

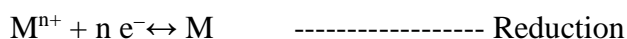
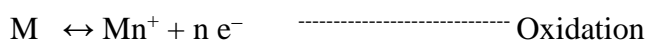
UNIT-I ELECTRODE SYSTEMS AND APPLICATIONS

(From the Academic year 2022-23 onwards)

Introduction: The electrical energy is a form of energy that has tremendous practical significance in our day-to-day life. A day without electricity from either the Power Corporation or batteries is far away from our imagination in technological society. **Electrochemistry** is an area of chemistry that deals with the inter conversion of electrical energy and chemical energy.

Electrochemical processes take place through oxidation- reduction reactions (redox reactions) in which the energy released by a spontaneous reaction is converted into electricity.

In oxidation, a species loses one or more electrons resulting in an increase in the oxidation number.



Electrochemical cells:

The basic apparatus used to the investigation of reactions in solution in terms of electrical measurements is an electrochemical cell. A cell consists of two electrodes, or metallic conductors, in contact with an electrolyte. Metallic conductor may be in the form of rod or sheet in contact with electrolytic solution, constitutes a half cell. The electrolyte is an ionic conductor which may be a solution, a liquid or a solid. (Solid electrolyte should melt at working temperature of the cell). The two electrodes may share the same electrolyte in which the electrode compartment will be one. If the two electrodes are in contact with two different electrolytic solutions the two compartments are joined by a salt bridge.

Classification of electrochemical cells:

The electrochemical cells are classified into two types, namely,

- (i) Galvanic cell and (ii) Electrolytic cell.

Galvanic cell:

A galvanic cell also called a voltaic cell is an electrochemical cell that produces electrical energy as a result of the spontaneous redox reactions occurring inside it.

E.g. Dry cell, Lead-acid accumulator, Ni-Cd battery.

Galvanic cells are further classified as,

- a) Primary cells
- b) Secondary cells
- c) Concentration cells

a) Primary (non rechargeable) cells:

The cells in which the cell reaction is not completely reversible are referred to as primary cells. They are not capable of being easily recharged electrically and, hence are discarded after discharge.

Eg. Dry cell (Lanclanche cell)

b) Secondary (rechargeable) cells:

The cells in which the cell reaction is reversible are termed as secondary cells. They are rechargeable. Secondary cells after discharge can be recharged electrically to their original condition by passing current through them in the opposite direction to that of discharge current. These are storage devices for electrical energy and referred to as storage batteries or accumulators.

Eg. Lead-acid battery, Ni-Cd battery.

c) Concentration cells:

The galvanic cells consisting of both anode and cathode made up of the same element (metal or non metal) in contact with the solutions of the same electrolyte but of different concentrations are referred to as concentration cells.

Eg. A concentration cell consisting of copper electrodes dipped in CuSO_4 solutions of different concentrations is represented as,



Electrolytic cells:

An electrochemical cell in which a non spontaneous reaction is driven by an external source of current is called an electrochemical cell. Or In electrolytic cell, external energy is required to carry out the chemical reactions. Electrolytic cells have a common electrolyte and no salt bridge.

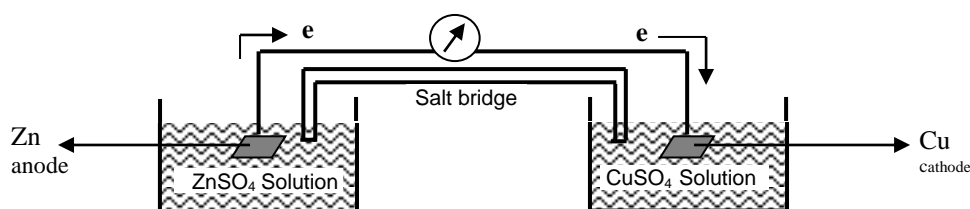
Eg. Electroplating of Gold.

Construction of a galvanic cell:

A person with silver fillings in his teeth may experience a strange and perhaps even unpleasant sensation while biting sweets or ice creams wrapped with aluminium foil. The cause for the said sensation is attributed to a very mild electric shock produced by the potential difference between silver fillings and the aluminium. This electrical energy arises from spontaneous redox reaction occurring in the cell created between the said metals and the cell is called a galvanic cell, named after Luigi Galvani.

Much of the early research was performed by Michael Faraday, a British scientist. In fact, it was he who coined the terms anode, cathode, electrode, electrolyte and electrolysis.

A galvanic cell is formed when two electrodes in contact with suitable electrolytes, are connected externally by a conducting material, i.e. a metallic wire and internally by means of a salt bridge and thereby produce an electric current.



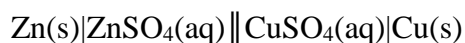
When two different electrolyte solutions are in contact in a cell, such a liquid-liquid contact introduces an additional potential known as liquid junction potential (across the interface of the two electrolytes). As a result, the observed emf will be more than the actual emf of the cell. The contribution of liquid junction potential to the emf of the cell can be reduced by joining the electrolyte compartments through a salt bridge. The success of the salt bridge lies in the fact that the liquid-liquid junction potentials at either end are largely independent of the concentration of the two dilute solutions, so they nearly cancel.

