**ELECTROCHEMISTRY**

Electrochemistry is the study of production of electricity from energy released during spontaneous chemical reactions and the use of electrical energy to bring about non-spontaneous chemical transformations. The subject is of importance both for theoretical and practical considerations. A large number of metals, sodium hydroxide, chlorine, fluorine and many other chemicals are produced by electrochemical methods. Batteries and fuel cells convert chemical energy into electrical energy and are used on a large scale in various instruments and devices. The reactions carried out electrochemically can be energy efficient and less polluting. Therefore, study of electrochemistry is important for creating new technologies that are ecofriendly. The transmission of sensory signals through cells to brain and vice versa and communication between the cells are known to have electrochemical origin. Electrochemistry, is therefore, a very vast and interdisciplinary subject. In this Unit, we will cover only some of its important elementary aspects.

- **Electrochemical Cells**

Let us consider the construction and functioning of Daniell cell as shown in figure. This cell converts the chemical energy liberated during the redox reaction:  $Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$
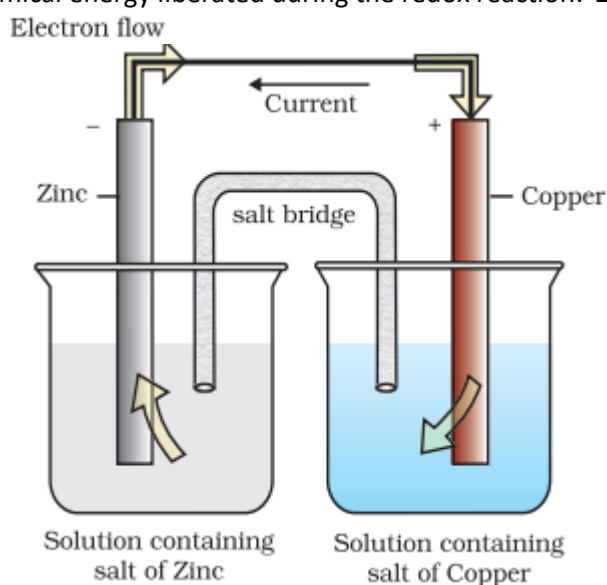


to electrical energy and has an electrical potential equal to 1.1 V when concentration of $Zn^{2+}$ and $Cu^{2+}$ ions is unity  1 mol dm$^{-3}$. Such a device is called a galvanic or a voltaic cell.

If an external opposite potential is applied in the galvanic cell and increased slowly, we find that the reaction continues to take place till the opposing voltage reaches the value 1.1 V 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. It now functions as an electrolytic cell, a device for using electrical energy to carry non-spontaneous chemical reactions. Both types of cells are quite important and we shall study some of their salient features in the following pages.

**Galvanic Cells**:

As mentioned earlier  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 a 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.

$$Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$$
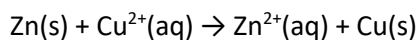
This reaction is a combination of two half reactions whose addition gives the overall cell reaction:

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

(ii) $Zn(s) \rightarrow Zn^{2+} + 2e^-$ (oxidation half reaction)
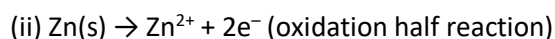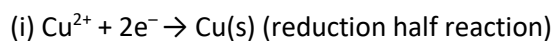
These reactions occur in two different portions of the Daniell cell. The reduction half reaction occurs on the copper electrode while the oxidation half reaction occurs on the zinc electrode. These two portions of the cell are also called half-cells or redox couples. The copper electrode may be called the reduction half cell and the zinc electrode, the oxidation half-cell.

We can construct innumerable number of galvanic cells on the pattern of Daniell cell by taking combinations of different half-cells. Each halfcell 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. Sometimes, both the electrodes dip in the same electrolyte solution and in such cases we do not require a salt bridge.
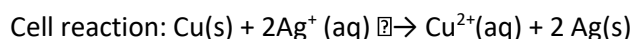
At each electrode-electrolyte interface there is a tendency of metal ions from the solution to deposit on the metal electrode trying to make it positively charged. At the same time, metal atoms of the electrode have a tendency to go into the solution as ions and leave behind the electrons at the electrode 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**. 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 now called standard electrode potentials. 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 current flow is opposite to that of electron flow.

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 now an accepted convention that we keep the anode on the left and the cathode on the right while representing the galvanic cell. 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
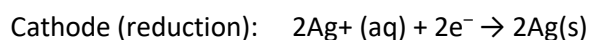
of the cell is positive and is given by the potential of the halfcell on the right hand side minus the potential of the half-cell on the left hand side i.e.,
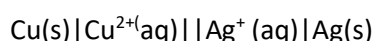
$E_{cell} = E_{right} - E_{left}$

This is illustrated by the following example:

Cell reaction: $Cu(s) + 2Ag^+ (aq) \rightarrow Cu^{2+}(aq) + 2 Ag(s)$

Half-cell reactions:

Cathode (reduction):  $2Ag+ (aq) + 2e^- \rightarrow 2Ag(s)$
Anode (oxidation):  $Cu(s) \rightarrow Cu^{2+}(aq) + 2e^-$

It can be seen that the sum of half-cell reactions leads to overall reaction in the cell and that silver electrode acts as a cathode and copper electrode acts as an anode. The cell can be represented as:

$Cu(s)|Cu^{2+}(aq)||Ag^+ (aq)|Ag(s)$

and we have $E_{cell} = E_{right} - E_{left}$
$= E_{Ag+ /Ag} - E_{Cu2+/Cu}$

Measurement of Electrode Potential:
The potential of individual half-cell cannot be measured. We can measure only the difference



