

Unit II

VI SEMISTER

ELECTROCHEMISTRY

KOHLRAUSCH LAW OF INDEPENDENT MIGRATION OF IONS

In 1874, Kohlrausch formulated the law of independent migration of ions based on the experimental data of conductivities of various electrolytes. This law can be stated as follows:

At infinite dilution, the dissociation of the electrolyte is complete and hence each ion makes definite contribution to the equivalent conductivity of the electrolyte irrespective of the nature of other ions associated with it.

Therefore the limiting equivalent conductivity of an electrolyte is the algebraic sum of limiting equivalent conductivities of its constituent ions.

i.e., The limiting equivalent conductivity of an electrolyte, $\Lambda_0^{\text{electrolyte}}$

$$\Lambda_0^{\text{electrolyte}} = \lambda_0^+ + \lambda_0^-$$

Where λ_0^+ and λ_0^- are the limiting equivalent conductivities of cation and anion respectively.

However the Kohlrausch law can also be stated in terms of molar conductivities as:

The limiting molar conductivity of an electrolyte is the sum of individual contributions of limiting molar conductivities of its constituent ions.

i.e., The molar equivalent conductivity of an electrolyte, $\mu_0^{\text{electrolyte}}$

$$\mu_0^{\text{electrolyte}} = n_+ \mu_0^+ + n_- \mu_0^-$$

Where μ_0^+ and μ_0^- are the limiting molar conductivities of cation and anion respectively.

And n_+ and n_- are the stoichiometric numbers of positive and negative ions formed during the dissociation of electrolyte.

EXPERIMENTAL BASIS AND THEORETICAL EXPLANATION OF KOHLRAUSCH LAW

Kohlrausch observed that at infinite dilutions, the difference between the conductivities of sodium and potassium salts is constant irrespective of the associated anions, as tabulated below.

Salt pair	Conductivity (mho cm ² equiv)	Difference
NaCl	108.90	21.20
KCl	130.10	
NaNO ₃	105.33	21.17
KNO ₃	126.50	
NaBr	111.10	21.20
KBr	132.30	

Kohlrausch argued that the constant difference in the conductivities of above pairs can be ascribed to the fact that the mobility of sodium and potassium ions at infinite dilution is not influenced by the nature of counter ions. The ions at such a low concentration migrate in the electric field as they are independent i.e., they show same ionic conductance irrespective of the nature of counter ion.

APPLICATIONS OF KOHLRAUSCH LAW

1) Calculation of limiting conductivities of weak electrolytes: The Kohlrausch law can be used to calculate the limiting conductivities of weak electrolytes.

E.g., The calculation of limiting equivalent conductance of acetic acid, a weak electrolyte is illustrated below.

According to Kohlrausch law, the limiting equivalent conductance values of CH₃COOH, CH₃COONa, HCl and NaCl can be written as follows:

$$\begin{aligned}\Lambda_o^{\text{CH}_3\text{COOH}} &= \lambda_o^{\text{CH}_3\text{COO}^-} + \lambda_o^{\text{H}^+} \\ \Lambda_o^{\text{CH}_3\text{COONa}} &= \lambda_o^{\text{CH}_3\text{COO}^-} + \lambda_o^{\text{Na}^+} \\ \Lambda_o^{\text{HCl}} &= \lambda_o^{\text{H}^+} + \lambda_o^{\text{Cl}^-} \\ \Lambda_o^{\text{NaCl}} &= \lambda_o^{\text{Na}^+} + \lambda_o^{\text{Cl}^-}\end{aligned}$$

Therefore,

$$\Lambda_o^{\text{CH}_3\text{COOH}} = \Lambda_o^{\text{CH}_3\text{COONa}} + \Lambda_o^{\text{HCl}} - \Lambda_o^{\text{NaCl}}$$

2) Determination of degree of ionization (α) of weak electrolyte: The degree of ionization of a weak electrolyte at a particular concentration is equal to the ratio of actual number of ions formed due to partial ionization to the expected number of ions formed upon complete dissociation.

$$\alpha = \frac{\text{Actual no of ions formed due to partial dissociation}}{\text{Expected no of particles formed due to complete dissociation}}$$

Since the conductance is proportional to the number of ions in the solution, the degree of ionization is equal to the conductance ratio as given below.

$$\alpha = \frac{\Lambda_c}{\Lambda_o} = \frac{\Lambda_c}{\lambda_o^+ + \lambda_o^-}$$

Where

Λ_c = equivalent conductivity at given concentration.

Λ_o = limiting equivalent conductivity.

λ_o^+ = limiting equivalent conductivity of cation.

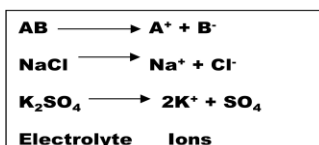
λ_o^- = limiting equivalent conductivity of anion.

Arrhenius Theory of Electrolytic Dissociation

In order to explain the properties of electrolytic solutions, Arrhenius put forth, in 1884, a comprehensive theory which is known as **theory of electrolytic dissociation or ionic theory**

The Main Points of the Theory are

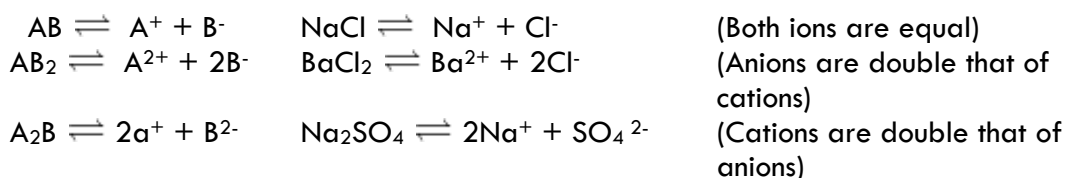
- ✓ An electrolyte, when dissolved in water, breaks up into two types of charged particles, one carrying a positive charge and the other a negative charge. These charged particles are called ions. Positively charged ions are termed cations and negatively charged as anions.



- ✓ In its modern form, the theory assumes that solid electrolytes are composed of ions which are held together by electrostatic forces of attraction. When an electrolyte is dissolved in a solvent, these forces are weakened and the electrolyte undergoes dissociation into ions. The ions are solvated.
- ✓ The process of splitting of the molecules into ions of an electrolyte is called ionization.
- ✓ The fraction of the total number of molecules present in solution as ions is known as degree of ionization or degree of dissociation. It is denoted by

$$\alpha = \frac{\text{Number of molecules dissociated into ions}}{\text{Total number of molecules}}$$

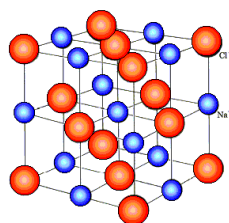
- ✓ It has been observed that all electrolytes do not ionize to the same extent. Some are almost completely ionized while others are feebly ionized. The degree of ionization depends on a number of factors.
- ✓ Ions present in solution constantly re-unite to form neutral molecules and, thus, there is a state of dynamic equilibrium between the ionized and non-ionized molecules, i.e., $AB \rightleftharpoons A^+ + B^-$
Applying the law of mass action to above equilibrium $\frac{[A^+][B^-]}{[AB]} = K$
K is known as ionization constant. The electrolytes having high value of K are termed strong electrolytes and those having low value of K as weak electrolytes.
- ✓ When an electric current is passed through the electrolytic solution, the positive ions (cations) move towards cathode and the negative ions (anions) move towards anode and get discharged, i.e., electrolysis occurs. The ions are discharged always in equivalent amounts, no matter what their relative speeds are.
- ✓ The electrolytic solution is always neutral in nature as the total charge on one set of ions is always equal to the total charge on the other set of ions. However, it is not necessary that the number of two sets of ions must be equal always



- ✓ The properties of electrolytes in solution are the properties of ions present in solution. For example, acidic solution always contains H^+ ions while basic solution contains OH^- ions and characteristic properties of solutions are those of H^+ ions and OH^- ions respectively.
- ✓ The ions act like molecules towards depressing the freezing point, elevating the boiling point, lowering the vapour pressure and establishing the osmotic pressure.
- ✓ The conductivity of the electrolytic solution depends on the nature and number of ions as the current is carried through solution by the movement of ions.
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Evidences in Favour of Ionic Theory

- ✓ A large number of experimental observations are available which support Arrhenius theory. A few of them are given below:



Ions Present in Solid Electrolytes

- ✓ X-ray diffraction studies have shown that electrolytes are composed of ions. For example, a crystal of NaCl does not contain NaCl units but Na^+ and Cl^- ions. Each Na^+ ion is surrounded by six Cl^- ions and each Cl^- ion in turn is surrounded by six Na^+ and Cl^- ions.
- ✓ The ionic compounds behave as good conductors in fused state. It can only be possible if ions are already present in ionic solids.

Ohm's Law Applicability

- ✓ The electrolytic solutions like metallic conductors obey Ohm's law, i.e., the strength of the current flowing through a conductor is directly proportional to potential difference (E) applied across the conductor and is inversely proportional to the resistance of the conductor. Mathematically, $I = E/R$

This can only be possible if ions are already present in the solution and no part of the current has only directive effect on the ions.

Ionic Reaction

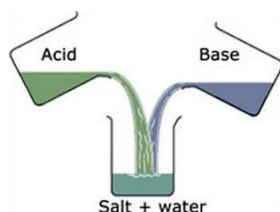
- ✓ Evidence for the existence of ions in aqueous solutions of electrolytes is furnished by well known reactions in inorganic chemistry. A white precipitate of silver chloride is obtained whenever Ag^+ ions come in contact with chloride ions.



But no precipitation occurs when AgNO_3 solution is added to CCl_4 , CHCl_3 or $\text{C}_2\text{H}_5\text{Cl}$ as these substances being non-electrolytes do not furnish Cl^- ions in solution. An acid which gives all tests of H^+ ions in aqueous solution, does not give the same tests when dissolved in any organic solvent because no ionization of the acid occurs in the common reaction.