Significance of Salt bridge: Salt bridge is used

1. to maintain electrical neutrality.
2. to connect two different solutions internally.
3. to overcome liquid junction potential.

Electrodes and Electrode reactions:

The representation of a Daniel cell (which represents a galvanic cell) and the electrode reactions are depicted below.



Anode

Cathode

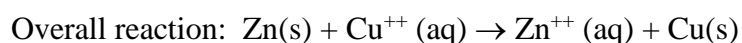
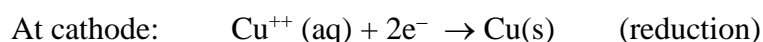
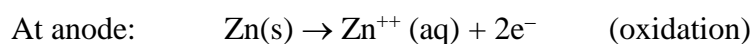
Electrode: An element in contact with its own ions in solution constitutes an electrode.

Anode: The electrode at which oxidation occurs is called the **anode**.

Cathode: The electrode at which reduction takes place is the **cathode**.

At anode, the metal passes into solution as metallic ions with the release of electrons.

At cathode, the metal ions present in the solution get deposited on the metal surface. These ions gain the electrons that are released at the anode and are conducted to the cathode through the external circuit and get reduced to metal atoms.



In a galvanic cell, the cathode carries a positive charge and anode carries a negative charge.

In an electrolytic cell, these charges are reversed.

Single electrode potential (E):

Electrode potential is the tendency of the electrodes to loose or gain electrons.

The potential that is developed when an element (metal or non-metal) is in equilibrium with its own ions in solution is called single electrode potential or half-cell potential.

In a galvanic cell, the cathode has a higher potential than the anode. The species undergoing reduction withdraws electrons from its electrode (cathode), so leaving a relative positive charge on it (corresponding to a high potential). At the anode, oxidation results in the transfer of electrons to the electrode, so giving a relative negative charge (corresponding to a low potential).

During the operation of a galvanic or voltaic cell, a chemical reaction occurs at each electrode as described above and it is the energy of these reaction which provide the electrical energy of the cell. In many cells, there is an overall chemical reaction and in such cases the energy of the overall reaction gets converted into electrical energy.

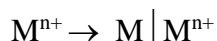
Origin of single electrode potential (E):

When a metal 'M' is dipped in a solution containing its own ions, M^{n+} , exhibits the following two tendencies.

- i) The metal has a tendency to pass into solution as positively charged metal ions.



- ii) Simultaneously, ions from the solution tend to discharge on to the metal.



Due to these tendencies, a potential difference arises and the origin of the potential can be explained as follows in two different cases.

1. When the concentration of metal ions in solution is very low.
2. When the concentration of metal ions in solution is very high.

- 1) If the concentration of metal ions in solution is very low, the metal tends to pass into solution as positively charged metal ions leaving behind the electrons. This makes the metal negatively charged. As the negative charge on the metal builds up, it becomes more difficult for the metal ions to leave the metal. The metal ions that have left the metal cause a positive charge to accumulate in the solution. This positive charge in the solution tends to collect near the negative charge on the metal. Thus an electric double layer, also known as Helmholtz double layer (HDL) is built up at the electrode-metal ion interface as depicted in the figure (a).

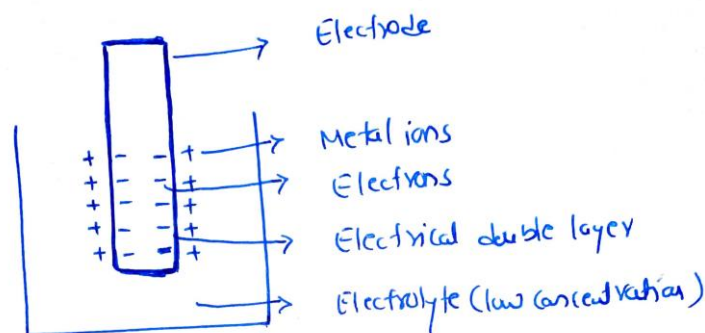


Figure (a)

- 2) When the concentration of metal ions in solution is high, the metal ions present in the solution, tend to get deposited on the metal surface rendering it positively charged. This

positively charged layer attracts the negatively charged anions present in the solution towards it. Thus, the anions collect at the surface as a layer of negative charges and an electrical double layer is built up as depicted in figure (b). The potential difference that exists across this electrical double layer is called single electrode potential.

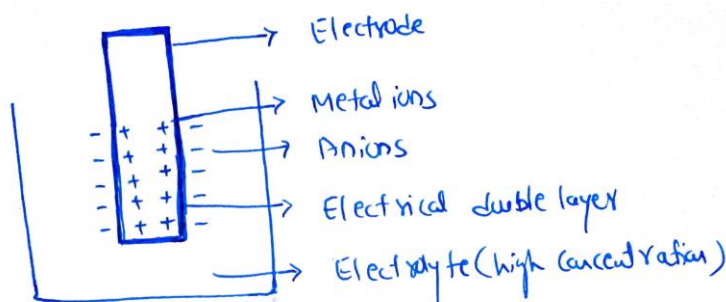
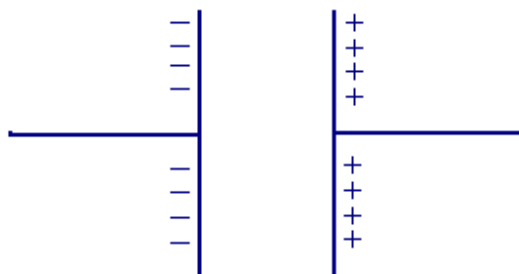


Figure (b)

The electrical double layer is like a capacitor with oppositely charged plates separated by a distance as depicted in figure. A potential difference exists across the electrical double layer and is referred to as single electrode potential.



