→ Types of reversible electrodes :→

1. Gas - metal ion electrodes
2. Metal - metal ion electrodes
3. Metal - insoluble metal salt electrodes
4. Redox electrodes

1. Gas - metal ion electrodes

(i) Hydrogen electrode :→

- Hydrogen gas bubbling in a 1M solution of an acid (say, HCl) forms an electrode of this type.
- The equilibrium in this case is represented as

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

- The electrode is reversible with respect to hydrogen ion.
- Since hydrogen gas is nonconducting, platinum or some other metal which is not attacked by the acid and easily comes into equilibrium with hydrogen, is used for making electrical contact in the circuit.
- The electrode is represented as

$$Pt, H_2(g), H^+$$

- It is called standard hydrogen electrode (SHE).

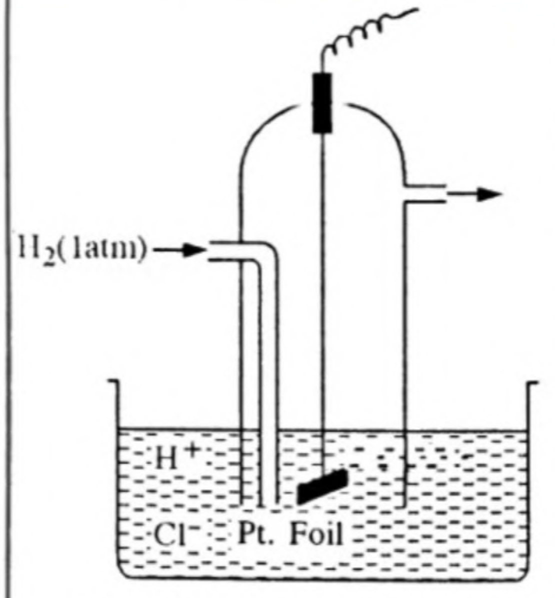


Fig. 1. The hydrogen electrode.

(ii) Chlorine electrode:→

- In this electrode, chlorine gas at a given pressure is bubbled into a solution of HCl.
- The electrode is represented as

$$Pt, Cl_2(g), Cl^-(aq)$$

- The electrode reaction is written as

$$\frac{1}{2} Cl_2(g) + e^- \rightleftharpoons Cl^-(aq.)$$

- The electrode is reversible with respect to chloride ion.

(iii) oxygen electrode:→

- In this electrode, oxygen gas at a given pressure is bubbled through a solution containing hydroxyl, OH^- ions.
- The electrode reaction is written as

$$O_2(g) + 2H_2O + 4e^- \rightleftharpoons 4OH^-(aq.)$$

But, since equilibrium between oxygen gas and hydroxyl ion in solution cannot be established quickly, oxygen electrode does not behave as a truly reversible electrode.

→ Types of reversible electrodes: →

1. Gas - metal ion electrodes
2. Metal - metal ion electrodes
3. Metal - insoluble metal salt electrodes
4. Redox electrodes

2. Metal - metal ion electrodes

- An electrode of this type consist of metal rod dipping in solution containing its own ion, as, for example, zinc rode dipping in zinc sulphate solution or a copper rod dipping in copper sulphate solution, as in the Daniell cell.
- If the metal is univalent, the electrode reaction may be represented as

$$M^+(aq) + e^- \rightleftharpoons M(s)$$

- If the metal rod behave as positive electrode (i.e., the reaction at the electrode involves reduction), the equilibrium will shift towards the right. The concentration of M^+ ions in solution will, therefore, decrease.
- If, on the other hand, the metal rod behave as negative electrode (i.e. the electrode reaction involves oxidation), the equilibrium will shift towards the left. The concentration of M^+ ions in solution will, therefore, increase.
- If metal is bivalent, the above equilibrium may be represented as

$$M^{2+}(aq) + 2e^- \rightleftharpoons M(s)$$

- In general, if the valency of metal is z, the equilibrium is represented as

$$M^{z+}(aq) + ze^- \rightleftharpoons M(s)$$

- The electrode, in general, is represented as

$$M(s), M^{z+}(aq.)$$

→ Types of reversible electrodes :→

1. Gas - metal ion electrodes
2. Metal - metal ion electrodes
3. Metal - insoluble metal salt electrodes
4. Redox electrodes

3. Metal - insoluble metal salt electrodes

- These electrodes consist of a metal and a sparingly soluble salt of the same metal dipping in a solution of a soluble salt having the same anion.
- Calomel electrode :→
- Calomel electrode electrode consist of mercury, solid mercurous chloride and a solution of potassium chloride.
- The electrode is represented as

$$Hg,\ Hg_2Cl_2(s),\ KCl\ (solution)$$

- In this electrode, high grade purity mercury is placed at the bottom of a glass tube having a side tube on each side (figure).
- Mercury is covered by a paste of mercurous chloride (calomel).
- A solution of potassium chloride introduced above the paste through the side tube shown on the right.
- The concentration of solution is either decinormal (N/10), normal (1N) or else the solution is fully saturated.
- The solution also fill the side tube ending in a jet on the left.

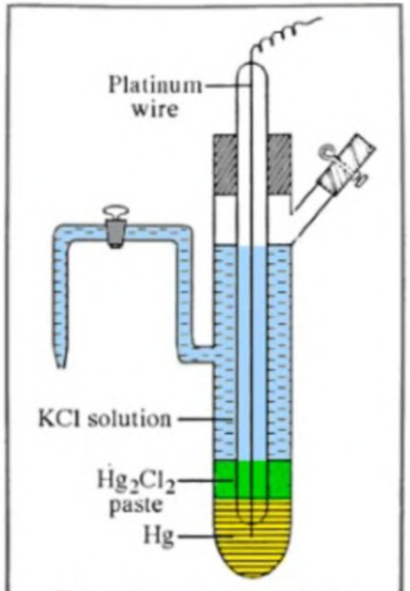


Fig. The calomel electrode.

