# ELECTRO CHEMISTRY

ELECTROCHEMICAL CELLS:

A device for producing an electrical current from a chemical reaction (spontaneous redox reaction) is called an **electrochemical cell** and also known as a **galvanic cell or Voltaic cell**. A simple voltaic cell is shown in Fig.1. Here the spontaneous reaction of zinc metal with an aqueous solution of copper sulphate is used.

$$Zn_{(s)} + Cu^{2+} \longrightarrow Zn^{2+} + Cu$$
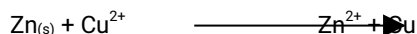
A bar of zinc metal (anode) is placed in zinc sulphate solution (where oxidation takes place) in the left container. A bar of copper metal (cathode) is immersed in copper sulphate solution (where reduction takes place) in the right container. In other words, each electrode may be regarded as a half-cell. The zinc and copper electrodes are joined by a copper wire. A salt bridge containing potassium sulphate solution interconnects the solutions in the anode compartment and the cathode compartment.

The oxidation half-reaction occurs in the anode compartment.

$$Zn(s) \longrightarrow Zn^{2+}(aq) + 2e^-$$
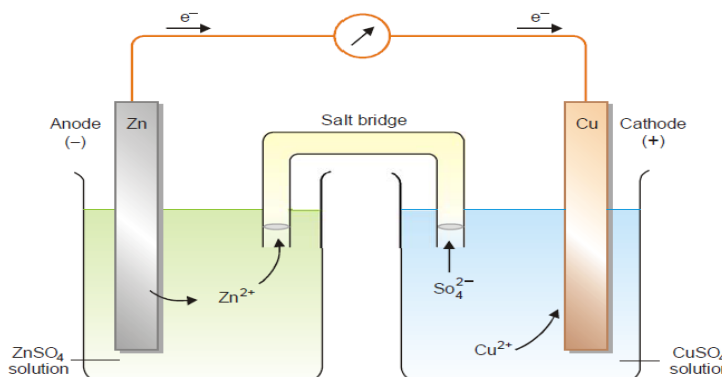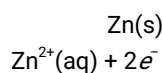
The reduction half-reaction takes place in the cathode compartment.

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

The cell reaction: $Zn(s) + Cu^{+2}(aq) \longrightarrow Zn^{+2}(aq) + Cu(s)$
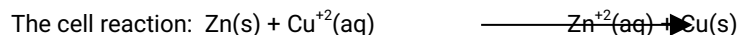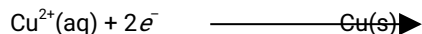
When the cell is set up, electrons flow from zinc electrode through the wire to the copper cathode. As a result, zinc dissolves in the anode solution to form Zn^{2+} ions. The Cu^{2+} ions in the cathode half-cell pick up electrons and are converted to Cu atoms on the cathode. At the same time, SO_4^{2-} ions from the cathode half-cell migrate to the anode half-cell through the salt bridge. Likewise, Zn^{2+} ions from the anode half-cell move into the cathode half-cell. This flow of ions from one half-cell to the other completes the electrical circuit which ensures continuous supply of current. The cell will operate till either the zinc metal or copper ion is completely used up.

CELL TERMINOLOGY:

Before taking up the study of the electrochemical cells, we should be familiar with a few common terms.

Current is the flow of electrons through a wire or any conductor.

Electrode: a metallic rod/bar/strip which conducts electrons into and out of a solution.

Anode is the electrode at which oxidation occurs. It sends electrons into the outer circuit. It has negative charge and is shown as (−) in cell diagrams.

Cathode is the electrode at which electrons are received (reduction occurs) from the outer circuit. It has a positive

charge and is shown as (+) in cell diagrams.

Electrolyte is the salt solutions in a cell.

Anode compartment is the compartment of the cell in which oxidation half-reaction occurs. It contains the anode.

Cathode compartment is the compartment of the cell in which reduction half-reaction occurs. It contains the cathode.

Half-cell. Each half of an electrochemical cell, where oxidation occurs and the half where reduction occurs, is called the half cell.

Salt bridge: A salt bridge is a U-shaped device containing concentrated solution of an inert electrolyte like KCl, KNO₃, etc. or a solidified solution of those electrolytes in agar-agar solution and gelatin to prevent intermixing of the solutions. It connects the oxidation and reduction half-cells of a galvanic cell. The inert electrolytes present do not take part in redox reaction of the cell and don't react with the electrolyte that has been used.

Daniel Cell: It is a typical voltaic cell. It was named after the British chemist John Daniel. It is a simple zinc-copper cell like the one described above (Fig. 2).

In this cell the salt-bridge has been replaced by a porous pot. Daniel cell resembles the above voltaic cell in all details except that Zn^{2+} ions and SO_4^{2-} ions flow to the cathode and the anode respectively through the porous pot instead of through the salt-bridge. In spite of this difference, the cell diagram remains the same.

Porous Pot

$$Zn \mid Zn^{2+} \parallel Cu^{2+} \mid Cu$$
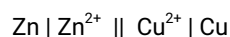
Anode   Cathode

Cell reaction:

The flow of electrons from one electrode to the other in an electrochemical cell is caused by the half-reactions taking place in the anode and cathode compartments. The net chemical change obtained by adding the two half-reactions is called the **cell reaction.** Thus, for a simple voltaic cell described above, we have
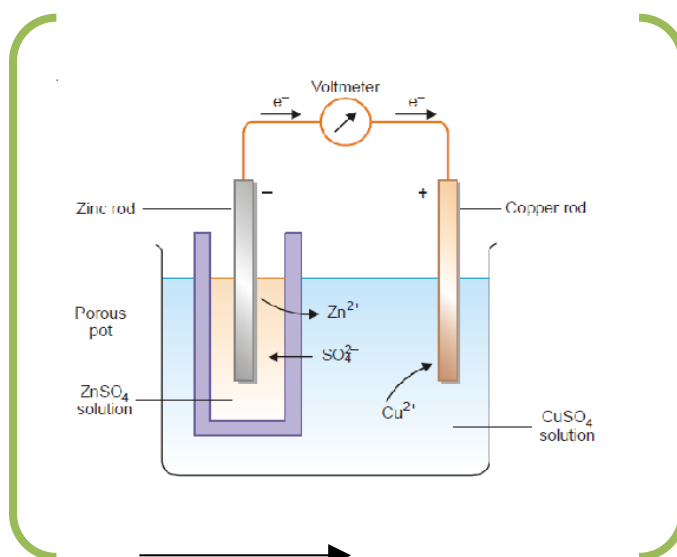

(a) Half-reactions:

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

$$Cu^{2+}(aq) + 2e^- \quad\quad Cu(s)$$

(b) Cell reaction $Zn(s) + Cu^{2+}(aq)$ $Zn^{2+}(aq) + Cu(s)$
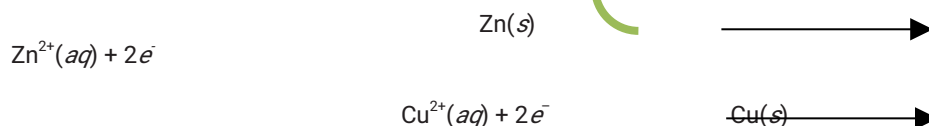
Cell diagram or Representation of a Cell

A cell diagram is an abbreviated symbolic depiction of an electrochemical cell. For this purpose, we will

consider that a cell consists of two half-cells. Each half-cell is again made of a metal electrode contact with metal ions in solution.

IUPAC Conventions: In 1953 IUPAC recommended the following conventions for writing cell diagrams. We will illustrate these with reference to Zinc-Copper cell.

(1) A **single vertical line (|)** represents a phase boundary between metal electrode and ion solution (electrolyte). Thus the two half-cells in a voltaic cell are indicated as

⌐— Phase boundary
↓

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

Anode Half-Cell   Cathode Half-Cell
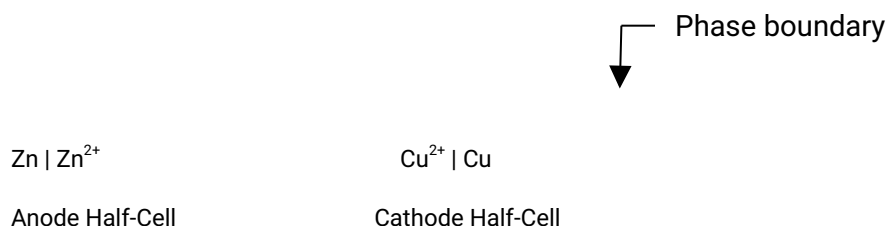
It may be noted that the metal electrode **in anode** half-cell is on the left, while **in cathode** half- cell it is on the right of the metal ion.

