Chemistry Notes for class 12 Chapter 3 Electrochemistry

Electrochemistry is that branch of chemistry which deals with 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.

Importance of Electrochemistry

1. Production of metals like Na, Mg. Ca and Al.
2. Electroplating.
3. Purification of metals.
4. Batteries and cells used in various instruments.

Conductors

Substances that allow electric current to pass through them are known as conductors.

Metallic Conductors or Electronic Conductors

Substances which allow the electric current to pass through them by the movement of electrons are called metallic conductors, e.g.. metals.

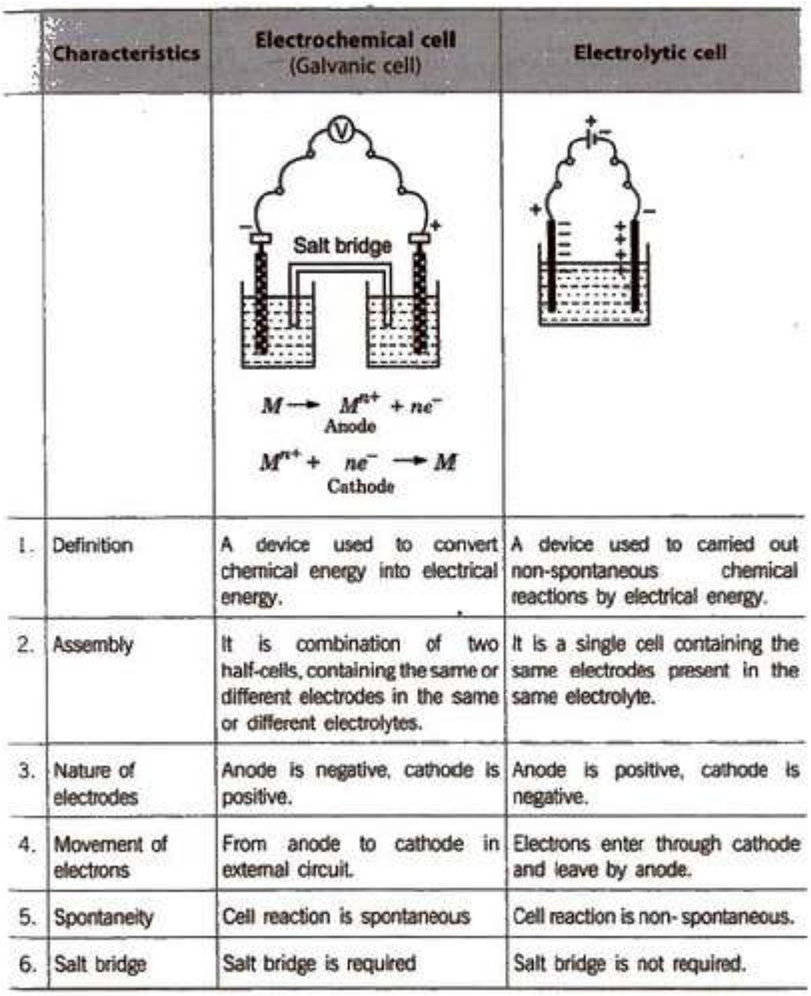
Electrolytic Conductors or Electrolytes

Substances which allow the passage of electricity through their fused state or aqueous solution and undergo chemical decomposition are called electrolytic conductors, e.g., aqueous solution of acids. bases and salts.

Electrolytes are of two types:

1. **Strong electrolytes** The electrolytes that completely dissociate or ionise into ions are called strong electrolytes. e.g., HCl, NaOH, K_2SO_4
2. **Weak electrolytes** The electrolytes that dissociate partially (ex < 1) are called weak electrolytes, e.g., CH_3COOH, H_2CO_3, NH_4OHH_2S, etc.

Electrochemical Cell and Electrolytic

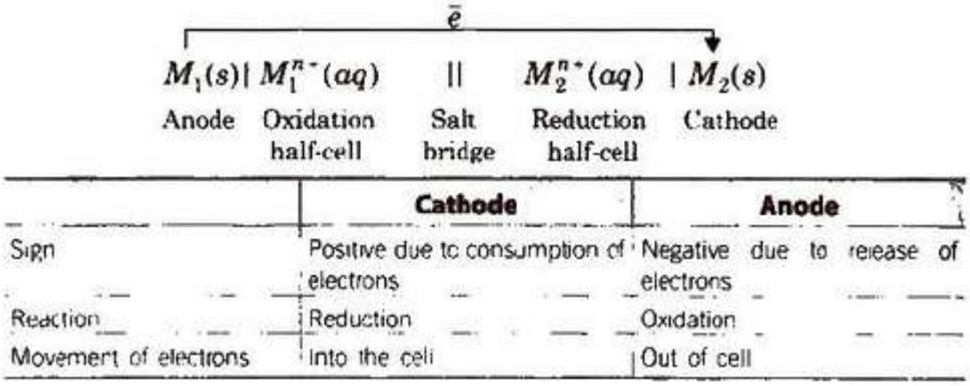


	Characteristics	Electrochemical cell (Galvanic cell)	Electrolytic cell
		$M \rightarrow M^{n+} + ne^-$ Anode $M^{n+} + ne^- \rightarrow M$ Cathode	
1.	Definition	A device used to convert chemical energy into electrical energy.	A device used to carried out non-spontaneous chemical reactions by electrical energy.
2.	Assembly	It is combination of two half-cells, containing the same or different electrodes in the same or different electrolytes.	It is a single cell containing the same electrodes present in the same electrolyte.
3.	Nature of electrodes	Anode is negative, cathode is positive.	Anode is positive, cathode is negative.
4.	Movement of electrons	From anode to cathode in external circuit.	Electrons enter through cathode and leave by anode.
5.	Spontaneity	Cell reaction is spontaneous	Cell reaction is non- spontaneous.
6.	Salt bridge	Salt bridge is required	Salt bridge is not required.

A cell of almost constant emf is called standard cell. The most common is Weston standard cell.

Galvanic cell is also called voltaic cell.