Heat of Neutralization

- ✓ When one gram equivalent of a strong acid is neutralized by one gram equivalent of a strong base, the heat evolved is always the same, i.e., 13.7 kcal. This can be explained on the basis of Arrhenius theory that an acid furnishes H^+ ions and base OH^- ions when dissolved in water and the process of neutralization involves the common reaction.



Thus, heat of neutralization is actually the heat of formation of H_2O from H^+ and OH^- ions.

Abnormal Colligative Properties

The abnormal behavior towards colligative properties as observed in the case of electrolytes can be explained on the basis of ionic theory. When an electrolyte is dissolved in water, the number of molecules actually dissolved due to ionization. The can't

Hoff factor,

$$\alpha = \frac{\text{Number of molecules dissociated into ions}}{\text{Toal number of molecules}}$$

is always more than one, i.e., $i = 1 + (n-1)$ where 'n' is the number of ions produced by the ionization of one molecule of the electrolyte and 'i' is the degree of ionization.

Colour of Solution

- ✓ The color of the electrolytes in solution. If any, is due to their ions, the CuSO_4 is blue in solution due to the presence of Cu^{2+} ions. Potassium permanganate (KMnO_4) is purple in solution due to the presence of ions.
- ✓ Ionic theory provides satisfactory explanations regarding various phenomena such as electrolysis, conductivity, salt hydrolysis, solubility product, etc.

Limitations of Arrhenius Theory

- ✓ Ostwald's dilution law which is based on Arrhenius theory is not applicable to strong electrolytes.
- ✓ Strong electrolytes conduct electricity infused state, i.e., in absence of water. this is in contradiction of Arrhenius theory according to which the presence of solvent is a must for ionization.
- ✓ Arrhenius theory assumes independent existence of ions but fails to account for the factors which influence the mobility of the ions.

Anomaly of Stong Electrolytes: Debye-Huckel-Onsager's Equation of strong electrolytes

In case of weak electrolytes increase in conductance with dilution may be due to the increase in degree of dissociation of the electrolyte. The reason for such a behaviour is due to the reason that as weak electrolytes are dissolved in water, only a small portion of it dissociates and a dynamic equilibrium is established between the dissociated species and undissociated molecules. Such equilibrium would lead to increase in concentration of ions with dilution. Therefore as per Arrhenius theory, at infinite dilution, weak electrolytes are completely dissociated. Hence, the degree of dissociation, α of such weak electrolytes can be obtained from the equation

$$\alpha = \frac{\Lambda c}{\Lambda_0}$$

Where Λ_c is the equivalent conductance of the electrolyte at a given concentration and Λ_0 is the equivalent conductance of the electrolyte at infinite dilution. But according to the modern theory of strong electrolytes, the degree of dissociation, α , of strong electrolytes is unity even at moderate concentrations. Therefore, the above relationship does not hold for strong electrolytes. Debye and Huckel suggested that increase in conductance the dilution in case of strong electrolytes is not due to increase in ionization but due to increase in mobilities of ions due to weaker interionic attraction. Debye and Huckel derived an equation which enabled them to calculate the magnitude of interionic effects. Debye-Huckel at 1923 later Onsagar at 1926 suggested that as a result of attractive forces between opposites ions, there is an aggregation around an ion by opposite ions besides to solvent molecules. Any ion is seem as a center of sphere which a rounded by opposites ions and solvent molecules .The ion in centre called **central ion** while the rounded ions and solvent molecules called **ion-atmosphere**. The net charge in ion atmosphere is equal of that for central ion but in opposite charge. The ion atmosphere is symmetrical at normal conditions (absence of applied voltage) due to the reason that the forces of attraction exerted by the atmosphere on the central ion is uniform in all directions and therefore cancels out. When the voltage is apply, there are two effects are caused:

1-Asymmetry effect

When an electric field is applied the ions are set in motion. As a result central ion moves in one direction and the atmosphere in the opposite direction. Thus if a positively charged central ion tends to move toward cathode while its negative atmosphere tend to move towards the anode. The symmetry of the atmosphere around the central ion thus gets distorted due to the reason that the force of become greater in the direction opposite to the one in which ion moves. Consequently the ion experience as retarding force, which tends to drag it backwards. The movement of ion is therefore slowed down. This drag on the central ion is known as asymmetry effect because it arises from the lack of symmetry in the ionic atmosphere. During its motion the central ion will build up its ionic atmosphere again where as the old one will die out. If the formation of new ionic atmosphere and the destruction of the old one occurs simultaneously, there will be no retarding force affecting the movement the movement of the central ion. But there is always a time gap between the formation of new ionic atmosphere and the destruction of the old one. This time gap is called time of relaxation. The asymmetric effect is represents as following

$$B=8.2 \times 10^5 \Lambda_0 / (DT)^{3/2}$$

Where D is the dielectric constant, η is the viscosity in poises, and T is the absolute temperature ($^{\circ}\text{K}$).

2-Electrophoretic effect

Another force which slows down the motion of ions at high concentration arises due to the water of hydration associated with the ionic atmosphere which moves in a direction opposite to that in which the central ion moves Thus, a positive ion which migrates towards cathode has to make its way through the medium which itself is moving with the negative ionic atmosphere towards the positive electrode. These counter currents slow down the ions in the same way as counter currents slow down a swimmer. A new retardation force arises on the central ion as a result of friction between central ion and solvent molecules. This force called *electrophoretic effect* which causes decreasing of equivalent conductance. The electrophoretic effect is represents as following:

$$A=82.4/(DT)^{1/2}\eta$$

where D is the dielectric constant, η is the viscosity in poises, and T is the absolute temperature ($^{\circ}\text{K}$).

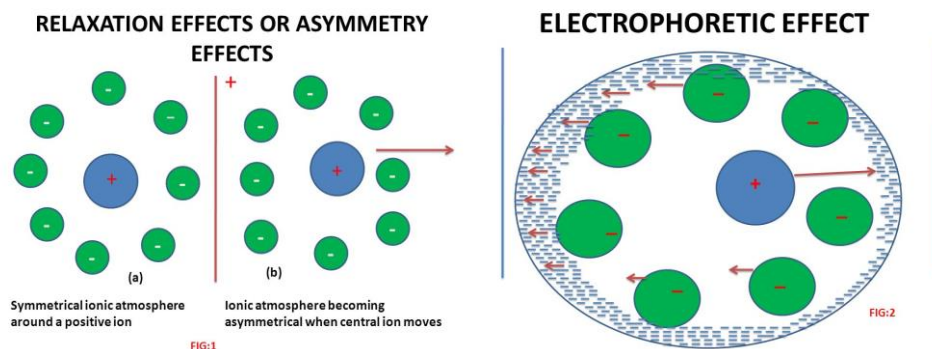
Debye Huckel and Onsagar worked out mathematically the magnitude of the asymmetry and electrophoretic effects in terms of factors such as valene of the ions, ionic concentration, dielectric constant and viscosity of the medium. For a uni-univalent electrolyte the following equation was derived.

$$\Lambda = \Lambda_0 - (A + B \Lambda_0) C^{1/2}$$

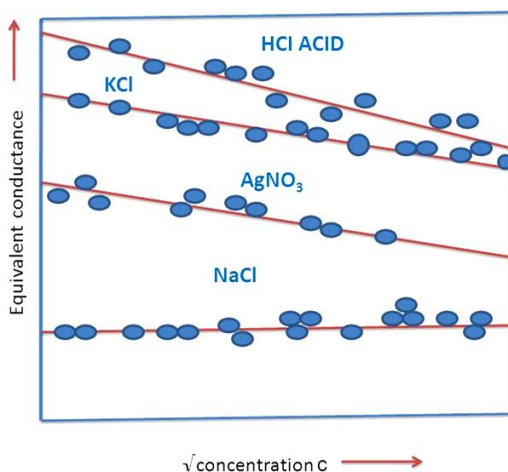
Or

$$\Lambda = \Lambda_0 - (82.4/(DT)^{1/2} \eta + 8.2 \times 10^5 \Lambda_0 / (DT)^{3/2} \Lambda_0) C^{1/2}$$

Here Λ is the equivalent electrical conductivity, Λ_0 is the equivalent electrical conductivity for infinite dilution, C is the concentration in moles per liter, and



If the equation is correct, then by plotting molar concentration, Λ against square root of the concentration $C^{1/2}$, a straight line of slope $A + B \Lambda_0$ should be obtained. This has been checked for a no of uni-uni valent electrolytes and found to be true up to the concentration of 0.02 M. But at higher concentrations slight deviations are observed from the normal. If the solution is at infinite dilution, i.e., if c tends to zero, then the second term on the right hand side of the equation becomes negligible and Λ approaches Λ_0



Transport Number

Transport number in electrochemistry, or just transference number, is described as a fraction of the total current carried by an ion. It is denoted by sets symbols such as t_+ and t_- or t_c and t_a or n_c and n_a .

According to the definition, we have

$$t_a = \frac{\text{Current carried by an anion}}{\text{Total current passed through the solution}}$$

$$t_c = \frac{\text{Current carried by a cation}}{\text{Total current passed through the solution}}$$

If u_+ and u_- are the speeds of the cation and anion respectively, then

Current carried by the cation = $k u_c$

Current carried by the anion = $k u_a$

Therefore total current carried = Current carried by the cation + Current carried by the anion

$$\begin{aligned} &= k u_c + k u_a \\ &= k(u_c + u_a) \end{aligned}$$

$$\text{Transport no of cation, } t_c = \frac{k u_c}{k(u_c + u_a)}$$

$$t_c = \frac{u_c}{u_c + u_a}$$

$$\text{Transport no of anion, } t_a = \frac{k u_a}{k(u_c + u_a)}$$

$$t_a = \frac{u_a}{u_c + u_a}$$

$$t_c + t_a = \frac{u_c}{u_c + u_a} + \frac{u_a}{u_c + u_a} = 1$$

$$t_c + t_a = 1$$

i.e., sum of transport numbers of cation and anion of an electrolyte is always unity. Thus, no current is lost in any other function and whole current is carried by the anions.