(2) A **double vertical line (||)** represents the salt bridge, porous partition or any other **means** of permitting ion flow while preventing the electrolyte from mixing.

(3) **Anode half-cell is written on the left** and **cathode half-cell on the right.**

(4) In the **complete cell diagram, the two half-cells are separated by a double vertical line (salt bridge) in between.** The zinc-copper cell can now be written as

⌐— Salt Bridge
↓

$Zn \mid Zn^{2+} \parallel Cu^{2+} \mid Cu$

Anode   Cathode

Half-cell   Half-cell
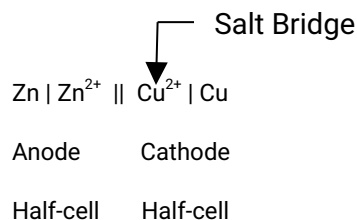
(5) The symbol for an **inert electrode,** like the platinum electrode is often enclosed in a bracket. For example,

⌐— Inert Electrode
↓

$Mg \mid Mg^{2+} \parallel H^{+} \mid H_2(Pt)$
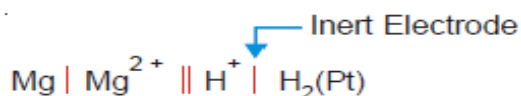
The value of emf of a cell is written on the right of the cell diagram. Thus a zinc-copper cell has emf 1.1V and is represented as

$Zn \mid ZnSO_4 \parallel CuSO_4 \mid Cu$ $E = + 1.1\ V$
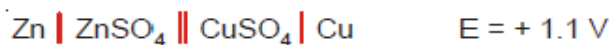
Electromotive force (emf) or Cell potential:

In a Zn-Cu voltaic cell, electrons are released at the anode and it becomes negatively charged. The negative electrode pushes electrons through the external circuit by electrical repulsions. The copper electrode gets positive charge due to the discharge of Cu^{2+} ions on it. Thus electrons from the outer circuit are attracted into this electrode. The flow of current through the circuit is determined by the 'push', of electrons at the anode and 'attraction' of

electrons at the cathode. These two forces constitute the 'driving force' or 'electrical pressure' that sends electrons through the circuit. This driving force is called the **electromotive force** (abbreviated **emf**) or **cell potential.** The emf of cell potential is measured in units of volts (V) and is also referred to as **cell voltage.**

The magnitude of the emf of a cell reflects the tendency of electrons to flow externally from one electrode to another. The electrons are transported through the cell solution by ions present and pass from the positive electrode (Cu in case of Daniel cell) to the negative electrode. This corresponds to a clockwise flow of electrons through the external circuit. Thus the emf of the cell is given the **+ve sign.** If the emf acts in the opposite direction through the cell circuit, it is quoted as **−ve value.** For example, Daniel cell has an emf of 1.1V and the copper electrode is positive. This can be expressed in two ways :

Zn | ZnSO$_4$ || CuSO$_4$ | Cu   E = + 1.1 V

Cu | CuSO$_4$ || ZnSO$_4$ | Zn   E = − 1.1 V

The negative sign indicates that the cell is not feasible in the given direction. The reaction will take place in the reverse direction.

Calculating the emf of a cell:

The electromotive force may be defined as the potential difference between two electrodes of a galvanic cell or voltaic cell. Or
The difference of potential, which causes the current to flow from an electrode at higher potential to the one of lower potential, is called the Electro motive force (emf) of the cell.

Mathematically, emf of an electrochemical cell is the algebraic sum of the single electrode potential; provided proper signs are being given according to the actual reaction taking place on the electrodes.

The emf of a cell can be calculated from the half-cell potentials of the two cells (anode and cathode) by using the following formula

Ecell = Ecathode − Eanode

       = E_R − E_L (IUPAC convention 3)

Where E_R and E_L are the reduction potentials of the right-hand and left-hand electrodes respectively.

Standard emf of a cell:

The emf generated by an electrochemical cell is given by the symbol E. It can be measured with the help of a potentiometer. The value of emf varies with the concentration of the reactants and products in the cell solutions and the temperature of the cell. When the emf of a cell is determined under standard conditions, it is called **the standard emf.** The standard conditions are (*a*) 1 M solutions of reactants and products; and (*b*) temperature of 25°C. Thus standard emf may be defined as: **the emf of a cell with 1 M solutions of reactants and products in solution measured at 25°C.** Standard emf of a cell is represented by the symbol **E°.** With gases 1 atm pressure is a standard condition instead of concentration. For a simple Zn-Cu voltaic cell, the standard emf, E°, is 1.10 V. This means that the emf of the cell operated with $[Cu^{2+}]$ and $[Zn^{2+}]$ both at 1 M and at 25°C is 1.10 V. That is,

Zn | Zn^{2+}(aq, 1M) || Cu^{2+}(aq,1M) | Cu   E = + 1.1 V
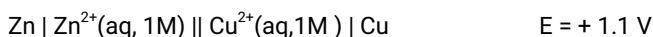
Single electrode potential:

An electrochemical cell consists of two half-cells. With an open-circuit, the metal electrode in each half-cell transfers its ions into solution. Thus an individual electrode develops a potential with respect to the solution. The potential of a single electrode in a half-cell is called the **Single electrode potential.** Thus in a Daniel cell in which the

electrodes are not connected externally, the anode Zn/Zn^{2+} develops a negative charge and the cathode Cu/Cu^{2+}, a positive charge. The amount of the charge produced on individual electrode determines its single electrode potential. The single electrode potential of a half-cell depends on: (*a*) concentration of ions in solution; (*b*) tendency to form ions; and (*c*) temperature.

The electrode potential can be defined as: The potential difference between the electrode and electrolytic solution surrounding it is called as electrode potential.

The tendency of an electrode to lose or gain electrons, when it is in contact with the solution of its own ions. The metal which has a greater tendency to lose electrons becomes the anode, while which has a greater tendency to gain electrons will behave as cathode.
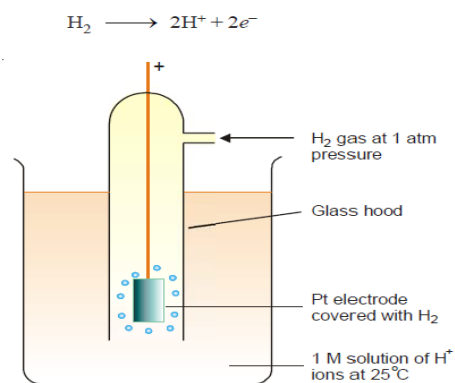

$$H_2 \longrightarrow 2H^+ + 2e^-$$

H₂ gas at 1 atm pressure

Glass hood

Pt electrode covered with H_2

1 M solution of H^+ ions at 25°C

Fig. 3 Standard hydrogen electrode

It may be noted that absolute values of these electrode potentials cannot be determined directly. These are found by connecting the half-cell with a standard hydrogen electrode whose reduction potential has been arbitrarily fixed as zero.

Determination of electrode potential or emf of a half-cell:

By a single electrode potential, we also mean the emf of an isolated half-cell or its half- reaction. The emf of a cell that is made of two half-cells can be determined by connecting them to a voltmeter. However, there is no way of measuring the emf of a single half-cell directly. A convenient procedure to do so is to combine the given half-cell with another standard half-cell. The emf of the newly constructed cell, E, is determined with a voltmeter. The emf of the unknown half-cell, E°, can then be calculated from the expression

$E_{measured} = E_R − E_L$

If the standard half-cell acts as anode, the equation becomes.

$E_R = E_{measured}$ ($\because E_L = 0$)

On the other hand, if standard half-cell is cathode, the equation takes the form

$E_L = − E_{measured}$ ($\because E_R = 0$)

The standard hydrogen half-cell or **Standard Hydrogen Electrode (SHE)** is selected for coupling with the unknown half-cell. It consists of a platinum electrode immersed in a 1 M solution of H^+ ions maintained at 25°C. Hydrogen gas at one atmosphere enters the glass hood and bubbles over the platinum electrode.

The hydrogen gas at the platinum electrode passes into solution, forming H^+ ions and electrons.

The standard hydrogen electrode:

The emf of the standard hydrogen electrode is arbitrarily assigned the value of zero volts. So, SHE can be used as a standard for other electrodes. The half-cell whose potential is desired is combined with the hydrogen electrode and the emf of the complete cell determined with a voltmeter. The emf of the cell is the emf of the half-cell.