H₂(g) at 1 bar

1.00 M H⁺

Finely divided platinum coated on platinum foil
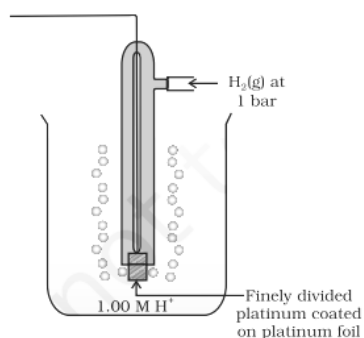
between the two half-cell potentials that gives the emf of the cell. If we arbitrarily choose the potential of one electrode (half-cell) then that of the other can be determined with respect to this. According to convention, a half-cell called standard hydrogen electrode represented by **Pt(s)/ H₂(g)/ H⁺ (aq)**, is assigned a zero potential at all temperatures corresponding to the reaction.

$$H^+ (aq) + e^- \rightarrow \frac{1}{2} H_2(g)$$
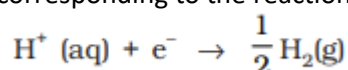
The standard hydrogen electrode consists of a platinum electrode coated with platinum black. The electrode is dipped in an acidic solution and pure hydrogen gas is bubbled through it. The concentration of both the reduced and oxidised forms of hydrogen is maintained at unity. This implies that the pressure of hydrogen gas is one bar and the concentration of hydrogen ion in the solution is one molar. At 298K the emf of the cell, standard hydrogen electrode ❚❚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 oxidised 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, $E^0_R$ of the given half-cell.
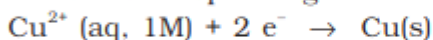
$$E^\ominus = E^\ominus_R - E^\ominus_L$$
As $E^\ominus_L$ for standard hydrogen electrode is zero.
$$E^\ominus = E^\ominus_R - 0 = E^\ominus_R$$

The measured emf of the cell:

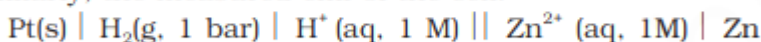$$Pt(s) \mid H_2(g, \text{ 1 bar}) \mid H^+ (aq, \text{ 1 M}) \parallel Cu^{2+} (aq, \text{ 1 M}) \mid Cu$$
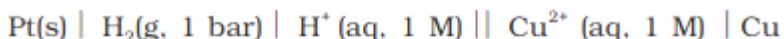
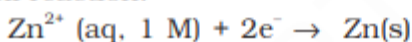is 0.34 V and it is also the value for the standard electrode potential of the half-cell corresponding to the reaction:

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

Similarly, the measured emf of the cell:

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

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

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

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 we can say that 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).

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

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

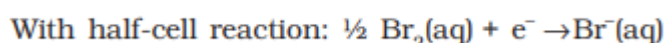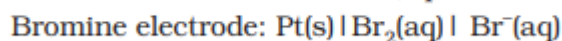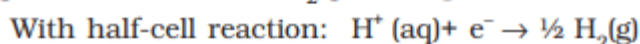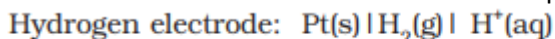Right electrode: $Cu^{2+} (aq, \text{ 1 M}) + 2 \, e^- \rightarrow Cu(s)$
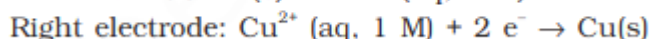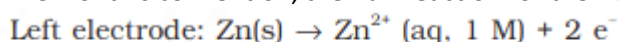
The overall reaction of the cell is the sum of above two reactions and we obtain the equation:

$$Zn(s) + Cu^{2+} (aq) \rightarrow Zn^{2+} (aq) + Cu(s)$$
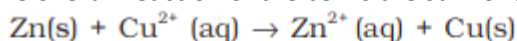
emf of the cell $= E^{\ominus}_{cell} = E^{\ominus}_{R} - E^{\ominus}_{L}$

$$= 0.34V - (-0.76)V = 1.10 \text{ V}$$

hey 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: $Pt(s) \mid H_2(g) \mid H^+(aq)$

With half-cell reaction: $H^+ (aq) + e^- \rightarrow \frac{1}{2} H_2(g)$

Bromine electrode: $Pt(s) \mid Br_2(aq) \mid Br^-(aq)$

With half-cell reaction: $\frac{1}{2} Br_2(aq) + e^- \rightarrow Br^-(aq)$

The standard electrode potentials are very important and we can extract a lot of useful information from them. The values of standard electrode potentials for some selected half-cell reduction reactions are given in Table table. If the standard electrode potential of an electrode is greater than zero then its reduced form is more stable 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 the table , 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.
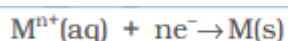
## Standard Electrode Potentials at 298 K

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

| Reaction (Oxidised form + ne⁻ →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* (left vertical axis)

*Increasing strength of reducing agent* (right vertical axis)

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.