General Representation of an Electrochemical Cell



$$\overset{\bar{e}\;\rightarrow}{M_1(s) \mid M_1^{n+}(aq) \parallel M_2^{n+}(aq) \mid M_2(s)}$$

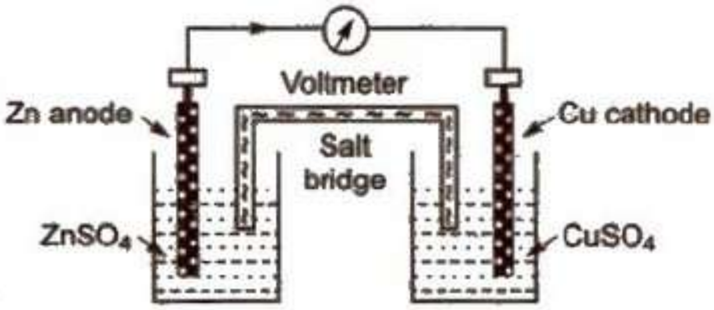
	Cathode	Anode
Sign	Positive due to consumption of electrons	Negative due to release of electrons
Reaction	Reduction	Oxidation
Movement of electrons	Into the cell	Out of cell

Other features of the electrochemical cell are

1. There is no evolution of heat.
2. The solution remains neutral on both sides.
3. The reaction and now of electrons stops after sometime.

Daniell Cell

An electrochemical cell of zinc and copper metals is known as Daniell cell. It is represented as



Cell diagram,

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

$$\begin{array}{lrcl} \text{LHS oxidation,} & \mathrm{Zn} & \longrightarrow & \mathrm{Zn}^{2+} + 2e^- \\ \text{RHS reduction,} & \mathrm{Cu}^{2+} + 2e^- & \longrightarrow & \mathrm{Cu} \\ \hline \text{Overall reaction,} & \mathrm{Zn} + \mathrm{Cu}^{2+}(aq) & \longrightarrow & \mathrm{Zn}^{2+}(aq) + \mathrm{Cu} \end{array}$$

By convention cathode is represented on the RHS and anode on the LHS.

Function of salt bridge

1. It completes the circuit and allows the flow of current.
2. It maintains the electrical neutrality on both sides. Salt-bridge generally contains solution of strong electrolyte such as KNO_3, KCL etc. KCI is preferred because the transport numbers of K^+ and $Cl^-$are almost same.

Transport number or Transference number The current flowing through an electrolytic solution is carried by the ions. The fraction of the current carried by an ion is called its transport number or transference number. Thus.

Transport number of cation. n_c = (current carried by cation/total current)

Transport number of cation. n_a = (current carried by anion/total current)

Evidently $n_c + n_a = 1$

Electrode Potential

When an electrode is in contact with the solution of its ions in a half-cell, it has a tendency to lose or gain electrons which is known as electrode potential. It is expressed in volts. It is an intensive property, i.e., independent of the amount of species in the reaction.

Oxidation potential The tendency to lose electrons in the above case is known as oxidation potential. Oxidation potential of a half-cell is inversely proportional to the concentration of ions in the solution.

Reduction potential The tendency to gain electrons in the above case is known as reduction potential. According to IUPAC convention, the reduction potential alone be called as the electrode potential unless it is specifically mentioned.

$E^\circ_{red} = -E^\circ_{oxidalion}$

It is not possible to determine the absolute value of electrode potential. For this a reference electrode [NHE or SHE] is required. The electrode potential is only the difference of potentials between two electrodes that we can measure by combining them to give a complete cell.

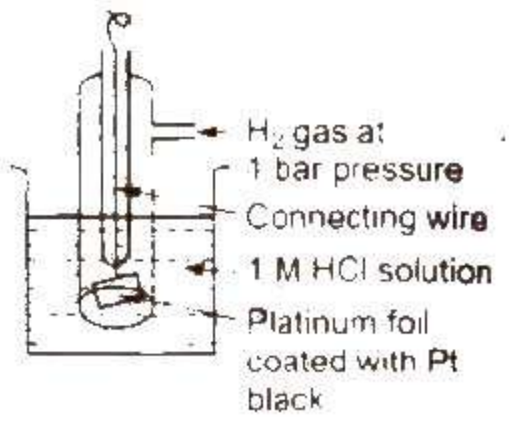
Standard electrode potential The potential difference developed between metal electrode and solution of ions of unit molarity (1M) at 1 atm pressure and 25°C (298 K) is called standard electrode potential.

It is denoted by E°.

Reference Electrode

The electrode of known potential is called reference electrode. It may be primary reference electrode like hydrogen electrode or secondary reference electrode like calomel electrode.

Standard hydrogen electrode (SHE) Standard hydrogen electrode (SHE). also known as normal hydrogen electrode (NHE), consists of platinum wire, carrying platinum foil coated with finely divided platinum black. The wire is sealed into a glass tube. placed in beaker containing 1 M HCl. The hydrogen gas at 1 atm pressure is bubbled through the solution at 298K. Half-cell is pt H_2 (1 atm) H^+ (1 M)



In SHE. at the surface of plantinum, either of (he following reaction can take place

$2H^+(ag) + 2e^- \rightarrow H_2G$ Reduction

$H_2(g) \rightarrow 2H^+(ag) + 2e^-$ Oxidation

The electrode potential of SHE has been fixed as zero at all temperatures.

Its main drawbacks are

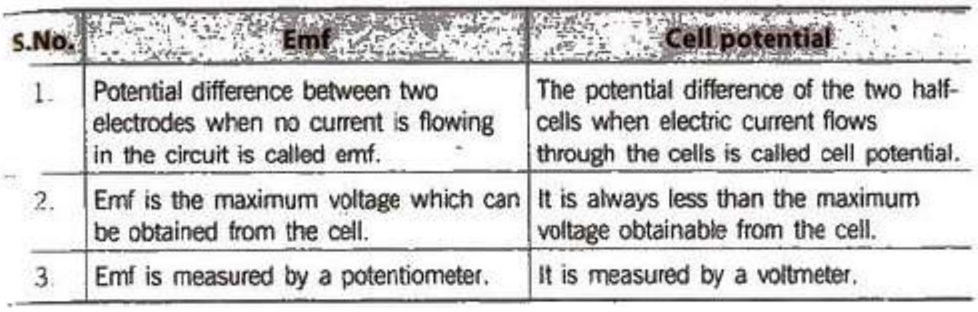
1. It is difficult to maintain 1 atm pressure of H_2 gas.
2. It is difficult to maintain H^+ ion concentration 1 M.
3. The platinum electrode is easily poisoned by traces of impurities.