For example, it is desired to determine the electrode potentiof the zinc electrode, $Zn \mid Zn^{2+}$. It is connected with the SHE as shown in Fig. 4. The complete electrochemical cell may be represented as:

Zn | Zn^{2+} || H$^+$ | H$_2$ (1 atm), Pt

E$_{cell}$ = E$_R$ − E$_L$

= 0 − 0.76 = − 0.76 V

The emf of the cell has been found to be − 0.76V which is the emf of the zinc half-cell. Similarly, the electrode potential of the copper electrode, Cu^{2+}|Cu can be determined by pairing it with the SHE when the electrochemical cell can be represented as:

Pt, H$_2$ (1 atm) | H$^+$ || Cu^{2+} | Cu

Fig. 5. The two situations are shown in
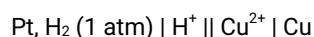
The emf of this cell has been determined to be 0.34 V which is the electrode potential of the copper half-cell.
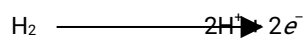
E$^0_{cell}$ = E$^0_{Cu|Cu}{}^{2+}$ - E$^0_{SHE}$

0.34 − 0 = 0.34 V

SHE can act both as cathode and anode when joined with another half-cell (Fig. 5).

When it is placed on the right-hand side of the Zinc electrode, the hydrogen electrode reaction is

2H$^+$ + 2e^- ⟶ H$_2$
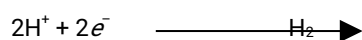
The electrons flow to the SHE and it acts as the cathode. When the SHE is placed on the left hand side, the electrode reaction is

H$_2$ ⟶ 2H$^+$ 2e^-

The electrons flow to the copper electrode and the hydrogen electrode as the anode. Evidently, **the SHE can act both as anode and cathode** and, therefore can be used to determine the emf of any other half-cell electrode (or single electrode).
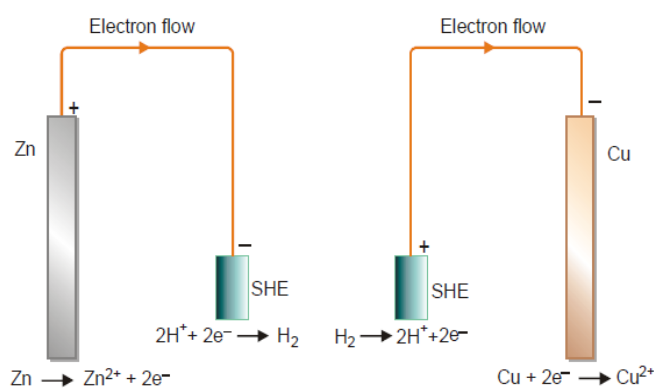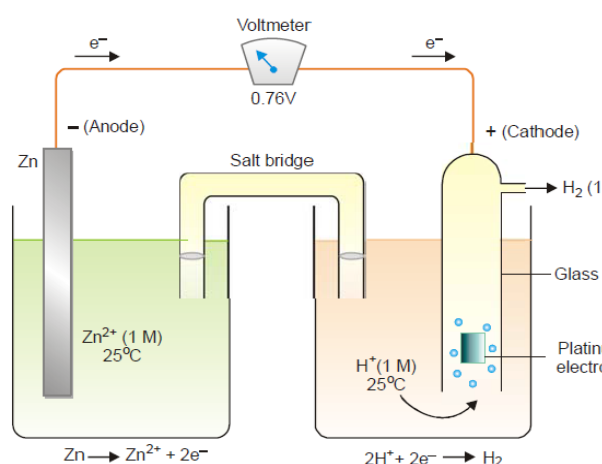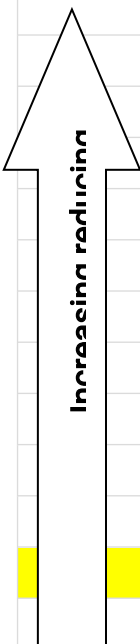
In the procedure for determining the emf of a given half-cell, the standard hydrogen electrode can be placed on the left-hand or the right-hand. The electrons flow from left-to-right and the given half-cell electrode gains electrons (reduction). The observed emf of the combined electrochemical cell is then the emf of the half-cell on the right-hand. Such emf values of half-cells, or half reactions, are known as the **Standard reduction potentials or Standard potentials.** However, if the SHE be placed on the right-hand side of the given half-cell, the potential so obtained is called as the **Standard oxidation potential.** The latter potentials are the standard potentials with the sign reversed, the only difference being that cells have been turned around.

According to IUPAC convention, the standard reduction potentials alone are the standard potentials.

Electrochemical series: The electrochemical series consists of a list of elements have been arranged in the increasing order of their standard electrode potentials. Or

When elements are arranged in increasing order of their standard electrode potential, a series called electrochemical series obtained.

Table 1. Standard reduction potentials or Standard potentials

	Element	Electrode Reaction (Reduction)	Standard Electrode Reduction potential E°, volt
Strong reductant	Li	$Li^+ + e^- \rightarrow Li$	-3.05
	K	$K^+ + e^- \rightarrow K$	-2.925
	Ca	$Ca^{2+} + 2e^- \rightarrow Ca$	-2.87
	Na	$Na^+ + e^- \rightarrow Na$	-2.714
	Mg	$Mg^{2+} + 2e^- \rightarrow Mg$	-2.37
	Al	$Al^{3+} + 3e^- \rightarrow Al$	-1.66
	Zn	$Zn^{2+} + 2e^- \rightarrow Zn$	-0.7628
	Cr	$Cr^{3+} + 3e^- \rightarrow Cr$	-0.74
	Fe	$Fe^{2+} + 2e^- \rightarrow Fe$	-0.44
	Cd	$Cd^{2+} + 2e^- \rightarrow Cd$	-0.403
	Ni	$Ni^{2+} + 2e^- \rightarrow Ni$	-0.25
	Sn	$Sn^{2+} + 2e^- \rightarrow Sn$	-0.14
	H₂	**$2H^+ + 2e^- \rightarrow H_2$**	**0.00**
	Cu	$Cu^{2+} + 2e^- \rightarrow Cu$	+0.337
	I₂	$I_2 + 2e^- \rightarrow 2I^-$	+0.535
	Ag	$Ag^+ + e^- \rightarrow Ag$	+0.799

Increasing reducing

Increasing oxidizing

Hg	$Hg^{2+} + 2e^- \rightarrow Hg$	+0.885	
Br_2	$Br_2 + 2e^- \rightarrow 2Br^-$	+1.08	
Cl_2	$Cl_2 + 2e^- \rightarrow 2Cl^-$	+1.36	
Au	$Au^{3+} + 3e^- \rightarrow Au$	+1.50	
F_2	$F_2 + 2e^- \rightarrow 2F^-$	+2.87	**(Strongest oxidant)**

Applications of electrochemical series:

1) Predicting the oxidizing or reducing ability 2) Predicting cell emf 3) Predicting feasibility of reaction 4) Predicting whether a metal will displace another metal from its salt solution or not 5) Predicting whether a metal will displace hydrogen from a dilute acid solution. 5) The relative corrosion tendencies of the metal.

Predicting the Oxidizing or Reducing Ability:

Let us consider a series of elements Cu, H_2, Ni, Zn and their ions. These four elements could act as reducing agents. On the other hand, their ions Cu^{2+}, H^+, Ni^{2+} and Zn^{2+} can act as electron acceptors or oxidizing agents. If we list the respective half-reactions (or electrodes) in order of increasing E° values, we will have placed the reducing agents in ascending order of their ability to attract electrons.

It is noteworthy that the value of E° becomes more positive down the series. This means that Cu^{2+} is the best oxidizing agent (most electron-attracting ion) of those in the list. That is, Cu^{2+} shows the greatest tendency to be reduced. Conversely, Zn^{2+} is the worst oxidizing agent, being the least electron-attracting ion. Of the elements Cu, H_2, Ni and Zn, Zn is the best reducing agent (best electron donor), since E° for the half-reaction has the most positive value. By the reasoning, Cu is the worst reducing agent.

$$Zn \longrightarrow Zn^{2+} + 2e^- \qquad E° = + 0.76 \text{ V}$$

The table of half reaction potentials above tells us that at standard conditions the following reactions occur spontaneously.

Some important points concerning the Table of Standard Reduction Potentials (Table 1) are:

(1) The more positive the value of E°, the better the oxidising ability (the greater the tendency to be reduced) of the ion or compound, on moving down ward in the Table.

(2) The more negative the value of E° the better the reducing ability of the ions, elements or compounds on moving upward in the Table.

(3) Under standard conditions, any substance in this Table will spontaneously oxidise any other substance higher than it in the Table.