Nernst Equation Equation:

We have assumed in the previous section that the concentration of all the species involved in the electrode reaction is unity. This need not be always true. Nernst showed that for the electrode reaction:

$$M^{n+}(aq) + ne^- \rightarrow M(s)$$

the electrode potential at any concentration measured with respect to standard hydrogen electrode can be represented by:

$$E_{(M^{n+}/M)} = E^{\ominus}_{(M^{n+}/M)} - \frac{RT}{nF} \ln \frac{[M]}{[M^{n+}]}$$

but concentration of solid M is taken as unity and we have

$$E_{(M^{n+}/M)} = E^{\ominus}_{(M^{n+}/M)} - \frac{RT}{nF} \ln \frac{1}{[M^{n+}]}$$

$E^0_{M/Mn+}$ V has already been defined, R is gas constant (8.314 JK$^{-1}$ mol$^{-1}$), F is Faraday constant (96487 C mol$^{-1}$), T is temperature in kelvin and [M$^{n+}$] is the concentration of the species, M$^{n+}$ .

In Daniell cell, the electrode potential for any given concentration of Cu$^{2+}$ and Zn$^{2+}$ ions, we write

For Cathode:

$$E_{(Cu^{2+}/Cu)} = E^{\ominus}_{(Cu^{2+}/Cu)} - \frac{RT}{2F} \ln \frac{1}{\left[Cu^{2+}(aq)\right]}$$

For Anode:

$$E_{(Zn^{2+}/Zn)} = E^{\ominus}_{(Zn^{2+}/Zn)} - \frac{RT}{2F} \ln \frac{1}{\left[Zn^{2+}(aq)\right]}$$

The cell potential, $E_{(cell)} = E_{(Cu^{2+}/Cu)} - E_{(Zn^{2+}/Zn)}$

$$= E^{\ominus}_{(Cu^{2+}/Cu)} - \frac{RT}{2F} \ln \frac{1}{\left[Cu^{2+}(aq)\right]} - E^{\ominus}_{(Zn^{2+}/Zn)} + \frac{RT}{2F} \ln \frac{1}{\left[Zn^{2+}(aq)\right]}$$

$$= E^{\ominus}_{(Cu^{2+}/Cu)} - E^{\ominus}_{(Zn^{2+}/Zn)} - \frac{RT}{2F} \left[ \ln \frac{1}{\left[Cu^{2+}(aq)\right]} - \ln \frac{1}{\left[Zn^{2+}(aq)\right]} \right]$$

$$E_{(cell)} = E^{\ominus}_{(cell)} - \frac{RT}{2F} \ln \frac{[Zn^{2+}]}{[Cu^{2+}]}$$

Equilibrium Constant from Nernst Equation:

If the circuit in Daniell cell is closed then we note that the reaction

$$Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$$
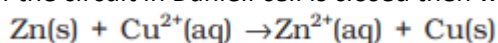
takes place and as time passes, the concentration of Zn$^{2+}$ keeps on increasing while the concentration of Cu$^{2+}$ keeps on decreasing. At the same time voltage of the cell as read on the voltmeter keeps on decreasing. After some time, we shall note that there is no change in the concentration of Cu$^{2+}$ and Zn$^{2+}$ ions and at the same time, voltmeter gives zero reading. This indicates that equilibrium has been attained. In this situation the Nernst equation may be written as:

$$E_{(cell)} = 0 = E^{\ominus}_{(cell)} - \frac{2.303RT}{2F} \log \frac{[Zn^{2+}]}{[Cu^{2+}]}$$

$$\text{or } E^{\ominus}_{(cell)} = \frac{2.303RT}{2F} \log \frac{[Zn^{2+}]}{[Cu^{2+}]}$$

But at equilibrium,

$$\frac{[Zn^{2+}]}{[Cu^{2+}]} = K_c \text{ for the reaction}$$

and at T = 298K the above equation can be written as

$$E^\ominus_{(cell)} = \frac{0.059\ V}{2}\ \log K_C = 1.1\ V \qquad (E^\ominus_{(cell)} = 1.1V)$$

$$\log K_C = \frac{(1.1V \times 2)}{0.059\ V} = 37.288$$

$$K_C = 2 \times 10^{37} \text{ at } 298K.$$

In general,

$$E^\ominus_{(cell)} = \frac{2.303RT}{nF}\ \log K_C$$

This equation gives a relationship between equilibrium constant of the reaction and standard potential of the cell in which that reaction takes place. Thus, equilibrium constants of the reaction, difficult to measure otherwise, can be calculated from the corresponding $E^0$ value of the cell.

Electrochemical Cell and Gibbs Energy of the Reaction:
Electrical work done in one second is equal to electrical potential multiplied by total charge passed. If we want to obtain maximum work from a galvanic cell then charge has to be passed reversibly. The reversible work done by a galvanic cell is equal to decrease in its Gibbs energy and therefore, if the emf of the cell is E and nF is the amount of charge passed and $\Delta_r G$ is the Gibbs energy of the reaction, then
$\Delta_r G = -nFE^0_{(cell)}$
It may be remembered that $E_{(cell)}$ is an intensive parameter but $\Delta_r G$ is an extensive thermodynamic property and the value depends on n. Thus, if we write the reaction