Standard electrode potential (E^0):

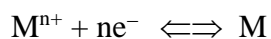
The potential that is developed when an element (metal or non-metal) is in equilibrium with a solution containing its own ions of unit concentration (1M) at 298K is called standard electrode potential.

If the electrode system involves gaseous substances, they must be passed at a partial pressure of one atmosphere.

Derivation of Nernst equation for single electrode potential:

Nernst* equation is a thermodynamic equation which relates the single electrode potential (E) with standard electrode potential (E^0), concentration of metal ions $[M^{n+}]$ in solution and temperature (T). It is derived using the concept of free energy (G).

Consider a metal ion-metal electrode of the type,



The free energy change (decrease in free energy) in a spontaneous process is the energy available to do work

$$\Delta G = W_{\max}$$

The maximum work available from a reversible chemical process is equal to the maximum amount of electrical energy that can be obtained.

$$W_{\max} = W_{\text{ele}}$$

Electrical energy in this case is the product of the electrode potential (volts) and the total electric charge (coulombs) that passes through the electrode.

$$\text{Electrical energy} = \text{volts} \times \text{coulombs}$$

The total charge is determined by the number of moles of electrons (n) that pass through the circuit. By definition,

$$\text{Total charge} = nF$$

Where F, the Faraday is the electrical charge contained in 1 mole of electrons.

$$W_{\max} = W_{\text{ele}} = -nFE$$

where E is the electrode potential.

The negative sign indicates that the electrical work is done by the system on the surroundings.

Since $\Delta G = W_{\max} = W_{\text{ele}}$

$$\Delta G = -nFE \quad \text{----- (1)}$$

The free energy change due to the transfer of 1 mole of ions across the double layer is related to the electrode potential (E).

Both n and F are positive quantities and ΔG is negative for a spontaneous process, so E is positive.

For reactions in which the reactants and products are in their standard states, equation (1) becomes

$$\Delta G^{\circ} = -nFE^{\circ} \quad \text{----- (2)}$$

E° is positive for spontaneous process.

ΔG is related to ΔG° and the equilibrium constant, K_c by the expression,

$$\Delta G = \Delta G^\circ + RT \ln K_c \quad \text{----- (3)}$$

$$\therefore -nFE = -nFE^\circ + RT \ln K_c \quad \text{----- (4)}$$

Since the equilibrium constant, $K_c = \frac{[\text{reduced form}]}{[\text{oxidised form}]} = \frac{[M]}{[M^{n+}]}$

Then equation (4) becomes,

$$-nFE = -nFE^\circ + RT \ln \frac{[M]}{[M^{n+}]} \quad \text{----- (5)}$$

Dividing equation (5) by $-nF$, we get

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

But for solids $[M] = 1$

$$\therefore E = E^\circ - \frac{RT}{nF} \ln \frac{1}{[M^{n+}]}$$

$$E = E^\circ + \frac{RT}{nF} \ln [M^{n+}] \quad \text{----- Basic Nernst equation}$$

$$\text{Or} \quad E = E^\circ + \frac{2.303 RT}{nF} \log_{10} [M^{n+}]$$

By substituting the values for the universal gas constant, R ($8.314 \text{ JK}^{-1}\text{mol}^{-1}$), Faraday, F ($96,500 \text{ JV}^{-1}\text{mol}^{-1}$) and putting the temperature (T) equal to 298K , the above equation further reduces to,

$$E = E^\circ + \frac{0.0591}{n} \log_{10} [M^{n+}]$$

*Walter Hermann Nernst, a noted electrochemist and also a discoverer of third law of thermodynamics was awarded Nobel Prize in 1920 for his contribution to thermodynamics.

Effect of metal ion concentration and temperature on single electrode potential:

Since both the metal ion concentration and temperature terms are found in the numerator of the Nernst equation, $E = E^\circ + \frac{RT}{nF} \ln [M^{n+}]$, the single electrode potential is directly

Proportional to the metal ion concentration and temperature.

EMF of a cell (emf or E_{cell}):

The work that given transfer of electrons can accomplish in a cell depends on the potential difference between the two electrodes and such a potential difference is called the cell potential.

It is represented as 'EMF' or 'emf' or ' E_{cell} ' or cell potential. It is expressed in volts.

The cell potential is said to be large, when a given number of electrons travelling between the electrodes can do a large amount of work. When the cell potential is small, the same number of electrons can do only a small amount of work. The cell potential becomes zero, when the overall cell reaction is at equilibrium and subsequently the cell can do no work.

EMF of a cell is the difference in the single electrode potentials of the two electrodes constituting the cell.