Predicting cell emf: The standard emf, E°, of a cell is the standard reduction potential of right- hand electrode (cathode) minus the standard reduction potential of the left-hand electrode anode). That is,

$$E°_{cell} = E°_{right} - E°_{left}$$

$$= \text{Cathode potential} - \text{Anode potential}$$

Let us predict the emf of the cell

$Zn(s) | Zn^{+2} (aq) || Ag^+(aq) | Ag$
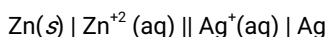
By using the E° values from the Table

$E°_{cell} = E°_{right} - E°_{left}$

$= 0.80 - (- 0.763) = 0.80 + 0.763 = 1.563$ V
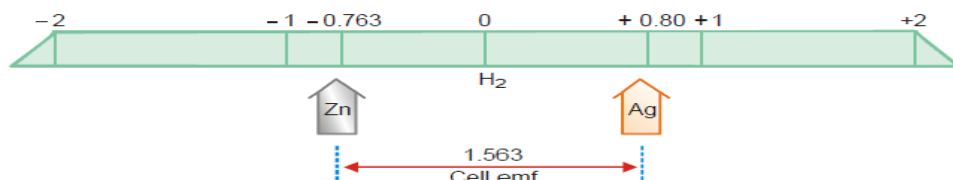
The answer is so clear from Fig. 6.

Figure 6. Diagrammatic representation of Cell emf.

Predicting Feasibility of Reaction: The feasibility of a redox reaction can be predicted with the help of the electrochemical series. The net emf of the reaction, E$_{cell}$, can be calculated from the expression
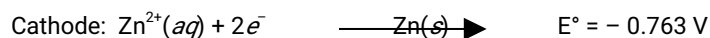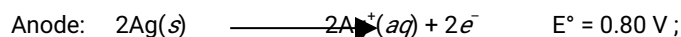
$E°_{cell} = E°_{cathode} - E°_{anode}$

In general, if E°cell = + ve, the reaction is feasible; E°$_{cell}$ = − ve, the reaction is not feasible

SOLVED PROBLEM 1. Predict whether the reaction

$2 Ag(s) + Zn^{2+} (aq) \longrightarrow Ag^+ (aq) + Zn(s)$ is feasible or not. Consult the table for the E° values.

SOLUTION: The cell half reactions are

Anode: $2Ag(s) \longrightarrow 2Ag^+(aq) + 2e^-$ E° = 0.80 V ;

Cathode: $Zn^{2+}(aq) + 2e^- \longrightarrow Zn(s)$ E° = − 0.763 V

$E°_{cell} = E°_{cathode} - E°_{anode}$

∴ E°cell = − 0.763 V − 0.80 = − 1.563

Since E°$_{cell}$ is negative, the given reaction is **not feasible**.

SOLVED PROBLEM 2. Determine the feasibility of the reaction

$2Al(s) + 2Sn^{4+}(aq) \longrightarrow 2Al^{3+} + 3Sn^{2+}(aq)$ Consult the table for the E° values.

**SOLUTION:** The given reaction consists of the following half reactions

Anode: $2Al(s) \longrightarrow 2Al^{3+} + 6e^-$ E° = − 1.66 V

Cathode: $3Sn^{4+} + 6e^- \longrightarrow 3Sn^{2+}$ E° = + 0.15
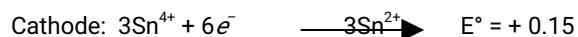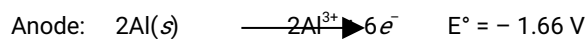
$E°_{cell} = 0.15 - (- 1.66) = 1.81$ V   Since E°$_{cell}$ is positive, the reaction is **feasible**.

Predicting whether a metal will displace another metal from its salt solution or not: As already shown, the metals near the top of the electrochemical series are strong reducing agents and are themselves oxidized to metal ions. On the contrary, the metals lying bottom in the series are strong oxidizing agents and their ions are readily reduced to the

metal itself. For example, zinc lying down above the series is oxidized to Zn^{2+} ion, while copper which is lower in the series is produced by reduction of Cu^{2+} ion.

$$Zn \xrightarrow{\hspace{3cm}} Zn^{2+} + 2e^-$$

$$Cu^{2+} + 2e^- \xrightarrow{\hspace{3cm}} Cu \downarrow$$
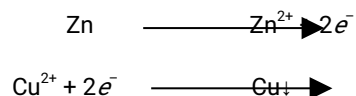
Thus when zinc is placed in $CuSO_4$ solution, Cu metal gets precipitated. In general we can say that **a metal higher up in the electrochemical series can precipitate the one lower down in the series.** Silver cannot precipitate Cu from $CuSO_4$, solution, since both metals have positions lower in the series and are strong oxidizing agents.

Predicting whether a metal will displace hydrogen from a dilute acid solution: Any metal below hydrogen in the electrochemical series is a weaker reducing agent than hydrogen itself and cannot reduce H^+ to H_2. Any metal above hydrogen is a stronger reducing agent than hydrogen and will convert H^+ to H_2. This explains why Zn lying above hydrogen reacts with dil H_2SO_4 to liberate H_2, while Cu lying below hydrogen does not react.

$$Zn + H^+ (dil\ H_2SO_4) \xrightarrow{\hspace{3cm}} Zn^{2+} + H_2 \uparrow$$

$$Cu + H^+ (dil\ H_2SO_4) \xrightarrow{\hspace{3cm}} \bigotimes + H_2$$
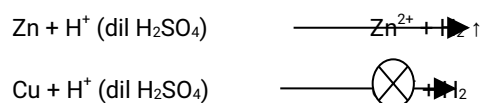
The relative corrosion tendencies of the metal. The metals above the hydrogen in the series can easily oxidised hence they undergo corrosion.

THE NERNST EQUATION:

The electrical energy generated by the galvanic cell can be quantitatively converted into work. So the emf of the cell is a measure of the maximum useful work that can be obtained under standard condition.

The electrical energy or electrical work is equal to the product of emf of the cell and the electrical charge that flow through the external circuit.

$W_{max} = nFE_{cell}$

Where, n is the no of moles of electrons transferred through wire

F is faraday constant i.e 96500 coloumbs

E_{cell} is the emf of the cell.

According to the thermodynamics, the free energy change (ΔG) for a process is equal to the maximum work that can be derived from a cell.

$W_{max} = \Delta G$

$\Delta G = -nFE_{cell}$ and $\Delta G^0 = -nFE^0_{cell}$

ΔG^0 = Standard free energy change

E^0_{cell} = Standard cell potential

The change in free energy is given by

$$\Delta G = \Delta G^0 + RT\ln Q \qquad \text{Where Q= reaction quotient}$$

On substituting the above expression

$$-nFE_{cell} = -nFE^0_{cell} + RTln\,Q$$

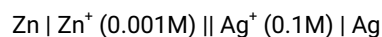On dividing the equation with $-nF$

$$E_{cell} = E^0_{cell} - \frac{RT}{nF}lnQ$$

Where, R= gas constant= 8.314 J; T= Temp in Kelvin, 298K; F= Faraday 96500 C

$$E_{cell} = E^0_{cell} - \frac{0.0592}{n}logQ$$

Where, $Q = \dfrac{[Product]}{[reactant]}$

$$E_{cell} = E^0_{cell} - \frac{0.0592}{n}log\frac{[product]}{[reactant]}$$

SOLVED PROBLEM. Calculate the emf of the cell.

$$Zn\,|\,Zn^+\,(0.001M)\,||\,Ag^+\,(0.1M)\,|\,Ag$$

The standard potential of Ag/Ag^+ half-cell is + 0.80 V and Zn/Zn^{2+} is − 0.76 V.

SOLUTION:

Step 1. Write the half-cell reactions of the anode and the cathode. Then add the anode and cathode half reactions to obtain the cell reaction and the value of $E^°_{cell}$.