- A platinum wire sealed into a glass tube serves to make electrical contact of the electrode with the circuit.
- If the electrode reaction involves reduction, the Hg_2^{+2} ions furnished by the sparingly soluble mercurous chloride would be discharged at the electrode. Hence, more of the calomel would pass into solution. The result is an increase in the concentration of chloride ions. The reactions may be represented as -

$$Hg_2^{+2}(aq.) + 2e^- \rightleftharpoons 2Hg(l)$$

$$Hg_2Cl_2(s) \rightleftharpoons Hg_2^{+2}(aq) + 2Cl^-(aq.)$$

- If, on the other hand, the electrode reaction involves oxidation, it would liberate electrons and send Hg_2^{+2} ions into solution. The Hg_2^{+2} ions would combine with Cl^- ions (furnished by KCl) forming sparingly soluble Hg_2Cl_2. The result is a fall in the concentration of chloride ions in the solution. The reactions may be represented as -

$$2Hg(l) \rightleftharpoons Hg_2^{+2}(aq.) + 2e^-$$

$$Hg_2^{+2}(aq) + 2Cl^-(aq) \rightleftharpoons Hg_2Cl_2(s)$$

- Thus, in the case of the calomel electrode, the electrode reaction may be represented as

$$Hg_2Cl_2(s) + 2e^- \rightleftharpoons 2Hg(l) + 2Cl^-(aq.)$$

The electrode, therefore, is reversible with respect to chloride ion.

- Silver - silver chloride electrode : →
- This type of electrode consist of a silver wire coated with a layer of silver chloride. This is inserted in a solution of KCl or HCl of known concentration.
- This electrode is represented as

$$Ag, AgCl(s), Cl^-(aq.)$$

The electrode is reversible with respect to Cl^- ion.

→ Types of reversible electrodes: →

1. Gas - metal ion electrodes
2. Metal - metal ion electrodes
3. Metal - insoluble metal salt electrodes
4. Redox electrodes

4. Redox electrodes

- Also known as Oxidation - Reduction electrodes.
- The term redox electrode or oxidation-reduction electrode is used for those electrodes in which the potential is developed due to the presence of the same substance in two different valence (i.e. oxidation) state.
- Such an electrode is setup by inserting an unattackable metal (e.g. platinum) in an appropriate solution.
- When platinum wire is inserted in a solution containing Fe^{+2} and Fe^{+3} ions, it is found that the wire aquires a potential.

  The same thing happens when a platinum wire is inserted in a solution containing Sn^{+2} and Sn^{+4} ions or Ce^{+3} and Ce^{+4} ions.
- The potential at the electrode arises from the tendency of the ions in one oxidation state to change into the other more stable oxidation state.
- The electrode reactions may be represented as follows -

$$Fe^{+3}(aq) + e^- \rightleftharpoons Fe^{+2}(aq)$$

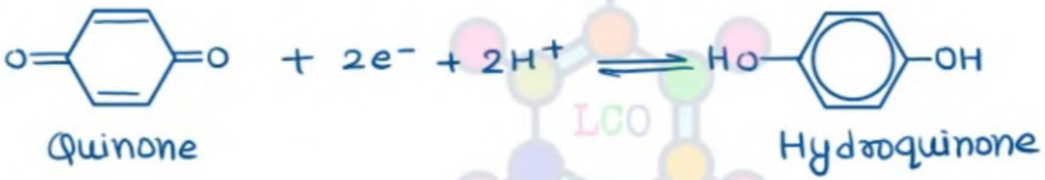
$$Sn^{+4}(aq) + 2e^- \rightleftharpoons Sn^{+2}(aq)$$

$$Ce^{+4}(aq) + e^- \rightleftharpoons Ce^{+3}(aq)$$

- The function of the platinum wire is to 'pick up' the electrons and to provide electrical contact to the electrode.

→ Quinhydrone electrode :-

- Another important but a slightly different type of oxidation - reduction electrode is so called quinhydrone electrode which consist of a platinum wire placed in a solution containing hydroquinone (QH_2) and quinone in equimolar amounts.
- The electrode reaction in this case is represented as follows:-



- This electrode is represented as

$$Pt, Q, QH_2, H^+(aq)$$

This is reversible with respect to H^+ ions.

→ Electrochemical cells:→

- Electrochemical cells can be broadly classified into two categories:-

(i) Electrolytic cells (ii) Galvanic cells

(i) Electrolytic cells:→

- In electrolytic cells, a chemical reaction (electrolysis) is carried out with the help of an electrical current.
- An electrolytic cell is a device which converts electrical energy into chemical energy.
- Consider an electrolytic cell involving the electrolysis of molten sodium chloride using platinum electrodes.
- The left side electrode is connected to the negative terminal of an external battery which supplies electrons to this electrode. It is because of this, the left side electrode becomes negative charged.
- The right side electrode is connected to the positive terminal of of the battery sucks electrons from this electrode. Thus this electrode aquires a positive charge.
- Within the solution, electricity is carried out by the movements of ions.
- The positive ions (i.e. cations) are attracted towards the negative electrode and the negative ions (i.e. anions) towards the positive.
- Since cations are attracted towards the negative electrode, the negative electrode is called cathode. Similarly the positive electrode is known as the anode.

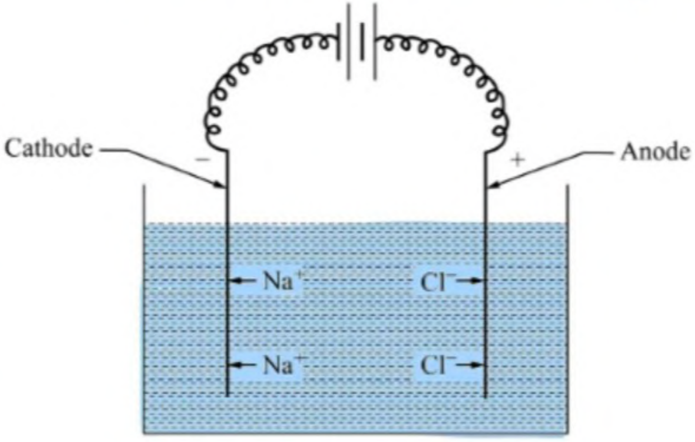


Fig:- Electrolytic cell

- Electrode reactions involve reduction at the cathode and oxidation at the anode. Thus in present case, we have

