Module 5: Electrochemistry

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5.1. INTRODUCTION

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. 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.
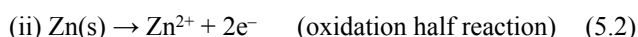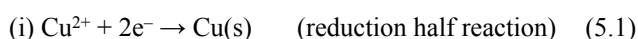
5.2. GALVANIC CELL

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.

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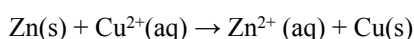
This reaction is a combination of two half reactions whose addition gives the overall cell reaction:

(i) $Cu^{2+} + 2e^- \rightarrow Cu(s)$ (reduction half reaction)   (5.1)

(ii) $Zn(s) \rightarrow Zn^{2+} + 2e^-$ (oxidation half reaction)   (5.2)

hese 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.
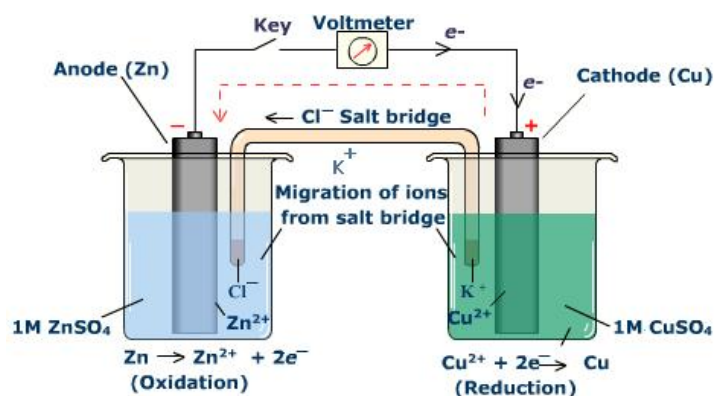

Fig. 5.1 Galvanic Cell

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 as shown in Fig. 5.1. Sometimes, both the electrodes dip in the same electrolyte solution and in such cases we do not require a salt bridge.
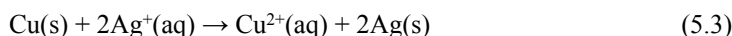
At each electrode-electrolyte interface there is a tendency of metal ions from the solution to deposit on the metal electrode trying to make it positively charged. At the same time, metal atoms of the electrode have a tendency to go into the solution as ions and leave behind the electrons at the electrode 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.,
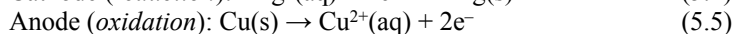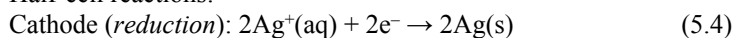
$E_{cell} = E_{right} - E_{left}$

This is illustrated by the following example:

Cell reaction:

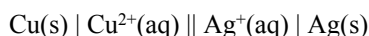$Cu(s) + 2Ag^+(aq) \rightarrow Cu^{2+}(aq) + 2Ag(s)$ (5.3)
Half-cell reactions:
Cathode (*reduction*): $2Ag^+(aq) + 2e^- \rightarrow 2Ag(s)$ (5.4)
Anode (*oxidation*): $Cu(s) \rightarrow Cu^{2+}(aq) + 2e^-$ (5.5)

It can be seen that the sum of (5.4) and (5.5) leads to overall reaction (5.3) 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 $E_{cell} = E_{right} - E_{left} = E_{Ag^+| Ag} - E_{Cu^{2+}| Cu}$ (5.6)

5.3. MEASUREMENT OF ELECTRODE POTENTIAL

The potential of individual half-cell cannot be measured. We can measure only the difference between the two half-cell potentials that gives the emf of the cell.
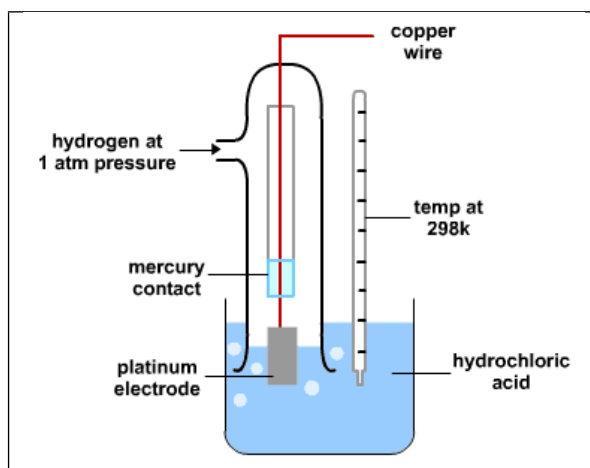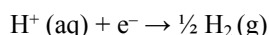

Fig. 5.2: Standard Hydrogen Electrode (SHE)

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 (Fig.5.2) represented by Pt(s)☐ H₂(g)☐ H⁺(aq), is assigned a zero potential at all temperatures corresponding to the reaction

$$H^+ (aq) + e^- \rightarrow \tfrac{1}{2} H_2 (g)$$

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 (Fig. 5.2). This implies that the pressure of hydrogen gas is one bar and the concentration of hydrogen ion in the solution is one molar.