Transport number, in fact, is an amount or a quantity, which is effectively used during a transport number calculation, also known as *electrochemical calculations*. As shown in the transport number equation above, transport number is always equivalent to the ratio between the velocity or mobility of an ion and the sum of the velocities of cation and anion. This is described as a characteristic, which is dependent on the mobilities of ions, concentrations and the temperature of the ions in an electrolytic solution.

Methods for Transport Number Calculation

Hittorf's Method

Hittorf's method is the most common method for calculating transport or transference number. It is a process to determine transport number wherein one determines changes in the composition of an electrolytic solution around its cathode and anode. This method is based upon the principle that fall in concentration around an electrode is proportional to the speed of the ion moving away from it.

$$\frac{\text{Fall in concentration around cathode}}{\text{Fall in concentration around anode}} = \frac{\text{Speed of anion}}{\text{Speed of cation}} = \frac{u_a}{u_c}$$

Since transport no of cation,

$$t_c = \frac{\text{speed of the cation}}{\text{speed of the cation} + \text{speed of the anion}}$$

$$t_c = \frac{\text{Fall in concentration around anode}}{\text{Fall in concentration around anode} + \text{Fall in concentration around cathode}}$$

$$t_c = \frac{\text{Fall in concentration around anode}}{\text{Total fall in concentration around both the electrodes}}$$

If the concentration is measured in terms of gram equivalents, then

$$t_c = \frac{\text{No of gram equivalents lost from the anodic compartment}}{\text{No of gram equivalents lost from both the compartments}}$$

Since no of ions/gram equivalents lost from both the anodic and cathodic compartments is equal to the no of ions/gram equivalents discharged/deposited on each electrode. Hence the transport no of cation is

$$t_c = \frac{\text{No of gram equivalents lost from the anodic compartment}}{\text{No of gram equivalents deposited on each electrode}}$$

Factors that Affect Transport Number

Rise in temperature is the main factor that affects a **transport number**. With a rise in temperature, the **transport number** or **transference number** of cation and anion comes closer to 0.5.

Transport number (or Transference number) and Ionic Mobility

Ionic Mobility, also known as Ionic Conductance, is defined as the conductivity of a solution containing 1 g ion at infinite dilution when two sufficiently large electrodes are placed 1cm apart.

Ionic mobilities (λ_a or λ_e) \propto speeds of ions (u_a or u_e)

Unit of ionic mobility is $\text{Ohm}^{-1} \text{cm}^2$ or $\text{V}^{-1}\text{S}^{-1} \text{cm}^2$

The following equation shows how Ionic Mobility and transport number are related to each other:

$$\lambda_a \text{ or } \lambda_e = t_a \text{ or } t_e \times \lambda_m$$

Absolute ionic mobility is the mobility with which an ion moves under unit potential gradient. Its unit is cm sec^{-1} .

$$\text{absolute ionic mobility} = \frac{\text{ionic mobility}}{96,500}$$

Moving boundary method:

The moving boundary method rests on the direct observation of migration of ions in an electric field. The principle may be explained with reference to the determination of transport no of H^+ ions in hydrochloric acid. The conductivity cell consists of a vertical tube of uniform bore filled with cadmium chloride and hydrochloric acid as shown below.

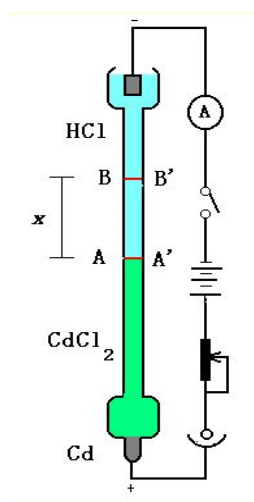
The formation of a sharp boundary is the crux of the method. Hydrochloric acid serves as a principle electrolyte while cadmium chloride serves as indicator electrolyte to enable the formation of an autogenic boundary. The concentration of the two solutions are so adjusted that hydrochloric acid solution has lower density than cadmium chloride solution so that hydrochloric acid floats over it. A sharp boundary appears between the two solutions. A care should be taken of the fact that cation of the indicator electrolyte should not move faster than the cation whose transport no is to be determined and the indicator electrolyte should have the anion common to principle electrolyte.

The anode is fitted at the bottom and is made up of cadmium metal while cathode at the top is a platinum foil. When current is passed through the cell the chloride ions move towards anode while hydrogen ions followed by cadmium ions move towards the cathode. As a result the boundary separating the two solutions move upwards.

If the boundary moves through distance x cm, from AA' to BB' then the volume of the liquid that has moved up is $X A \text{ cm}^3$. Let the concentration of the acid be C gram equivalents per litre. Then the no of gram equivalents of H^+ ions carried towards the cathode = $XAC/1000$. Since each gram equivalent carries one faraday of electricity, the electricity carried by H^+ ions = $XAC/1000Q$

Since total quantity of electricity that flows in the same time as measured in the coulometer, is equal to Q faradays then,

Transport no of H^+ ions = $XAC/1000Q$

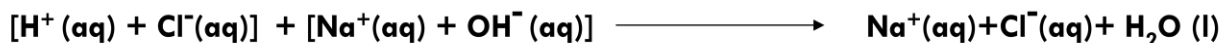


Conductometric Titrations

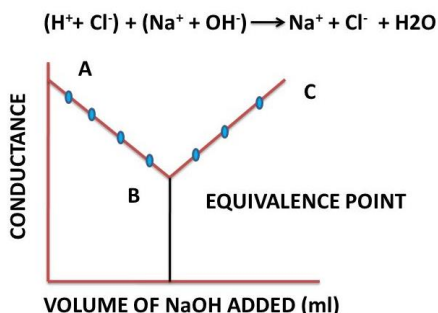
Conductometric measurements are frequently employed to find the end points of the acid-base and other titrations. In such titrations variation of the equivalent conductance by the addition of titrant is measured. In conductometric titrations advantage is taken on the fact that conductivity of a solution is dependent upon the no of ions and their conductance.

The addition of one electrolyte to the other one producing no appreciable change in volume will alter the conductance of the solution according to whether the ionic reactions are producing or not. If no ionic reaction takes place then the conductivity also does not change and if ionic reaction occurs, change in conductivity occurs.

Strong acid Vs Strong base: Consider the titration of strong acid, like hydrochloric acid with a strong base such as sodium hydroxide. The acid is taken in a conductivity vessel and alkali in a burette. The conductance of hydrochloric acid is due to the presence of hydrogen and chloride ions. As the alkali is added gradually, the hydrogen ions are replaced by the slow moving sodium ions as represented below.

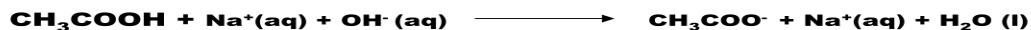


As sodium hydroxide is added the H^+ ions are removed as slightly ionized water. Therefore, the conductance will decrease as Na^+ ions don't possess much mobility. At the neutralization point the solution contains Na^+ and Cl^- ions and will have a considerably less conductance than the original value. Any subsequent addition of the alkali will result in introducing fast moving hydroxyl ions. The conductance will therefore begin to rise after reaching a certain minimum value. On plotting the conductance values as ordinate against millilitres of titrant added as abscissa, the points will lie on two straight lines, the point of intersection of which gives equivalence point.

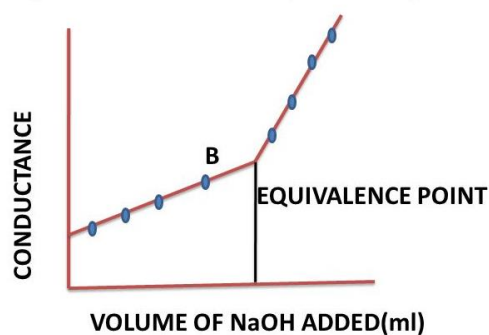


Weak acid Vs Strong base:

The solution containing weak acid such as acetic acid has a very low conductance due to its poor dissociation. During the titration of acetic acid with a strong base such as sodium hydroxide, a highly ionized salt such as sodium acetate is formed. In spite of the common ion effect, neutral salt which is formed during the first part of the titration tends to suppress the ionization of the acetic acid still present. The conductance increases because the conducting power of the highly ionized salt exceeds that of the acid and the reaction may be represented as

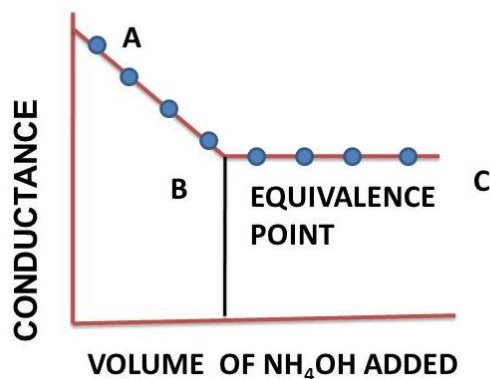


At end point when acid is completely neutralized further addition of alkali introduces the excess of fast moving hydroxyl ions, therefore, conductance increases rapidly. On plotting the conductance versus volume of the alkali added two straight lines are obtained and the point where they meet gives the end point of the titration.