At Cathode $Na^+ + e^- \longrightarrow Na(s)$

At Anode $Cl^- \longrightarrow \frac{1}{2} Cl_2(g) + e^-$

The overall transformation is

$$Na^+ + Cl^- \longrightarrow Na(s) + \frac{1}{2} Cl_2(g)$$

→ Electrochemical cells:→

- Electrochemical cells can be broadly classified into two categories:-

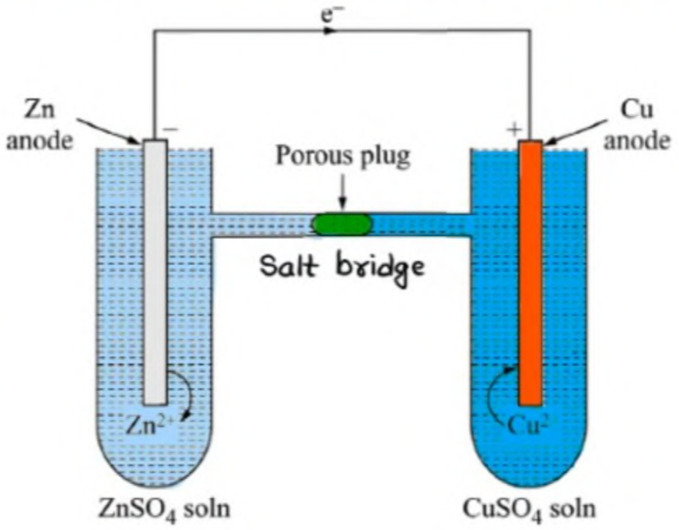
(i) Electrolytic cells (ii) Galvanic cells

(ii) Galvanic cells:→

- Also called voltaic cell.
- In galvanic cell, electrical current is produced as a result of some spontaneous chemical reaction.
- The galvanic cell is a device which converts chemical energy into electrical energy.
- Such a cell, usually, conists of two electrodes immersed in one or more suitable electrolytes. when the electrodes are connected externally as well as internally, if required, a chemical reaction occurs in the cell involving oxidation at one electrode and reduction at the other electrode.
- Example:→

→ Daniell cell:→

- In this cell, a copper rod dipping in copper sulphate solution and zinc rod dipping in a solution of zinc sulphate.
- The two metal rods are connected through an ammeter and two solutions are connected through a salt bridge i.e. an inverted U-shaped glass tube filled with a solution of KCl.
- As soon as the circuit is closed, current starts flowing which is indicated by deflection in the ammeter.



- The flow of current is due to following processes:

  The zinc metal passes into solution as Zn^{+2} ions liberating two electrons. The process involves oxidation.

  $$Zn \rightarrow Zn^{+2} + 2e^-$$

  The liberating electrons move into the ammeter and then enter the copper rod. Cu^{+2} ions extract two electrons each from the copper rod and are discharged as copper metal on the copper electrode. The process involves reduction.

  $$Cu^{+2} + 2e^- \rightarrow Cu$$

  The overall chemical reaction or cell reaction is, thus,

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

- Since in the present case electrons are generated at the zinc electrode and consumed at the copper electrode, the flow of electrons, in the cell is from zinc electrode to copper electrode.

- The SO_4^{-2} ions left unpaired due to reduction of Cu^{+2} ions to metallic copper migrate through the salt bridge to other segment of cell where they combine with Zn^{+2} ion produced by the oxidation of zinc
- Thus while electrons move from the zinc rod to copper rod in the outside circuit, the SO_4^{-2} ions move from the solution surrounding the copper rod to the solution surrounding the zinc rod through the salt bridge. This completes the electrical circuit of the cell.

- With the passage of time, the concentration of Zn^{+2} ion increases and that of Cu^{+2} decreases. This pushes the cell reaction in the backward direction. Ultimately, a state of equilibrium is reached and cell stops producing electricity.

→ Reversible and Irreversible cells:→

- For thermodynamic treatment of galvanic cell it is essential that these cells operate in a thermodynamically reversible manner.

(a) Reversible cells:→

- A cell is said to work reversibly in the thermodynamic sense when it is generating infinitesimally small current so that the cell reaction always remains virtually in a state of equilibrium.
- In order to find out if a given cell is reversible or not, it is connected to an external source of EMF acting in opposite direction.
- The cell will be reversible if it satisfies the following conditions:

(i) opposing EMF = Cell EMF

If the opposing EMF is exactly equal to that of the cell itself, no current is given out by the cell and no chemical reaction takes place in the cell.

(ii) opposing EMF < Cell EMF

If the opposing EMF is infinitesimally smaller than that of the cell itself, an extremally small current is given out by the cell and small amount of the chemical reaction takes place in the cell.

(iii) opposing EMF > Cell EMF

If the opposing EMF is infinitesimally greater than that of the cell itself, an extremely small current flow through the cell in the opposite direction and a small amount of the chemical reaction also takes place in reverse direction.

Example:-

- Daniell cell

$$Zn \mid \underset{Sol.}{ZnSO_4} \mid \underset{Sol.}{CuSO_4} \mid Cu$$

- Cell reaction

$$Zn + Cu^{+2} \rightleftharpoons Zn^{+2} + Cu$$

If opposing EMF < Cell EMF, cell reaction proceeds from left to right.

If opposing EMF > Cell EMF, cell reaction proceeds from right to left.

Hence the cell works in reversible manner.

(b) Irreversible cells :→

- A cell is said to be an irreversible one which does not satisfy the three conditions of revesibility.

Example:-

$$Zn \mid aq.\ H_2SO_4 \mid Cu$$

- cell reaction

$$Zn + 2H^+ \rightarrow Zn^{+2} + H_2\uparrow$$

If opposing EMF < Cell EMF, cell reaction proceeds as above

If opposing EMF > Cell EMF, cell reaction proceeds as below

$$Cu + 2H^+ \rightarrow Cu^{+2} + H_2\uparrow$$

Hence the cell works in irreversible manner.

→ Conventional representation of electrochemical cells: →

(i) A half cell, such as zinc rode dipped in a solution of Zn^{+2} ion of concentration, m is indicated as :-

$$Zn \mid Zn^{+2}(m)$$

The vertical line denotes a solid phase in contact with liquid phase.