Cathode : $2Ag^+ + 2e^- \longrightarrow 2Ag$ E° = +0.80 V

Anode : $Zn \longrightarrow Zn^{2+} + 2e^-$ E° = − 0.76 V

Cell reeaction: $Zn + 2Ag^+ \longrightarrow Zn^{2+} + 2Ag$ E° = 1.56 V
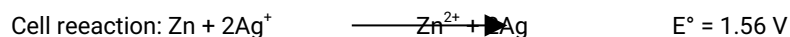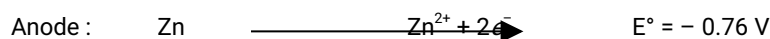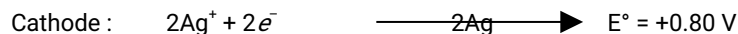
Step2.

$$Q \text{ for the cell reaction } = \frac{[Zn^{+2}]}{[Ag^+]^2}$$

Substitute the given values in the Nernst equation and solving for E_{cell}, we have

$$E_{cell} = E^0_{cell} - \frac{0.0592}{n}logQ$$

$$E_{cell} = 1.56 - \frac{0.0592}{2}log\frac{[Zn^{+2}]}{[Ag^+]^2}$$

$$E_{cell} = 1.56 - \frac{0.0592}{2}log\frac{[10^{-3}]}{[10^{-1}]^2}$$

$$= 1.56 + 0.02955 = \mathbf{1.58955\ V}$$

Nernst equation of electrode potential:

We know experimentally that the potential of a single electrode or half-cell varies with the concentration of ions in the cell. In 1889 Walter Nernst derived a mathematical relationship which enable us to calculate the half-cell potential, E, from the standard electrode potential, E°, and the temperature of the cell.

This relation known as the **Nernst equation** can be stated as

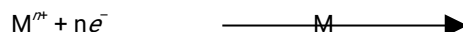$$E = E^0 - \frac{2.303RT}{nF} \log Q \qquad (1)$$

Where   E° = standard electrode potential; R = gas constant; T = Kelvin temperature

n = number of electrons transferred in the half-reaction F = Faraday of electricity

Q = reaction quotient

Calculation of Half-cell potential:

For a reduction half-cell reaction

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

The Nernst equation takes the form

$$E = E^0 - \frac{2.303RT}{nF} \log \left[\frac{M}{M^{n+}} \right] \qquad (2)$$

The concentration of solid metal [M] is considered as unity. Therefore, the Nernst equation can be written as

$$E = E^0 - \frac{2.303RT}{nF} \log \frac{1}{[M^{n+}]} \qquad (3)$$

Substituting the values of R, F and T at 25°C, the quantity 2.303 RT/F comes to be 0.0592. Thus the Nernst equation (3) can be written in its simplified form as

$$E = E^0 - \frac{0.0592}{n} \log \frac{1}{[M^{n+}]}$$

This is the equation for a half-cell in which reduction occurs. In case it is an oxidation reaction, the sign of E will have to be reversed.

SOLVED PROBLEM. What is the potential of a half-cell consisting of copper electrode in 0.015M CuSO4 solution at 25°C, E° =0.34 V.

SOLUTION: The half-cell reaction is

$$Cu^{2+} + 2e^- \longrightarrow Cu \qquad (reduction)$$
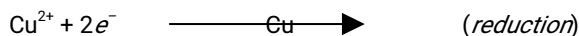
The Nernst equation for the oxidation half-cell reaction is

$$E = E^0 - \frac{0.0592}{n} \log \frac{[Cu]}{[Cu^{2+}]}$$

The number of electrons transferred n = 2 and E° = 0.34 V. and solid copper [Cu] concentration is unity. Substituting these values in the Nernst equation we have

$$E = 0.34 - \frac{0.0592}{2} \log \frac{1}{0.015}$$

$$E = 0.296 \, V$$

Calculation of Equilibrium constant for the cell reaction

The Nernst equation for a cell is

$$E_{cell} = E^0_{cell} - \frac{0.0592}{n} \log Q$$

At equilibrium ΔG=0 and E=0 and Q=K., Then
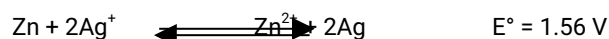
$$0 = E^0_{cell} - \frac{0.0592}{n} \log K$$

$$\log K = \frac{nE^0_{cell}}{0.0592}$$

SOLVED PROBLEM. Calculate the equilibrium constant for the reaction between silver nitrate and metallic zinc.

SOLUTION:

Step 1. Write the equation for the reaction

$$Zn + 2Ag^+ \rightleftharpoons Zn^{2+} + 2Ag \qquad E° = 1.56 \text{ V}$$

Step 2. Substitute values in the Nernst equation at equilibrium

$$\log K = \frac{nE^0_{cell}}{0.0592}$$

$$0 = 1.56 - 0.03 \log K$$

$$-1.56 = -0.03 \log K$$

$$\log K = \frac{-1.56}{0.05 - 0.03} = 52$$

$$K = 1 \times 10^{52}$$

Reference electrodes: The electrode of standard potential, with which we can compare the potential of another electrode, is called as reference electrode. Reference electrodes are broadly divided into two types:

1) Primary reference electrode   example: standard hydrogen electrode(SHE)

2) Secondary reference electrode example: standard calomel electrode,

Standard hydrogen electrode (SHE), (Primary reference electrode)

Construction: It consists of a platinum electrode covered in a glass hood immersed in a 1 M solution of H^+ ions maintained at 25°C. Hydrogen gas at one atmosphere enters the glass hood and bubbles over the platinum electrode (Fig. 3). The hydrogen gas at the platinum electrode passes into solution, forming H^+ ions and electrons.

The emf of the standard hydrogen electrode is arbitrarily assigned the value of zero volts.   So, SHE can be used as a standard for other electrodes (see page No. 6).

- The SHE may be represented as: H_2 (1atm) pt $|$ H^+(C=1)

- Depending on half cell to which it is attached hydrogen electrode can act as a cathode or anode.

When hydrogen electrode act as cathode, reduction reaction takes place

$$2H^+ + 2e^- \longrightarrow H_2(g)$$
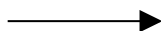
When hydrogen electrode act as anode, oxidation reaction takes place

$$H_2 (g) \qquad 2H^+ + 2e^-$$

Determination of p^H of a solution by using standard hydrogen electrode:

A standard hydrogen electrode is coupled with another hydrogen electrode which contains the solution of unknown pH (Fig. 7). In both half-cells hydrogen gas is used at 1 atm pressure and 25°C. The emf of the complete cell is recorded experimentally.

$$Pt \mid H_2(1atm) \mid H^+(unknown) \| H^+(1M) \mid H_2(1atm) \mid pt$$

Hydrogen electrode reaction is:

$$2H^+ + 2e^- \longrightarrow H_2$$

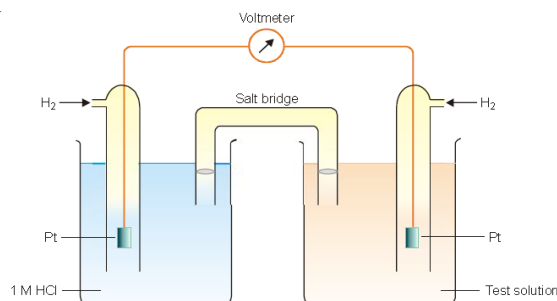$$E = E^0 - \frac{2.303RT}{nf} \log \frac{[H_2]}{[H^+]^2}$$

Fig. 7 A standard hydrogen electrode is coupled with another hydrogen electrode
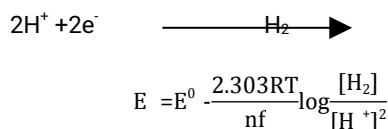
$$E = E^0 - \frac{2.303RT}{nf} \log \frac{1}{[H^+]^2}$$

$$E = E^0 + \frac{0.0592V}{2} 2 \log[H^+]$$

$$E = 0 + 0.0592 \, V \log[H^+]$$

$$E = -0.0592V \, P^H$$

The emf of the E_{cell}, is given as $\qquad E_{cell} = E_{right} - E_{left}$

$$E_{cell} = 0 - (-0.0592 \, V \, P^H)$$

$$P^H = \frac{Ecell}{0.0592 \, V}$$

Limitations: 1) The standard hydrogen electrode (SHE) is not the most convenient standard electrode to use in the laboratory. The gas has to be carefully controlled and hydrogen gas can form explosive mixtures with air. 2) It cannot be used in solutions containing redox systems. 3) It cannot be used in the presence of ions of many metals.

Any other electrode system whose potential has been determined relative to the SHE can also be used as **Secondary standard electrode.**

The Calomel Electrode: It is the most commonly used **secondary standard reference electrode**. The
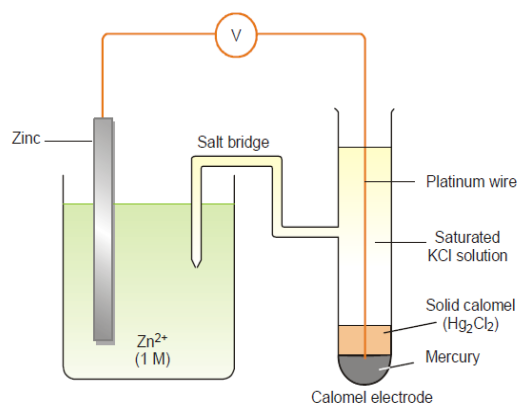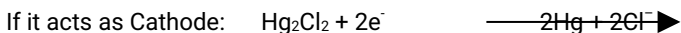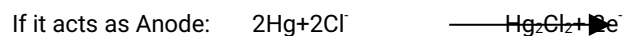

Fig. 8 The calomel electrode coupled with zinc electrode to determine its emf

standard calomel electrode, **SCE,** consists of a wide glass-tube with a narrow side-tube. It is set up as illustrated in Fig. 8. A platinum wire is dipping into liquid mercury covered with mercury solid mercurous chloride (Hg_2Cl_2, calomel). The tube is filled with a 1 M solution of KCl (or saturated KCl solution). The side-tube containing KCl solution provides the salt bridge which connects the electrode to any other electrode (Fig 8).

