ELECTRO CHEMISTRY

TOPIC-6
Standard electrodes and electrochemical series, characteristics and applications

VERY SHORT ANSWER QUESTIONS

1. What is electrode potential?
When a metal is placed in a solution of its ions, the metal acquires either a positive or negative charge with respect to the solution. On account of this, a definite potential difference is developed between the metal and the solution. This potential difference is called electrode potential.

2. What is oxidation and reduction?

(a) **Oxidation**: It is process in which **m**etal ions pass from the electrode into solution leaving an excess of electrons and thus a negative charge on the electrode.

(b) **Reduction:** It is process in which Metal ions in solution gain electrons from the electrode leaving a positive charge on the electrode.

3. What is standard electrode potential?

Ans: In order to compare the electrode potentials of various electrodes, it is necessary to specify the concentration of the ions present in solution in which the electrode is dipped and the temperature of the half-cell. The potential difference developed between metal electrode and the solution of its ions of unit molarity (1M) at 25°C (298 K) is called **standard electrode potential.**

SHORT ANSWER QUESTIONS

1. Explain what are reversible and irreversible cells?

Ans: Daniel cell has the emf value 1.09 volt. If an opposing emf exactly equal to 1.09 volt is applied to the cell, the cell reaction,

$$Zn + Cu^{2+} \text{-->} Cu + Zn^{2+}$$

stops but if it is increased infinitesimally beyond 1.09 volt, the cell reaction is reversed.

$$Cu + Zn^{2+} \text{-->} Zn + Cu^{2+}$$

Such a cell is termed a **reversible cell**. Thus, the following are the two main conditions of reversibility:

(i) The chemical reaction of the cell stops when an exactly equal opposing emf is applied.

(ii) The chemical reaction of the cell is reversed and the current flows in opposite direction when the opposing emf is slightly greater than that of the cell.

Any other cell which does not obey the above two conditions is termed as irreversible. A cell consisting of zinc and copper electrodes dipped into the solution of sulphuric acid is **irreversible**. Similarly, the cell

$$Zn|H_2S0_4(aq)|Ag$$

is also irreversible because when the external emf is greater than the emf of the cell, the cell reaction,

$$Zn + 2H^+ \text{-->} Zn^{2+} + H_2$$

is not reversed but the cell reaction becomes

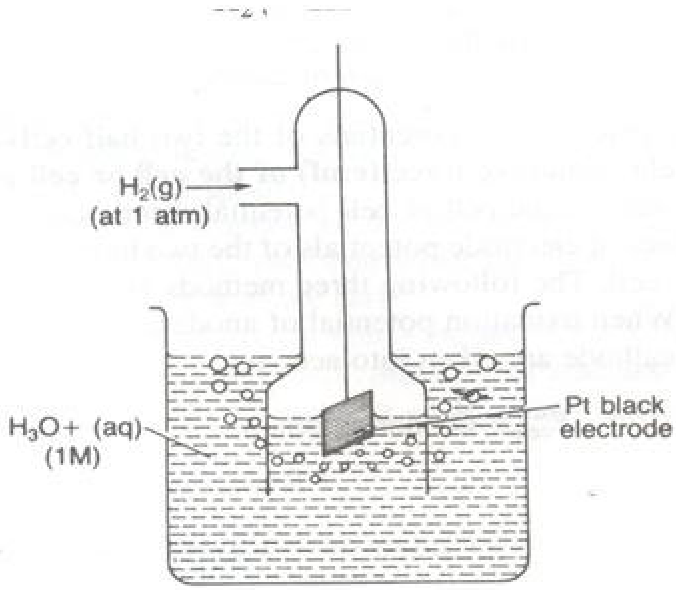
$$2Ag + 2H^+ \text{-->} 2Ag^+ + H_2$$

2. Explain Standard Hydrogen Electrode?

Ans: STANDARD HYDROGEN ELECTRODE, (SHE OR NHE)

Hydrogen electrode is the primary standard electrode. It consists of a small platinum strip coated with platinum black as to adsorb hydrogen gas. A platinum wire is welded to the platinum strip and sealed in a glass tube as to make contact with the outer circuit through mercury. The platinum strip and glass tube is surrounded by an outer glass tube which has an inlet for hydrogen gas at the top and a number of holes at the base for the escape of excess of hydrogen gas. The platinum strip is placed in an acid solution which has H^+ ion concentration 1 M. Pure hydrogen gas is circulated at one atmospheric pressure. A part of the gas is adsorbed and the rest escapes through holes. This gives equilibrium between the adsorbed hydrogen and hydrogen ions in the solution.

$$\mathbf{H_2 \text{<-->} 2H^+ + 2e^-}$$



The temperature of the cell is maintained at 25^{0}C. By international agreement the standard hydrogen electrode is arbitrarily assigned a potential of exactly ± 0.000 . .. volt.