(ii) A galvanic cell may be represented as

$$Zn \mid Zn^{+2}(m) \parallel Cu^{+2}(m) \mid Cu$$

The two vertical lines in between the two half cells represent the liquid function.

(iii) The electrode potential is given a positive sign if the electrode reaction involves reduction and a negative sign if the electrode reaction involves oxidation.

(iv) The emf of cell is the algebric sum of the potential of the two half cells. For example, in a general cell,

$$A \mid A^{+} \parallel B^{+} \mid B$$

The emf of the cell is given by the potential difference of two electrodes i.e.

$$\therefore \; E_{cell} = \left\{ \begin{matrix} \text{Reduction potential of right hand} \\ \text{electrode} \end{matrix} \right\} - \left\{ \begin{matrix} \text{Reduction potential of left hand} \\ \text{electrode} \end{matrix} \right\}$$

(v) The potential of the same electrode acting as anode will be opposite in sign to one acting as cathode.

(vi) The emf of a cell is arbitrarily given a positive sign if the electrode written at left is negative and the electrode at the right is positive.

$$\overset{\xrightarrow{\quad e \quad}}{- A \mid A^{+} \parallel B^{+} \mid B +} \qquad (\text{E is positive})$$

$$\overset{\xleftarrow{\quad e \quad}}{+ B \mid B^{+} \parallel A^{+} \mid A -} \qquad (\text{E is negative})$$

If E is positive, oxidation occurs at left hand electrode and reduction takes place at the right hand electrode.

If E is negative, reduction takes place at the left hand electrode and oxidation occurs at the right hand electrode.

→ Nernst equation :→ (Derivation of cell EMF and single electrode potential)

- Suppose the reaction occuring in a reversible cell is represented by the general equation

$$aA + bB \rightleftharpoons cC + dD$$

- The decrease in free energy, $-\Delta G$, accompanying the process is given by the well known thermodynamic equation

$$-\Delta G = -\Delta G^\circ - RT\ln Q \quad — ①$$

Where $-\Delta G^\circ$ is the decrease in free energy accompanying the same process when all the reactant and products are in standard states of unit activity and Q stands for the reaction quotient of the activities of the products and the reactants at any given stage of the reaction, that is

$$Q = \frac{(a_C)^c (a_D)^d}{(a_A)^a (a_B)^b}$$

- If E is the EMF of the cell in volts and cell reaction involves the passage of n faradys, i.e. nF coulombs, the electrical energy produced by the cell is nFE volt coulombs i.e. joules.

Hence
$$-\Delta G = nFE$$
and
$$-\Delta G^\circ = nFE^\circ$$

Where E = Electromotive force of cell

E° = std Electromotive force of cell i.e. when the activity, or to be approximation, concentration, of each of the reactants and products of the cell reaction is unity.

Substitute the value of $-\Delta G$ and ΔG° in eq. ①

$$nFE = nFE^\circ - RT\ln Q \quad - ②$$

Divide both side of eq ② by nF

$$\frac{nFE}{nF} = \frac{nFE^\circ}{nF} - \frac{RT}{nF}\ln Q$$

or $$E = E^\circ - \frac{RT}{nF}\ln Q \quad - ③$$

or $$E = E^\circ - \frac{2.303\,RT}{nF}\log Q \quad - ④$$

At 25°C $$\frac{2.303RT}{F} = \frac{2.303 \times 8.314\ \mathrm{J\,K^{-1}\,mol^{-1}} \times 298\ \mathrm{K}}{96485\ \mathrm{C\,mol^{-1}}} = 0.0591\ \text{volt}$$ (Joule = volt coulomb)

Eq. ④ may be written as

$$E = E^\circ - \frac{0.0591}{n}\log Q \quad - ⑤$$

or $$E = E^\circ - \frac{0.0591}{n}\log\frac{(a_C)^c(a_D)^d}{(a_A)^a(a_B)^b} \quad - ⑥$$

or $$E = E^\circ - \frac{0.0591}{n}\log\frac{[C]^c[D]^d}{[A]^a[B]^b} \quad - ⑦$$

Eq. ⑦ gives the effect of the concentrations of reactants and product involved in the cell reaction on the EMF of the cell. Eq. ⑦ is called Nernst equation.

With the help of eq. ⑦ we can calculate cell EMF.

→ Derivation of single electrode potential: →

- The general expression for the electrode potential of a metal M in contact with M^{n+} ions, involving the electrode reaction

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

may be written as

$$E_{el} = E^\circ_{el} - \frac{RT}{nF} \ln \frac{[M]}{[M^{n+}]}$$

$$\text{or} \quad E_{el} = E^\circ_{el} - \frac{RT}{nF} \ln \frac{1}{[M^{n+}]} \qquad \because [M] \text{ is taken unity}$$

$$\text{or} \quad E_{el} = E^\circ_{el} + \frac{RT}{nF} \ln [M^{n+}]$$

$$\text{or} \quad E_{el} = E^\circ_{el} + \frac{0.0591}{n} \log [M^{n+}] \text{ at } 25^\circ C \quad - ⑧$$

- In Case of redox electrodes such as Fe^{+3}, Fe^{+2} electrode

$$Fe^{3+}(aq) + e^- \rightleftharpoons Fe^{2+}(aq)$$

$$\text{Hence} \quad E_{el} = E^\circ_{el} - \frac{RT}{F} \ln \frac{[Fe^{2+}]}{[Fe^{3+}]} = E^\circ_{el} + \frac{RT}{F} \ln \frac{[Fe^{3+}]}{[Fe^{2+}]} \quad - ⑨$$

- It follows from the above discussion that if we write the electrode reaction, in general, as

$$\text{oxidised state} + ne^- \rightleftharpoons \text{reduced state}$$

the potential of the electrode is given by

$$E_{el} = E^{\circ}_{el} - \frac{RT}{F} \ln \frac{[\text{Reduced state}]}{[\text{oxidised state}]} \quad - ⑩$$

$$E_{el} = E^{\circ}_{el} + \frac{RT}{F} \ln \frac{[\text{oxidised state}]}{[\text{Reduced state}]} \quad - ⑪$$

→ Single electrode potential and standard hydrogen electrode (Reference electrode) :→