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

$$\Delta_r G = -2FE_{(cell)}$$

If the concentration of all the reacting species is unity, then $E_{(cell)} = E^0_{(cell)}$ and we have

$$\Delta_r G^\ominus = -nFE^\ominus_{(cell)}$$

Thus, from the measurement of $E^0_{(cell)}$ we can obtain an important thermodynamic quantity, $\Delta_r G^0$, standard Gibbs energy of the reaction. From the latter we can calculate equilibrium constant by the equation:

$$\Delta_r G^\ominus = -RT \ln K.$$

- **Conductance of Electrolytic Solutions**:
The electrical resistance of any object is directly proportional to its length, l, and inversely proportional to its area of cross section, A. That is
$R \propto \dfrac{l}{A}$ or $R = \rho \dfrac{l}{A}$
The electrical resistance is represented by the symbol 'R' and it is measured in ohm ($\Omega$) which in terms of SI base units is equal to (kg m$^2$ )/(S$^3$ A$^2$ ). It can be measured with the help of a Wheatstone bridge. The constant of proportionality, $\rho$ (Greek, rho), is called resistivity (specific resistance). Its SI units are ohm-metre ($\Omega$ m) and quite often its submultiple, ohm-centimetre ($\Omega$ cm) is also used. Physically, the resistivity for a substance is its resistance when it is one metre long and its area of cross section is one m$^2$.
The inverse of resistance, R, is called conductance, G, and we have the relation:
$G = \dfrac{1}{R} = \dfrac{A}{\rho l} = \kappa \dfrac{A}{l}$
The SI unit of conductance is siemens, represented by the symbol 'S' and is equal to ohm$^{-1}$ (also known as mho) or $\Omega^{-1}$. The inverse of resistivity, called conductivity (specific conductance) is

represented by the symbol, κ (Greek, kappa). The SI units of conductivity are $S\ m^{-1}$ but quite often, κ is expressed in $S\ cm^{-1}$. Conductivity of a material in $S\ m^{-1}$ is its conductance when it is 1 m long and its area of cross section is $1\ m^2$.

Electrical conductance through metals is called metallic or electronic conductance and is due to the movement of electrons.
The electronic conductance depends on
(i) the nature and structure of the metal
(ii) the number of valence electrons per atom
(iii) temperature (it decreases with increase of temperature).

As the electrons enter at one end and go out through the other end, the composition of the metallic conductor remains unchanged. The mechanism of conductance through semiconductors is more complex.

The conductance of electricity by ions present in the solutions is called electrolytic or ionic conductance.
The conductivity of electrolytic (ionic) solutions depends on:
(i) the nature of the electrolyte added
 (ii) size of the ions produced and their solvation
(iii) the nature of the solvent and its viscosity
 (iv) concentration of the electrolyte
 (v) temperature (it increases with the increase of temperature).
 Passage of direct current through ionic solution over a prolonged period can lead to change in its composition due to electrochemical reactions.

Measurement of the Conductivity of Ionic Solutions: We know that accurate measurement of an unknown resistance can be performed on a Wheatstone bridge. However, for measuring the resistance of an ionic solution we face two problems. Firstly, passing direct current (DC) changes the composition of the solution. Secondly, a solution cannot be connected to the bridge like a metallic wire or other solid conductor. The first difficulty is resolved by using an alternating current (AC) source of power. The second problem is solved by using a specially designed vessel called conductivity cell.
Basically it consists of two platinum electrodes coated with platinum black (finely divided metallic Pt is deposited on the electrodes electrochemically). These have area of cross section equal to 'A' and are separated by distance 'l'. Therefore, solution confined between these electrodes is a column of length l and area of cross section A. The resistance of such a column of solution is then given by the equation:
$$R = \rho\ \frac{l}{A}$$
$$= \frac{l}{\kappa A}$$
The quantity $\frac{l}{A}$ is called cell constant denoted by the symbol, G*. It depends on the distance between the electrodes and their area of cross-section and has the dimension of length$-1$ and can be calculated if we know l and A. Measurement of l and A is not only inconvenient but also unreliable. The cell constant is usually determined by measuring the resistance of the cell containing a solution whose conductivity is already known. For this purpose, we generally use KCl solutions whose conductivity is known accurately at various concentrations and at different temperatures. The cell constant, G*, is then given by the equation:

$$G* = \frac{l}{A} = R\kappa$$

Once the cell constant and the resistance of the solution in the cell is determined, the conductivity of the solution is given by the equation:

$$K = \frac{cell\ constant}{R} = \frac{G*}{R}$$

The conductivity of solutions of different electrolytes in the same solvent and at a given temperature differs due to charge and size of the Fig. 3.5: Arrangement for measurement of resistance of a solution of the ions in which they dissociate, the concentration of ions or ease with which the ions move under a potential gradient. It, therefore, becomes necessary to define a physically more meaningful quantity called molar conductivity denoted by the symbol $\Lambda_m$ (Greek, lambda). It is related to the conductivity of the solution by the equation:

$$\Lambda_m = \frac{\kappa}{C}$$

If we use S cm$^{-1}$ as the units for $\kappa$ and mol cm$^{-3}$, the units of concentration, then the units for $\Lambda_m$ are S cm$^2$ mol$^{-1}$. It can be calculated by using the equation:

$$\Lambda_m = \frac{1000\kappa}{C}$$

**Variation of Conductivity and Molar Conductivity with Concentration**:

Both conductivity and molar conductivity change with the concentration of the electrolyte.

Conductivity always decreases with decrease in concentration both, for weak and strong electrolytes. This can be explained by the fact that the number of ions per unit volume that carry the current in a solution decreases on dilution. The conductivity of a solution at any given concentration is the conductance of one unit volume of solution kept between two platinum electrodes with unit area of cross section and at a distance of unit length.