Hence, calomel electrodes are conveniently used as reference electrodes, It consists of mercury in contact with Hg_2 Cl_2 (calomel) paste in a solution of KCl.

Electromotive Force (emf) of a Cell

It is the difference between the electrode potentials of two half-cells and cause flow of current from electrode at higher potential to electrode at lower potential. It is also the measure of free energy change. Standard emf of a cell,

$$E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode} = E^\circ_{right} - E^\circ_{left} = E^\circ_{red} + E^\circ_{oxi}$$

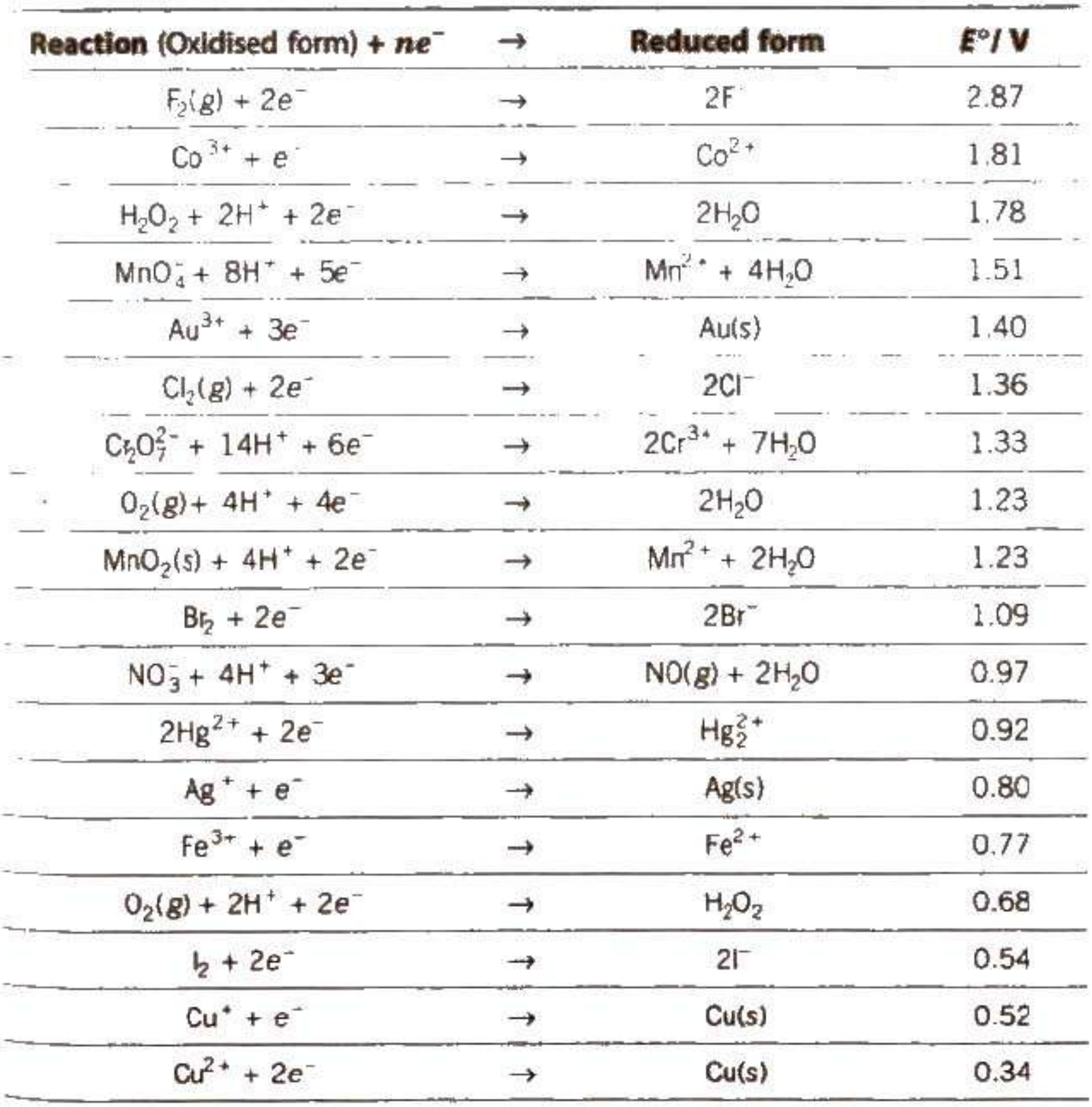


S.No.	Emf	Cell potential
1.	Potential difference between two electrodes when no current is flowing in the circuit is called emf.	The potential difference of the two half-cells when electric current flows through the cells is called cell potential.
2.	Emf is the maximum voltage which can be obtained from the cell.	It is always less than the maximum voltage obtainable from the cell.
3.	Emf is measured by a potentiometer.	It is measured by a voltmeter.