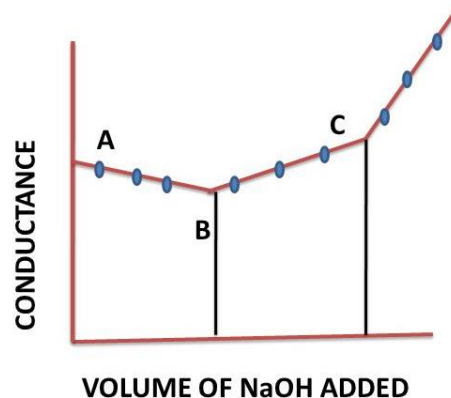
Strong acid Vs Weak base:

If we titrate strong acid like hydrochloric acid with a weak base such as ammonium hydroxide, then addition of weak base to a strong acid will cause the conductance to decrease first as H^+ ions are replaced by slow moving ammonium ions. After neutralization of the acid, further addition of the weakly ionized ammonium hydroxide will cause no appreciable change in the conductance. The titration curves obtained are shown in figure below.



Mixture of a Weak and a Strong acid Vs Strong base:

When a mixture of weak and a strong acid like acetic acid and hydrochloric acid is titrated against a strong base like sodium hydroxide, a curve of the type shown in the figure below is obtained. In presence of a strong acid ionization of a weak acid is suppressed due to common ion effect. So strong acid is neutralized first followed by a weak acid. Therefore, first point of intersection, i.e point B refers to the neutralization of a strong acid and point C refers to the complete neutralization of an acid mixture.



Electrochemical Cells

An electrochemical cell is a single arrangement of two electrodes and an electrolyte for producing an electric current due to chemical action within the cell, or for producing chemical action due to passage of electricity. Thus electrochemical cells may be used for two purposes namely.

- (i) to convert chemical energy into electrical energy.
- (ii) to convert electrical energy into chemical energy.

The common galvanic (or voltaic) cell, dry cell and lead storage battery are devices for converting chemical energy into electrical energy, while the electrolytic cell used for the purification of metals is the device in which electrical energy is used in causing a chemical reaction (electrolysis)

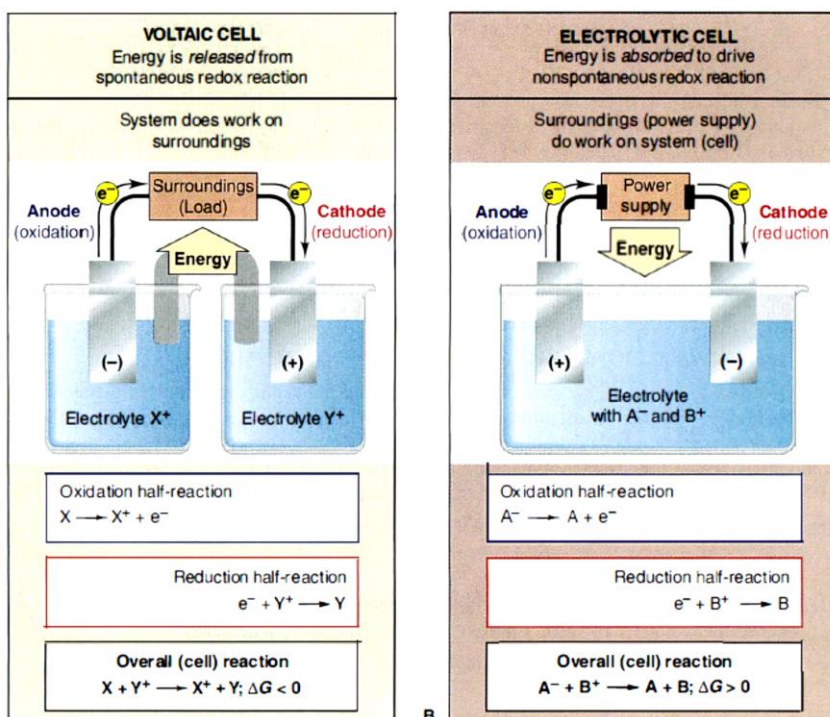
We distinguish two types of electrochemical cells based on the general thermodynamic nature of the reaction:

1. A voltaic cell (or galvanic cell) uses a spontaneous reaction ($\Delta G < 0$) to generate electrical energy. In the cell reaction, the difference in chemical potential energy between higher energy reactants and lower energy products is converted into electrical energy. This energy is used to operate the load-flashlight bulb, CD player, car starter motor, or other electrical device. In other words, the system does work on the surroundings. All batteries contain voltaic cells.
2. An electrolytic cell uses electrical energy to drive a nonspontaneous reaction ($\Delta G > 0$). In the cell reaction, electrical energy from an external power supply converts lower energy reactants into higher energy products. Thus, the surroundings do work on the system. Electroplating and recovering metals from ores involve electrolytic cells.

The two types of cell have certain design features in common. Two electrodes, which conduct the electricity between cell and surroundings, are dipped into an electrolyte, a mixture of ions (usually in aqueous solution) that are involved in the reaction or that carry the charge. An electrode is identified as either anode or cathode depending on the half-reaction that takes place there:

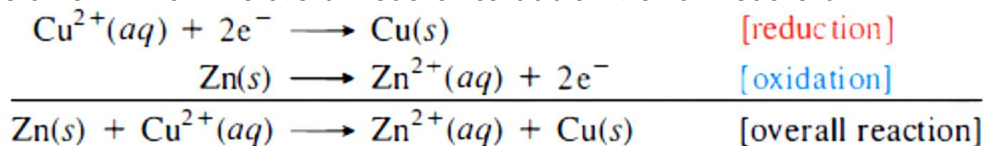
- The oxidation half-reaction occurs at the anode. Electrons are lost by the substance being oxidized (reducing agent) and leave the cell at the anode.
- The reduction half-reaction occurs at the cathode. Electrons are gained by the substance being reduced (oxidizing agent) and enter the cell at the cathode.

As shown in Figure, the relative charges of the electrodes are opposite in the two types of cell. These opposite charges result from the different phenomena that cause the electrons to flow.



Voltaic Cells: Using Spontaneous Reactions To Generate Electrical Energy

If you put a strip of zinc metal in a solution of Cu^{2+} ion, the blue color of the solution fades as a brown-black crust of Cu metal forms on the Zn strip. Judging from what we see, the reaction involves the reduction of Cu^{2+} ion to Cu metal, which must be accompanied by the oxidation of Zn metal to Zn^{2+} ion. The overall reaction consists of two half-reactions:



Construction and Operation of a Voltaic Cell

Electrons are being transferred in the Zn/Cu $^{2+}$ reaction, but the system does not generate electrical energy because the oxidizing agent (Cu^{2+}) and the reducing agent (Zn) are in the same beaker. If, however, the half-reactions are physically separated and connected by an external circuit, the electrons are transferred by traveling through the circuit, thus producing an electric current.

This separation of half-reactions is the essential idea behind a voltaic cell. The components of each half-reaction are placed in a separate container, or half-cell, which consists of one electrode dipping into an electrolyte solution. The two half-cells are joined by the circuit, which consists of a wire and a salt bridge. In order to measure the voltage generated by the cell, a voltmeter is inserted in the path of the wire connecting the electrodes. A switch (not shown)

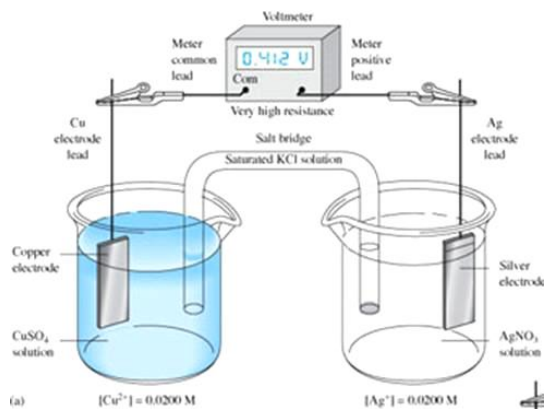
closes (completes) or opens (breaks) the circuit. By convention, the oxidation half-cell (anode compartment) is shown on the left and the reduction half-cell (cathode compartment) on the right. Here are the key points about the Zn/Cu^{2+} voltaic cell:

1. **The oxidation half-cell.** In this case, the anode compartment consists of a zinc bar (the anode) immersed in a Zn^{2+} electrolyte (such as a solution of zinc sulfate, ZnSO_4). The zinc bar is the reactant in the oxidation half-reaction, and it conducts the released electrons out of its half-cell.

2. **The reduction half-cell.** In this case, the cathode compartment consists of a copper bar (the cathode) immersed in a Cu^{2+} electrolyte [such as a solution of copper(II) sulfate, CuSO_4]. The copper bar is the product in the reduction half reaction, and it conducts electrons into its half-cell.

3. **Relative charges on the electrodes.** The electrode charges are determined by the source of electrons and the direction of electron flow through the circuit. In this cell, zinc atoms are oxidized at the anode to Zn^{2+} ions and electrons. The Zn^{2+} ions enter the solution, while the electrons enter the bar and then the wire. The electrons flow left to right through the wire to the cathode, where Cu^{2+} ions in the solution accept them and are reduced to Cu atoms. As the cell operates, electrons are continuously generated at the anode and consumed at the cathode. Therefore, the anode has an excess of electrons and a negative charge relative to the cathode. In any voltaic cell, the anode is negative and the cathode is positive.

The purpose of the salt bridge. The cell cannot operate unless the circuit is complete. The oxidation half-cell originally contains a neutral solution of Zn^{2+} and SO_4^{2-} ions, but as Zn atoms in the bar lose electrons, the solution would develop a net positive charge from the Zn^{2+} ions entering. Similarly, in the reduction half-cell, the neutral solution of Cu^{2+} and SO_4^{2-} ions would develop a net negative charge as Cu^{2+} ions leave the solution to form Cu atoms. A charge imbalance would arise and stop cell operation if the half-cells were not neutral. To avoid this situation and enable the cell to operate, the two half-cells are joined by a salt bridge, which acts as a "liquid wire," allowing ions to flow through both compartments and complete the circuit. The salt bridge shown in Figure below is an inverted U tube containing a solution of the nonreacting ions Na^+ and SO_4^{2-} in a gel. The solution cannot pour out, but ions can diffuse through it into and out of the half-cells. To maintain neutrality in the reduction half-cell (right; cathode compartment) as Cu^{2+} ions change to Cu atoms, Na^+ ions move from the salt bridge into the solution (and some SO_4^{2-} ions move from the solution into the salt bridge). Similarly, to maintain neutrality in the oxidation half-cell (left; anode compartment) as Zn atoms change to Zn^{2+} ions, SO_4^{2-} ions move from the salt bridge into that solution (and some Zn^{2+} ions move from the solution into the salt bridge). Thus, the circuit is completed as electrons move left to right through the wire, while anions move right to left and cations move left to right through the salt bridge.