Molar conductivity of a solution at a given concentration is the conductance of the volume V of solution containing one mole of electrolyte kept between two electrodes with area of cross section A and distance of unit length. Therefore,

$$\Lambda_m = \kappa\ V$$

Molar conductivity increases with decrease in concentration. This is because the total volume, V, of solution containing one mole of electrolyte also increases. It has been found that decrease in $\kappa$ on dilution of a solution is more than compensated by increase in its volume. When concentration approaches zero, the molar conductivity is known as limiting molar conductive ity and is represented by the symbol $\Lambda^0_m$. The variation in $\Lambda_m$ with concentration is different for strong and weak electrolytes.
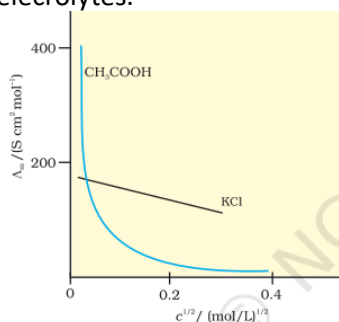


**Strong Electrolytes**: For strong electrolytes, $\Lambda_m$ increases slowly with dilution and can be represented by the equation: $\Lambda_m = \Lambda^0_m - A\ c^{1/2}$ .It can be seen that if we plot $\Lambda_m$ against c 1/2, we obtain a straight line with intercept equal to Ëm ° and slope equal to '–A'. The value of the constant 'A' for a given solvent and temperature depends on the type of electrolyte i.e., the charges on the cation and anion produced on the dissociation of the electrolyte in the solution. All electrolytes of a particular type have the same value for 'A'.

Kohlrausch examined $\Lambda^0_m$ values for a number of strong electrolytes and observed certain regularities. He noted that the difference in $\Lambda^0_m$ of the electrolytes NaX and KX for any X is nearly constant. For example at 298 K:

$\Lambda^0_m$ (KCl) $- \Lambda^0_m$ (NaCl)$= \Lambda^0_m$ (KBr) $- \Lambda^0_m$ (NaBr) $= \Lambda^0_m$ (KI) $- \Lambda^0_m$ (NaI) $\simeq$ 23.4 S cm$^2$ mol$^{-1}$ .

and similarly it was found that:
$\Lambda^0_m$ (NaBr)$- \Lambda^0_m$ (NaCl)$= \Lambda^0_m$ (KBr) $- \Lambda^0_m$ (KCl) $\simeq$ 1.8 S cm$^2$ mol$^{-1}$.

On the basis of the above observations he enunciated **Kohlrausch law of independent migration of ions.**
*The law states that limiting molar conductivity of an electrolyte can be represented as the sum of the individual contributions of the anion and cation of the electrolyte*. Thus,
$\Lambda^0_m$ (NaCl) $= \lambda^0_{Na+} + \lambda^0_{Cl-}$
In general, if an electrolyte on dissociation gives v+ cations and v− anions then its limiting molar conductivity is given by:
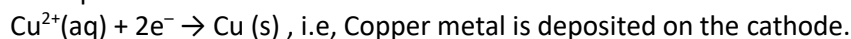$\Lambda^0_m = v+ \lambda^0_+ + v- \lambda^0_-$
Here, $\lambda^0_+$ and $\lambda^0_-$ are the limiting molar conductivities of the cation and anion respectively.

**Weak Electrolytes**: Weak electrolytes like acetic acid have lower degree of dissociation at higher concentrations and hence for such electrolytes, the change in $\Lambda_m$ with dilution is due to increase in the degree of dissociation and consequently the number of ions in total volume of solution that contains 1 mol of electrolyte. In such cases $\Lambda_m$ increases steeply on dilution, especially near lower concentrations. Therefore, $\Lambda^0_m$ cannot be obtained by extrapolation of $\Lambda_m$ to zero concentration. At infinite dilution (i.e., concentration c $\rightarrow$ zero) electrolyte dissociates completely ($\alpha$ =1), but at such low concentration the conductivity of the solution is so low that it cannot be measured accurately. Therefore, $\Lambda^0_m$ for weak electrolytes is obtained by using Kohlrausch law of independent migration of ions.
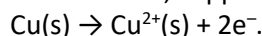For example, $\Lambda^0_m$ for NaCl, HCl and NaAc are 126.4, 425.9 and 91.0 S cm$^2$ mol$^{-1}$ respectively. Thus,
$\Lambda_m^0{}_{(HAc)} = \lambda^0_{H+} + \lambda^0_{AC-}$

$\qquad = \lambda^0_{H+} + \lambda^0_{Cl-} + \lambda^0_{Na+} + \lambda^0_{AC-} - \lambda^0_{Na+} + \lambda^0_{Cl-}$

$\qquad = \Lambda_m^0{}_{(HCl)} + \Lambda_m^0{}_{(NaAc)} - \Lambda_m^0{}_{(NaCl)}$

$\qquad = (425.9 + 91.0 - 126.4 )$ S cm$^2$ mol$^{-1}$

$\qquad =390.5$ S cm$^2$ mol$^{-1}$.

**Electrolytic Cells and Cells andCells and Electrolysis**: In an electrolytic cell external source of voltage is used to bring about a chemical reaction. One of the simplest electrolytic cell consists of two copper strips dipping in an aqueous solution of copper sulphate. If a DC voltage is applied to the two electrodes, then Cu$^{2+}$ ions discharge at the cathode (negatively charged) and the following reaction takes place:
$Cu^{2+}(aq) + 2e^- \rightarrow Cu$ (s) , i.e, Copper metal is deposited on the cathode.
At the anode, copper is converted into Cu$^{2+}$ ions by the reaction:
$Cu(s) \rightarrow Cu^{2+}(s) + 2e^-$.
Thus copper is dissolved (oxidised) at anode and deposited (reduced) at cathode. This is the basis for an industrial process in which impure copper is converted into copper of high purity.