The hydrogen electrode thus obtained forms one of two half-cells of a voltaic cell. When this half-cell is connected with any other half-cell, a voltaic cell is constituted. The hydrogen electrode can act as cathode or anode with respect to other electrode.

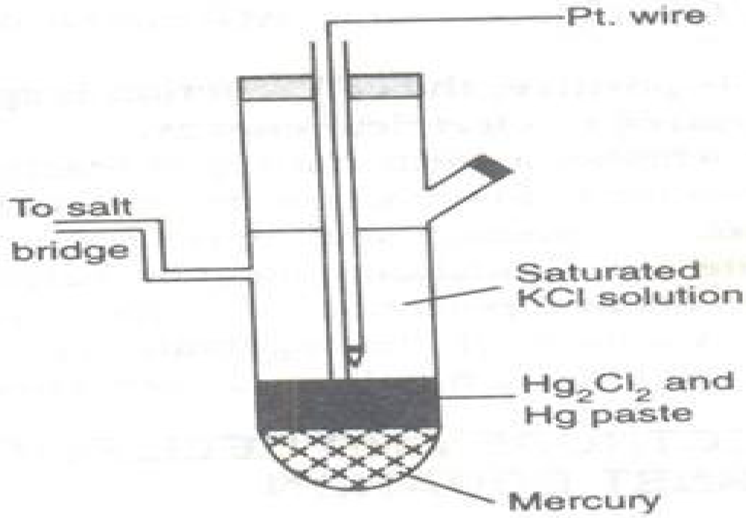
SHE half reaction	Electrode potential
H_2 --> $2H^+ + 2e^-$	0.0 V (Anode)
$2H^+ + 2e^-$ --> H_2	0.0 V (Cathode)

3 . Explain Standard Calomel Electrode?

Calomel electrode: It consists of mercury at the bottom over which a paste of mercury-mercurous chloride is placed. A solution of potassium chloride is then placed over the paste. A platinum wire sealed in a glass tube helps in making the electrical contact. The electrode is connected with the help of the side tube on the left through a salt bridge with the other electrode to make a complete cell.

The potential of the calomel electrode depends upon the concentration of the potassium chloride solution. If potassium chloride solution is saturated, the electrode is known as saturated calomel electrode (SCE) and if the potassium chloride solution is 1 N, the electrode is known as normal calomel electrode (NCE) while for 0.1 N potassium chloride solution, the electrode is referred to as decinormal calomel electrode (DNCE).

The electrode reaction when the electrode acts as cathode is:



$\frac{1}{2} Hg_2Cl_2 + e^- \longleftrightarrow Hg + Cl^-$

The reduction potentials of the calomel electrodes on hydrogen scale at 298K are as follows:

Saturated KC1	**0.2415 V**
1.0NKC1	**0.2800 V**
0.1NKC1	**0.3338 V**

The electrode potential of any other electrode on hydrogen scale can be measured when it is combined with calomel electrode. The emf of such a cell is measured. From the value of electrode potential of calomel electrode, the electrode potential of the other electrode can be evaluated.

LONG ANSWER QUESTIONS

1. What is electrochemical series and what are its characteristics and applications?

Ans: ELECTROCHEMICAL SERIES

By measuring the potentials of various electrodes versus standard hydrogen electrode (SHE), a series of standard electrode potentials has been established. When the electrodes (metals and non-metals) in contact with their ions are arranged oh the basis of the values of their standard reduction potentials or standard oxidation potentials, the resulting series is called the **electrochemical** or **electromotive** or **activity series** of the elements.

