H_2 couple.

The standard electrode potentials are very important and give a lot of useful information about the half cells. The values of standard electrode potentials for some selected half-cell reduction reactions are given in Table 1. If the standard electrode potential of an electrode is greater than zero then its reduced form is more stable as compared to hydrogen gas. Similarly, if the standard electrode potential is negative then hydrogen gas is more stable than the reduced form of the species. It can be seen that the standard electrode potential for fluorine is the highest in the Table indicating that fluorine gas (F_2) has the maximum tendency to get reduced to fluoride ions (F^-) and therefore fluorine gas is the strongest oxidising agent and fluoride ion is the weakest reducing agent. Lithium has the lowest electrode potential indicating that lithium ion is the weakest oxidising agent while lithium metal is the most powerful reducing agent in an aqueous solution. It may be seen that as we go from top to bottom in Table 1, the standard electrode potential decreases and with this decreases the oxidising power of the species on the left and increases the reducing power of the species on the right hand side of the reaction. Electrochemical cells are extensively used for determining the pH of solutions, solubility product, equilibrium constant and other thermodynamic properties and for potentiometric titrations.

In view of this convention, the half reaction for the Daniell cell in Fig.1 can be written as:

Left electrode: $Zn(s) \rightarrow Zn^{2+}(aq,\ 1\ M)\ +\ 2e^{-}$

Right electrode: $Cu^{2+}(aq,\ 1\ M)\ +\ 2\ e^{-} \rightarrow Cu(s)$

The overall reaction of the cell is the sum of above two reactions and given as below:

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

Emf of the cell = $E^o = E^o_R - E^o_L$ = 0.34 V – (– 0.76) V = 1.10 V

Example 1: How would you determine the standard electrode potential of the system $Mg^{2+}|Mg$?

Solution: The standard electrode potential of the system $Mg^{2+}|Mg$ can be determined by using it as a cathode and standard hydrogen electrode as anode in an electrochemical cell. Standard hydrogen electrode potential is always zero and it is represented as:

$Pt(s), H_2(g)\ (1\ atm)|H^+\ (aq)$ and

The electrode $Mg^{2+}|Mg$ is made by dipping Magnesium wire in a 1M $MgSO_4$ solution.

From the formula: $E^o_{cell} = E^o_{cathode} - E^o_{anode}$, $E^o_{cathode}$ can be calculated.

Hence $E^o_{cell} = E^o_{Mg|Mg2+}$ (as $E^o_{anode} = 0$ and $E^o_{cathode} = E^o_{Mg|/Mg2+}$)

Prediction of cell potentials: Given the E^0 values for two half reactions, you can easily predict the potential difference of the corresponding cell: simply add the reduction potential of the reduction half-cell to the negative of the reduction potential (that is, to the oxidation potential) of the oxidation reaction.

Example 2: Find the standard electrode potential of the cell;

$Cu(s)|Cu^{2+}|Cl^-||AgCl(s)|Ag(s)$ and predict the direction of electron flow when the two electrodes are connected.

Solution. The reactions corresponding to this cell will be:

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

$AgCl(s) + e^- \rightarrow Ag(s) + Cl^-(aq)$ Cathode reaction (reduction)

Net Reaction

$$Cu(s) + 2AgCl(s) \rightarrow Cu^{2+}(aq) + 2Cl^-(aq) + 2Ag(s)$$

$$E_{\text{cell}} = E_{\text{Right}} - E_{\text{Left}}$$
$$= (0.22 - 0.34)\ \text{V}$$
$$= -0.12\ \text{V}$$

Since this potential is negative, then the reaction will proceed to the left, and electrons will be withdrawn from the silver-silver chloride electrode and flow through the external circuit into the copper electrode. Note carefully that in combining these half-cell potentials, we did *not* multiply the E^0 for the silver-silver chloride electrode by two.

Example 3: a) Can you store copper sulphate solution in a zinc pot?

Solution: Copper sulphate cannot be stored in a zinc pot because zinc being more reactive will displace copper and slowly form zinc sulfate and in doing so, the area of the pot which is in contact with copper sulphate will develop holes and the solution will eventually drain out, or leak out from the pot.

b) Consult the table of standard electrode potentials given above and suggest three substances that can oxidize ferrous ions under suitable conditions.

Solution: Any substance that has greater standard electrode potential than Fe^{+3}/Fe^{+2} can oxidize ferrous ions. $Fe^{3+} \rightarrow Fe^{2+} + e^-$; $E^{\circ} = +0.77$ V

This means that the substances that have higher reduction potentials than +0.77 V can oxidize ferrous ions to ferric ions. Examples of three such substances are O_2, F_2 and Cl_2.