At 298 K 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 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^-_R of the given half-cell.

$$E^- = E^-_R - E^-_L$$

As E^-_L for standard hydrogen electrode is zero.

$$E^- = E^-_R - 0 = E^-_R$$
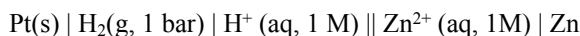
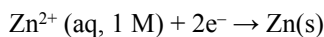The measured emf of the cell:
Pt(s) | H₂(g, 1 bar) | H⁺ (aq, 1 M) ‖ Cu²⁺ (aq, 1 M) | Cu
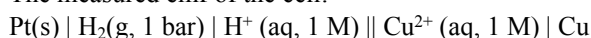
is 0.34 V and it is also the value for the standard electrode potential of the half-cell corresponding to the reaction:

Cu²⁺ (aq, 1M) + 2 e⁻ → Cu(s)
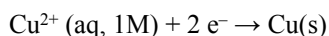
Similarly, the measured emf of the cell:

Pt(s) | H₂(g, 1 bar) | H⁺ (aq, 1 M) ‖ Zn²⁺ (aq, 1M) | Zn

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

Zn²⁺ (aq, 1 M) + 2e⁻ → Zn(s)

The positive value of the standard electrode potential in the first case indicates that Cu²⁺ ions get reduced more easily than H⁺ ions. The reverse process cannot occur, that is, hydrogen ions cannot oxidize 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 Galvanic cell in Fig. 5.1 can be written as:
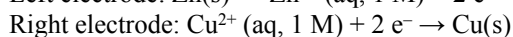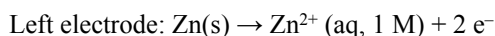
Left electrode: Zn(s) → Zn²⁺ (aq, 1 M) + 2 e⁻
Right electrode: Cu²⁺ (aq, 1 M) + 2 e⁻ → Cu(s)
The overall reaction of the cell is the sum of above two reactions and we obtain the equation:
Zn(s) + Cu²⁺ (aq) → Zn²⁺ (aq) + Cu(s)
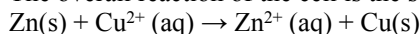
emf of the cell = $E^0_{cell} = E^0_R - E^0_L$

   $= 0.34V - (- 0.76)V = 1.10$ V

5.4. NERNST EQUATION

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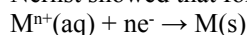
$$E_{(M^{n+}/M)} = E^-_{(M^{n+}/M)} - \frac{RT}{nF} \ln \frac{[M]}{[M^{n+}]}$$

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

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

$E^-_{(M^{n+}/M)}$ = Standard electrode potential in the oxidised/reduced form.
R is gas constant (8.314 JK⁻¹ mol⁻¹)
F is Faraday constant (96487 C mol⁻¹)
T is temperature in kelvin.
[M^{n+}] is the concentration of the species, M^{n+}.

Table 5.1 Standard Reduction Potentials at 25°C

	Reduction Half-Reaction		$E°$ (V)
Stronger oxidizing agent	$F_2(g) + 2e^-$	$\longrightarrow 2F^-(aq)$	2.87
	$H_2O_2(aq) + 2H^+(aq) + 2e^-$	$\longrightarrow 2H_2O(l)$	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
Weaker oxidizing agent	$Mg^{2+}(aq) + 2e^-$	$\longrightarrow Mg(s)$	−2.37
	$Na^+(aq) + e^-$	$\longrightarrow Na(s)$	−2.71
	$Li^+(aq) + e^-$	$\longrightarrow Li(s)$	−3.04

(Weaker reducing agent → Stronger 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.

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

For Cathode:

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

For Anode:

$$E_{(Zn^{2+}/Zn)} = E^-_{(Zn^{2+}/Zn)} - \frac{RT}{2F} \ln \frac{1}{[Zn^{2+}(aq)]} \qquad (3)$$

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

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

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

$$E_{(cell)} = E^-_{(cell)} - \frac{RT}{2F} \ln \frac{[Zn^{2+}]}{[Cu^{2+}]} \qquad (4)$$

It can be seen that E(cell) depends on the concentration of both Cu^{2+} and Zn^{2+} ions. It increases with increase in the concentration of Cu^{2+} ions and decrease in the concentration of Zn^{2+} ions.