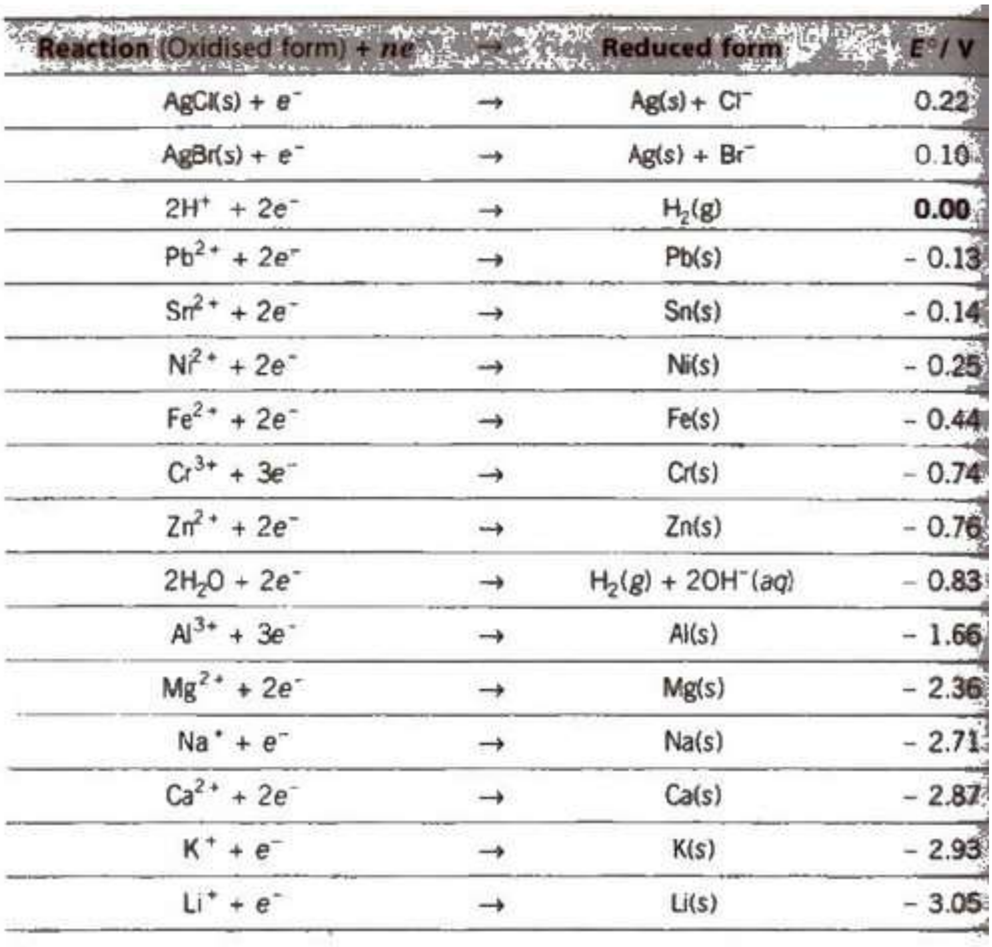
Electrochemical Series

It is the arrangement of electrodes in the increasing order of their standard reduction potentials.

Standard Electrode Potential at 298 K



Reaction (Oxidised form) + ne^-	→	**Reduced form**	**E°/ V**
$F_2(g) + 2e^-$	→	$2F^-$	2.87
$Co^{3+} + e^-$	→	Co^{2+}	1.81
$H_2O_2 + 2H^+ + 2e^-$	→	$2H_2O$	1.78
$MnO_4^- + 8H^+ + 5e^-$	→	$Mn^{2+} + 4H_2O$	1.51
$Au^{3+} + 3e^-$	→	$Au(s)$	1.40
$Cl_2(g) + 2e^-$	→	$2Cl^-$	1.36
$Cr_2O_7^{2-} + 14H^+ + 6e^-$	→	$2Cr^{3+} + 7H_2O$	1.33
$O_2(g) + 4H^+ + 4e^-$	→	$2H_2O$	1.23
$MnO_2(s) + 4H^+ + 2e^-$	→	$Mn^{2+} + 2H_2O$	1.23
$Br_2 + 2e^-$	→	$2Br^-$	1.09
$NO_3^- + 4H^+ + 3e^-$	→	$NO(g) + 2H_2O$	0.97
$2Hg^{2+} + 2e^-$	→	Hg_2^{2+}	0.92
$Ag^+ + e^-$	→	$Ag(s)$	0.80
$Fe^{3+} + e^-$	→	Fe^{2+}	0.77
$O_2(g) + 2H^+ + 2e^-$	→	H_2O_2	0.68
$I_2 + 2e^-$	→	$2I^-$	0.54
$Cu^+ + e^-$	→	$Cu(s)$	0.52
$Cu^{2+} + 2e^-$	→	$Cu(s)$	0.34



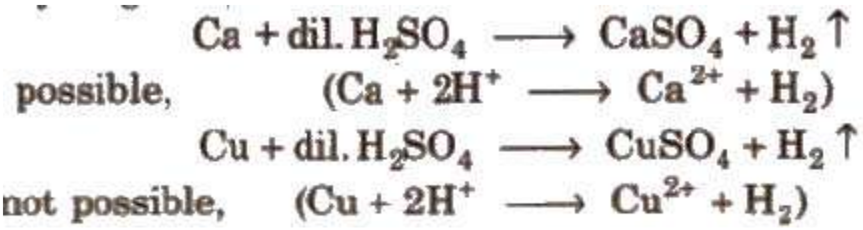
Reaction (Oxidised form) + ne	→	Reduced form	E°/ V
$AgCl(s) + e^-$	→	$Ag(s) + Cl^-$	0.22
$AgBr(s) + e^-$	→	$Ag(s) + Br^-$	0.10
$2H^+ + 2e^-$	→	$H_2(g)$	**0.00**
$Pb^{2+} + 2e^-$	→	$Pb(s)$	- 0.13
$Sn^{2+} + 2e^-$	→	$Sn(s)$	- 0.14
$Ni^{2+} + 2e^-$	→	$Ni(s)$	- 0.25
$Fe^{2+} + 2e^-$	→	$Fe(s)$	- 0.44
$Cr^{3+} + 3e^-$	→	$Cr(s)$	- 0.74
$Zn^{2+} + 2e^-$	→	$Zn(s)$	- 0.76
$2H_2O + 2e^-$	→	$H_2(g) + 2OH^-(aq)$	- 0.83
$Al^{3+} + 3e^-$	→	$Al(s)$	- 1.66
$Mg^{2+} + 2e^-$	→	$Mg(s)$	- 2.36
$Na^+ + e^-$	→	$Na(s)$	- 2.71
$Ca^{2+} + 2e^-$	→	$Ca(s)$	- 2.87
$K^+ + e^-$	→	$K(s)$	- 2.93
$Li^+ + e^-$	→	$Li(s)$	- 3.05

Appications of Electrochemical Series (ECS)

1. The lower the value of E°, the greater the tendency to form cation.

$M \rightarrow M^{n+} + ne^-$

Metals placed below hydrogen in ECS replace hydrogen from di1 acids but metals placed above hydrogen cannot replace hydrogen from dil acids.