Notation for a Voltaic Cell

A useful shorthand notation describes the components of a voltaic cell. For example, the notation for the Zn/Cu²⁺ cell is

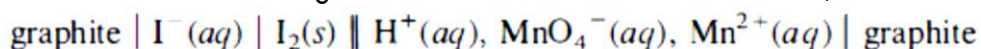


Key parts of the notation are

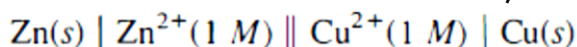
- The components of the anode compartment (oxidation half-cell) are written to the left of the components of the cathode compartment (reduction half-cell).

A vertical line represents a phase boundary. For example, Zn(s) | Zn²⁺(aq) indicates that the solid Zn is a different phase from the aqueous Zn²⁺.

A comma separates the half-cell components that are in the same phase. For example, the notation for the voltaic cell housing the reaction between iodine and MnO₄⁻ is



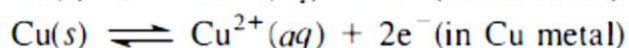
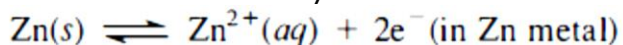
That is, in the cathode compartment, H⁺, MnO₄⁻, and Mn²⁺ ions are all in aqueous solution with solid graphite immersed in it. Often, we specify the concentrations of dissolved components; for example, if the concentrations of Zn²⁺ and Cu²⁺ are 1 M, we write



- Half-cell components usually appear in the same order as in the half-reaction, and electrodes appear at the far left and right of the notation.
- A double vertical line separates the half-cells and represents the phase boundary on either side of the salt bridge (the ions in the salt bridge are omitted because they are not part of the reaction).

Why Does a Voltaic Cell Work?

By placing a light bulb in the circuit or looking at the voltmeter, we can see that the Zn/Cu²⁺ cell generates electrical energy. But what principle explains how the reaction takes place, and why do electrons flow in the direction shown? Let's examine what happens when the switch is open and no reaction is occurring. In each half-cell, we can consider the metal electrode to be in equilibrium with the metal ions in the electrolyte and the electrons residing in the metal:



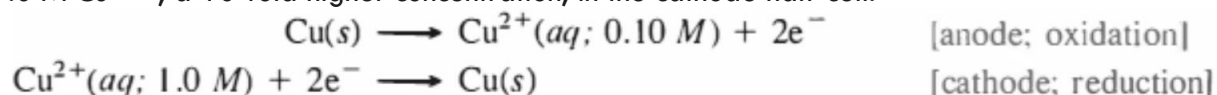
From the direction of the overall spontaneous reaction, we know that Zn gives up its electrons more easily than Cu does; thus, Zn is a stronger reducing agent. Therefore, the equilibrium position of the Zn half-reaction lies farther to the right: Zn produces more electrons than Cu does. You might think of the electrons in the Zn electrode as being subject to a greater electron "pressure" than those in the Cu electrode, a greater potential energy (referred to as electrical potential) ready to "push" them through the circuit. Close the switch, and electrons flow from the Zn to the Cu electrode to equalize this difference in electrical potential. The flow disturbs the equilibrium at each electrode. The Zn half-reaction shifts to the right to restore the electrons flowing out, and the Cu half-reaction shifts to the left to remove the electrons flowing in. Thus, the spontaneous reaction occurs as a result of the different abilities of these metals to give up their electrons and the ability of the electrons to flow through the circuit.

Concentration Cells

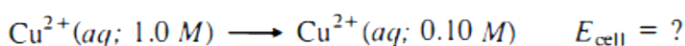
If you mix a concentrated solution and a dilute solution of a salt, you know that the final concentration equals some intermediate value. A concentration cell employs this phenomenon to generate electrical energy. The two solutions are in separate half-cells, so they do not mix; rather, their concentrations become equal as the cell operates.

How a Concentration Cell Works

Suppose both compartments of a voltaic cell house the Cu/Cu^{2+} half-reaction. The cell reaction is the sum of identical half reactions, written in opposite directions, so the standard half-cell potentials cancel ($E^\circ_{\text{copper}} - E^\circ_{\text{copper}}$) and E°_{cell} is zero. This occurs because standard electrode potentials are based on concentrations of 1 M. In a concentration cell, however, the half-reactions are the same but the concentrations are different. As a result, even though E°_{cell} equals zero, the nonstandard cell potential, E_{cell} does not equal zero because it depends on the ratio of concentrations. A concentration cell has 0.10 M Cu^{2+} in the anode half cell and 1.0 M Cu^{2+} , a 10-fold higher concentration, in the cathode half-cell:



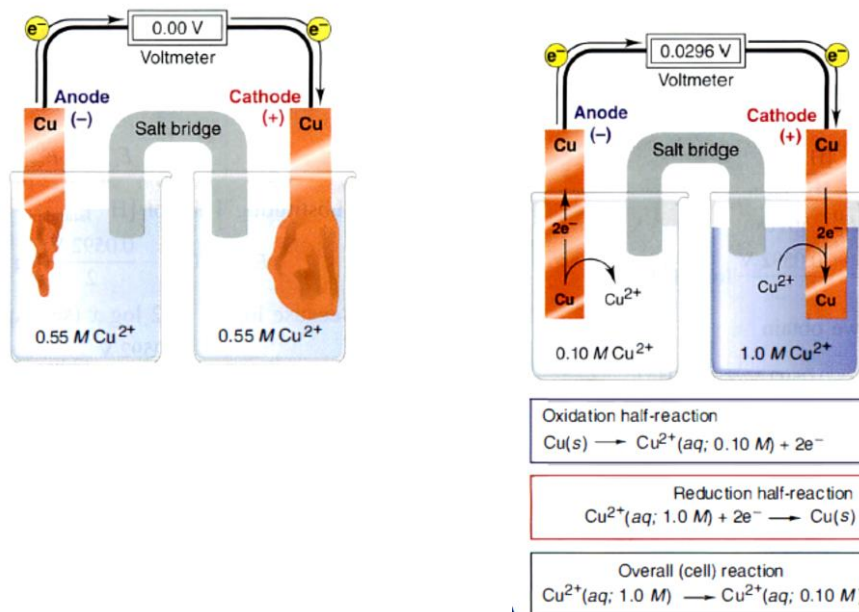
The overall cell reaction is the sum of the half-reactions:



The cell potential at the initial concentrations of 0.10 M (dilute) and 1.0 M (concentrated) with $n = 2$, is obtained from the Nernst equation:

$$\begin{aligned} E_{\text{cell}} &= E^\circ_{\text{cell}} - \frac{0.0592 \text{ V}}{2} \log \frac{[\text{Cu}^{2+}]_{\text{dil}}}{[\text{Cu}^{2+}]_{\text{conc}}} = 0 \text{ V} - \left(\frac{0.0592 \text{ V}}{2} \log \frac{0.10 \text{ M}}{1.0 \text{ M}} \right) \\ &= 0 \text{ V} - \left[\frac{0.0592 \text{ V}}{2} (-1.00) \right] = 0.0296 \text{ V} \end{aligned}$$

As you can see, because E°_{cell} for a concentration cell equals zero, E_{cell} for nonstandard conditions depends entirely on the $[(0.0592 \text{ V} / n) \log Q]$ term. What is actually going on as this cell operates? In the half-cell with dilute electrolyte (anode), the Cu atoms in the electrode give up electrons and become Cu^{2+} ions, which enter the solution and make it more concentrated. The electrons released at the anode flow to the cathode compartment. There, Cu^{2+} ions in the concentrated solution pick up the electrons and become Cu atoms, which plate out on the electrode, so that solution becomes less concentrated. As in any voltaic cell, E_{cell} decreases until equilibrium is attained, which happens when $[\text{Cu}^{2+}]$ is the same in both half-cells. The same final concentration would result if we mixed the two solutions, but no electrical work would be done.



Standard reduction potential (E°) :

It is defined as potential developed at the interface between the metal and the solution, when a metal is dipped in a solution containing its own ions of unit concentration at 298K. [If the electrodes involve gases then it is one atmospheric pressure] It is denoted as E° .

Electromotive force (EMF):

It is defined as the potential difference between the two electrodes of a galvanic cell which causes the flow of current from an electrode with higher reduction potential to the electrode with lower reduction potential.

It is denoted as E_{cell} .

$$E_{\text{cell}} = E_{\text{right}} - E_{\text{left}}$$

$$E_{\text{cell}} = E_{\text{cathode}} - E_{\text{anode}}$$

Electrochemical series:

The arrangement of elements in the order of their standard reduction potential is referred to as emf or electrochemical series. Such a arrangement of few elements given in the table.

M^{n+}/M	E° (volts)	M^{n+}/M	E° (volts)
Li^+/Li	-3.05	H^+/H_2	0.00
K^+/K	-2.93	Sn^{4+}/Sn^{2+}	+0.15
Mg^{2+}/Mg	-2.37	Cu^{2+}/Cu	+0.16
Al^{3+}/Al	-1.66	Cu^+/Cu	+0.52
Zn^{2+}/Zn	-0.76	I_2/I^-	+0.54
Cr^{3+}/Cr	-0.74	Fe^{3+}/Fe^{2+}	+0.77
Fe^{2+}/Fe	-0.44	Hg^{2+}/Hg^+	+0.79
Cr^{3+}/Cr^{2+}	-0.41	Ag^+/Ag	+0.80
Cd^{2+}/Cd	-0.40	Hg^{2+}/Hg	+0.85
Ni^{2+}/Ni	-0.25	Pt^{2+}/Pt	+1.20
Sn^{2+}/Sn	-0.14	Cr^{3+}/Cr^{2+}	+1.31
Pb^{2+}/Pb	-0.13	$Cl_2/2Cl^-$	+1.36
Fe^{3+}/Fe^{2+}	-0.041	Au^{3+}/Au	+1.50

1) A negative value indicates oxidation tendency and a positive value indicates reduction tendency with respect to hydrogen.