- Galvanic cell is made up of two electrodes.
- At one electrode oxidation takes place, i.e., electrons are involved.
- At the other electrode reduction takes place, i.e., electrons are taken up.
- The tendency of an electrode to lose or gain electrons when it is in contact with its own ion in solution, is called electrode potential.
- The tendency to gain electrons means also the tendency to get reduced, this tendency is called reduction potential.
- The tendency to lose electrons means the tendency to get oxidised, this tendency is called oxidation potential.
- Oxidation potential is the reverse of reduction potential. Thus, if the reduction potential of an electrode under given condition is 1.5 volts, then its oxidation potential is taken as −1.5 volts and vice-versa.
- It is not possible to determine experimentally the potential of a single electrode (i.e. of a half cell). It is only the difference of potential between two electrodes that we can measure by combining them to give a complete cell.
- By arbitrarily fixing potential of one electrode as zero, it is possible to assign numerical value to potentials of the various other electrodes.
- Accordingly, the potential of a reversible hydrogen electrode has been fixed as zero. The electrode is known as standard hydrogen electrode (SHE) and is represented as

$$Pt\ ;\ H_2(g)(1\,atm),\ H^+(aq)\,(c = 1M)$$

- All other single electrode potential measured with respect to standard hydrogen electrode are referred to as potential on the hydrogen scale.
- If it is required to find the electrode potential of, say, zinc electrode, all that is needed is to combine it with the SHE electrode so as to have a complete cell represented as:

$$Zn, Zn^{2+} \text{ solution} \mid H^+(aq)(C = 1M),\ H_2(g)\ (1\,atm);\ Pt$$

The EMF of the cell, determined potentiometrically, is then equal to the potential of the zinc electrode since potential of the SHE is taken as zero.

- In this case, reduction occurs at the hydrogen electrode and oxidation takes place at the zinc electrode, as shown below:

Hydrogen electrode : $2H^+(aq) + 2e^- \rightleftharpoons H_2(g)$

Zinc electrode : $Zn(s) \rightleftharpoons Zn^{2+}(aq) + 2e^-$

∴ The net reaction is

$$Zn(s) + 2H^+(aq) \rightleftharpoons Zn^{2+}(aq) + H_2(g)\ (1\,atm)$$

- It is not convenient to use the standard hydrogen electrode as the reference electrode. This is because it is difficult to maintain the activity of H+ ions in the solution at unity and to keep the pressure of the gas uniformly at one atomsphere. A far better reference electrode is the calomel electrode.

→ Sign conventions or sign of electrode potential: →

- According to the latest convention adopted by IUPAC, the electrode potential is given a positive sign if the electrode reaction involves reduction (i.e. taking up of electrons from the electrode) when connected to the standard hydrogen electrode and a negative sign if the electrode reaction involves oxidation (i.e. liberation of electrons) when connected to the standard hydrogen electrode whose potential is taken zero.
- When copper electrode (copper rod dipping in solution of a copper sulphate) is connected with a standard hydrogen electrode, reduction takes place at the copper electrode. The electrode reactions are as follows:

Copper electrode : $Cu^{2+}(aq.) + 2e^- \rightleftharpoons Cu(s)$ (Reduction)

Hydrogen electrode : $H_2(g) \rightleftharpoons 2H^+(aq.) + 2e^-$ (oxidation)

Hence, according to the above convention, the potential of copper electrode is taken as positive. Thus $E_{(Cu^{2+}, Cu)}$ is positive.

- However, if zinc electrode is connected with the standard hydrogen electrode, oxidation takes place at the zinc electrode. The electrode reactions are as follows:

Zinc electrode : $Zn(s) \rightleftharpoons Zn^{2+}(aq.) + 2e^-$ (oxidation)

Hydrogen electrode : $2H^+(aq.) + 2e^- \rightleftharpoons H_2(g)$ (Reduction)

Hence, the potential of the zinc potential is taken as negative. Thus, $E_{(Zn^{2+}, Zn)}$ is negative.

→ Standard electrode potential : Electrochemical series and its significance:→

- The potential of an electrode, at a given temperature, depends upon the concentration of the ions in the surrounding solution.
- If the concentration of the ions is unity and the temperature is 25°c, the potential of the electrode is termed as the standard electrode potential.
- The standard electrode potential of number of electrodes are given in table. These values are said to be on hydrogen scale since in these determinations the potentials of the standard hydrogen electrode, used as the reference electrode, has been taken as zero.
- The values of standard electrode potential arranged in the decreasing order in the table and the series is called electrochemical series.

Electrode	Electrode Reaction	E°_{el} (volts)
$F_2(g); 2F^-$	$F_2 + 2e^- \rightleftharpoons 2F^-$	+2·87
$Co^{3+}, Co^{2+}; Pt$	$Co^{3+} + e^- \rightleftharpoons Co^{2+}$	+1·82
$Ce^{4+}, Ce^{3+}; Pt$	$Ce^{4+} + e^- \rightleftharpoons Ce^{3+}$	+1·61
$Mn^{2+}, MnO_4^-; Pt$	$MnO_4^- + 8H^+ + 5e^- \rightleftharpoons Mn^{2+} + 4H_2O$	+1·51
Au^{3+}, Au	$Au^{3+} + 3e^- \rightleftharpoons Au$	+1·50
$Cl_2(g), 2Cl^-; Pt$	$Cl_2(g, 1\text{ atm}) + 2e^- \rightleftharpoons 2Cl^-$	+1·36
$Cr^{3+}, Cr_2O_7^{2-}$	$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightleftharpoons 2Cr^{3+} + 7H_2O$	+1·33
Tl^{3+}, Tl^+	$Tl^{3+} + 2e^- \rightleftharpoons Tl^+$	+1·25
$Br_2(l), 2Br^-; Pt$	$Br_2(l) + 2e^- \rightleftharpoons 2Br^-$	+1·06
$Hg^{2+}, Hg_2^{2+}; Pt$	$2Hg^{2+} + 2e^- \rightleftharpoons Hg_2^{2+}$	+0·92
$Ag^+; Ag$	$Ag^+ + e^- \rightleftharpoons Ag$	+0·80
$Fe^{3+}, Fe^{2+}; Pt$	$Fe^{3+} + e^- \rightleftharpoons Fe^{2+}$	+0·77
$Hg_2SO_4(s), SO_4^{2-}; Hg$	$Hg_2SO_4(s) + e^- \rightleftharpoons 2Hg + SO_4^{2-}$	+0·61