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

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

$$E^{\circ}_{\text{cell}} = E^{\circ}_{\text{cathode}} - E^{\circ}_{\text{anode}}$$

Nernst equation is also used to calculate the emf of cells.

$$E_{\text{cell}} = E^{\circ}_{\text{cell}} + \frac{0.0591}{n} \log_{10} \frac{[\text{Reactants}]}{[\text{Products}]}$$

$$E_{\text{cell}} = E^{\circ}_{\text{cell}} + \frac{0.0591}{n} \log_{10} \frac{[\text{oxidised state}]}{[\text{reduced state}]}$$

It is apparent from the Nernst equation that the emf of a cell changes with the concentrations of the ions involved in the cell reaction. Thus the cell potential measurements provide a way to measure and monitor ion concentrations in aqueous solutions.

In an operating galvanic cell or battery, the voltage gradually decreases as the reactants are consumed. When the cell reaction approaches equilibrium, the voltage will drop to zero. The battery is said to be dead.

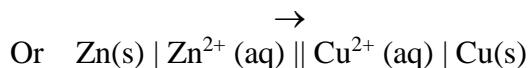
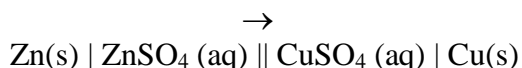
Cell notation and cell conventions

Notation:

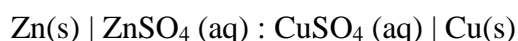
- (i) The phase boundaries, i.e. the interface between the metal and the solution containing its own ions, are denoted by a vertical line.
- (ii) A double vertical line represents the salt bridge.

(iii) An arrow mark is used to indicate the flow of electrons from one electrode to other.

The Daniel cell in which the liquid junction potential is assumed to be eliminated is denoted as,



A liquid junction is denoted by : so the Daniel cell is written as,



Conventions:

- (i) The electrode at which oxidation takes place i.e. anode is always written on the left side while the electrode at which reduction occurs i.e. cathode is written on the right side.
- (ii) The electrode potential always refers to reduction potential and is represented as $E_{M^{n+}|M}$.

Sign conventions:

- 1) Electrode potential:** In a cell, oxidation takes place at anode and reduction at cathode. Accordingly, the potential at anode is called oxidation potential and that at cathode is called reduction potential. As per convention, the electrode potential is generally expressed as reduction potential. The reduction potential of anode can be obtained by simply reversing the sign of its oxidation potential.

Eg: Oxidation potential of $\text{Zn}|\text{Zn}^{++} = + 0.76 \text{ V}$

Reduction potential of $\text{Zn}^{++}|\text{Zn} = - 0.76 \text{ V}$

The following latest convention has been followed in respect of sign conventions for electrode potential.

- i) The electrode at which reduction occurs with respect to standard hydrogen electrode (SHE) has positive sign for reduction potential or assigned negative sign for oxidation potential. The potential of the electrode $M^{n+}|M$ is a measure of tendency of the metal ions to get discharged, i.e. for the ions to be reduced.

For example, copper undergoes reduction when connected to SHE .So its potential is called as reduction potential and as a positive sign i.e $\text{Cu}^{++}|\text{Cu} = 0.34\text{V}$

And oxidation potential can be written by changing sign i.e $\text{Cu}|\text{Cu}^{++} = - 0.34\text{V}$

- ii) The electrode at which oxidation occurs with respect to standard hydrogen electrode has negative sign for the reduction potential or assigned positive sign for oxidation potential. The potential of the electrode $M|M^{n+}$ represents the tendency for the metal to pass into solution as ions, i.e. for the metal atoms to be oxidised.

Eg: Oxidation potential of $Zn|Zn^{++} = + 0.76 \text{ V}$

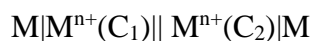
Reduction potential of $Zn^{++}|Zn = - 0.76 \text{ V}$

- 2) **EMF:** The emf of a cell is assigned a positive sign when the left hand electrode acts as a source of electrons (i.e. releases electrons by undergoing oxidation), while the right hand electrode removes them with the redox reaction being spontaneous in the forward direction (i.e. metal ions gain electrons and thereby get reduced). If the emf of a cell is negative, the reverse is true.

Concentration cells:

The galvanic cells consisting of both anode and cathode made up of the same metal in contact with the solutions of the same electrolyte of different concentrations are referred to as concentration cells.

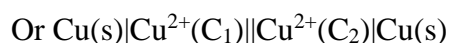
A concentration cell consisting of the electrodes of the same metal, M dipped in solutions of their own ions, M^{n+} of concentrations C_1 and C_2 is represented as,



Anode Cathode

In a concentration cell, the electrode at which the metal ion concentration is low compared to the other would become an anode while the other electrode at which the metal ion concentration is high would act as a cathode. It is apparent that the electrode potential depends on the concentrations of the ions used.

Eg: A concentration cell consisting of copper electrodes dipped in CuSO_4 solutions of different concentrations is represented as,



Consider a case of copper electrodes put into two aqueous solutions of CuSO_4 at 0.1M and 1.0M concentrations. The two solutions are connected by a salt bridge, and the electrodes are connected by a wire.