$Ca + \text{dil.}\, H_2SO_4 \longrightarrow CaSO_4 + H_2\uparrow$

possible, $(Ca + 2H^+ \longrightarrow Ca^{2+} + H_2)$

$Cu + \text{dil.}\, H_2SO_4 \longrightarrow CuSO_4 + H_2\uparrow$

not possible, $(Cu + 2H^+ \longrightarrow Cu^{2+} + H_2)$

3. Oxides of metals placed below hydrogen are not reduced by H_2 but oxides of iron and metals placed above iron are reduced by H_2·

- SnO, PbO, CuO are reduced by H_2
- CaO, K_2O are not reduced by H_2·

4. Reducing character increases down the series.

5. Reactivity increases down the series.

6. Determination of emf; emf is the difference of reduction potentials of two half-cells.

- $E_{emf} = E_{RHS} - E_{LHS}$

If the value of emf is positive. then reaction take place spontaneously, otherwise not.

7. Greater the reduction potential of a substance, oxidising power. (e.g.. $F_2 > Cl_2 > Br_2 > I_2$)

8. A negative value of standard reduction potential shows that it is the site of oxidation.

9. Oxides of metals having $E^\circ_{red} \geq 0.79$ will be decomposed by heating to form O_2 and metal.

$HgO(s) \rightarrow Hg(l)(1/2)O_2(g)$

$(E^\circ_{Hg^{2+}/Hg} = 0.79V)$

Nernst Equation

The relationship between the concentration of ions and electrode potential is given by Nernst equation.

$$M^{n+} + ne^- \longrightarrow M$$

$$E_{M^{n+}/M} = E^\circ_{M^{n+}/M} - \frac{2.303\,RT}{nF}\log\frac{1}{[M^{n+}]}$$

$$E_{M^{n+}/M} = E^\circ_{M^{n+}/M} - \frac{0.0591}{n}\log\left[\frac{1}{M^{n+}}\right]$$

For a electrochemical cell,

$$aA + bB \longrightarrow cC + dD$$

$$E_{cell} = E^\circ_{cell} - \frac{2.303RT}{nF}\log\frac{[C]^c[D]^d}{[A]^a[B]^b}$$

Concentration of pure solids and liquids is taken as unity.

Nernst equation and K_c

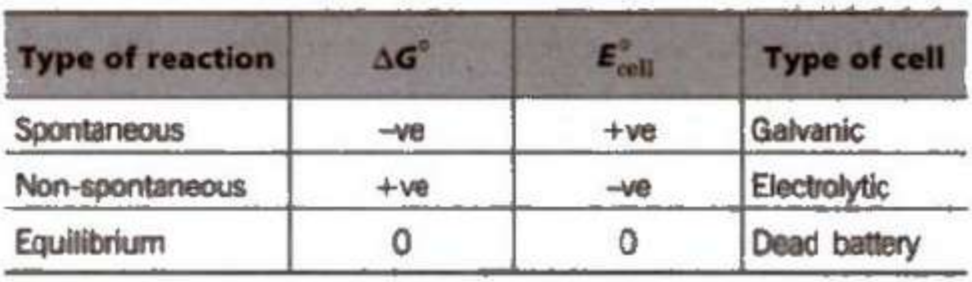
At equilibrium

$$\because \text{ At equilibrium, } E_{cell} = 0$$

$$E^\circ_{cell} = \frac{0.0591}{n} \log K_c \text{ at } 298\text{K}$$

$$\Delta G^\circ = -nFE^\circ_{cell}$$

Here, ΔG° is the standard Gibbs free energy change.



Type of reaction	ΔG°	E°_{cell}	Type of cell
Spontaneous	–ve	+ve	Galvanic
Non-spontaneous	+ve	–ve	Electrolytic
Equilibrium	0	0	Dead battery

Relationship between free energy change and equilibrium constant

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

Concentration Cells

(i) Electrode concentration cells Two hydrogen electrodes or different pressures are dipped In the same solution of electrolyte,

e.g..

$$\text{Pt, } H_2(p_1)|H^+|H_2(p_2)\text{Pt, } p_1 > p_2$$

$$E_{cell} = \frac{2.303RT}{nF} \log \frac{p_2}{p_1}$$

(ii) Electrolyte concentration cells Electrodes are the same but electrolyte solutions have different concentrations, e.g..

$$\text{Zn}|\text{Zn}^{2+}(C_1)||\text{Zn}^{2+}(C_2)|\text{Zn, } C_2 > C_1$$

$$E_{cell} = \frac{2.303RT}{nF} \log \frac{C_2}{C_1} = \frac{0.0591}{n} \log \frac{C_2}{C_1}$$

Conductance (G)

It is the ease of flow of electric current through the conductor. It is reciprocal of resistance (R).

$G = (1/R)$, units ohm^{-1} mhos or Ω^{-1}

Specific Conductivity (K)

It is the reciprocal of specific resistance.

$$\kappa = \frac{1}{\rho} = \frac{l}{R.a} = G \times \frac{l}{a} = G \times \text{cell constant } (G^*)$$

$$\left(\frac{l}{a} = \text{cell constant}\right)$$

$$\text{Units of } \kappa = \Omega^{-1}\text{cm}^{-1}$$
$$= \text{S cm}^{-1} (\Omega^{-1} = \text{S } \textit{i.e.}, \text{ Siemens})$$

Unit of cell constant is cm^{-1} or m^{-1}.

Specific conductivity decreases on dilution. This is because concentration of ions per cc decreases upon dilution.

Molar Conductivity (Λ_m)

The conductivity of all the ions produced when 1 mole of an electrolyte is dissolved in V mL of solution is known as molar conductivity.

It is related to specific conductance as

$\Lambda_m = (k \times 1000/M)$

where. M = molarity.

It units are Ω^{-1} cm^2 mol^{-1} or S cm^2 mol^{-1}.

Equivalent conductivity (Λ_m)

The conducting power of all the ions produced when 1 g-equivalent of an electrolyte is dissolved in V mL of solution, is called equivalent conductivity. It is related to specific conductance as

$\Lambda_m = (k \times 1000/N)$

where. N = normality.

Its units are ohm^{-1} cm^2 (equiv^{-1}) or mho cm^2 (equiv^{-1}) or S cm^2 (g-equiv^{-1}).