$I_2(s)$; $2I^-$; Pt	$I_2(s) + 2e^- \rightleftharpoons 2I^-$	+0·53
Cu^+, Cu	$Cu^+ + e^- \rightleftharpoons Cu$	+0·52
Cu^{2+}, Cu	$Cu^{2+} + 2e^- \rightleftharpoons Cu$	+0·34
$Hg_2Cl_2(s)$, Cl^- ; Hg	$Hg_2Cl_2(s) + 2e^- \rightleftharpoons 2Hg + 2Cl^-$	+0·28
$AgCl(s)$, Cl^- ; Ag	$AgCl(s) + e^- \rightleftharpoons Ag(s) + Cl^-$	+0·22
Sn^{4+}, Sn^{2+} ; Pt	$Sn^{4+} + 2e^- \rightleftharpoons Sn^{2+}$	+0·15
Cu^{2+}, Cu^+	$Cu^{2+} + e^- \rightleftharpoons Cu^+$	+0·15
$Hg_2Br_2(s)$, Br^- ; Hg	$Hg_2Br_2(s) + 2e^- \rightleftharpoons 2Hg + 2Br^-$	+0·13
$AgBr(s)$, Br^- ; Ag	$AgBr(s) + e^- \rightleftharpoons Ag(s) + Br^-$	+0·07
$2H^+$, $H_2(g)$; Pt	$2H^+ + 2e^- \rightleftharpoons H_2(g, 1\ atm)$	0·00
Pb^{2+}, Pb	$Pb^{2+} + 2e^- \rightleftharpoons Pb$	−0·13
Sn^{2+}, Sn	$Sn^{2+} + 2e^- \rightleftharpoons Sn$	−0·15
$AgI(s)$, I^- ; Ag	$AgI(s) + e^- \rightleftharpoons Ag(s) + I^-$	−0·15
Ni^{2+}, Ni	$Ni^{2+} + 2e^- \rightleftharpoons Ni$	−0·24
Co^{2+}, Co	$Co^{2+} + 2e^- \rightleftharpoons Co$	−0·27
Tl^+, Tl	$Tl^+ + e^- \rightleftharpoons Tl$	−0·34
Cd^{2+}, Cd	$Cd^{2+} + 2e^- \rightleftharpoons Cd$	−0·40
Fe^{2+}, Fe	$Fe^{2+} + 2e^- \rightleftharpoons Fe$	−0·44
Cr^{3+}, Cr	$Cr^{3+} + 3e^- \rightleftharpoons Cr$	−0·74
Zn^{2+}, Zn	$Zn^{2+} + 2e^- \rightleftharpoons Zn$	−0·76
Mn^{2+}, Mn	$Mn^{2+} + 2e^- \rightleftharpoons Mn$	−1·18
Al^{3+}, Al	$Al^{3+} + 3e^- \rightleftharpoons Al$	−1·66
Mg^{2+}, Mg	$Mg^{2+} + 2e^- \rightleftharpoons Mg$	−2·52
Na^+, Na	$Na^+ + e^- \rightleftharpoons Na$	−2·71
Ca^{2+}, Ca	$Ca^{2+} + 2e^- \rightleftharpoons Ca$	−2·87
Ba^{2+}, Ba	$Ba^{2+} + 2e^- \rightleftharpoons Ba$	−2·90
K^+, K	$K^+ + e^- \rightleftharpoons K$	−2·92
Li^+, Li	$Li^+ + e^- \rightleftharpoons Li$	−3·04

- The higher is the positive value, the greater is the tendency of the oxidised form to get reduced by accepting electrons.
- The greater the negative value, the greater is the tendency of the reduced form to get oxidised by donating electrons.

→ Importance:→

- The electrochemical series can be used to predict the chemical behaviour of different elements.
- The electrochemical series offers a very good method of studying the displacement reactions.
- From the values of standard electrode potentials, EMF of the cell can be calculated.
- The phenomenon of rusting of iron is an electrochemical process. This can be explained by means of the series.

→ EMF of a cell and its computation:→

- In the Daniell cell, electrons flow from Zn electrode to copper electrode. This is due to fact that Zn atom can be more easily oxidised to Zn^{2+} ion than Cu atom to Cu^{2+} ion.
- on the other side, Cu^{2+} ion can be more easily reduced than the Zn^{2+} ion.
- Consequently, Zn atom is oxidised to Zn^{2+} ion and the electrons set free at the Zn electrode move towards Cu electrode where Cu^{2+} ion is reduced to Cu atom.
- The flow of electrons is due to the difference of oxidation tendencies of the two atoms or it is due to the difference of reduction tendencies of the two ions.
- The relative oxidation tendencies of atoms can be represented by the oxidation potentials.
- A more easily oxidizable atom will have a larger value of oxidation potential and less easily oxidizable atom have a low value of oxidation potential.
- Thus, Zn atom has a higher oxidation potential than the Cu atom.
- Electrons in the external circuit flow from the electrode of higher oxidation potential to the electrode of lower oxidation potential.
- The difference in potential which causes a current to flow from the electrode of higher potential to the lower potential is known as the electromotive force, abbreviated as EMF, of the cell and is expressed in volts.
- EMF of cell is represented by the symbol E_{cell}. Thus

$$E_{cell} = \text{Higher oxidation potential} - \text{Lower oxidation potential} \quad - ①$$

→ EMF in terms of reduction potential:→

- By convention, E_{cell} is expressed in terms of reduction potential (Known as standard electrode potential) of the two electrodes.