**Faraday's Laws of Electrolysis** : After his extensive investigations on electrolysis of solutions and melts of electrolytes, Faraday published his results during 1833-34 in the form of the following well known Faraday's two laws of electrolysis:
(i) **First Law**: The amount of chemical reaction which occurs at any electrode during electrolysis by a current is proportional to the quantity of electricity passed through the electrolyte (solution or melt). W$\propto$Q , or, W=ZQ, where Z is called electrochemical equivalent.

(ii) Second Law: The amounts of different substances liberated by the same quantity of electricity passing through the electrolytic solution are proportional to their chemical equivalent weights (Atomic Mass of Metal ÷ Number of electrons required to reduce the cation).

i.e $W \propto E$

or, $\dfrac{W1}{E1} = \dfrac{W2}{E2}$

**Products of Electrolysis**: Products of electrolysis depend on the nature of material being electrolysed and the type of electrodes being used. If the electrode is inert (e.g., platinum or gold), it does not participate in the chemical reaction and acts only as source or sink for electrons. On the other hand, if the electrode is reactive, it participates in the electrode reaction. Thus, the products of electrolysis may be different for reactive and inert electrodes. The products of electrolysis depend on the different oxidising and reducing species present in the electrolytic cell and their standard electrode potentials. Moreover, some of the electrochemical processes although feasible, are so slow kinetically that at lower voltages these do not seem to take place and extra potential (called overpotential) has to be applied, which makes such process more difficult to occur.

1. **Electrolysis of molten NaCl**: Here we have only one cation ($Na^+$) which is reduced at the cathode ($Na^+ + e^- \rightarrow Na$) and one anion ($Cl^-$) which is oxidised at the anode ($Cl^- \rightarrow \frac{1}{2}Cl_2 + e^-$).

2. **Electrolysis of aqueous solution of NaCl**: During the electrolysis of aqueous sodium chloride solution, the products are NaOH, $Cl_2$ and $H_2$.

In this case besides $Na^+$ and $Cl^-$ ions we also have $H^+$ and $OH^-$ ions along with the solvent molecules, $H_2O$.

At the cathode there is competition between the following reduction reactions:

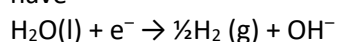$Na^+ (aq) + e^- \rightarrow Na (s)$ , $E^o_{cell} = -2.71$ V

$H^+(aq) + e^- \rightarrow 1/2 H_2(g)$ , $E^o_{cell} = 0.00$ V
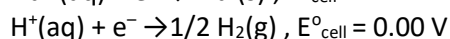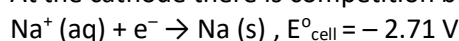
The reaction with higher value of $E^0$ is preferred and therefore, the reaction at the cathode during electrolysis is:
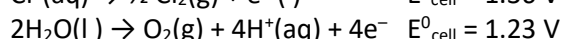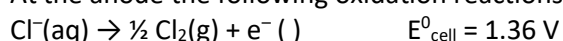
$H^+(aq) + e^- \rightarrow 1/2 H_2(g)$.
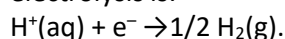
but $H^+(aq)$ is produced by the dissociation of $H_2O$, i.e., $H_2O (l) \rightarrow H^+ (aq) + OH^-(aq)$
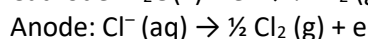
Therefore, the net reaction at the cathode may be written as the sum of the above reactions and we have

$H_2O(l) + e^- \rightarrow \frac{1}{2}H_2 (g) + OH^-$

At the anode the following oxidation reactions are possible:

$Cl^-(aq) \rightarrow \frac{1}{2} Cl_2(g) + e^- ( )$          $E^0_{cell} = 1.36$ V
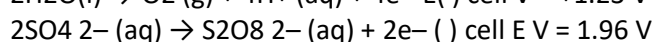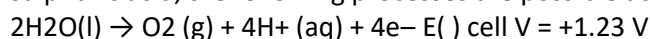
$2H_2O(l) \rightarrow O_2(g) + 4H^+(aq) + 4e^-$   $E^0_{cell} = 1.23$ V

he reaction at anode with lower value of $E^0$ is preferred and therefore, water should get oxidised in preference to $Cl^-$ (aq). However, on account of overpotential of oxygen, the first reaction is preferred. Thus, the net reactions may be summarised as:

$NaCl (aq) \rightarrow Na^+ (aq) + Cl^- (aq)$

Cathode: $H_2O(l) + e^- \rightarrow \frac{1}{2} H_2 (g) + OH^- (aq)$

Anode: $Cl^- (aq) \rightarrow \frac{1}{2} Cl_2 (g) + e$

Net reaction:

$NaCl(aq) + H_2O(l) \rightarrow Na+ (aq) + OH^- (aq) + \frac{1}{2}H_2 (g) + \frac{1}{2}Cl_2 (g)$
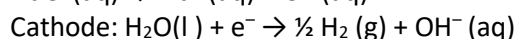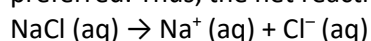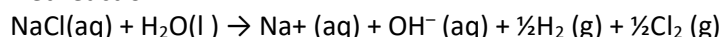
3. **Electrolysis of $H_2SO_4$**: The standard electrode potentials are replaced by electrode potentials given by Nernst equation to take into account the concentration effects. During the electrolysis of sulphuric acid, the following processes are possible at the anode:

$2H2O(l) \rightarrow O2 (g) + 4H+ (aq) + 4e-$ E( ) cell V = +1.23 V

$2SO4 2- (aq) \rightarrow S2O8 2- (aq) + 2e-$ ( ) cell E V = 1.96 V

For dilute sulphuric acid, first reaction is preferred but at higher concentrations of $H_2SO_4$ ,second reaction is preferred.