By converting the natural logarithm in Eq. (4) to the base 10 and substituting the values of R, F and T = 298 K, it reduces to

$$E_{(cell)} = E^-_{(cell)} - \frac{0.059}{2} \log \frac{[Zn^{2+}]}{[Cu^{2+}]} \qquad (5)$$

$$E_{(cell)} = E^-_{(cell)} + \frac{0.059}{2} \log \frac{[Cu^{2+}]}{[Zn^{2+}]} \qquad (6)$$

5.5. 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.

5.5.1. 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 (Fig.5.3). 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: $MnO_2 + NH_4^+ + e^- \rightarrow MnO(OH) + NH_3$
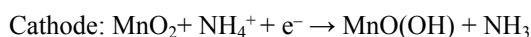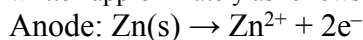
In the reaction at cathode, manganese is reduced from the + 4 oxidation state to the +3 state. Ammonia produced in the reaction forms a complex with Zn^{2+} to give $[Zn(NH_3)_4]^{2+}$. The cell has a potential of nearly 1.5 V.
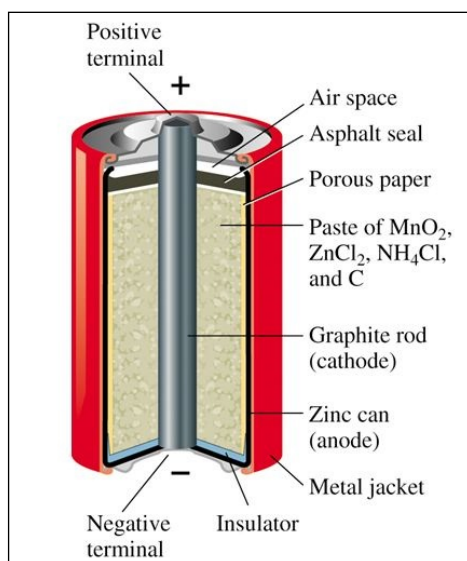

Fig. 5.3: A commercial dry cell

Mercury cell, (Fig. 5.4) 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.
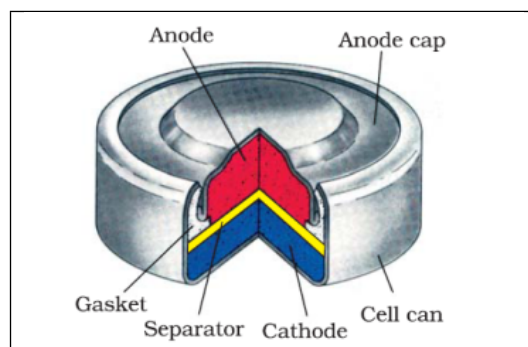
Fig. 5.4: Mercury cell

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.
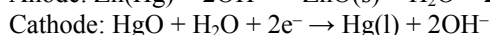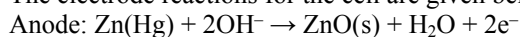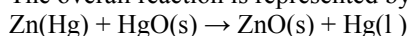
5.5.2. Secondary Batteries

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 (Fig. 5.5) 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: $PbO_2(s) + SO_4^{2-}(aq) + 4H^+(aq) + 2e^- \rightarrow PbSO_4(s) + 2H_2O(l)$
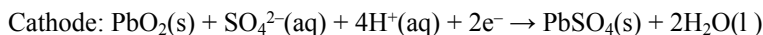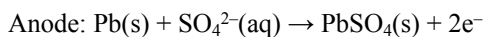
i.e., overall cell reaction consisting of cathode and anode reactions is:

$Pb(s) + PbO_2(s) + 2H_2SO_4(aq) \rightarrow 2PbSO_4(s) + 2H_2O(l)$
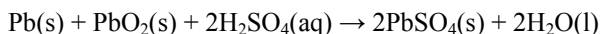
On charging the battery the reaction is reversed and $PbSO_4(s)$ on anode and cathode is converted into Pb and PbO_2, respectively.
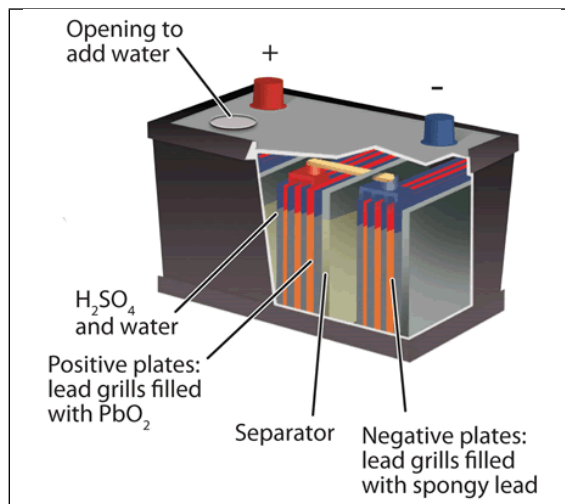
Fig. 5.5: The Lead storage battery