By international convention, the standard potentials of electrodes are tabulated for reduction half reactions, indicating the tendencies of the electrodes to behave as cathodes towards SHE. Those with positive E° values for reduction half reactions do in fact act as cathodes versus SHE, while those with negative E° values of reduction half reactions behave instead as anodes versus SHE. The electrochemical series is shown in the following table.

Standard Aqueous Electrode Potentials at 25°C 'The Electrochemical Series'

Element	**Electrode Reaction (Reduction)**	**Standard Electrode Reduction potential E^o, volt**
Li	$Li^+ + e^- = Li$	-3.05
K	$K^+ + e^- = K$	-2.925
Ca	$Ca^{2+} + 2e^- = Ca$	-2.87
Na	$Na^+ + e^- = Na$	-2.714
Mg	$Mg^{2+} + 2e^- = Mg$	-2.37
Al	$Al^{3+} + 3e^- = Al$	-1.66
Zn	$Zn^{2+} + 2e^- = Zn$	-0.7628
Cr	$Cr^{3+} + 3e^- = Cr$	-0.74
Fe	$Fe^{2+} + 2e^- = Fe$	-0.44
Cd	$Cd^{2+} + 2e^- = Cd$	-0.403
Ni	$Ni^{2+} + 2e^- = Ni$	-0.25
Sn	$Sn^{2+} + 2e^- = Sn$	-0.14
H_2	$2H^+ + 2e^- = H_2$	0.00

Cu	$Cu^{2+} + 2e^- = Cu$	+0.337
I_2	$I_2 + 2e^- = 2I^-$	+0.535
Ag	$Ag^+ + e^- = Ag$	+0.799
Hg	$Hg^{2+} + 2e^- = Hg$	+0.885
Br_2	$Br_2 + 2e^- = 2Br^-$	+1.08
Cl_2	$Cl_2 + 2e^- = 2Cl^-$	+1.36
Au	$Au^{3+} + 3e^- = Au$	+1.50
F_2	$F_2 + 2e^- = 2F^-$	+2.87

Characteristics of Electrochemical series

(i) The negative sign of standard reduction potential indicates that an electrode when joined with SHE acts as anode and oxidation occurs on this electrode. For example, standard reduction potential of zinc is -0.76 volt. When zinc electrode is joined with SHE, it acts as anode (-ve electrode) i.e., oxidation occurs on this electrode. Similarly, the +ve sign of standard reduction potential indicates that the electrode when joined with SHE acts as cathode and reduction occurs on this electrode.

(ii) The substances which are stronger reducing agents than hydrogen are placed above hydrogen in the series and have negative values of standard reduction potentials. All those substances which have positive values of reduction potentials and placed below hydrogen in the series are weaker reducing agents than hydrogen.

(iii) The substances which are stronger oxidising agents than H^+ ion are placed below hydrogen in the series.

(iv) The metals on the top (having high negative values of standard reduction potentials) have the tendency to lose electrons readily. These are active metals. The activity of metals decreases from top to bottom. The non-metals on the bottom (having high positive values of standard reduction potentials) have the tendency to accept electrons readily. These are active non-metals. The activity of non-metals increases from top to bottom.

Applications of Electrochemical series

(i) Reactivity of metals:

The activity of the metal depends on its tendency to lose electron or electrons, i.e., tendency to form cation (M^{n+}). This tendency depends on the magnitude of standard reduction potential. The metal which has high negative value (or smaller positive value) of standard reduction potential readily loses the electron or electrons and is converted into cation. Such a metal is said to be chemically active.

The chemical reactivity of metals decreases from top to bottom in the series. The metal higher in the series is more active than the metal lower in the series. For example,

(a) Alkali metals and alkaline earth metals having high negative values of standard reduction potentials are chemically active. These react with cold water and evolve hydrogen. These readily dissolve in acids forming corresponding salts and combine with those substances which accept electrons.

(b) Metals like Fe, Pb, Sn, Ni, Co, etc., which lie a little down in the series do not react with cold water but react with steam to evolve hydrogen.

(c) Metals like Cu, Ag and Au which lie below hydrogen are less reactive and do not evolve hydrogen from water.

(ii) Electropositive character of metals:

The electropositive character also depends on the tendency to lose electron or electrons. Like reactivity, the electropositive character of metals decreases from top to bottom in the electrochemical series. On the basis of standard reduction potential values, metals are divided into three groups:

(a) Strongly electropositive metals: Metals having standard reduction potential near about -2.0 volt or more negative like alkali metals, alkaline earth metals are strongly electropositive in nature.