2) The metal with lower electrode potential is more reactive and as the electrode potential increases, the reactivity decreases, and metals with higher electrode potentials are nobler.

3) Metals with lower electrode potentials have the tendency to replace metals with higher electrode potential from their solutions for example, Zn displaces Cu, and Cu displaces Ag

4) Metals with negative electrode potentials can liberate hydrogen from acidic solutions.

Derivation of Nernst Equation for Electrode potential:

In 1889 Nernst derived a quantitative relationship between the electrode potential and the concentrations of metal ions are involved. The maximum work available from a reversible chemical process is equal to the maximum amount of electrical energy that can be obtained; it shows decrease in free energy.

$$W_{\text{max}} = - \Delta G \text{-----}[1]$$

And

W_{max} = difference in potential between two electrode x total quantity of charge flowing through the cell

Total quantity of charge flowing through the cell = (No. of moles of electrons) x (Faradays constant)

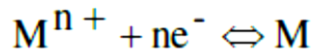
So $W_{\max} = nFE_{\text{cell}}$ -----[2]
 equate eqn [1] & [2]

$$\Delta G = -nFE \text{ -----[3]}$$

under std.condition,

$$\Delta G^0 = -nFE^0$$

Consider a reversible electrode reaction,



for the above reaction , equilibrium constant K_c can be written as

$$K_c = \frac{[M]}{[M^{n+}]} \text{ -----[4]}$$

K_c ΔG and ΔG^0 are related by a 'vant hoff reaction isotherm',

$$\Delta G = \Delta G^0 + RT \ln K_c \text{ -----[5]}$$

substitute the values of K_c ΔG and ΔG^0 to the above equation,

$$-nFE = -nFE^0 + RT \ln \frac{[M]}{[M^{n+}]}$$

divide both the sides by $-nF$

$$E = E^0 - \frac{RT}{nF} \ln \frac{[M]}{[M^{n+}]}$$

under standard condition, $[M] = 1$

$$E = E^0 + \frac{2.303RT}{nF} \log[M^{n+}] \text{ -----[6]}$$

Where,

E = Electrode potential

E^0 = standard electrode potential

n = no. of electrons

$[M^{n+}]$ = Concentration of metal ions

R = Universal gas constant = $8.314 \text{ J K}^{-1} \text{ mol}^{-1}$

T = Temperature (In Kelvin) = 298 K

$$E_{\text{cell}} = E^0 + \frac{0.0591}{n} \log[M^{n+}] \text{ -----[7]}$$

$$E_{cell} = E^0 - \frac{0.0591}{2} \log K_c \text{ where } K_c = \frac{[\text{product}]}{[\text{reactant}]}$$

$$E_{cell} = E^0 + \frac{0.0591}{2} \log \frac{[\text{Species at cathode}]}{[\text{Species at anode}]}$$

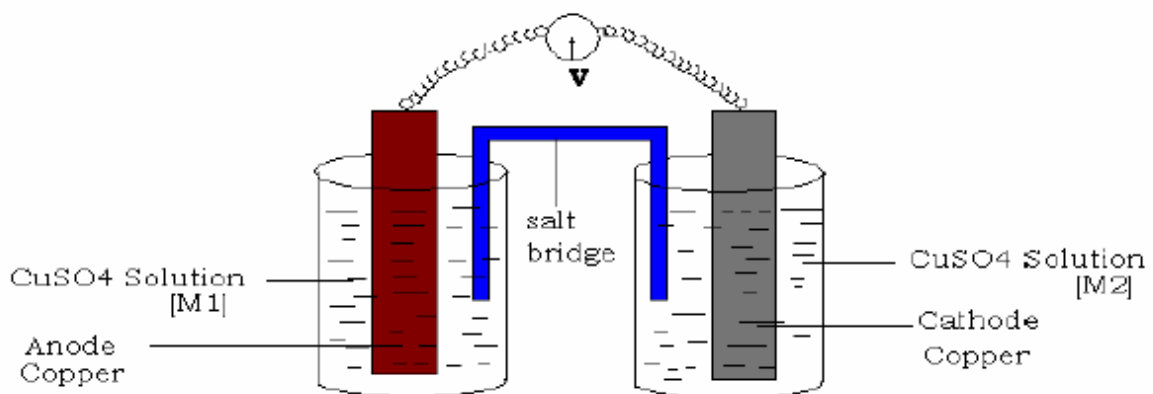
Concentrations cells:

“A concentration cell is an electrochemical cell in which electrode materials and electrolytes of two half cells are composed of same material but the concentration of two solutions are different”

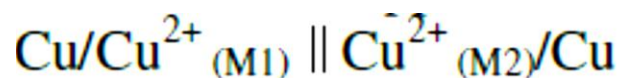
Ex- $\text{Cu}/\text{Cu}^{2+}(\text{M1}) \parallel \text{Cu}^{2+}(\text{M2})/\text{Cu}$

A concentration cell consists of two same metal electrode dipped into their own ionic solutions of two different concentration.

Thus in a concentration cell, the electrode with lower electrolyte concentration acts as anode and the one with higher electrolyte concentration acts as cathode. The concentration of ions at anode increases and at cathode decreases, when the cell is in operation

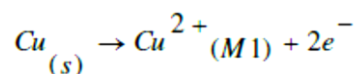


Consider two copper rods are dipped into their own ionic solutions of M1 and M2 and it is represented as

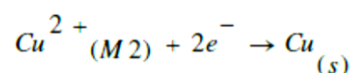


By electrochemical conventions, if $\text{M2} > \text{M1}$ then, we have the following reactions.

At anode



At cathode



The e.m.f of the concentration cell will be

$$E_{cell} = E^0 + \frac{0.0591}{2} \log M_2 - \left[E^0 + \frac{0.0591}{2} \log M_1 \right]$$

$$E_{cell} = \frac{0.0591}{2} \log \frac{M_2}{M_1}$$

The emf of the cell is +ve only if $M_2 > M_1$

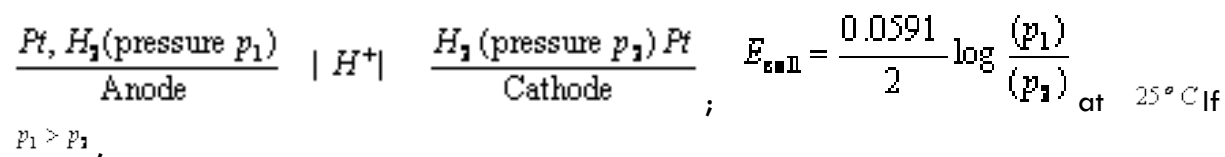
The following characteristics of concentration cell can be noted:

1. When $M_2 = M_1$, the concentration cell does not generate electrical energy.
2. When $M_2 > M_1$, the E_{cell} is +ve.
3. When $M_2 < M_1$, E_{cell} is -ve.
4. Higher the ratio of M_2/M_1 , greater is the cell potential

The concentration cells can be divided in two groups these are

- (1) Electrode concentration cell,
- (2) Electrolyte concentration cell,

(1) Electrode concentration cell: Consists of two cells where identical electrodes are dipped in the same solution with different levels of concentration. For instance, consider two hydrogen electrodes that are placed at a different gaseous pressure in the same solution consisting of hydrogen ions. In these cells, the potential difference is developed between two electrodes at different concentrations dipped in the same solution of the electrolyte. For example, two hydrogen electrodes at different gaseous pressures in the same solution of hydrogen ions constitute a cell of this type.



oxidation occurs at L. H. S. electrode and reduction occurs at R. H. S. electrode.

In the amalgam cells, two amalgams of the same metal at two different concentrations are immersed in the same electrolytic solution. $M(Hg C_1) \mid M^{n+} \mid Zn(Hg C_2)$ The e.m.f of the cell is given

$$E_{cell} = \frac{0.0591}{n} \log \frac{C_1}{C_2} \text{ at } 25^\circ C$$

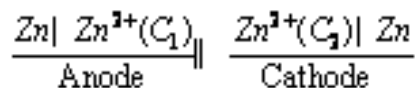
by the expression,

(2) Electrolyte concentration cell: Electrolyte Concentration cell comprises of two same electrodes that are dipped in an electrolyte which possesses different concentration level. An electrolyte has a tendency to diffuse from a solution of higher concentration level to a solution of lower concentration level. With a period of time, the two concentrations tend to be equal. In these cells, electrodes are identical but these are immersed in solutions of the same electrolyte of different concentrations. The source of electrical energy in the cell is the tendency of the electrolyte to diffuse from a solution of higher concentration to that of lower concentration. With the expiry of time, the two concentrations tend to become equal. Thus, at the start the emf

of the cell is maximum and it gradually falls to zero. Such a cell is represented in the following manner (C_2 is greater than C_1).



or



The emf of the cell is given by the following expression,

$$E_{\text{cell}} = \frac{0.0591}{n} \log \frac{C_{2(M^{n+})}}{C_{1(M^{n+})}} \quad \text{at } 25^\circ \text{C}$$

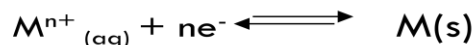
The concentration cells are used to determine the solubility of sparingly soluble salts, valency of the cation of the electrolyte and transition point of the two allotropic forms of metal used as electrodes, etc.