Debye-Huckel Onsagar equation It gives a relation between molar conductivity, Λ_m at a particular concentration and molar conductivity Λ_m at infinite dilution.

$\Lambda_m = \Lambda^0_m - \sqrt{C}$

where, b is a constant. It depends upon the nature of solvent and temperature.

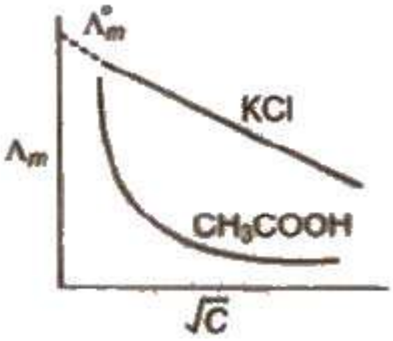
Factors Affecting Conductivity

(i) Nature of electrolyte The strong electrolytes like KNO_3 KCl. NaOH. etc. are completely ionised in aqueous solution and have high values of conductivity (molar as well as equivalent).

The weak electrolytes are ionised to a lesser extent in aqueous solution and have lower values of conductivity (molar as well as equivalent) .

ii) Concentration of the solution The concentrated solutions of strong electrolytes have SIgnificant interionic attractions. which reduce the speed of ions and lower the value of Λ_m. and Λ_{eq}.

The dilution decreases such attractions and increase the value of Λ_m and Λ_{eq}.



The limiting value, Λ^0_m or Λ^∞_m. (the molar conductivity at zero concentration (or at infinite dilution) can be obtained extrapolating the graph.

In case of weak electrolytes, the degree of ionisation increases dilution which increases the value of $\Lambda_m$and Λ_{eq}. The liminting value Λ^0_m cannot be obtained by extrapolating the graph. ~ limiting value, Λ^0_m, for weak electrolytes is obtained by Kohlrausch law.

(iii) Temperature The increase of temperature decreases inter-ionic attractions and increases kinetic energy of ions and their speed. Thus, Λ_m and Λ_{eq} increase with temperature.

Kohlrausch's Law

At infinite dilution, the molar conductivity of an electrolyte is the sum of the ionic conductivities of the cations and anions, e.g., for A_xB_y.

$$\Lambda^0_m (A_xB_y) = x\Lambda^0_{A^+} + y\Lambda^0_{B^-}$$

$$\Lambda^0_{eq} = \Lambda^0_{A^+} + \Lambda^0_{B^-}$$

Applications

(i) Determination of equivalent/molar conductivities of weak electrolytes at infinite dilution, e.g.,

$$\Lambda^\infty_{CH_3COOH} = \Lambda^\infty_{CH_3COONa} + \Lambda^\infty_{HCl} - \Lambda^\infty_{NaCl}$$

$$\Lambda^\infty_{NH_4OH} = \Lambda^\infty_{NH_4Cl} + \Lambda^\infty_{NaOH} - \Lambda^\infty_{NaCl}$$

(ii) Determination of degree of dissociation (α) of an electrolyte at a given dilution.

$$\alpha = \frac{\text{molar conductance at concentration `}C\text{'}}{\text{molar conductance at infinite dilution}} = \frac{\Lambda^C_m}{\Lambda^\infty_m}$$

The dissociation constant (K) of the weak electrolyte at concentration C of the solution can be calculated by using the formula

$k_c = (C\alpha^2/1 - \alpha)$

where, α is the degree of dissociation of the electrolyte.

(iii) Salts like $BaSO_4$ .., $PbSO_4$‘ AgCl, AgBr and AgI which do not dissolve to a large extent in water are called sparingly soluble salts.

The solubility of a sparingly soluble salt can be calculated as

$$\Lambda^\circ_m = \frac{\kappa \times 1000}{\text{solubility (in mol L}^{-1})}$$

$$\text{Solubility (in mol L}^{-1}) = \frac{\kappa \times 1000}{\Lambda^\circ_m}$$

Electrolysis

It is the process of decomposition of an electrolyte when electric current is passed through either its aqueous solution or molten state,

1. In electrolytic cell both oxidation and reduction takes place in the same cell.

2. Anode is positively charged and cathode is negatively charged, In electrolytic cell.
3. During electrolysis of molten electrolyte, cations are liberated at cathode. while anions at the anode.
4. When two or more ions compete at the electrodes. the ion with higher reduction potential gets liberated at the cathode while the ion with lower reduction potential at the anode.

For metals to be deposited on the cathode during electrolysis, the voltage required is almost the same as the standard
electrode potential. However for liberation of gases, some extra voltage is required than the theoretical value of the standard electrode potential. The extra voltage thus required is called over voltage or bubble voltage.

How to Predict the Products of Electrolysis?

When an aqueous solution of an electrolyte is electrolysed, if the cation has higher reduction potential than water (-0.83 V), cation is liberated at the cathode (e.g.. in the electrolysis of copper and silver salts) otherwise H_2 gas is liberated due to reduction of water (e.g., in the electrolysis of K, Na, Ca salts, etc.) Similarly if anion has higher oxidation potential than water (- 1.23 V), anion is liberated (e.g., Br^-), otherwise O^2 gas is liberated due to oxidation of water (e.g., in caseof F^-, aqueous solution of Na_2SO_4 as oxidation potential of $SO^{2-}{}_4$ is – 0.2 V).

Discharge potential is defined as the minimum potential that must be applied acrossthe electrodes to bring about the electrolysis and subsequent discharge of the ion on the electrode.

Faraday's Laws of Electrolysis

1. First law

The amount of the substance deposited or liberated at cathode directly proportional to the quantity of electricity passed through electrolyte.

$W \propto I \times t = I \times t \times Z = Q \times Z$

- I current in amp, t = time in sec,
- Q = quantity of charge (coulomb)
- Z is a constant known as electrochemical equivalent.

When I = 1 amp, t = 1 sec then Q = 1 coulomb, then w = Z.