(b) Moderately electropositive metals: Metals having values of reduction potentials between 0.0 and about -2.0 volt are moderately electropositive. Al, Zn, Fe, Ni, Co, etc., belong to this group.

(c) Weakly electropositive metals: The metals which are below hydrogen and possess positive values of reduction potentials are weakly electropositive metals. Cu, Hg, Ag, etc., belong to this group.

(iii) Displacement reactions:

(a) To predict whether a given metal will displace another, from its salt solution. A metal higher in the series will displace the metal from its solution which is lower in the series, i.e., the metal having low standard reduction potential will displace the metal from its salt's solution which has higher value of standard reduction potential. A metal higher in the series has greater tendency to provide electrons to the cations of the metal to be precipitated.

(b) Displacement of one nonmetal from its salt solution by another nonmetal: A nonmetal higher in the series (towards bottom side), i.e., having high value of reduction potential will displace another nonmetal with lower reduction potential i.e., occupying position above in the series. The nonmetal's which possess high positive reduction potentials have the tendency to accept electrons readily. These electrons are provided by the ions of the nonmetal having low value of reduction potential. Thus, Cl_2 can displace bromine and iodine from bromides and iodides.

$Cl_2 + 2KI \rightarrow 2KC1 + I_2$

$21^- \rightarrow I_2 + 2e^-$ (Oxidation)

$Cl_2 + 2e- \rightarrow 2C1^-$ (Reduction)

[The activity or electronegative character or oxidising nature of the nonmetal increases as the value of reduction potential increases.]

(c) Displacement of hydrogen from dilute acids by metals: The metal which can provide electrons to H^+ ions present in dilute acids for reduction, evolve hydrogen from dilute acids.

$Mn \rightarrow Mn''^+ + ne^-$ (Oxidation)

$2H^+ + 2e^- \rightarrow H_2$ (Reduction)

The metal having negative values of reduction potential possess the property of losing electron or electrons.

Thus, the metals occupying top positions in the electrochemical series readily liberate hydrogen from dilute acids and on descending in the series tendency to liberate hydrogen gas from dilute acids decreases.

The metals which are below hydrogen in electrochemical series like Cu, Hg, Au, Pt, etc., do not evolve hydrogen from dilute acids.

(d) Displacement of hydrogen from water: Iron and the metals above iron are capable of liberating hydrogen from water. The tendency decreases from top to bottom in electrochemical series.

Alkali and alkaline earth metals liberate hydrogen from cold water but Mg, Zn and Fe liberate hydrogen from hot water or steam.

(iv) Reducing power of metals:

Reducing nature depends on the tendency of losing electron or electrons. More the negative reduction potential, more is the tendency to lose electron or electrons. Thus, reducing nature decreases from top to bottom in the electrochemical series. The power of the reducing agent increases as the standard reduction potential becomes more and more negative.

Sodium is a stronger reducing agent than zinc and zinc is a stronger reducing agent than iron.

Element	Na	Zn	Fe
Reduction potential	-2.71	-0.76	-0.44

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Reducing nature decreases

Alkali and alkaline earth metals are strong reducing agents.

(v) Oxidising nature of nonmetals:

Oxidising nature depends on the tendency to accept electron or electrons. More the value of reduction potential, higher is the tendency to accept electron or electrons. **Thus, oxidising nature increases from top to bottom in the electrochemical series.** The strength of an oxidising agent increases as the value of reduction potential becomes more and more positive.

F_2 (Fluorine) is a stronger oxidant than Cl_2, Br_2 and I_2.

Cl_2 (Chlorine) is a stronger oxidant than Br_2 and I_2.