Single Electrodes or Half Cells: Types

A single electrode or a half cell is composed of an electronic conductor, in contact with an electrolytic conductor. An electronic conductor may be a metal, a gas adsorbed on metal or a metal coated with sparingly soluble salt and an electrolytic conductor may be electrolytic solution, or fused salts. At the junction of the metallic and electrolytic conductor, a potential difference is established due to transfer of electrons or ions. Such a potential difference set up between these two types of conductors is known as electrode potential, or half cell potential.

Various types of single electrodes or half cells are

1. **Metal-Metal ion electrode:** This type of an electrode consists of a metal rod dipped in a solution of its own ions. E.g., zinc rod dipped in zinc sulfate solution or a copper rod dipped in copper sulfate solution. The electrode reaction may be represented as



If the metal behaves as a positive electrode (electrode involves reduction), then equilibrium will shift towards right. The concentration of M^{n+} ions in solution will, therefore, decrease.

If the metal rod behaves as a negative electrode (electrode involves oxidation) the above equilibrium will shift towards left. The concentration of M^{n+} ions in solution will, therefore, increase.

Thus the electrode is reversible w. r. t M^{n+} ions and is represented as $M(s), M^{n+}(\text{aq})$.

2. **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. An important electrode of this type is the calomel electrode. It consists of mercury, its sparingly soluble salt, solid mercurous chloride and a solution of potassium chloride having a common ion (Cl^-) with sparingly soluble salt, mercurous chloride. The electrode may be represented as
 $\text{Hg} : \text{Hg}_2\text{Cl}_2(s) ; \text{KCl}(\text{soln})$

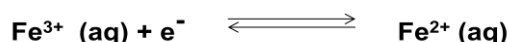
An other example of this type is Silver-Silver Chloride-Hydrochloric Acid electrode.

3. **Gas Electrode:** These electrodes consist of a gases continuously bubbling through solutions of their ions at a steady value of gas pressure. In this type of electrodes, a gaseous non metal is in contact with the solution of its own ions. Since the gases are non conductors of electricity, an inert metal such as platinum, gold or graphite is dipped in the solution containing the ions of the gas and the gas is bubbled over it. The metal absorbs the gaseous non metal and the equilibrium rapidly gets established between the gaseous non metal and its ions.

Examples of this type of electrode are; Hydrogen electrode, Oxygen electrode, Chlorine electrode.

4. Inert metal Oxidation Reduction electrodes:

The term oxidation reduction electrode is used for those electrodes in which potential is developed due to the presence of ions of the same substance in two different oxidation states. This type of electrode consists of an inter electrode (Pt/Au) immersed in a mixed solution containing the substance in both the oxidized and reduced forms, e.g, when a Pt wire is inserted into the solution containing Fe^{2+} and Fe^{3+} ions, it is found that wire acquires a potential. This potential at the electrode arise from the tendency o f the ions in one oxidation state to change into the other more stable oxidation state. The electrode reaction ma be represented as



The function of the inert metal is to pick up electrons and to provide the electrical contact to the electrode.

Reference Electrodes:

“Reference electrode are the electrode with reference to those, the electrode potential of any electrode can be measured.”

It can acts both as an anode or cathode depending upon the nature of other electrode.

The Reference Electrodes can be classified in to two types

- i) **Primary reference electrodes** Ex: Standard hydrogen electrode
- ii) **Secondary reference electrodes** Ex: Calomel and Ag/Agcl electrodes

Standard Hydrogen Electrode (SHE):

Construction and working of Standard Hydrogen Electrode (SHE):

It is composed of a platinum foil, coated with finely divided platinum black which is immersed in a solution containing hydrogen ions at one molar concentration. The hydrogen gas at one atmospheric pressure is constantly bubbled through the solution. The platinum wire itself acts as a medium to transfer electrons which is governed by the overall cell reaction.

SHE when coupled with other electrode acts either as anode or cathode.

When SHE acts as an anode, oxidation takes place at the electrode and the cell reaction is given by



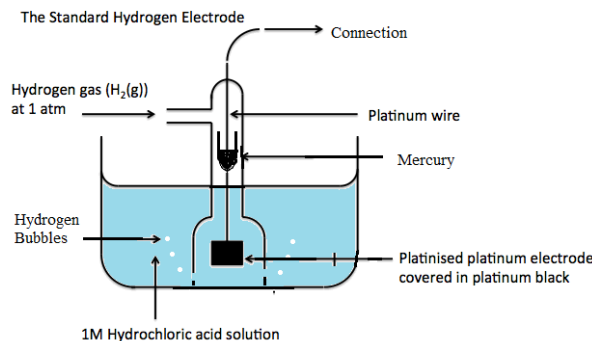
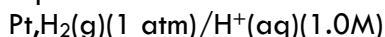
i.e., some hydrogen gas passes into the solution as H^+ ions

When SHE acts as an cathode, reduction takes place at the electrode and the cell reaction is given by



i.e., some H^+ ions from the solution changes into hydrogen gas.

These reactions shows that this electrode is reversible with respect to H^+ ions. SHE is represented as



The electrode whose electrode potential is to be determined is coupled with the SHE and the cell is set up. The cell potential is the sum of oxidation potential of the anode and reduction potential of the cathode. Since one of the electrodes involved in a cell reaction is SHE and its electrode potential is taken as zero, the cell potential will therefore, will be the electrode potential of the electrode under investigation. The direction of flow of current will indicate whether the electrode under investigation is an anode or cathode and accordingly the potential of the electrode is termed as oxidation potential or reduction potential. Since electrode reactions are carried under standard conditions, the electrode potential is called standard electrode potential and is denoted by E^0

e.g., in order to determine the electrode potential of Zn/Zn^{2+} electrode, a cell is set up by coupling this electrode with SHE and the cell is operated. The EMF of a cell is found to be 0.76 Volt. Since the electrode potential of SHE is taken as zero. Therefore, standard electrode potential of the Zn/Zn^{2+} is 0.76 volts. Further the direction of flow of current indicates that oxidation takes place at the Zn/Zn^{2+} electrode. Hence 0.76 is the standard oxidation potential of the Zn/Zn^{2+} electrode. Or in terms of reduction potential the standard reduction potential of this electrode is -0.76 volts.

SHE has two main Limitations:

- i) The construction of SHE is difficult. It is very difficult to maintain the concentration of H^+ as 1M and pressure H_2 gas at 1 atm
- ii) Platinum electrode is poisoned by the impurities of the gas

Construction and working of Standard Calomel electrode (SCE):

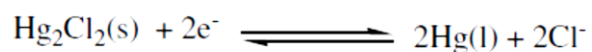
1. Calomel electrode is a metal-metal salt ion electrode.
2. It consists of mercury, mercurous Chloride and a solution of KCl. Mercury is placed at the bottom of a glass tube.
3. A paste of mercury and mercurous chloride is placed above the mercury. The space above the paste is filled with a KCl solution of known concentration.
4. A platinum wire is kept immersed into the mercury to obtain electrical contact.
5. Calomel electrode can be represented as,



The calomel electrode can act as anode or cathode depending on the nature of the other electrode of the cell.

The net cell reversible electrode reaction is,

The net cell reversible electrode reaction is,



$$\text{Electrode potential, } E = E^0 - \frac{2.303RT}{nF} \cdot \log[\text{Cl}^-]^2$$

$$E = E^0 - \frac{2.303RT}{F} \cdot \log[\text{Cl}^-] \quad \text{Where } n=2$$

$$E = E^0 - 0.0591 \log[\text{Cl}^-] \text{ at } 298\text{K}$$

Therefore electrode potential of calomel electrode is depending upon the concentration of KCl.

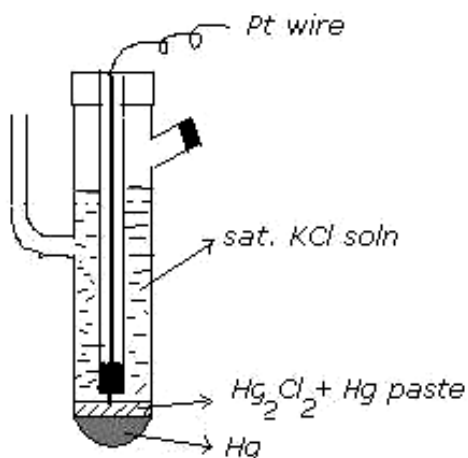
The electrode is reversible with chloride ions.

The potential of the calomel electrode depends on the concentration of the KCl.

For saturated KCl, the potential is 0.241V;

For 1M KCl, 0.280V;

For 0.1M KCl, 0.334V.



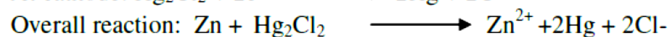
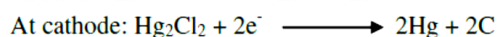
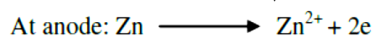
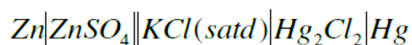
Measurement Of Single Electrode Potential Using Calomel Electrode:

Electrode potential of a given electrode can be measured by using calomel electrode as a reference electrode.

Example-1: To measure the electrode potential of zinc: To measure the potential of the Zn-electrode, the

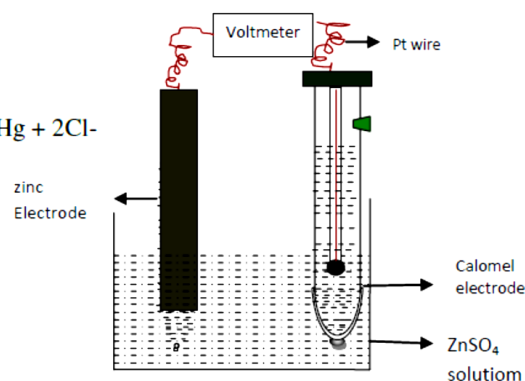
Zn- electrode is coupled with the SCE through a salt bridge. The anode and the cathode of the cell can be

identified by connecting the electrodes to the appropriate terminals of the voltmeter. Proper measurements can be made only when the Zn-electrode is connected to the -ve terminal and the calomel electrode to the +ve terminal of the voltmeter indicating that Zinc electrode is anode & the calomel electrode is a cathode.