Thus, electrochemical equivalent I" the amount of the substance deposited or liberated by passing 1A current for 1 sec (i.e.. 1 coulomb, I x t = Q)

2. Second law

When the same quantity of electricity is passed through different electrolytes. the amounts of the substance deposited or liberated at the electrodes arc directly proportional to their equivalent weights, Thus,

$$\frac{\text{Mass of } A}{\text{Mass of } B} = \frac{\text{eq. wt. of } A}{\text{eq. wt. of } B}$$

$$\frac{\omega_1}{\omega_2} = \frac{E_1}{E_2} \Rightarrow \frac{Z_1 Q}{Z_2 Q} = \frac{E_1}{E_2}$$

Hence, electrochemical equivalent ∝ equivalent weight.

Batteries

These are source of electrical energy which may have one or more cells connected in series. For a good quality battery it should be reasonably light. compact and its voltage should not vary appreciably during its use.

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.

(i) Dry cell or Leclanehe cell

Anode-Zinc container

Cathode-Graphite rod surrounded by MnO_2 powder

Electrolyte-Paste of $NH_4Cl + ZnCl_2$

Cathode reaction,

$2MnO_2(s) + 2\ NH^+_4(aq) + 2e^- \rightarrow Mn_2O^3(s) + 2NH_3(g) + H_2O(l)$

Anode reaction,

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

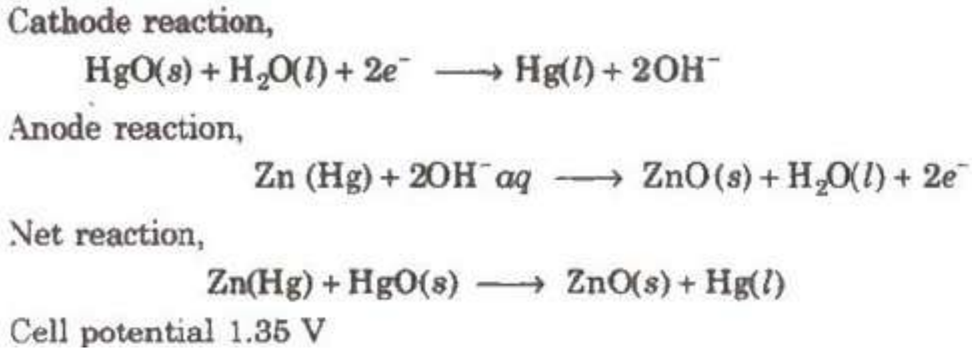
Cell potential 1.25 V to 1.5 V

(ii) Mercury cell

Anode-Zn-Hg amalgam

Cathode-Paste of (HgO + C)

Electrolyte-Moist paste of KOH-ZnO



Cathode reaction,

$$HgO(s) + H_2O(l) + 2e^- \longrightarrow Hg(l) + 2OH^-$$

Anode reaction,

$$Zn\ (Hg) + 2OH^-\ aq \longrightarrow ZnO(s) + H_2O(l) + 2e^-$$

Net reaction,

$$Zn(Hg) + HgO(s) \longrightarrow ZnO(s) + Hg(l)$$

Cell potential 1.35 V

Secondary Batteries

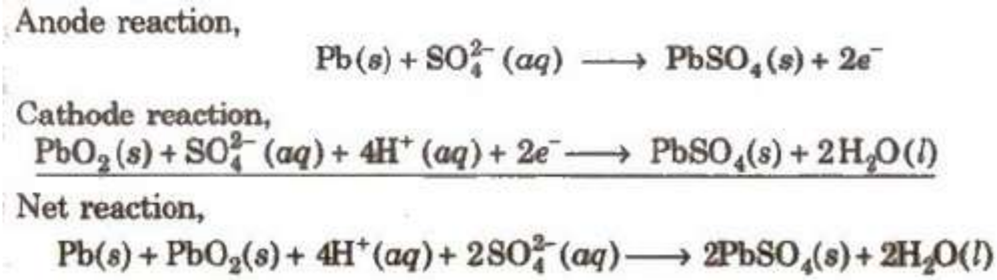
These cells can be recharged and can be used again and again, e.g.,

(i) Lead Storage battery

Anode-Spongy lead

Cathode-Grid of lead packed with PbO_2

Electrolyte-38% H_2SO_4 by mass



Anode reaction,

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

Cathode reaction,

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

Net reaction,

$$Pb(s) + PbO_2(s) + 4H^+(aq) + 2SO_4^{2-}(aq) \longrightarrow 2PbSO_4(s) + 2H_2O(l)$$

When recharged the cell reactions are reversed.