Example 4: Predict the anode and the cathode in the cell consisting of the following half-cells and write the overall cell reaction. Also calculate the cell potential, is it a voltaic cell or an electrochemical cell?

An iron (Fe) electrode in a solution of $Fe(NO_3)_3$ and a silver (Ag) electrode in a solution of $AgNO_3$.

Solution:

Step I: Analyze:

Given: A half-cell consists of Fe(*s*) with $Fe(NO_3)_3$ (*aq*) and a second half-cell consists of Ag(*s*) with $AgNO_3$ (*aq*).

Step II: Plan

i. Look up E^0 for each half-reaction (written as reductions) in Table 1.

$$Fe^{3+}(aq) + 3e^- \rightarrow Fe(s) \qquad E^0 = -0.04\ \text{V}$$

$$Ag^+(aq) + e^- \rightarrow Ag(s) \qquad E^0 = +0.80\ \text{V}$$

ii. Find the cathode and anode.

Fe in $Fe(NO_3)_3$ is the anode because it has a lower reduction potential than Ag.

Ag in $Ag(NO_3)$ is therefore the cathode.

Step III: Compute:

i. The overall cell reaction can be determined as follows:

Multiply the Ag half-reaction by 3 so that the number of electrons lost in the reduction half-reaction equals the number of electrons gained in the oxidation half. Reverse the iron half-reaction to make it an oxidation half-reaction and add the two half reactions.

ii. $3Ag^+(aq) + Fe(s) \rightarrow 3Ag(s) + Fe^{3+}(aq)$

iii. Calculate the cell potential by $E^0_{\text{cell}} = E^0_{\text{cathode}} - E^0_{\text{anode}}$.

Hence, $E^0_{\text{cell}} = E^0_{\text{cathode}} - E^0_{\text{anode}} = +0.80\ \text{V} - (-0.04)\text{V} = +0.84\ \text{V}$

Step IV: Evaluate:

The calculated value for E^0_{cell} is positive, which confirms that current is produced as a result of the spontaneous reaction between silver ions and iron and therefore it is a voltaic cell.

Practice:

1. Write the half-cell reactions and the cell notation for the following reaction:

$$Mg(s) \ + \ 2Ag^{+}(aq) \rightarrow Mg^{2+}(aq) \ + \ Ag(s)$$

2. For each pair of half-cells, determine the overall electrochemical reaction that proceeds spontaneously and the E^0 value.
   a. $Cr_2O_7^{2-}/Cr^{3+}$ and Ni^{2+}/Ni
   b. SHE and Fe^{2+}/Fe^{3+}

Other Reference Electrodes:

SHE though is the most standard but not most common reference electrode used as it is difficult to maintain the pressure of hydrogen exactly 1 bar. The hydrogen electrode is cumbersome to handle and also prone to poisoning. The most important requirement of a reference electrode is that it should be easy to prepare and maintain, and that its potential should be stable which means that the concentration of any ionic species involved in the electrode reaction must be a fixed value. Other reference electrodes that are very frequently used in the laboratories are:

a. *Silver-Silver Chloride Electrode* : Ag│AgCl│Cl^-

$$AgCl\,(s) \ + \ e^{-} \rightleftarrows Ag(s) \ + \ Cl^{-} \qquad E^0 = +\,0.222 \text{ V}$$

b. *Calomel Electrode:* Mercury-Mercurous chloride electrode

$$\tfrac{1}{2}\, Hg_2Cl_2\,(s) \ + e^{-} \rightleftarrows Hg\,(l) \ + \ Cl^{-} \qquad E^0 = +\,0.268 \text{ V}$$

Summary

Electrochemistry deals with applications of redox reactions to electricity or production of current. Half-cell is an electrode immersed in an electrolyte solution. In an electrolytic cell, the anode is the electrode where oxidation takes place and the reduction takes place at the electrode called cathode. The cell consists of electrodes connected by a wire along which the electron travels and a salt bridge (or porous barrier) through which ions transfer to balance the charge. In an electrochemical cell, the chemical reactions produce electrical energy or electric current produces chemical change. Electrolytic cells are cells in which electrical energy from an external source causes a nonspontaneous reaction to occur. An electrolytic cell has an E^0 *cell* value that is negative. The potential difference (EMF) of a cell can be predicted from the given standard half- cell potential (E^0) values of the two electrodes in a cell. The addition of reduction potential of the reduction half-cell to the negative of the oxidation potential of the oxidation reaction gives the potential difference of the corresponding cell.