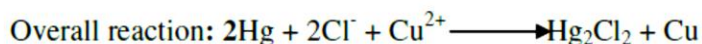
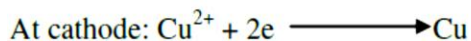
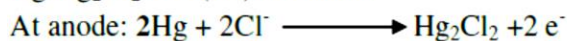
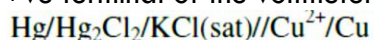


$$\begin{aligned} E_{\text{cell}} &= E_{\text{cathode}} - E_{\text{anode}} \\ &= E_{\text{SCE}} - E_{\text{Zn}^{2+}/\text{Zn}} \\ &= 0.2422\text{V} - E_{\text{Zn}^{2+}/\text{Zn}}^0 \\ E_{\text{Zn}^{2+}/\text{Zn}} &= 0.2422 - E_{\text{cell}} \\ E_{\text{Zn}^{2+}/\text{Zn}} &= 0.2422 - 1.001 \end{aligned}$$

$$E_{\text{Zn}^{2+}/\text{Zn}} = -0.76\text{V}$$

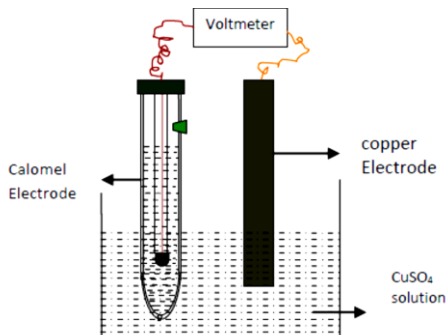


Example-2: To measure the electrode potential of copper: Similarly to determine the copper electrode potential of the cell, the cell is constructed as follows. Calomel electrode being the anode is connected to -ve terminal of the voltmeter and copper electrode being the cathode is connected to the +ve terminal of the voltmeter.



$$\begin{aligned} E_{\text{cell}} &= E_{\text{cathode}} - E_{\text{anode}} \\ &= E_{\text{Cu}^{2+}/\text{Cu}} - E_{\text{SCE}} \\ E_{\text{Cu}^{2+}/\text{Cu}} &= E_{\text{cell}} + 0.2422 \\ E_{\text{Cu}^{2+}/\text{Cu}} &= 0.1 + 0.2422 \end{aligned}$$

$$E_{\text{Cu}^{2+}/\text{Cu}} = +0.34\text{V}$$



Advantages of calomel electrode:-

1. It is easily setup (simple to construct).
2. The cell potential is reproducible and stable over a long period.
3. It is used as a secondary reference electrode in the measurement of single electrode potential.

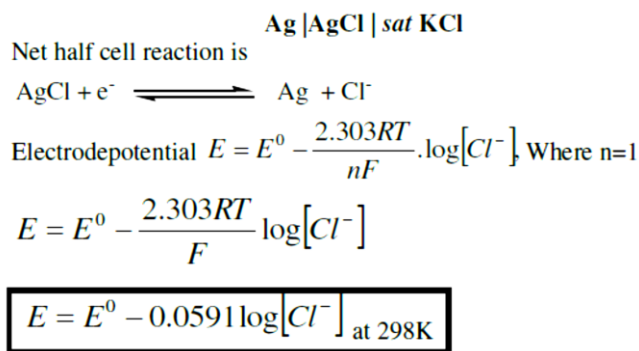
4. It is the most commonly used reference electrode in all potentiometric determinations and to measure pH of the given solution

Applications:

1. It is used as secondary reference electrode in the measurement of single electrode.
2. It is used as reference electrode in all potentiometer determinations and to measure pH of the given solution.

Construction and working of Silver- Silver Chloride electrode:

1. Silver-Silver chloride is also a metal-metal salt ion electrode.
2. Silver and its sparingly soluble salt silver chlorides are in contact with a solution of chloride solution ions. Generally a silver wire is coated with AgCl and dipped in a solution of KCl .
3. Cell representation is as follows



- Therefore electrode potential of calomel electrode is depending upon the concentration of KCl.
- The electrode is reversible with chloride ions.
- The potential of the calomel electrode depends on the concentration of the KCl.

-For 1N solution, the electrode potential is 0.223V and for saturated solution is 0.199V at 298K

Applications:

1. Used as secondary reference electrode in ion selective electrode.
2. In determining the distribution of potential on the ship hull and pipe lines.

Ion selective electrode (ISE):

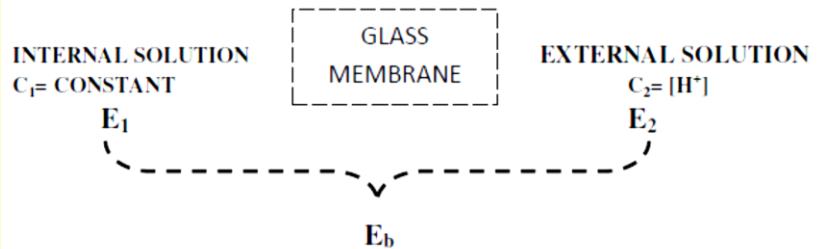
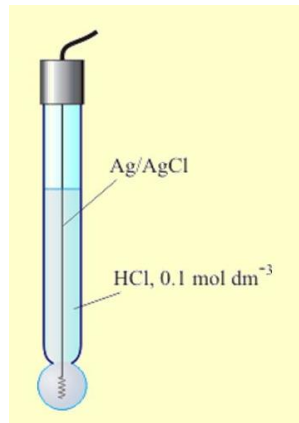
“Ion selective electrode is one which selectively responds to a specific ion in a mixture and the potential developed at the electrode is a function of the concentration of that ion in the solution”

Construction and working of Glass electrode:

A glass electrode is an ion selective electrode where potential depends upon the pH of the medium.

1. The glass electrode consists of a glass bulb made up of special type of glass (sodium silicate type of glass) with high electrical conductance.
2. The glass bulb is filled with a solution of constant pH (0.1MHCl) and insert with a Ag-AgCl electrode, which is the Internal reference electrode and also serves for the external electrical contact.
3. The electrode dipped in a solution containing H^+ ions as shown in the figure.
4. The electrode representation is,

Glass | 0.1M HCl | Ag/AgCl.



The glass electrode works on the principle that when a thin glass membrane is in contact with a solution, a boundary potential E_b is developed at layers of the glass membrane. This potential arises due to difference in the concentration of H^+ ion inside and outside the membrane.

Boundary potential, $E_b = E_2 - E_1$ ----- (1)

$$E_1 = E^0 + \frac{0.0591}{n} \cdot \log C_1$$

$$E_2 = E^0 + \frac{0.0591}{n} \log C_2$$

Where, C_1 and C_2 are concentration of H^+ ions inner and outer membrane. Substitute the values of E_1 & E_2 into eqn (1), we get

$$E_b = E^0 + \frac{0.0591}{n} \cdot \log C_2 - \left[E^0 + \frac{0.0591}{n} \log C_1 \right]$$

$$E_b = \frac{0.0591}{n} \log C_2 - \frac{0.0591}{n} \log C_1 \quad (n = 1)$$

$$E_b = 0.0591 \log C_2 - 0.0591 \log C_1$$

($n = 1$, Since the concentration of the inner solution is constant, C_1 is constant & ($C_2 = (H^+)$))

$$E_b = \text{Const} + 0.0591 \log [H^+]$$

Where $\text{Const} = K = -0.0591 \log C_1$

$$E_b = K - 0.0591 pH$$

The glass electrode potential is sum of the

- i) Boundary potential E_b ,
- ii) Ag-AgCl electrode potential $E_{Ag/AgCl}$ and
- iii) Asymmetry potential E_{asy} .

$$E_G = E_b + E_{Ag/AgCl} + E_{asy}$$

Theoretically, $E_b = 0$ for $C_1 = C_2$. However, a small additional potential is exists called Easy potential.

$$E_G = K - 0.0591 pH + E_{Ag/AgCl} + E_{asy}$$

$$E_G = E_G^0 - 0.0591 pH$$

$$\text{where } E_G^0 = K + E_{Ag/AgCl} + E_{asy}$$

Determination of pH using glass electrode:

Procedure: glass electrode is immersed in the solution; the pH is to be determined. It is combined with a reference electrode such as a calomel electrode through a salt bridge. The cell assembly is represented as,

$Hg | Hg_2Cl_2 | Cl^- | \text{Solution of unknown pH} | \text{glass} | 0.1M HCl | Ag | AgCl$

The emf of the above cell, E_{cell} is measured using an electronic voltmeter with a pH meter.

The emf of the cell is given by

$$E_{cell} = E_{cathode} - E_{anode} \dots\dots\dots (1)$$

$$E_{cell} = E_G - E_{SCE} \dots\dots\dots (2)$$

Since E_{SCE} is knowing emf the cell,

E glass can be evaluated.

$$E_G = E_G^0 - 0.0591 pH \dots\dots\dots (3)$$

$$E_{cell} = E_G^0 - 0.0591 pH - E_{SCE} \dots\dots\dots (4)$$

$$pH = \frac{E_G^0 - E_{cell} - E_{SCE}}{0.0591}$$

Advantages

1. This electrode can be used to determine PH in the range 0-9, with special type of glass even up to 12 can be calculated.
2. It can be used even in the case of strong oxidizing agents.
3. The equilibrium is reached quickly.
4. It is simple to operate, hence extensively used in various laboratories.

Limitations

1. The glass membrane though it is very thin, it offers high resistance. Therefore ordinary potentiometers cannot be used; hence it is necessary to use electronic potentiometers.