**Batteries**: Any battery (actually it may have one or more than one cell connected in series) or cell that we use as a source of electrical energy is basically a galvanic cell where the chemical energy of the redox reaction is converted into electrical energy. However, for a battery to be of practical use it should be reasonably light, compact and its voltage should not vary appreciably during its use. There are mainly two types of batteries.

**Primary Batteries**: In the primary batteries, the reaction occurs only once and after use over a period of time battery becomes dead and cannot be reused again.

- The most familiar example of this type is the **dry cell** (known as **Leclanche cell** after its discoverer) which is used commonly in our transistors and clocks.

The cell consists of a zinc container that also acts as anode and the cathode is a carbon (graphite) rod surrounded by powdered manganese dioxide and carbon. The space between the electrodes is filled by a moist paste of ammonium chloride ($NH_4Cl$) and zinc chloride ($ZnCl_2$). The electrode reactions are complex, but they can be written approximately as follows :

Anode: $Zn(s) \rightarrow Zn^{2+} + 2e^-$

Cathode: $MnO_2 + NH_4^+ + e^- \rightarrow MnO(OH) + NH_3$

In the reaction at cathode, manganese is reduced from the + 4 oxidation state to the +3 state. Ammonia produced in the reaction forms a complex with $Zn^{2+}$ to give $[Zn(NH_3)_4]^{2+}$. The cell has a potential of nearly 1.5 V.

- **Mercury cell**, suitable for low current devices like hearing aids, watches, etc. consists of zinc – mercury amalgam as anode and a paste of HgO and carbon as the cathode. The electrolyte is a paste of KOH and ZnO. The electrode reactions for the cell are given below:

  Anode: $Zn(Hg) + 2OH^- \rightarrow ZnO(s) + H_2O + 2e^-$

  Cathode: $HgO + H_2O + 2e^- \rightarrow Hg(l) + 2OH^-$

  The overall reaction is represented by $Zn(Hg) + HgO(s) \rightarrow ZnO(s) + Hg(l)$

  The cell potential is approximately 1.35 V and remains constant during its life as the overall reaction does not involve any ion in solution whose concentration can change during its life time.

**Secondary Batteries**: A secondary cell after use can be recharged by passing current through it in the opposite direction so that it can be used again. A good secondary cell can undergo a large number of discharging and charging cycles.

- The most important secondary cell is the lead **storage battery** commonly used in automobiles and invertors. It consists of a lead anode and a grid of lead packed with lead dioxide ($PbO_2$) as cathode. A 38% solution of sulphuric acid is used as an electrolyte.

The cell reactions when the battery is in use are given below:

Anode: $Pb(s) + SO_4^{2-}(aq) \rightarrow PbSO_4(s) + 2e^-$

Cathode: $PbO_2(s) + SO_4^{2-}(aq) + 4H^+(aq) + 2e^- \rightarrow PbSO_4(s) + 2H_2O(l)$

i.e., overall cell reaction consisting of cathode and anode reactions is:

$Pb(s) + PbO_2(s) + 2H_2SO_4(aq) \rightarrow 2PbSO_4(s) + 2H_2O(l)$

On charging the battery the reaction is reversed and $PbSO_4(s)$ on anode and cathode is converted into Pb and $PbO_2$, respectively.

Another important secondary cell is the nickel-cadmium cell which has longer life than the lead storage cell but more expensive to manufacture. The overall reaction during discharge is:

$Cd(s) + 2Ni(OH)_3(s) \rightarrow CdO(s) + 2Ni(OH)_2(s) + H_2O(l)$

*Thermodynamics of cell reaction*: The potential of the cell is 2.0 volts. As current is drawn from the cell, the cell potentialdoes not drop very much so the power is near the reversible value, rather large currents-hundreds of amperes-can be drawn from the fully charged device without dropping the potential excessively. When the cell needs to be recharged, we use an external power source to force current through the cell in the reverse direction. The potential difference that must be impressed to recharge the cell has to be greater than the potential difference during discharge, but not excessively larger. The voltage efficiency of the cell is defined as :

The voltage efficiency $=\dfrac{\text{average voltage during discharge}}{\text{average voltage during charge}}$

The voltage efficiency of the lead-acid cell is about 80 %. This near reversibility is a consequence of the rapidity of the chemical reactions in the cell. As we have seen, the ability to supply large currents at potentials near the open-circuit potential means that the chemical reactions at the electrodes are fast ; as the charge is drained away by the current,the potential should drop, but the chemical reaction occurs rapidly enough to rebuild the potential. If we compare the quantity of charge obtained from the lead-acid cell to the quantity that must be passed in to charge the cell, we obtain values of 90 to 95 %, or even higher in special circumstances. This means that very little of the charging current is dissipated in side reactions (such as electrolysis of water). Overall, the lead storage cell is an extra ordinary device : It is highly efficient ; its larger versions can last 20 to 30 years (if carefully attended) ; and it can be cycled thousands of times. Its chief disadvantages are its great weight (low energy storage to weight ratio), and that if left unused in partially charged condition it can be ruined in a short time by the growth of relatively large $PbSO_4$ crystals,which are not easily reduced or oxidized by the charging current ; this disaster is known as " sulfation." For the standard Gibbs energy change in the lead-acid cell we have (for a two electron change) :