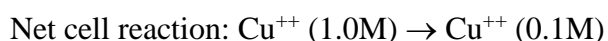
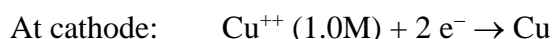
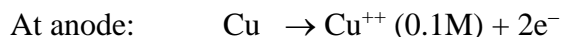
According to Le Chatlier's principle, the tendency for the reduction $\text{Cu}^{++}(\text{aq}) + 2 \text{e}^- \rightarrow \text{Cu}(\text{s})$ increases with increasing concentration of Cu^{++} ions. Therefore, reduction should occur in the more concentrated compartment (cathode) and oxidation should take place on the more dilute side (anode). The cell notation is



Anode

Cathode

Half-cell reactions:



EMF of a concentration cell:

The emf of a concentration cell, $\text{M} | \text{M}^{n+} (\text{C}_1) || \text{M}^{n+}(\text{C}_2) | \text{M}$ is given by,

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

$$= (E^{\circ} + \frac{0.0591}{n} \log_{10} \text{C}_2) - (E^{\circ} + \frac{0.0591}{n} \log_{10} \text{C}_1)$$

$$E_{\text{cell}} = \frac{0.0591}{n} \log_{10} \frac{\text{C}_2}{\text{C}_1}$$

E° for concentration cells is zero.

The emf of concentration cells is generally small and decreases continually during the operation of the cell as the concentrations in the compartments approach each other.

when $\text{C}_1 = \text{C}_2$, E_{cell} becomes zero.

$\text{C}_1 > \text{C}_2$, E_{cell} is negative.

$\text{C}_2 > \text{C}_1$, E_{cell} is positive.

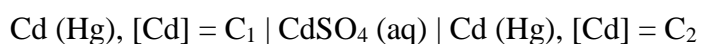
Concentration cells with transference and without transference:

Concentration cells with transference: In a concentration cell where the two solutions connected through a salt bridge. Such a cell is called a concentration cell with transference.

Eg: A concentration cell consisting of copper electrodes dipped in CuSO_4 solutions of different concentrations.

Concentration cells without transference: there are some concentration cells where the two half-cells are not connected through a salt bridge. They are connected through solutions of same electrolyte of equal concentration but contain different quantities of metal electrodes dissolved in mercury. Such cells are called concentration cells without transference.

A typical example of concentration cell without transference is the Weston cell. It is represented using the cell notation,



Significance of concentration cell: Membrane potentials, the potentials established across the membrane of a biological cell due to unequal concentrations of the same ions can be calculated by treating the cell as a concentration cell.

Types of electrodes:

The electrodes constituting a reversible cell must themselves be reversible. Several types of such electrodes are known. They are,

1. Electrodes of the first kind
2. Electrodes of the second kind

Electrodes of the first kind or metal-metal ion electrodes:

The electrodes of this kind consist of an element (metal or non-metal) in contact with a solution of its own ions.

Eg. Zn in ZnSO₄ solution,

Cu in CuSO₄ solution,

Hydrogen in solution containing H⁺ ions,

Oxygen in solution containing OH⁻ ions.

The electrodes of this type are reversible w.r.t. ions of the electrode material.

Electrodes of the second kind or metal-metal insoluble salt electrodes:

The electrodes of this kind consist of a metal and a sparingly soluble salt of the metal in contact with a solution of a soluble salt of the same anion.

Eg. Calomel electrode, Hg(l)|Hg₂Cl₂(s), KCl(solution)

Ag(s)|AgCl(s); KCl(solution)

The electrodes of this type are reversible w.r.t. a common anion, i.e., the chloride ion in the above electrodes.

Electrodes of second kind are of great value in electrochemistry, because they permit the ready establishment of an electrode reversible with respect to anions.

Reference electrodes:

The electrodes of standard potentials with which the potentials of other electrodes can be computed are known as reference electrodes.

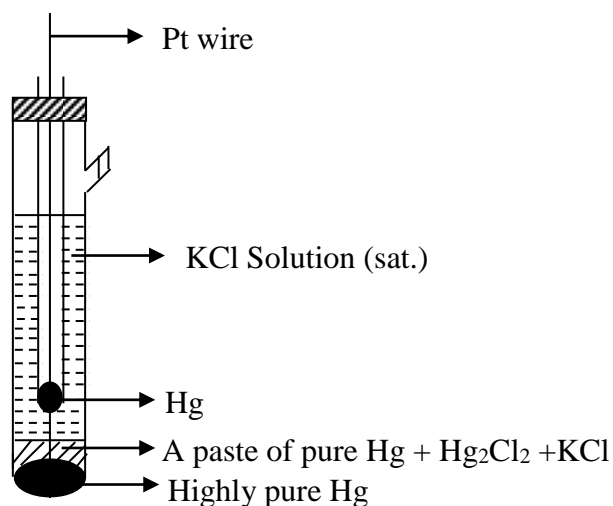
Eg. Standard hydrogen electrode (primary), Standard calomel electrode (secondary).

Limitations or drawbacks of using hydrogen electrode as a reference electrode:

1. It is difficult to maintain hydrogen ion concentration always unity.
2. It is difficult to pass hydrogen gas always at 1 atmosphere.
3. The deposition of impurities on platinum foil causes hindrance in maintaining the equilibrium between the gas and H^+ ions.
4. Hydrogen electrode cannot be used in solutions containing oxidising agents such as nitrates, permanganates, ferric salts, etc.

Calomel electrode:

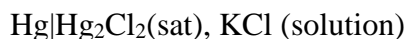
Calomel electrode is a secondary reference electrode.