- The reduction potentials measure reduction tendencies of ions and their values are simply negative of the oxidation potentials of the corresponding atoms.
- This follows from the fact that an atom with the maximum tendency of oxidation (i.e. highest value of oxidation potential) will yield an ion with the least tendency of reduction (i.e. the minimum reduction potential) and vice versa.
- Thus, eq ① may be written as

$$E_{cell} = \text{Higher reduction potential} - \text{Lower reduction potential} \quad -②$$

- Example:- The two half-cell reactions in the Daniell cell are thus written as

(i) $Cu^{2+}(aq.) + 2e^- \rightleftharpoons Cu(s)$: $E^\circ_{el} = +0.34\ V$

(ii) $Zn^{2+}(aq.) + 2e^- \rightleftharpoons Zn(s)$: $E^\circ_{el} = -0.76\ V$

Substracting eq. (ii) from eq. (i) we get

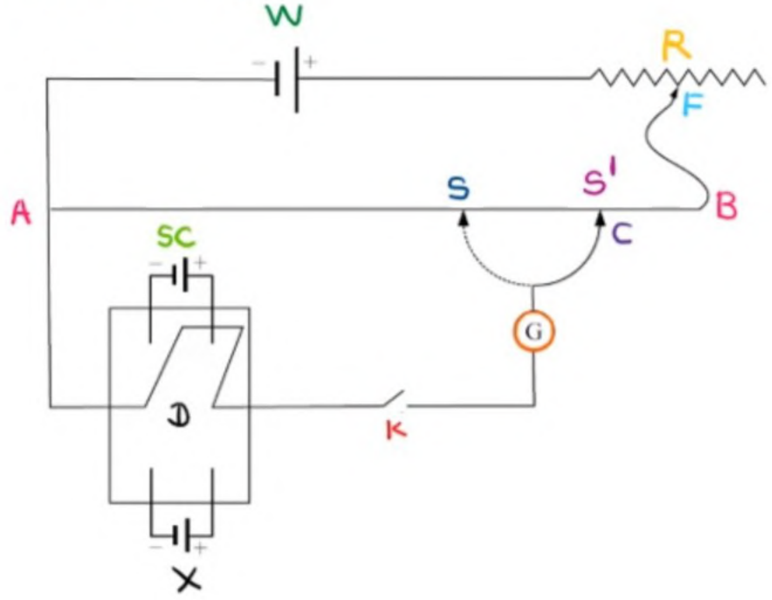
$$Cu^{2+}(aq.) + Zn(s) \rightleftharpoons Cu(s) + Zn^{2+}(aq.)$$

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

→ Measurement of cell EMF :→

- The EMF of a cell cannot be determined by voltmeter directly. Since it draws some current from the cell, which will change the EMF due to following reasons–
  (i) The change in concentration of species caused by electrode reactions.
  (ii) Current flow part of the EMF will have to be utilized to overcome the internal resistance of of the cell.

  Hence the potential measured on the voltmeter will not be the accurate cell EMF.
- The precise value of the EMF of a cell can be determined by using potentiometric method. In this method an unknown EMF is opposed by another EMF until the two are equal.
- Figure illustrates the experimental setup for determining the EMF of a cell with the potentiometric method.

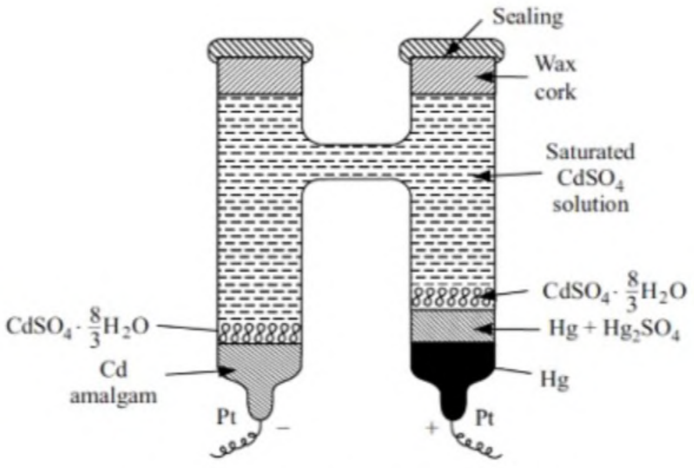


- AB is the uniform wire. The resistance of wire is directly proportional to its length and is calibrated in volts.
- SC is the standard cell, whose EMF is reproducible, constant with time. Usually a standard cadmium cell is used whose EMF is 1.0183 volts at 20°C.
- X is unknown cell, whose EMF is to be determined.
- W is a working cell, whose potential is larger than SC and X. All three cells have their negative terminals attached to one end of the wire AB.
- R is a resistor of variable resistance.
- G is a galvanometer.

- First, the pointer C is set at a point S' along AB corresponding to the value of EMF of the standard cell.
- Next, SC is connected with the circuit and F is moved along the resistor R until the galvanometer G shows no deflection. When this balance is estabilished, the current flowing through AB is of such a magnitude as to make the potential drop between A and S' exactly 1·0183 V and the voltage drop anywhere along AB is the same as the voltage marking on the slide wire.
- Now the given cell X is connected with the circuit and the pointer C is moved along AB until a point S is found at which the galvanometer G again shows no deflection. The reading of the slide wire at S gives the voltage directly.

→ Standard cell :→

- The standard cell should be such that its potential should be reproducible, constant with time and also it should be reversible.
- It should not suffer permanent damage due to passage of current and should preferably have a low temperature coefficient of EMF.
- The cells that most closely approximate these requirements are Weston unsaturated and saturated standard cells.



Weston Saturated Cell

→ Calculation of thermodynamic quantities of cell reaction (ΔG, ΔH and K) :→

1 Calculation of free energy change (ΔG) :→

- The free energy change accompanying a cell reaction can be obtained from the EMF of the cell through the relation.

$$\Delta G = -nFE$$

where n = no. of electrons participited in cell reaction

F = Faraday (96485 Coulombs)

2. Calculation of enthalpy change (ΔH) :→

- The change in enthalpy of the cell reaction can also be determined if the temperature dependance of the EMF of the cell is available. For this, we make use of the Gibbs - Helmholtz equation

$$\Delta G = \Delta H + T\left[\frac{\partial(\Delta G)}{\partial T}\right]_P \quad - ①$$

We know that

$$\Delta G = -nFE \quad - ②$$

substitute value of ΔG in eq. ①

$$-nFF = \Delta H + T\left[\frac{\partial(-nFE)}{\partial T}\right]_P$$

or $$-nFF = \Delta H - nFT\left(\frac{\partial E}{\partial T}\right)_p$$

or $$\Delta H = -nFE + nFT\left(\frac{\partial E}{\partial T}\right)_p$$

or $$\Delta H = -nF\left[E - T\left(\frac{\partial E}{\partial T}\right)\right]_p \quad — ③$$

Thus, ΔH of the cell reaction can be determined from the knowlegde of E and $(\partial E/\partial T)_p$. Since, E and F are expressed respectively in volt and coulomb, the units of ΔH in volt-coulomb and is equal to the joule unit.