The calomel electrode is represented as: Cl^- (1M) | Hg_2Cl_2, Hg

The half-cell reactions are: Based on the Reduction potential values, the Calomel electrode can be used as Anode or Cathode.

If it acts as Anode: $2Hg + 2Cl^- \longrightarrow Hg_2Cl_2 + 2e^-$

If it acts as Cathode: $Hg_2Cl_2 + 2e^- \longrightarrow 2Hg + 2Cl^-$

Note. The potential of the calomel electrode depends on the concentration of KCl solution taken in the half-cell.

Kcl concentration	0.1N	1N	Saturated
Electrode potential(in volts)	0.3335	0.2810	0.2422

Determination of emf of the standard zinc half-cell using calomel electrode: The zinc half- cell is connected with the standard calomel electrode as shown in Fig. 8. The emf of the complete cell is then measured with the help of a voltmeter. It is found to be 1.040 V. Since zinc forms the negative electrode of the cell, its emf with respect to calomel electrode will be − 1.040 V. The addition of 0.280 gives the standard electrode potential of zinc. (− 1.040 + 0.280) = − 0.76 V

Determination of p^H of unknown solution by using calomel electrode instead of SHE: The electrode can be coupled with Hydrogen electrode containing solution of unknown P^H.

Pt, H_2 (1 atm) | H^+(unknown) || KCl(satd)|Hg_2Cl_2(s),Hg
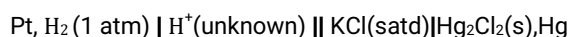
The Emf of the cell   = −

$$= E_{calomel} - E_{hydrogen}$$

$$E_{cell} = 0.2422 - (-0.0592 \, P^H)$$

$$P^H = \frac{E_{cell} - 0.2422}{0.0592 \, V}$$

Quinhydrone Electrode: It is a widely used secondary standard electrode. It involves the redox reaction between quinone (Q) and hydroquinone (QH2), or, simply
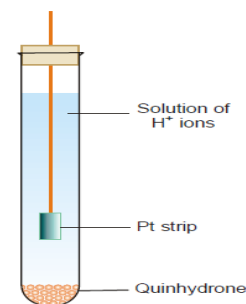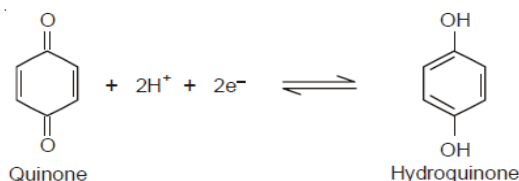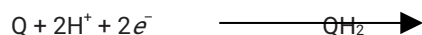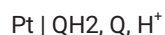

Quinone $+ 2H^+ + 2e^- \rightleftharpoons$ Hydroquinone

Figure–.17 The Quinhydrone electrode

$$Q + 2H^+ + 2\bar{e} \xrightarrow{\hspace{2cm}} QH_2$$

The hydroquinone half-cell consists of a platinum strip immersed in a saturated solution of quinhydrone at a definite H$^+$ ion concentration. Quinhydrone is a molecular compound which gives equimolar amounts of quinone and hydroquinone in solution. The electrode system may be represented as

Pt | QH2, Q, H$^+$

The potential developed is measured against a hydrogen electrode or calomel electrode.

$$Q + 2H^+ + 2\bar{e} \xrightarrow{\hspace{2cm}} QH_2$$

The electrode potential at 25^{0}c is given by Nernst equation

$$E_Q = E_Q^0 - \frac{2.303RT}{nf} \log \frac{[QH_2]}{[Q][H^+]^2}$$

$$E_Q = E_Q^0 - \frac{0.0592\ V}{2} \log \frac{[QH_{2]}}{[Q][H^+]^2}$$

Since quinone and hydroquinone are taken in

equimolar amounts i.e., [Q] = [QH$_2$] = 1

$$E_Q = E_Q^0 - \frac{0.0592\ V}{2} \log \frac{1}{[H^+]^2}$$

$$E_Q = E_Q^0 + \frac{0.0592\ V}{2} 2 \log[H^+]$$

Fig. 10 Quinhydrone electrode coupled with saturated calomel electrode (dipping calomel electrode)

$$E_Q = E_Q^0 + 0.0592\ V \log[H^+]$$

$$E_Q = E_Q^0 - 0.0592\ V\ P^H$$
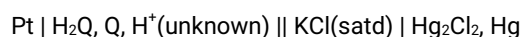
$[-\log[H^+] = P^H]$ $\qquad$ $E_Q = 0.6994V - 0.0592\ VP^H$

Since the electrode potential of the quinhydrone electrode depends upon the concentration of hydrogen ions, it can be used for the determination of P^H value just like a hydrogen electrode.

Construction:

Quinhydrone electrode can very easily be set up by adding a pinch quinhydrone powder (a sparingly soluble solid) to the experimental solution with stirring, until the solution is saturated and a slight excess of it remains undissolved. Then, indicator electrode, usually of bright platinum, is inserted in it. For determining the P^H value, this half cell is combined with any other reference electrode, usually saturated calomel electrode and the emf of the cell so-formed (Fig. 10) is determined potentiometrically. The complete cell may be represented as
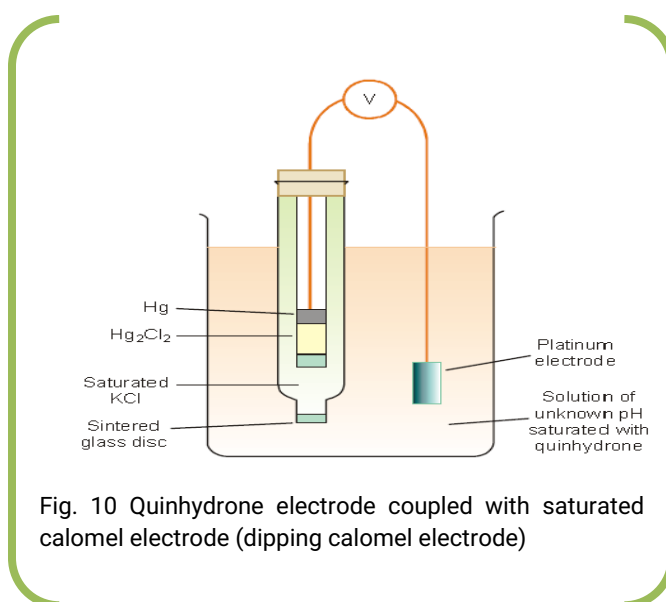
Pt | H$_2$Q, Q, H$^+$(unknown) || KCl(satd) | Hg$_2$Cl$_2$, Hg

$$= E_R - E_L$$

$$= E_{calomel} - E_{quinhydrone}$$

$$= 0.2422 - (0.6994v - 0.0592 \text{ V } P^H)$$

$$P^H = \frac{E_{cell} - 0.2422 + 0.6994}{0.0592}$$

Advantages:

1. The electrode is very easy to setup. 2) The P^H value obtained is very accurate. 3) Very small quantities of the solution are sufficient for the measurement.

Limitations: The electrode cannot be used in alkaline solutions ($P^H > 8.5$) 2) It cannot be used in solutions containing redox system, which would react with either quinhydrone or quinone. (Ex: Fe^{+2}, Mno_2, etc.,)
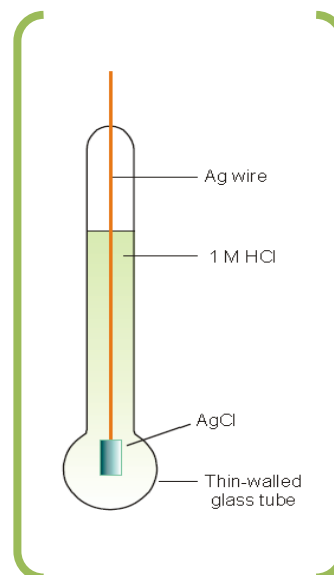
Ion-selective electrode (ISE): Ion selective electrode posses the ability to respond only to certain specific ions, there by developing a potential with respect to that species only in a mixture and ignoring the other ions totally.