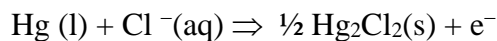
Calomel electrode consists of a long glass tube having two side tubes as depicted in figure. Highly pure mercury is placed at the bottom of the tube and is covered by a paste of pure mercury, calomel (Hg_2Cl_2) and potassium chloride solution. The electrical connection is made by means of platinum wire sealed into another small glass tube having little mercury at its bottom. The rest of the tube is filled with an appropriate concentration of saturated KCl

solution. The calomel electrode can be connected to another electrode to make the cell complete by means of a salt bridge.

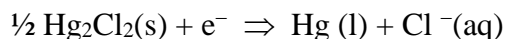
Calomel electrode can be represented as,



The reaction that occurs at calomel electrode when it acts as anode is



The reaction that occurs at calomel electrode when it acts as cathode is



The electrode potential of calomel electrode depends on the concentration of KCl solution with which the tube is filled. The reduction potentials for the various KCl concentrations at 25°C are,

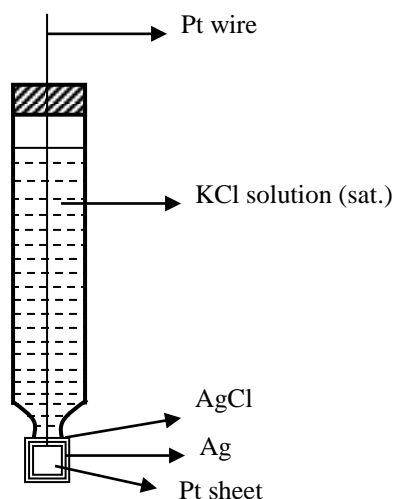
0.1M KCl solution	0.3338V
1.0M KCl solution	0.281V
Saturated KCl solution	0.2415V

Advantages of calomel electrode:

1. It is simple to construct and operate.
2. It gives reproducible electrode potentials.

Silver-silver chloride electrode:

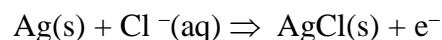
In recent times, silver-silver chloride electrode has been frequently employed as a reference electrode for the accurate determination of standard electrode potentials. Since it is a reversible electrode, it can be used to determine the E° values by the use of cells which contain chlorides and are free from liquid junction potentials. Silver-silver chloride electrode is constructed as follows.



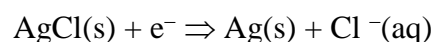
A small sheet or a short foil of platinum is first coated with silver by electrolysis of an argentocyanide solution. The silver is then partly converted into silver chloride by making it an anode in KCl solution and by passing a current of low density for 30 minutes. Finally it is sealed to a platinum wire and dipped in KCl or HCl solution in a glass tube. The electrode is reversible with respect to chloride ions.

The silver-silver chloride electrode is represented as, $\text{Ag(s)} \mid \text{AgCl(s)}, \text{KCl (aq)}$

The reaction that occurs at silver-silver chloride electrode when it acts as anode is



The reaction that occurs at silver-silver chloride electrode when it acts as cathode is



The potential of Ag-AgCl electrode is 0.2224V at 25°C (1M KCl)

The potential of Ag-AgCl electrode is 0.199V at 25°C (saturated KCl)

Ion selective electrodes:

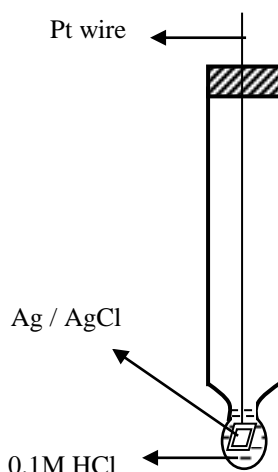
The electrodes that are able to respond to certain specific ions only and develop a potential while ignoring the other ions in a solution are called ion selective electrodes.

Eg. Glass electrode

The chemists have devised ways of measuring, monitoring, and even controlling the concentrations of a large variety of chemical species in solution using these ion selective electrodes.

Glass electrode:

Glass electrode is an ion selective electrode which responds to hydrogen ions in a solution and develops potential while it ignores the other ions. One of the most advances in the recent years in connection with the determination of pH is the use of glass electrode.

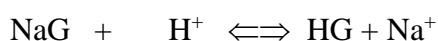


The glass electrode consists of a glass tube having a small bulb at its bottom. The bulb is made up of a special type of thin walled glass of relatively low melting point and high electrical conductivity. The bulb contains a solution of a buffer or 0.1M hydrochloric acid solution. Electrical connection is made by a platinum wire coated with Ag-AgCl and is dipped in a buffer solution or 0.1 M hydrochloric acid solution.

Glass electrode can be represented as,



The reaction that occurs at glass electrode is not clearly understood. The probable reaction is,



(On the surface (in solution)
of glass membrane)

Limitations of glass electrode:

1. Glass electrode cannot give satisfactory results with the solutions having pH greater than 9. As the pH increases, alkalinity of the solution increases leading to increase in salt effects.
2. In very acidic solutions of $\text{pH} < 1$, the salt effects due to anions are observed.
3. It does not function satisfactorily in pure alcohol or in pure acetic acid.

Advantages:

The glass electrode has the following outstanding advantages.