Another important secondary cell is the nickel-cadmium cell (Fig. 5.6) which has longer life than the lead storage cell but more expensive to manufacture. We shall not go into details of working of the cell and the electrode reactions during charging and discharging. The overall reaction during discharge is:

$Cd(s) + 2Ni(OH)_3(s) \rightarrow CdO(s) + 2Ni(OH)_2(s) + H_2O(l)$
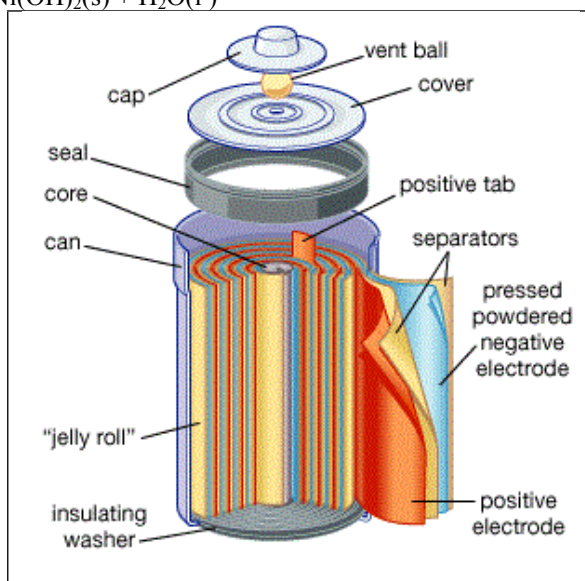
Fig. 5.6: Rechargeable nickel-cadmium cells in a jelly roll arrangement and separated by a layer soaked in moist sodium or potassium hydroxide.

Example 5.1. Calculate the e.m.f. of a concentration cell at $25^0C°C$ consisting of two Zn electrodes immersed in solution of Zn^{2+} ions of 0.1 M and 0.01 M concentrations.

Solution

$$E_{(cell)} = \frac{0.059}{2} \log \frac{C_2}{C_1}$$

Where $C_2 > C_1$

Now for Zn^{2+} / Zn electrode, n = 2 $[Zn^{2+} + 2e^- \rightarrow Zn]$

$$E_{(cell)} = \frac{0.059}{2} \log \frac{0.1}{0.01} = 0.0296 \log 10$$

$$= 0.0296 \times 1 = \textbf{0.0296 V}$$

Example 5.2. Calculate the e.m.f. of a galvanic cell at $25^0C^\circ C$, when the concentration of $ZnSO_4$ and $CuSO_4$ are 0.001 M and 0.1 M respectively. The standard potential of the cell is 1.2 volts.

Solution: Cell is: $Zn\ (s)\ |\ Zn^{2+}\ (0.001\ M)\ \|\ Cu^{2+}\ (0.1\ M)\ |\ Cu\ (s)$

$$E_{(cell)} = E^-_{(cell)} + \frac{0\ 059}{2}\ \log\frac{[Cu^{2+}]}{[Zn^{2+}]}$$

$$= 1.1 + 0.0296\ \log\ (0.1/\ 0.001)$$

$$= 1.1 + 0.0296 \times 2 = 1.1 + 0.592 = \textbf{1.1592 V}$$

Example 5.3. Why do electrochemical cell stop working after some time?
Solution: An electrochemical cell produces electrical energy at the cost of redox reaction. When the redox reaction is completed, the cell stop working, since it is now incapable of undoing redox reaction any more.

Example 5.4. Why does a dry cell becomes dead after a long time, even if has not been used.

Ans. Acidic NH_4Cl slowly corrodes the zinc container of the dry cell, even when the cell is not in the use. Hence, dry cell becomes dead after a long time, even it is not used.

Example 5.5. Why is salt bridge used in the construction of cell?

Ans: A wire cannot be used to connect two electrodes internally in an electrochemical cell, because it produces a voltage drop. Consequently, accurate electric cell measurement cannot be done. In order to make accurate electric measurements in solution, a salt bridge is employed. Salt bridge completes the electrical circuit, thereby permitting the ions to move from one solution to another without direct contact (or mixing) of the two solutions. Moreover, it maintains electrical neutrality of the solutions in the two half-cells.

Example 5.6. The emf of a concentration cell gradually decreases why?