(ii) Nickel-cadmium storage cell

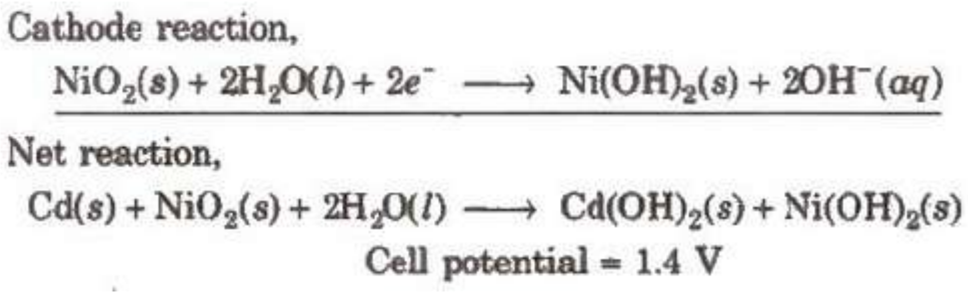
Anode-Cadmium

Cathode-Metal grid containing NiO_2

Electrolyte-KOH solution

Anode reaction,

$Cd(s) + 2OH^-(aq) \rightarrow Cd(OH)_2(s) + 2e^-$



Cathode reaction,

$$NiO_2(s) + 2H_2O(l) + 2e^- \longrightarrow Ni(OH)_2(s) + 2OH^-(aq)$$

Net reaction,

$$Cd(s) + NiO_2(s) + 2H_2O(l) \longrightarrow Cd(OH)_2(s) + Ni(OH)_2(s)$$

Cell potential = 1.4 V

Fuel Cells

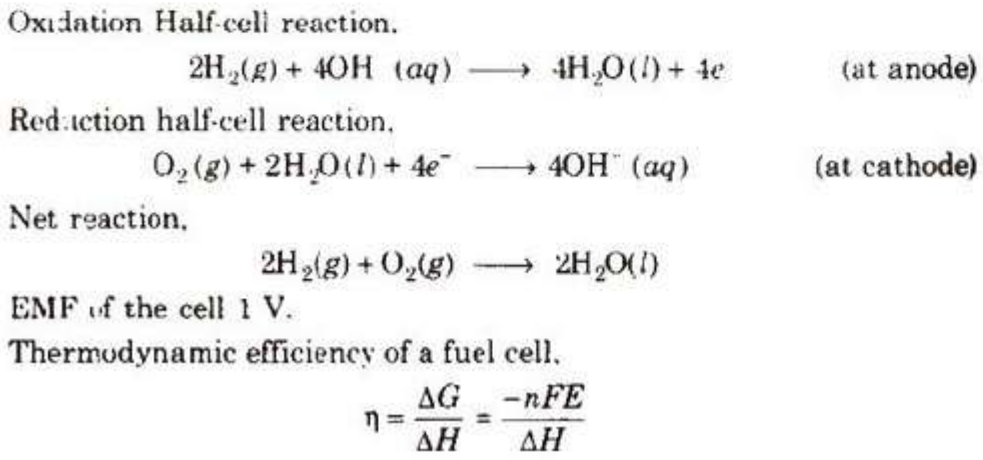
Galvanic cells which use energy of combustion of fuels like H_2, CH_4, CH_3OH, etc., as the source to produce electrical energy are called fuel cells. The fuel cells are pollution free and have high efficiency.

Hydrogen-Oxygen Fuel Cell

Electrodes-Made of porous graphite impregnated with catalyst (Pt, Ag or a metal oxide).

Electrolyte-Aqueous solution of KOH or NaOH

Oxygen and hydrogen are continuously fed into the cell.



Oxidation Half-cell reaction.

$$2H_2(g) + 4OH^-(aq) \longrightarrow 4H_2O(l) + 4e^- \qquad \text{(at anode)}$$

Reduction half-cell reaction.

$$O_2(g) + 2H_2O(l) + 4e^- \longrightarrow 4OH^-(aq) \qquad \text{(at cathode)}$$

Net reaction.

$$2H_2(g) + O_2(g) \longrightarrow 2H_2O(l)$$

EMF of the cell 1 V.

Thermodynamic efficiency of a fuel cell.

$$\eta = \frac{\Delta G}{\Delta H} = \frac{-nFE}{\Delta H}$$

Corrosion

Slow formation of undesirable compounds such as oxides, sulphides or carbonates at the surface of metals by reaction with moisture and other atmospheric gases is known as corrosion.

Factors Affecting Corrosion

1. Reactivity of metals
2. Presence of moisture and atmospheric gases like CO_2, SO_2, etc.
3. Presence of impurities
4. Strains in the metal

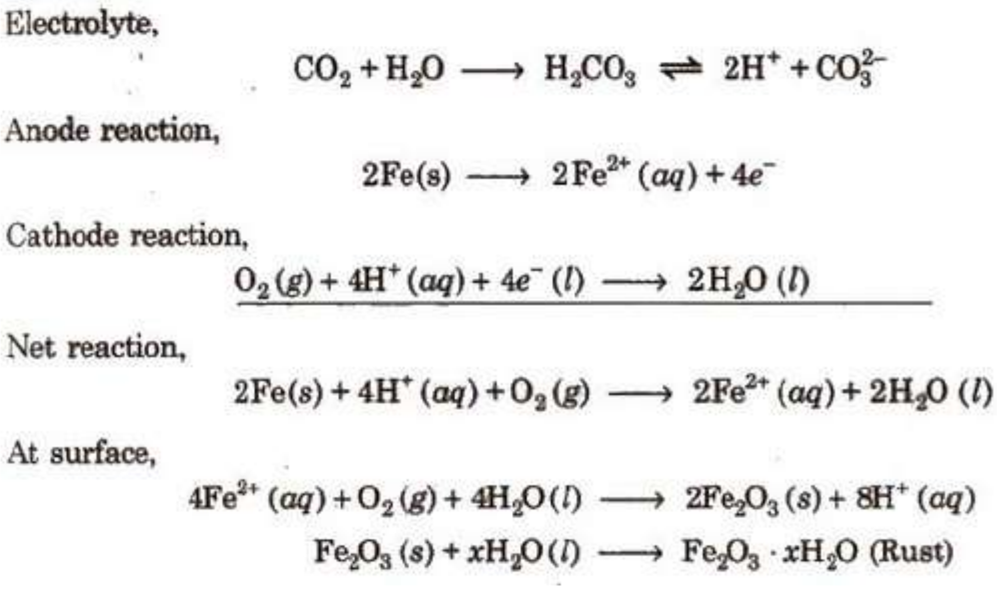
5. Presence of electrolyte

Rusting of Iron-Electrochemical Theory

An electrochemical cell, also known as corrosion cell, is developed at the surface of iron.

Anode- Pure iron

Cathode-Impure surface



Electrolyte,

$$CO_2 + H_2O \longrightarrow H_2CO_3 \rightleftharpoons 2H^+ + CO_3^{2-}$$

Anode reaction,

$$2Fe(s) \longrightarrow 2Fe^{2+}(aq) + 4e^-$$

Cathode reaction,

$$\underline{O_2(g) + 4H^+(aq) + 4e^-(l) \longrightarrow 2H_2O(l)}$$

Net reaction,

$$2Fe(s) + 4H^+(aq) + O_2(g) \longrightarrow 2Fe^{2+}(aq) + 2H_2O(l)$$

At surface,

$$4Fe^{2+}(aq) + O_2(g) + 4H_2O(l) \longrightarrow 2Fe_2O_3(s) + 8H^+(aq)$$

$$Fe_2O_3(s) + xH_2O(l) \longrightarrow Fe_2O_3 \cdot xH_2O \text{ (Rust)}$$

Rusting of iron can be prevented by the following methods :

1. Barrier protection through coating of paints or electroplating.
2. Through galvanisation or coating of surface with tin metal.
3. By the use of antirust solutions (bis phenol).
4. By cathodic protection in which a metal is protected from corrosion by connecting it to another metal that is more easily oxidised.