Element	I_2	Br_2	Cl_2	F_2
Reduction potential	+0.53	+1.06	+1.36	+2.85

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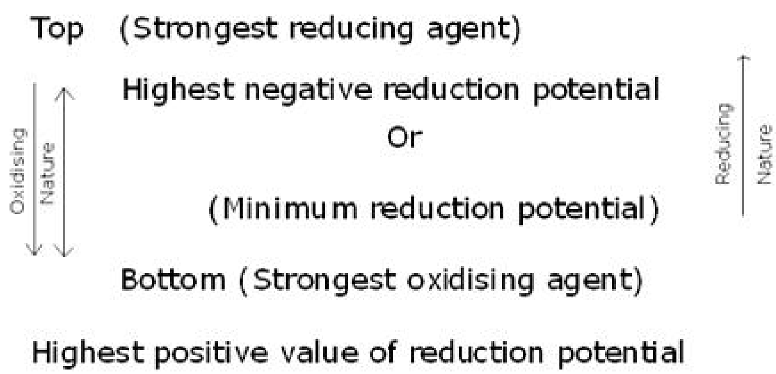
Oxidising nature increases

Thus, in electrochemical series

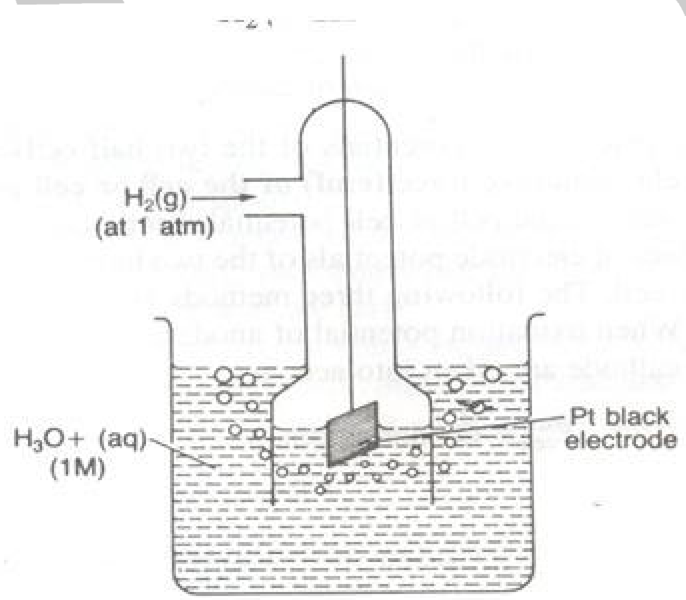


2. What is standard Hydrogen electrode and what are its applications?

Ans: STANDARD HYDROGEN ELECTRODE (SHE OR NHE)

Hydrogen electrode is the primary standard electrode. It consists of a small platinum strip coated with platinum black as to adsorb hydrogen gas. A platinum wire is welded to the platinum strip and sealed in a glass tube as to make contact with the outer circuit through mercury. The platinum strip and glass tube is surrounded by an outer glass tube which has an inlet for hydrogen gas at the top and a number of holes at the base for the escape of excess of hydrogen gas. The platinum strip is placed in an acid solution which has H^+ ion concentration 1 M. Pure hydrogen gas is circulated at one atmospheric pressure. A part of the gas is adsorbed and the rest escapes through holes. This gives equilibrium between the adsorbed hydrogen and hydrogen ions in the solution.

$$H_2 \text{ <--> } 2H^+ + 2e^-$$



The temperature of the cell is maintained at 25^0C. By international agreement the standard hydrogen electrode is arbitrarily assigned a potential of exactly ± 0.000 . .. volt.

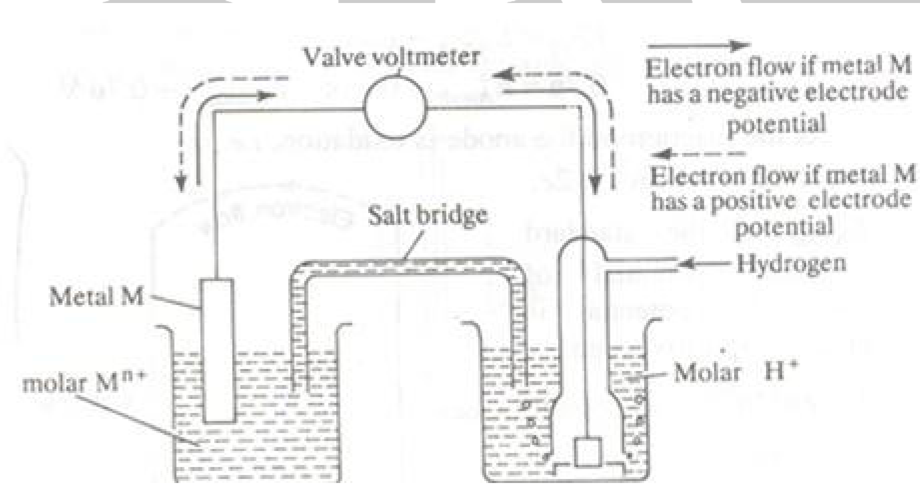
The hydrogen electrode thus obtained forms one of two half-cells of a voltaic cell. When this half-cell is connected with any other half-cell, a voltaic cell is constituted. The hydrogen electrode can act as cathode or anode with respect to other electrode.