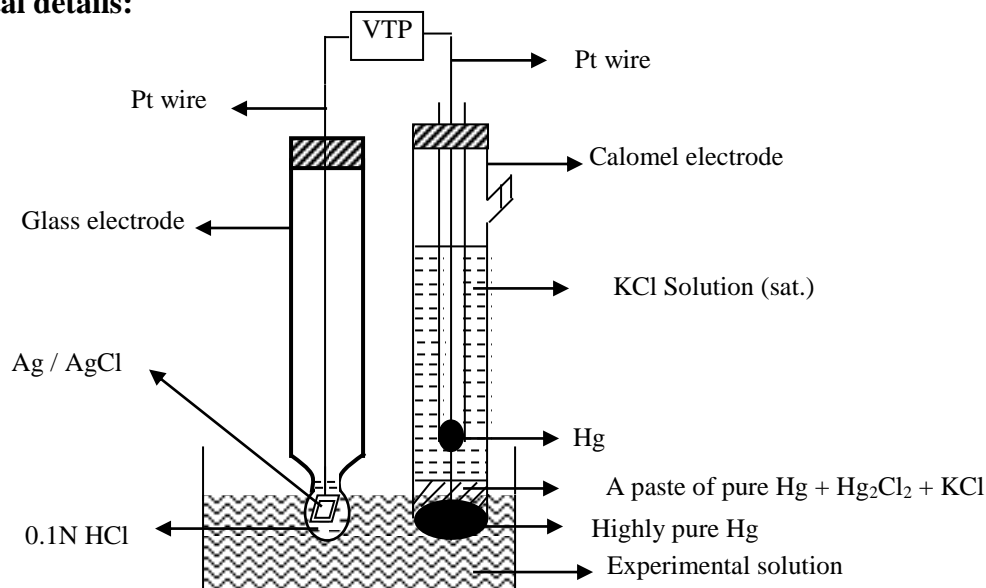
1. It can be employed in the presence of strong oxidising or reducing or organic substances.
2. It can be used in the presence of metal ions.
3. It can be used in unbuffered solutions and can be adopted for measurements with very small quantities of liquids or solutions.
4. It is simple to operate and therefore extensively used in chemical, industrial, agricultural and biological laboratories.

Determination of pH of a solution using glass electrode:

Principle: When a thin glass membrane is placed between two solutions of different pH values (inside and outside the glass membrane), a potential difference exists across the membrane. The potential difference varies, as the pH of the two solutions varies. In actual practice, the pH of one of these two solutions i.e. inside the glass bulb is made to remain

constant. Therefore, the electrode potential depends on the pH of another solution. In fact, the potential is proportional to the pH of the experimental solution.

Experimental details:



The bulb of the glass electrode is placed in the experimental solution, i.e. the solution whose pH is to be determined. The glass electrode is coupled to a reference electrode, calomel electrode and emf of the resulting cell is determined using special vacuum tube potentiometer.

The emf of the cell is given by,

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

$$E_{\text{cell}} = E_{\text{SCE}} - E_{\text{G}}$$

Since E_{SCE} is known, by knowing emf of the cell, E_{G} can be evaluated.

The potential of the glass electrode E_{G} is given by,

$$E_{\text{G}} = \frac{RT}{nF} \ln \frac{a_1}{a_2}$$

where, a_1 is the H^+ ion concentration of the solution present inside the glass bulb and a_2 is the H^+ ion concentration of the experimental solution.

$$E_{\text{G}} = \frac{RT}{nF} \ln a_1 - \frac{RT}{nF} \ln a_2$$

Since the H^+ ion concentration inside the glass bulb is a constant, the first term on RHS of the above equation becomes a *constant*.

$$\therefore E_{\text{G}} = \text{constant} - \frac{RT}{nF} \ln a_2$$

By substituting the values for the gas constant, R, Faraday, F and keeping the temperature equal to 298K and converting natural logarithm to logarithm base 10, the above equation reduces to,

$$E_G = \text{constant} - 0.0591 \log_{10} a_2$$

n = 1 because the system involves H⁺ ions

$$E_G = \text{constant} - 0.0591 \log_{10} [H^+]$$

$$E_G = \text{constant} + 0.0591 \text{ pH} \quad - \log_{10} [H^+] = \text{pH}$$

$$\therefore \text{pH} = \frac{E_G - \text{constant}}{0.0591}$$

$$\therefore \text{pH} = \frac{0.242 - E_{\text{cell}} - \text{constant}}{0.0591}$$

The *constant* for a particular glass electrode is a constant and its value can be determined by calibrating the glass electrode with a series of buffer solutions.

PROBLEMS

- 1) Calculate the $E_{\text{Zn}^{++}/\text{Zn}}$ for the reaction $\text{Zn}^{++} + 2 e^- \rightarrow \text{Zn}$. Given, $E_{\text{Zn}^{++}/\text{Zn}}^0 = -0.76 \text{ V}$ and $[\text{Zn}^{++}] = 0.1 \text{ M}$.

Solution:

$$\begin{aligned} E_{\text{Zn}^{++}/\text{Zn}} &= E_{\text{Zn}^{++}/\text{Zn}}^0 + \frac{0.0591}{n} \log_{10} [\text{Zn}^{++}] \\ &= -0.76 + \frac{0.0591}{2} \log_{10}(0.1) \\ &= -0.76 + 0.0295 (-1) \\ &= -0.7895 \text{ V} \end{aligned}$$

- 2) Calculate the $E_{\text{Cu}^{++}/\text{Cu}}$, given $E_{\text{Cu}^{++}/\text{Cu}}^0 = 0.296 \text{ V}$ and $[\text{Cu}^{++}] = 0.015 \text{ M}$.