Ans: The concentration cell produces electric energy, due to transfer of metallic ions from the solution of a higher concentration to the solution of lower concentration. As this process continues, the difference in concentration between two half- cell concentration cells decreases. Consequently, the emf of the cell also gradually decreases, since the emf is given by:

$$E_{(cell)} = \frac{2.3.3\ RT}{nF}\ \log\frac{C_2}{C_1}$$

and the ratio $C_2/\ C_1$ goes on decreasing gradually and finally the cell stops working when C_2 becomes equal to C_1.

5.6. CORROSION

"Corrosion is the process of gradual deterioration of a metal from its surface due to the unwanted chemical or electrochemical interaction of metal with its environment". 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. The most familiar example of corrosion is rusting of iron exposed to the atmospheric conditions. The chemistry of corrosion is quite complex but it may be considered essentially as an electrochemical phenomenon.

$$2\ Fe(s) + \frac{3}{2}\ O_2(g) + x\ H_2O(l) \longrightarrow Fe_2O_3 . x\ H_2O(s)$$
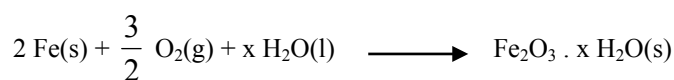
(Chemical composition of rust)

Fig. 5.7: Corrosion of iron in atmosphere

5.7. EFFECTS OF CORROSION

Effects of corrosion are briefly given below:

1.   Production related consequences:
i.   Loss of useful properties of metal and thus loss of efficiency.
ii.   Decrease in production rate, because efficiency is less and replacement of corroded equipment is time consuming.
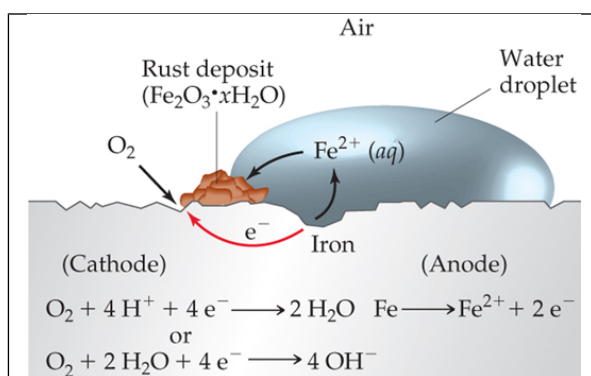iii.   Increase in maintenance and production cast.
iv.   Contamination of product.
2.   Health and safety related consequences:
i.   Unpredictable failure of machinery, sometimes lead to loss of life.
ii.   Contamination of drinking water.
iii.   Leakage of toxic liquid or gas.
iv.   Leakage of inflammable gas from corrodes pipe or instrument which can cause fire hazards.

5.8. FACTORS AFFECTING CORROSION

The rate of corrosion is affected by following factors.
1.   The more reactive metals are more prone to corrosion.
2.   Air and moisture are quite helpful in corrosion. The presence of gases like CO_2 and SO_2 in air makes it still faster. e.g., if iron is kept in vacuum, then no rusting is formed.
3.   Presence of impurities helps in setting up a corrosion cell and increases the rate of corrosion. e.g., pure iron does not rust.
4.   Strains in metal also help in corrosion. e.g., in iron articles, rusting is more pronounced on the areas having bends, dust, scratches, nicks and cuts.
5.   The presence of electrolytes also makes the corrosion process faster, e.g., iron rust more rapidly in saline water in comparison to pure water.

5.9. TYPES OF CORROSION

Corrosion of the metals occurs by the attack of surrounding materials on the surface of metal. Corrosion is classified as:
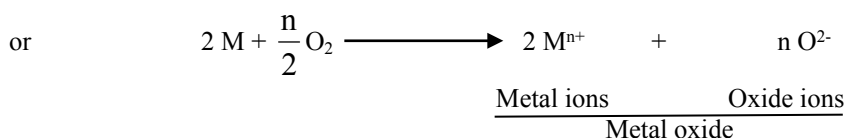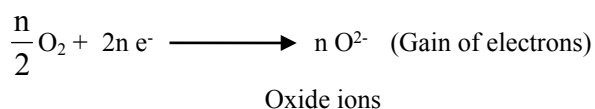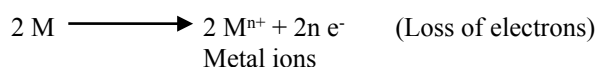1.   Dry corrosion or direct chemical corrosion
2.   Wet corrosion or immersed corrosion or electro-chemical corrosion.