$\Delta G^0 = -376.97$ kJ/mol ;

$\Delta H^0 = -227.58$ kJ/mol ;
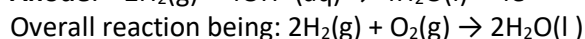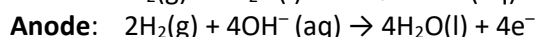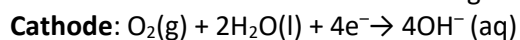
$Q_{rev} = T\Delta S =.= +149.39$ kJ/mol
.

Note that the reaction is endothermic if the cell performs reversibly. These figures mean that not only is the energy change, the $\Delta H$, available to provide electrical work but also the quantity of heat, $Q_{rev} = T\Delta S$, that flows from the surroundings to keep the cell isothermal can be converted to electrical work. The ratio

$\dfrac{-\Delta G}{-\Delta H} = \dfrac{376.97}{277.58} = 1.36$

compares the electrical work that can be produced to the decrease in enthalpy of the materials. The extra 36 % is the energy that flows in from the surroundings.

**Fuel Cells**: Galvanic cells that are designed to convert the energy of combustion of fuels like hydrogen, methane, methanol, etc. directly into electrical energy are called **fuel cells**.

$H_2$-$O_2$ Fuel Cell: One of the most successful fuel cells uses the reaction of hydrogen with oxygen to form water. The cell was used for providing electrical power in the Apollo space programme. The water vapours produced during the reaction were condensed and added to the drinking water supply for the astronauts. In the cell, hydrogen and oxygen are bubbled through porous carbon electrodes into concentrated aqueous sodium hydroxide solution. Catalysts like finely divided platinum or palladium metal are incorporated into the electrodes for increasing the rate of electrode reactions. The electrode reactions are given below:

**Cathode**: $O_2(g) + 2H_2O(l) + 4e^- \rightarrow 4OH^-$ (aq)

**Anode**:  $2H_2(g) + 4OH^-$ (aq) $\rightarrow 4H_2O(l) + 4e^-$

Overall reaction being: $2H_2(g) + O_2(g) \rightarrow 2H_2O(l)$

The cell runs continuously as long as the reactants are supplied. Fuel cells produce electricity with an efficiency of about 70 % compared to thermal plants whose efficiency is about 40%.

The power available is limited by the relatively slow reduction of oxygen at the cathode surface; this problem exists with any fuel cell that uses an oxygen electrode. At present, platinum seems to be the best catalyst, but even platinum is not nearly as good as we would like. The rate of the anodic reaction, the oxidation of hydrogen at the platinum surface, is relatively rapid. However, it would be nice if we could use something less expensive than platinum as a catalyst. At higher temperatures, the reaction rates are faster and the cell performance is better.

**Corrosion**: Corrosion slowly coats the surfaces of metallic objects with oxides or other salts of the metal. The rusting of iron, tarnishing of silver, development of green coating on copper and bronze are some of the examples of corrosion. It causes enormous damage to buildings, bridges, ships and to all objects made of metals especially that of iron. We lose crores of rupees every year on account of corrosion. In corrosion, a metal is oxidised by loss of electrons to oxygen and formation of oxides. Corrosion of iron (commonly known as rusting) occurs in presence of water and air. The chemistry of corrosion is quite complex but it may be considered essentially as an electrochemical phenomenon. At a particular spot  of an object made of iron, oxidation takes place and that spot behaves as anode and we can write the reaction:

**Anode**: $2 Fe (s) \rightarrow 2Fe^{2+} + 4e^-$ , $E^0_{Fe2+/Fe} = -0.44$ V

Electrons released at anodic spot move through the metal and go to another spot on the metal and reduce oxygen in presence of $H^+$ (which is believed to be available from $H_2CO_3$ formed due to dissolution of carbon dioxide from air into water. Hydrogen ion in water may also be available due to dissolution of other acidic oxides from the atmosphere). This spot behaves as cathode with the reaction

**Cathode**: $O_2(g) + 4 H^+(aq) + 4 e^- \rightarrow 2 H_2O(l)$ ,   $E^0_{H+/O2/H2O} = 1.23$ V

The overall reaction being:

$2Fe(s) + O_2(g) + 4H^+ (aq) \rightarrow 2Fe^{2+}(aq) + 2H_2O (l)$, $E^0_{cell} =1.67$V

The ferrous ions are further oxidised by atmospheric oxygen to ferric ions which come out as rust in the form of hydrated ferric oxide $(Fe_2O_3.xH_2O)$ and with further production of hydrogen ions.

**Prevention** of corrosion is of prime importance. It not only saves money but also helps in preventing accidents such as a bridge collapse or failure of a key component due to corrosion. One of the simplest methods of preventing corrosion is to prevent the surface of the metallic object to come in contact with atmosphere. This can be done by covering the surface with paint or by some chemicals (e.g. bisphenol). Another simple method is to cover the surface by other metals (Sn, Zn, etc.) that are inert or react to save the object. An electrochemical method is to provide a sacrificial electrode of another metal (like Mg, Zn, etc.) which corrodes itself but saves the object.