3. Calculation of equilibrium constant K :→

- The equilibrium constant of a reaction is related to the free energy of the reaction by the relation

$$\Delta G = -RT\ln K \quad — ①$$

we know that

$$\Delta G = -nFE \quad — ②$$

From eq. ① and ②

$$-nFE = -RT\ln K$$

or $$nFE = RT\ln K$$

or $$\ln K = \frac{nF}{RT}$$

or $$2.303 \log K = \frac{nF}{RT}$$

or $$\log K = \frac{nF}{2.303RT} \quad — ③$$

→ Polarization: →

- When a simple galvanic cell operates, it is observed that the electromotive force of the cell decreases with time.
- This is due to fact that a layer of hydrogen is deposited on the copper electrode. Due to this current strength rapidly diminishes and finally falls practically to zero. This effect is known as polarization of the cell.
- The polarisation may be explained as follows:

(i) When the two plates of a galvanic cell are connected by an external wire, the H^+ ions move towards the copper plate. These H^+ ions should then deliver charge and bubbles away. But actually a film of neutral hydrogen is found to collect on the copper plate. This neutral hydrogen is a bad conductor of electricity. As the thickness of this layer increases, its resistance to current increases and, thus, the strength of the current decreases continuously.

$$H_2SO_4 \rightleftharpoons 2H^+ + SO_4^{2-}$$

$$SO_4^{2-} + H_2O \rightleftharpoons H_2SO_4 + O^{2-}$$

$$2H^+ + 2e^- \rightleftharpoons H_2 \text{ (cathode)}$$

$$2O^{2-} \rightleftharpoons 2O_2 + 4e^- \text{ (anode)}$$

(ii) Due to the deposition of neutral hydrogen gas on the copper electrode, the incoming H^+ ions are not completely delivering their charges to the positive copper plate and, thus, the strength of the current may further diminish.

(iii) Hydrogen being electropositive with respect to zinc, local current starts flowing from hydrogen layer to zinc i.e., in the direction copper to zinc. This opposes the main current flowing from zinc to copper and sets up a back EMF (also called polarisation EMF), this reduces the EMF of the cell. A stage is soon reached when the back EMF does not permit any further H^+ ions from moving towards the copper plate. At this point the current finally falls to zero and the cell is known to be completely polarised.

→ Concentration polarization:→

- As the current passes through the cell, there occurs concentration changes at the electrodes and these changes develop a back EMF. This changes the resultant EMF of the cell. This phenomenon is called concentration polarization.

→ Elimination of polarisation:→

- Mechanical method:- By brushing off hydrogen layer from copper plate
- Electrochemical method:- In this method two solutions are used so that liberated hydrogen comes in contact with second solution.
- Chemical method:- Polarisation of cells may be minimised by using some strong oxidising agents such as chromic acid, nitric acid, manganese dioxide etc. which may convert hydrogen into water.

$$H_2 + \frac{1}{2}O_2 \rightarrow H_2O$$

✲ The substaces which are used to remove polarization completely or partly are known as depolarisers. e.g. Solid MnO_2, O_2 etc.

→ Overvoltage or overpotential :→

- By the application of the opposing EMF, the cell reaction can be reversed.
- Usually the opposing voltage required to reverse the cell reaction is much greater than the EMF of the cell and not greater only by an infinitesimal quantity.
- Suppose we have a cell like

$$Pt \mid H_2\,(1\,atm) \mid HCl \mid Pt \mid O_2\,(1\,atm)$$

The voltage of this cell is 1.12 volts. If the opposing voltage is slightly greater than 1.12, the cell reaction should get reversed and evolution of H_2 and O_2 should start. In reality this is not true, and an opposing voltage of 1.7 volts is required.

Thus, an excess of 1.7 - 1.2 or 0.58 volt is required, to cause the reverse reaction to the place. This excess of voltage, over the voltage of the cell that is necessary to cause the reverse reaction, is termed as overvoltage.

→ Factors Affecting Overvoltage :→

- Current density
- Impurities
- Hydrogen ion concentration (pH)
- Pressure
- Temperature

→ Importance of overvoltage :→

- The concept of overvoltage is of great importance in the electrolytic reduction of organic compounds.
- It is utilized in the industrial production of chlorine and sodium hydroxide by the electrolysis of sodium chloride solution.
- The presence of hydrogen over voltage makes it possible to deposit metals (Zn, Cd etc.) electrolytically having more negative potentials than hydrogen from an acid solution.

→ Hydrogen overvoltage :→

- If a dilute solution is electrolysed with platinised platinum electrodes, hydrogen is liberated at the reversible hydrogen potential of the solution.
- With electrodes other than platinised electrodes a more potential is required to secure its liberation.
- This variation in the potential is explained by the difference in polarisation and depends upon the nature of electrodes.
- The difference of potential at which hydrogen gas is actually evolved during electrolysis and theoritical value at which it happens is known as hydrogen overvoltage.
- At platinised platinum and at zero current density, the hydrogen overvoltage is zero.

→ Measurement of hydrogen overvoltage :→

- In order to measure hydrogen overvoltage, the solution should be from oxygen or other reducible material.
- Then the solution is generally saturated with hydrogen at one atm.
- Now the current of definite strength is passed through the solution for a sufficient time so as to become constant.
- The cathode potential is then measured by combining it with reference electrode.

Electrode	Hydrogen overvoltage (volt)
Platinised platinum	0·00
Iron	0·08
Smooth platinum	0·09
Nickel	0·22
Cadmium	0·48
Lead	0·64
Zinc	0·70
Mercury	0·80