5.9.1. Dry corrosion or direct chemical corrosion

This type of corrosion occurs mainly through the direct chemical action of environment/ atmospheric gases such as oxygen, halogen, hydrogen sulphide, sulphur dioxide, nitrogen or anhydrous inorganic liquid with metal surfaces in immediate proximity. There are three main types of chemical corrosion.
   i.   Oxidation corrosion
   ii.   Corrosion by other gases
   iii. Liquid metal corrosion

i. Oxidation Corrosion: This type of corrosion is brought about by the direct action of oxygen at low or high temperatures on metals, usually in the absence of moisture. At ordinary temperatures, metal, in general, are very slightly attacked. However, alkali metals (Li, Na, K, Rb, etc.) and alkaline earth metals (Be, Ca, Sr, etc.) are even rapidly oxidised at low temperatures. At high temperatures, almost all metals (except Ag, Au and Pt) are oxidised. The reactions in the oxidation corrosion are:

$$2\,M \longrightarrow 2\,M^{n+} + 2n\,e^- \quad \text{(Loss of electrons)}$$
Metal ions

$$\frac{n}{2}O_2 + 2n\,e^- \longrightarrow n\,O^{2-} \quad \text{(Gain of electrons)}$$
Oxide ions

or $\qquad 2\,M + \dfrac{n}{2}O_2 \longrightarrow 2\,M^{n+} \qquad + \qquad n\,O^{2-}$

$$\underset{\text{Metal oxide}}{\underline{\text{Metal ions} \qquad\qquad \text{Oxide ions}}}$$

ii. Corrosion by Other Gases: Dry gases such as SO_2, CO_2, Cl_2, H_2S, F_2 etc., also cause corrosive effect on the metals. The extent of corrosion effect depends mainly on the chemical affinity to the metal and gas involved. Like in case of oxidation corrosion by atmospheric air, hence also the degree of attack depends on the formation of protective or non protective layers, on the metal surface.

i.   If the layer formed is non-porous or protective, the extent of attack decreases, because the layer formed protects the metal surface from further attack. For example, AgCl layer resulting from the attack of chlorine on silver metal.

ii.   If the layer formed is porous or non-protective, the total metal surface is gradually decayed. e.g. , dry Cl_2 gas attacks on tin forming volatile tin(iv) chloride, which volatilizes immediately from the metal surface, thereby leaving fresh metal surface for further attack. Similarly, at high temperature, hydrogen sulphide attacks steel forming scale of FeS, which hinders the normal operations in petroleum industry.

iii. Liquid Metal Corrosion: This type of corrosion has been found to occur in devices used for nuclear power. Liquid metal corrosion occurs due to the chemical action of flowing liquid metal at high temperatures on solid metal or alloy. This type of corrosion results in weakening of the solid metal either (i) dissociation of a solid metal by a liquid metal, or (ii) internal penetration of the liquid metal into the solid metal.

5.9.2. Wet Corrosion or Electrochemical Corrosion

This type of corrosion occurs: (i) where a conducting liquid is in contact with metal or (ii) when two dissimilar metal or alloys or either immersed or dipped partially in a solution. This corrosion involves flow of electron current between the anodic and cathodic areas. At anodic area, oxidation reaction (i.e., liberation of free electrons) takes place, so anodic metal is destroyed by either dissolving or assuming combined state (such as oxide, etc.). Hence, corrosion always occurs at anodic areas.

At anodic areas: $M \longrightarrow M^{n+} + ne^-$ (Oxidation)

On the other hand, the cathodic reaction consumes electrons with either by: (a) evolution of hydrogen or (b) absorption of oxygen, depending on the nature of the corrosive environment.

(a) **Evolution of hydrogen:** This type corrosion occurs, usually in acidic environments. Considering metal like Fe, the anodic reaction is dissolution of iron as ferrous ions with the liberation of electrons.

$Fe \longrightarrow Fe^{2+} + 2e^-$ (Oxidation)
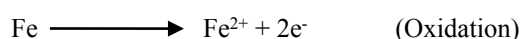
These electrons flow through the metal, from anode to cathode, where H^+ ions (of acidic solution) are eliminated by hydrogen gas.

$2H^+ + 2e^- \longrightarrow H_2 \uparrow$ (Reduction)
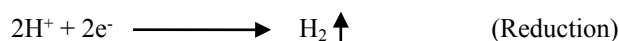
The overall reaction is: $Fe + 2H^+ \longrightarrow Fe^{2+} + H_2 \uparrow$

Thus, this type of corrosion causes "displacement of hydrogen ions from, the acidic solution by metal ions." Consequently, all metals above hydrogen in the electrochemical series have a tendency to get dissolved in acidic solution with simultaneous evolution of hydrogen.

Note: It may be pointed here that in hydrogen evolution type of corrosion, the anodes are, usually very large areas; whereas cathode are small areas.