SHE half reaction	Electrode potential
$H_2 \rightarrow 2H^+ + 2e^-$	0.0 V (Anode)
$2H^+ + 2e^- \rightarrow H_2$	0.0 V (Cathode)

Applications:

MEASUREMENT OF ELECTRODE POTENTIAL

The measurement of electrode potential of a given electrode is made by constituting a voltaic cell, i.e., by connecting it with a standard hydrogen electrode (SHE) through a salt bridge. 1 M solution is used in hydrogen half-cell and the temperature is



maintained at 25^oC. The emf of the cell is measured either by a calibrated potentiometer or by a high resistance voltmeter, i.e., a valve voltmeter. The reading of the voltmeter gives the electrode potential of the electrode in question with respect to the hydrogen electrode. The standard electrode potential of a metal may be determined as it is the potential difference in volt developed in a cell consisting of two electrodes: the pure metal is contact with a molar solution of one of its ions and the standard hydrogen electrode.

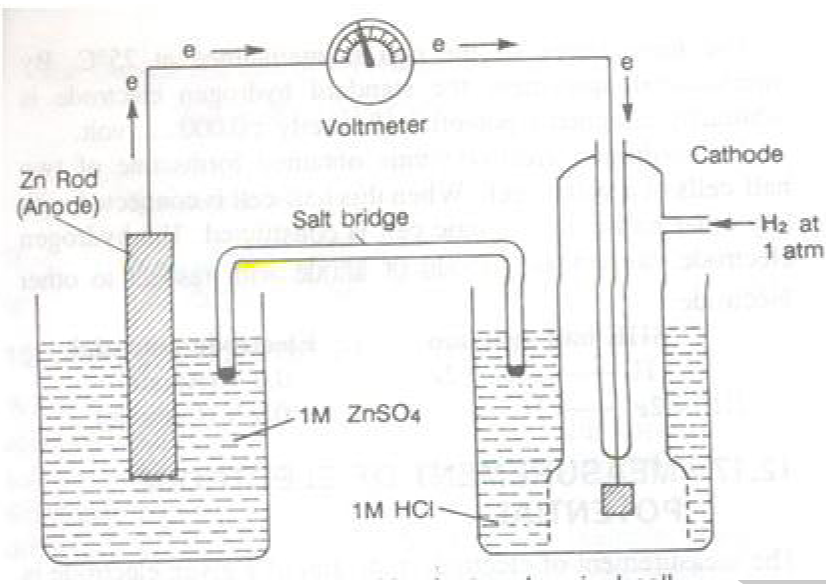
(i) Determination of standard electrode potential of Zn/Zn^{2+} electrode:

A zinc rod is dipped in 1 M zinc sulphate solution. This half-cell is combined with a standard hydrogen electrode through a salt bridge. Both the electrodes are connected with a voltmeter as shown in Fig. 12.12. The deflection of the voltmeter indicates that current is flowing from hydrogen electrode to metal electrode or the electrons are moving from zinc rod to hydrogen electrode. The zinc electrode acts as an anode and the hydrogen electrode as cathode and the cell can be represented as

$Zn|Zn^{2+}$ (aq)/Anode(-) || 2H(aq)| H_2 (g)/Cathode (+)

$Zn \text{-->} Zn^{2+} + 2e^-$; $2H^+ + 2e^- \text{-->} H_2\uparrow$

(Oxidation) (Reduction)