Example: glass electrode is only H^+ ions selective.

Glass electrode: When two solutions of different P^H values are separated by a thin glass membrane, there develops a difference of potential between the two surfaces of the membrane. The potential difference developed is proportional to the difference in P^H values. The Glass membrane functions as an Ion-exchange Resin. There is an equilibrium set up between the Na^+ ions of glass and H^+ ions in the solution. The potential difference varies with the H^+ ions concentration of the solution. The electrode potential is given by

At 25^0c $E_G = E_G^0 - 0.0592 \log[H^+]$

$E_G = E_G^0 + 0.0592 P^H$

Construction:

A glass electrode is a type of ion-selective electrode and consists of thin walled glass bulb containing AgCl coated Ag electrode or simply a Pt electrode in 0.1M HCl (Fig. 11). The glass electrode may be shown schematically

Ag │ AgCl(s), HCl(0.1M) │ Glass or Pt,0.1M HCl │ Glass

Determination of p^H of solution by using glass electrode: Glass electrode is dipped in a solution whose P^H is to be determined and it is coupled with saturated calomel electrode (Fig. 12). The EMF of the cell is measured. The EMF of complete cell is given by

$E_{cell} = E_{right} - E_{left}$
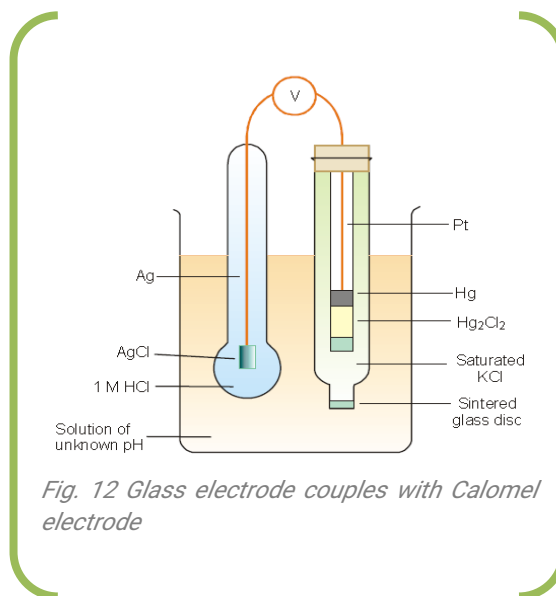
$E_{cell} = E_{SCE} - E_{GLASS}$

$= 0.2422V - [E_G^0 + 0.0592 P^H]$

Fig. 12 Glass electrode couples with Calomel electrode

$$P^H = \frac{0.2422\ V - E_{cell} - E_G^0}{0.0592\ V}$$

The value of the potential of calomel electrode is known while E_{cell} can be found experimentally. Therefore, we can find P^H of a given solution if $E°_G$ is known. The $E°_G$ value of a glass electrode can be determined by using a solution of known P^H in the cell and measuring E_{cell}. This value of $E°_G$ is constant for a particular glass electrode and can be used for any subsequent determinations of pH of unknown solutions

Advantages of glass electrode: 1) It is simple and can easily be used. 2) Equilibrium is rapidly achieved 3) The results are accurate 4) It is not easily poisoned.

Limitations of glass electrode: 1) The glass electrode can be used in solutions with P^H range of 0-10. Electrodes composed of special glasses can be used for measurements up to a P^H of 12. However, above 12 P^H cations of solution affect the glass interface and render the electrode useless. 2) Although, glass membranes of electrode is very thin, yet its resistance is very high, which cannot be measured by ordinary potentiometers. It is therefore, necessary to use special electronic potentiometers.

Potentiometric titrations

A titration in which the equivalent or the end point of the reaction is determined with the help of measurement of potential of a reaction mixture is known as potentiometric titrations.

In a potentiometric titration, a suitable electrode immersed in the solution to be titrated acts as the 'indicator' (Fig. 14). The **indicator electrode** is paired with a reference electrode and the two electrodes are connected to an electronic voltmeter. The emf of the indicator electrode changes gradually with the change of concentration of ions caused by the addition of titrant from the burette. The equivalence
Point is indicated by a sharp change in electrode potential.

Since the reference electrode potential has a constant value, any change in the indicator electrode potential is reflected by a similar change in the cell potential. Therefore, the equivalence point can be found by plotting a graph between the cell emf and the volume of titrant added from the burette. A sharp rise of the curve shows the equivalence point and the corresponding volume on the graph is the volume of the solution used for the titration.

The potentiometric titrations may be of three types:
1) Acid-base titrations 2) Oxidation-reduction titrations 3) Precipitation titrations

Acid-base titrations:
The Acid solution whose strength has to be determined is taken in a beaker and the Hydrogen electrode or glass electrode and Calomel electrode were dipped in the solution. The electrodes were connected to the potentiometer and the emf is measured. A standard Alkali solution is taken in a burette and added to the beaker which has Acid solution. The solution is stirred thoroughly and the emf of the cell is recorded.

The readings are recorded by repeating the procedure of addition of standard Alkali.
The volume of Alkali added is plotted against emf observed. The steepest portion of the curve indicates the equivalent point of the titration.

In the similar way plot of ΔE/ΔV against the volume of the base. The sharp point of the curve indicates the end point of titration.
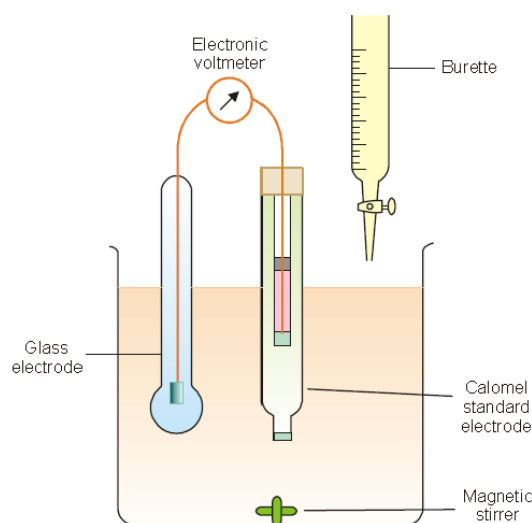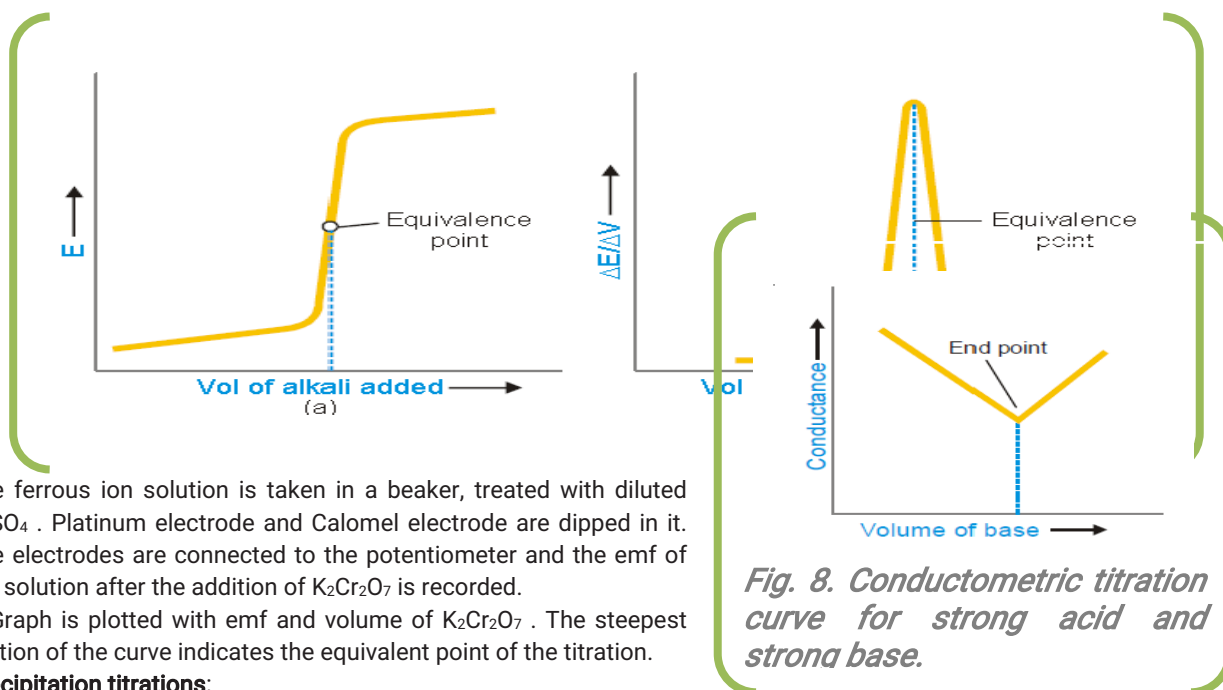

Fig. 14 Apparatus for potentiometric acid-base titrations.