(b) **Absorption of Oxygen:** Rusting of iron in neutral aqueous solution of electrolytes (like NaCl solution) in the presence of atmospheric oxygen is a common example of this type of corrosion. The surface of iron is, usually coated with at thin film of iron oxide. However, if this iron oxide film develops some cracks, acidic areas are created on the surface; while the well metal parts act as cathodes. It follows that the anodic areas are small surface parts; while nearly rest of the surface of the metal forms large cathodes.

At the anodic areas of the metal (iron) dissolve as ferrous ions with liberation of electrons.

$Fe \longrightarrow Fe^{2+} + 2e^-$ (Oxidation)
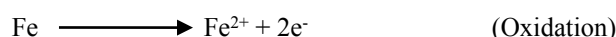
The liberated electrons flow from anodic to cathodic areas, through iron metal, where electrons are intercepted by the dissolved oxygen as:

$$\frac{1}{2} O_2 + H_2O + 2e^- \longrightarrow 2OH^-$$ (Reduction)
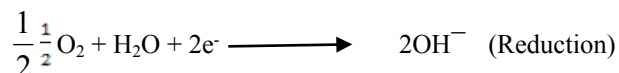
The Fe^{2+} ions (at anode) and OH^- ions (at cathode) diffuse and when they meet, ferrous hydroxide is precipitated.

$Fe^{2+} + 2OH^- \longrightarrow Fe(OH)_2 \downarrow$
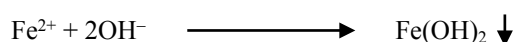
(i) If enough oxygen is present, ferrous hydroxide is easily oxidised ferric hydroxide.

$Fe(OH)_2 + O_2 + 2H_2O \longrightarrow 4Fe(OH)_3$
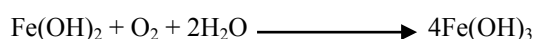
This product, called yellow rust, actually corresponds to $Fe_2O_3 . H_2O$.

(ii) If the supply of oxygen is limited, the corrosion product may be even black anhydrous magnetite, Fe_3O_4.

In other words, any corrosion process can be termed as an electrochemical process in which cathode and anode are formed on the metal surface and an electrolyte (water or salt or acid) must be present to permit ionic flow to form corrosion products.

Note: 1. It may be pointed out that through the two reactants Fe^{2+} and OH^- originate from the anode and cathode respectively, but their combination occurs, more commonly near the cathode, because the smaller Fe^{2+} diffuse more rapidly than the larger OH^- ions. So corrosion occurs at the anode, but rust is deposited at or near the cathode.

2. An increase in oxygen content has two effects: (i) it forces the cathodic reaction to the right, producing more OH⁻ ions, and (ii) it removes more electrons and, therefore, accelerates the corrosion at the anode. Each of these effects, in-turn, supply more reactants for the rust-forming reaction. Evidently, presence of oxygen greatly accelerates both corrosion and rust-formation, with the corrosion occurring at the anode, but the rust forming at or near the cathode.

5.10. CORROSION CONTROL METHODS

There are varieties of corrosion control techniques as the corrosion depends on the nature of environment. The important corrosion control methods are given in the following sections:

1. Design and material selection

2. Protective coatings

3. Cathodic protection

4. Anodic protection

5. Corrosion inhibitors

5.10.1. Design and material selection

The designing of the material should be such that corrosion if it occurs is uniform and does not result in intense and localized corrosion. Some of the important design principles are:

1. If two different metals have to be in contact, they should be selected and their oxidation potential is as close as possible.

2. Heat treatment (annealing) helps to reduce internals stresses and reduce corrosion.

3. The anodic metal should not be painted or coated when in contact with a different cathodic metal, because any crack in coating would lead to it rapid localized corrosion.

4. If moisture of electrolyte solution is present, suitable inhibitors should be employed.

5. The contact between dissimilar metals in the presence of corrosive solution should be avoided. If this principle is not obeyed, then corrosion is localized on the more active metal, while the less reactive metal remains protected.

6. If an active metal is used, it should be insulated from more cathodic metals.

7. Whenever, the direct joining of different metals, is unavoidable, an insulating fitting may be used in between them to avoid direct metal- metal electrical contact.

8. Impingement attack can be reduced by careful filtration of suspended solids from the liquid stream and by preventing turbulent flow.

9. By adjusting the acidity or alkalinity of the environment, corrosion can be controlled. If control of pH is not possible, inert coating and inactive metals are used to control the pH.

5.10.2. Protective coatings

These are used to prevent corrosion at the surfaces of materials. Protective coatings include metallic coatings, chemical conversion coatings, ceramic coatings and organic coatings.