The emf of the cell is 0.76 volt

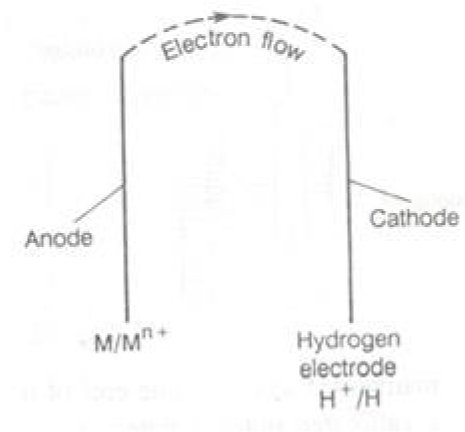
$E_{Cell} = E^o_{Anode} + E^o_{Cathode}$

$0.76 = E^o_{Anode} + 0$ or $E^o_{Anode} = +0.76$ V

As the reaction on the anode is oxidation, i.e.,

$Zn \text{-->} Zn^{2+} + 2e$,

E^o_{Anode} is the standard oxidation potential of zinc. This potential is given the positive sign.



E^o_{ox} (Zn/Zn^{2+}) = +0.76 volt

So standard reduction potential of Zn, i.e., E^o (Zn/Zn^{2+})

= E^o_{ox} = -(+0.76)

= -0.76 volt

The emf of such a cell gives the positive value of standard oxidation potential of metal M. The standard reduction potential (E^o) is obtained by reversing the sign of standard oxidation potential.

(i) Determination of standard electrode potential of Cu^{2+}/Cu, electrode:

A copper rod is dipped in 1 M solution of CuSO4. It is combined with hydrogen electrode through a salt bridge. Both the electrodes joined through a voltmeter. The deflection of the voltmeter indicates that current is flowing from copper electrode towards hydrogen electrode, i.e., the electrons ate moving from hydrogen to copper electrode. The hydrogen electrode acts as an anode and the copper electrode as a cathode. The cell can be represented as

H_2 (g)|$2H^+$ (aq) ||Cu^{2+} (aq) |Cu

Anode (-) Cathode (+)

$H_2 \rightarrow 2H^+ + 2e^-$; Cu^{2+} $2e^-$ --> Cu

Oxidation Reduction

The emf of the cell is 0.34 volt.

$$\mathbf{E^o_{Cell} = E^o_{Anode} + E^o_{Cathode}}$$

$0.34 = 0 + E^o_{Cathode}$

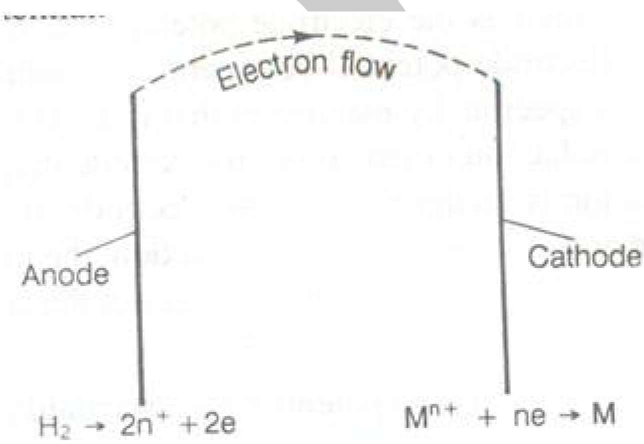
Since the reaction on the cathode is reduction, i.e.,
$Cu^{2+} + 2e^- \rightarrow Cu$, $E^o_{Cathode}$ is the standard reduction potential of copper. This is given the +ve sign.

E°, i.e., standard reduction potential of Cu^{2+}/Cu = 0.34 volt

So $E°_x$ (standard oxidation potential of copper) = -0.34 volt

The emf of such a cell gives positive value of reduction potential of metal electrode. The standard oxidation potential of this electrode is obtained by reversing the sign of standard reduction potential.

The emf of such a cell gives the positive value of standard oxidation potential of metal M. The standard reduction potential (E°) is obtained by reversing the sign of standard oxidation potential.



It is thus concluded that at the metal electrode which acts as anode with respect to hydrogen electrode (cathode), the reduction potential is given the minus sign and at the metal electrode which acts as cathode with respect to hydrogen electrode (anode), the reduction potential is given the positive sign.

The standard electrode potentials (oxidation or reduction) of various elements can be measured by combining the electrode in question with a standard hydrogen electrode and measuring the emf of the cell constituted.