Oxidation-reduction titrations:

The titrations for Oxidation and reduction are similar to that of Acid Base titrations. The only difference is the electrode reversible to Hydrogen ions is replaced by a bright Platinum electrode.

e.g.: Fe^{+2} titrated against $K_2Cr_2O_7$

The ferrous ion solution is taken in a beaker, treated with diluted H_2SO_4 . Platinum electrode and Calomel electrode are dipped in it. The electrodes are connected to the potentiometer and the emf of the solution after the addition of $K_2Cr_2O_7$ is recorded.
A Graph is plotted with emf and volume of $K_2Cr_2O_7$. The steepest portion of the curve indicates the equivalent point of the titration.

Precipitation titrations:

In precipitation reactions or titrations also an electrode reversible to one of the ions is involved.
e.g.: Titrations of $AgNO_3$ with NaCl where AgCl precipitates out.

Here Silver electrode is used along with Calomel electrode. The NaCl is taken in the burette and $AgNO_3$ is taken in the beaker containing electrodes. The emf of the cell is measured and plotted against volume of NaCl added. The steepest portion of the curve indicates the equivalent point of the titration.

Advantages of potentiometric titrations:

1)   Coloured solutions can be titrated without the use of an indicator.
2)   Even weak acids, weak base titrations can be carried out.
3)   Results obtained are very accurate.
4)   The apparatus required is inexpensive, reliable and readily available.
5)   can be used in the titrations of mixture of acids, bases, halides

CONDUCTOMETRIC TITRATIONS:

Titrations in which conductance measurements are made use of in determining the end-point of acid-alkali reactions, some displacement reactions or precipitation reactions are called conductometric titrations. In these titrations, advantage is taken of the fact that the conductance **of a solution at a constant temperature depends upon the number of ions present in it and their mobility.** For this purpose, the titrant is added from a burette into a measured volume of the solution to be titrated which is taken in a conductance cell and the conductance readings corresponding to the various additions are plotted against the volume of the titrant. In this way two linear curves are obtained, the point of intersection of which is the end-point.

The shapes of curves obtained in certain types of titration are discussed below:

### (1) Titration of a Strong acid against a Strong base:

Consider the reaction in which hydrochloric acid solution is titrated against a solution of sodium hydroxide (Fig. 8). In these titrations, alkali (NaOH) solution is generally taken in the burette and a known volume of the acid solution (HCl) is taken in the conductivity cell. Before the addition of alkali, the conductance of the solution is high due to presence of H^+ and Cl^- ions. Since hydrogen ions possess the greatest mobility of any ion, the greater part of the conductance is due to it. As alkali solution is added, the hydrogen ions are removed by combination with the hydroxyl ions forming feebly ionized water molecules and their place is taken up by comparatively slow moving Na^+ ions.

$H^+ + Cl^- + Na^+ + OH^- \longrightarrow Na^+ + Cl^- + H_2O(\textit{feebly ionized})$
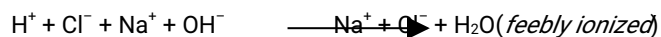
As a result of this, the conductance of the solution decreases and continues to fall with every subsequent addition of alkali till the end-point is reached. After the equivalence point is reached the further addition of sodium hydroxide solution results in an increase of conductance since the hydroxyl ions are no longer removed in the chemical reaction in the form of feebly ionized water. The point of minimum conductance, therefore, coincides with the end-point of the titration.

(2) Titration of a Weak acid against a Strong base:

When a weak acid like acetic acid is titrated against a strong alkali like sodium hydroxide, we get a curve of the type shown in Fig. 9. The initial conductance of the solution is low because of the poor dissociation of the weak acid. On adding alkali, highly ionised sodium acetate is formed. The acetate ions at first tend to suppress the ionization of acetic acid still further due to *Common Ion Effect* but after a while the conductance begins to increase because the conducting power of highly ionized salt exceeds that of the weak acid.

$CH_3COOH + Na^+ + OH^- \longrightarrow CH_3COO^- + Na^+ + H_2O$
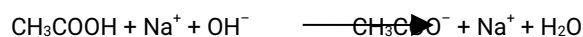
Immediately after the end point, further addition of sodium hydroxide introduces the fast moving hydroxyl ions. Thus, the conductance value shows a sharp increase. The point of intersection of the two curves, gives the end-point.

(3) Titration of a Strong acid against a Weak base

The curve obtained for the titration of a strong acid against a weak base is shown in Fig. 10. In this case, the conductance of the solution will first decrease due to the decrease of the fast moving H^+ ions and their replacement by slow moving NH_4^+ ions.

$H^+Cl^- + NH_4OH \longrightarrow NH_4^+ + Cl^- + H_2O(\textit{feebly ionized})$

After the end-point has been reached, the addition of ammonium hydroxide will not cause any appreciable change in conductance value as it is a weak electrolyte and its conductance is very small compared with that of the acid or its salt. The shape of this part of the curve will, therefore, be as shown in the figure 10.
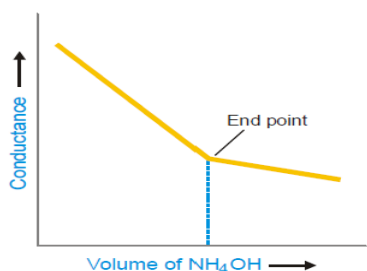

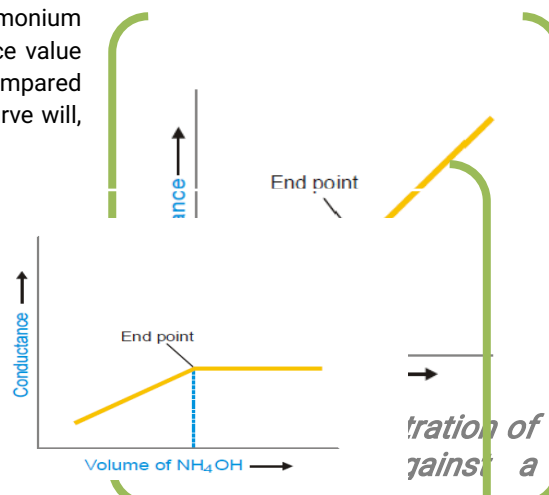Fig. 10. Curve for titration of a strong acid(HCl) against a weak base(NH₄OH) .

Fig. 11. Curve for titration of acetic acid against ammonium hydroxide.

(4) Titration of a Weak acid against a Weak base:

The conductometric method is particularly suitable as such titrations do not give a sharp end- point with indicators. Consider the titration of acetic acid with ammonium hydroxide. The complete titration curve is shown in Fig 11. The initial conductance of the solution in this case is also low due to the poor dissociation of the weak acid. But it starts increasing as the salt CH_3COONH_4 is formed. After the equivalence point, the conductivity remains almost constant because the free base NH_4OH is a weak electrolyte. The end-point is quite sharp.

Advantage of Conductometric Titrations:

(1) Colored solutions where no indicator is found to work satisfactorily can be successfully titrated by this method.

(2) This method is useful for the titration of weak acids against weak bases which do not give a sharp change of colour with indicators in ordinary volumetric analysis.

(3) More accurate results are obtained because the end -point is determined graphically.

Precautions. (*i*) It is necessary to keep the temperature constant throughout the experiment. (*ii*) In acid-alkali titrations, the titrant should be about 10 times stronger than the solution to be titrated so that the volume change is as little as possible.

DIFFERENCES BETWEEN CONDUCTOMETRIC AND VOLUMETRIC TITRATIONS

Conductometric Titrations	Volumetric Titrations
Conductance measurements are done to check end points.	Volume measurements are done to check end points.
Titrations can be carried out even with coloured solution.	These titrations fail in coloured solutions as suitable indicators are not available some times.
Accurate results are obtained.	Results are not so accurate.
End point is determined graphically.	End point is determined by change in colour of indicator.
In case of polybasic acids conductometric titrations can be used.	In case of polybasic acids volumetric titrations do not give correct end points.
These are successful even in weak acids and strong bases.	These are not successful in weak acids and strong bases.