5.10.3. Cathodic protection

The corrosion of metal takes place at the anodic region where as at the cathodic region, metal is unaffected. The principle of cathodic protection involves the elimination of anodic sites and conversion of the entire metal into cathodic site. This can be achieved by providing electrons from an external source so that the specimen always remains cathode. This technique of offering protection to a specimen against corrosion by providing electrons from an external source is called cathodic protection. It can be achieved by the following two methods:

i. Sacrificial anode method: In this method, the metal structure is converted into a cathode by connective into a more active metal, which acts as an auxiliary anode. The most commonly used auxiliary anodes are Zn, Mg and Al. These metals being more active, acts as anode and undergo preferential corrosion, thus protecting the metal structure. Since the anode metals are sacrificed to protect the metal structure, this method is known as sacrificial anode method. New auxiliary anodes replace exhausted sacrificial anodes as and when required. For examples,

(a) Magnesium block connected to underground pipelines.

(b) Magnesium bars are fixed to the sides of the ships.

ii. Impressed current method: Another method of providing cathodic protection is by applying a direct current larger than the corrosion current. The protected metal is made cathodic by connecting it to the negative terminal of a DC source. Positive terminal is connected to an inert anode like graphite. The metal structure being cathode does not undergo corrosion.

5.10.4. Anodic protection

The prevention of corrosion by impressed anodic current method is called anodic protection. Few metals like Ti and alloys like steel, when made as anode exhibits passivity by forming their oxide layers. In case of metals, such as Ti, Ni, Cr and their alloys, application of suitable anodic current makes them passive and decreases their rate of dissolution. The potential required to protect the metal can be obtained from potential current curve. The advantage of the method is that it requires a small current. However, the corrosion rate cannot be reduced to zero as in cathodic protection. A drawback of the method is that it cannot be applied to metals that do not passivate. This method of anodic protection is utilized in the transportation of concentrated acids.

5.10.5. Corrosion inhibitors

These inhibitors reduce corrosion by retarding either anodic or cathodic reactions.

i. Anodic inhibitors: Anodic reaction is the oxidation of metals, that is, for example in rusting of iron, Fe^{2+} ions are formed at anode. Anodic inhibitors prevent the formation of Fe^{2+} ions (anodic reaction), and thereby retard the corrosion process. This is achieved by the addition of anions such as chromate, tungstate, molybdate, etc., which combine with metal ions formed at anodic region, forming sparingly soluble salts. These salts are deposited on the anodic sites forming protective films, which acts as barriers between metal surface and corrosion medium, prevent further anodic reaction and hence corrosion.

ii. Cathodic inhibitors: These act by inhibiting the cathodic reactions which involve the liberation of hydrogen in acidic solutions and OH^- ions in alkaline solution. These can be of two types:

a) Organic cathodic inhibitors such as amines, mercaptans, thioureas, sulphoxides form a protective layers on cathodic regions, prevent the evolution of hydrogen; thus decreasing the rate of corrosion.

b) Inorganic cathodic inhibitors such as sulphates of Mg, Mn, Ni, and Zn are used in neutral or alkaline medium. These inhibitors react with OH- ions liberated at cathode, forming insoluble hydroxide, which form protective film over cathodes areas and prevent corrosion.

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EXERCISE

1. Write short note on electrode potential.
2. What is standard electrode potential?
3. Describe the construction and working of galvanic cell.
4. Explain the function of salt bridge.
5. What do you understand by electrochemical series?

6.   Discuss the working principle of secondary batteries.
7.   Derive Nernst equation for the calculation of cell emf.
8.   Describe the construction of lead storage battery.
9.   What is electrochemical corrosion? Write down the mechanism involved in the said reaction.
10.   Describe the process of galvanization of iron? How does it prevent the corrosion of iron?
11.   Explain the mechanism of hydrogen evolution and oxygen absorption in electrochemical corrosion. Give figures.
12.   What is corrosion? Describe the mechanism of electrochemical corrosion by (i) Hydrogen evolution (ii) Oxygen absorption
13.   Explain sacrificial anodic and impressed cathodic protection method for prevention of corrosion.
14.   Explain why pure metal rod half immersed vertically in water starts corroding at the bottom?
15.   Discuss any four method of corrosion control.
16.   Define the term corrosion. Discuss in brief the electrochemical theory of corrosion.
17.   What are the factors which affect corrosion?
18.   What is corrosion of metals? Explain the basic reason of metallic corrosion.
19.   How is corrosion prevented by cathodic protection?
20.   Define corrosion.
21.   Write a short note on corrosion inhibitors.
22.   Discuss the mechanism of electrochemical corrosion.