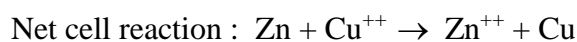
Solution:

$$\begin{aligned} E &= E^0 + \frac{0.0591}{n} \log_{10} [M^+] \\ E_{\text{Cu}^{++}/\text{Cu}} &= E_{\text{Cu}^{++}/\text{Cu}}^0 + \frac{0.0591}{n} \log_{10} [\text{Cu}^{++}] \\ \therefore E_{\text{Cu}^{++}/\text{Cu}} &= E_{\text{Cu}^{++}/\text{Cu}}^0 - \frac{0.0591}{n} \log_{10} [\text{Cu}^{++}] \\ &= 0.296 - \frac{0.0591}{2} \log_{10}(0.015) \\ &= 0.296 - 0.02955 (-1.8239) \\ &= 0.296 + 0.0538 \\ &= 0.3498 \text{ V} \end{aligned}$$

- 3) Write the half-cell and net cell reactions for the following cell, $\text{Zn} | \text{ZnSO}_4(\text{aq}) || \text{CuSO}_4(\text{aq}) | \text{Cu}$. Calculate the emf of the cell. Given, $E_{\text{Zn}^{++}/\text{Zn}}^{\circ} = -0.76 \text{ V}$ and $E_{\text{Cu}^{++}/\text{Cu}}^{\circ} = 0.34 \text{ V}$.

Solution:

Half-cell reactions:

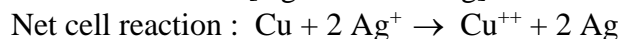


$$\begin{aligned} E_{\text{cell}} &= E_{\text{cathode}} - E_{\text{anode}} \\ &= E_{\text{Cu}^{++}/\text{Cu}} - E_{\text{Zn}^{++}/\text{Zn}} \\ &= 0.34 - (-0.76) \\ &= 1.10 \text{ V} \end{aligned}$$

- 4) Write the half-cell and net cell reactions for the cell, $\text{Cu} | \text{Cu}^{++}(1\text{M}) || \text{Ag}^{+}(1\text{M}) | \text{Ag}$. Calculate the emf of the cell. Given, $E_{\text{Cu}^{++}/\text{Cu}}^{\circ} = 0.34 \text{ V}$ and $E_{\text{Ag}^{+}/\text{Ag}}^{\circ} = 0.8 \text{ V}$.

Solution:

Half-cell reactions:

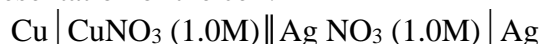


$$\begin{aligned} E_{\text{cell}} &= E_{\text{cathode}} - E_{\text{anode}} \\ &= E_{\text{Ag}^{+}/\text{Ag}} - E_{\text{Cu}^{++}/\text{Cu}} = 0.8 - 0.34 = 0.46 \text{ V} \end{aligned}$$

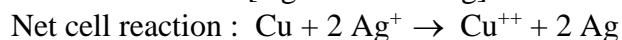
- 5) A cell consists of the following two electrodes,
- Cu rod immersed in 1M copper nitrate solution
 - Ag rod immersed in 1M silver nitrate solution
- Give the representation of the cell
 - Write the net cell reaction
 - In which direction will the reaction proceeds spontaneously?
 - Do electrons flow from Ag to Cu in the external circuit or the other way?

Solution:

- a) Representation of the cell:



- b) Half-cell reactions:



- The reaction is spontaneous from anode to cathode, i.e., from copper to silver electrode.
- Flow of electrons is from copper to silver electrode in the external circuit.

- 5) A cell uses $\text{Ag}^+ | \text{Ag}$ and $\text{Zn} | \text{Zn}^{++}$ couples. Which couple is negative? What is the cell voltage? Write the net cell reaction. Given, $E^\circ_{\text{Ag}^+/\text{Ag}} = 0.8 \text{ V}$ and $E^\circ_{\text{Zn}^{++}/\text{Zn}} = -0.76 \text{ V}$.

Solution:

Cell representation: $\text{Zn} | \text{Zn}^{++}(\text{aq}) || \text{Ag}^+(\text{aq}) | \text{Ag}$

Half-cell reactions:

At anode : $\text{Zn} \rightarrow \text{Zn}^{++} + 2 \text{e}^-$

At cathode : $[\text{Ag}^+ + \text{e}^- \rightarrow \text{Ag}] \times 2$

Net cell reaction : $\text{Zn} + 2 \text{Ag}^+ \rightarrow \text{Zn}^{++} + 2 \text{Ag}$

$$\begin{aligned} E_{\text{cell}} &= E_{\text{cathode}} - E_{\text{anode}} \\ &= E_{\text{Ag}^+/\text{Ag}} - E_{\text{Zn}^{++}/\text{Zn}} \\ &= 0.8 - (-0.76) \\ &= 1.56 \text{ V} \end{aligned}$$

$\text{Zn} | \text{Zn}^{++}$ couple is negative.

- 7) Calculate $E_{\text{Zn}^{++}/\text{Zn}}$, if the emf of $\text{Zn} | \text{Zn}^{++}(\text{a}=1) || \text{Ni}^{++}(\text{a}=1) | \text{Ni}$ is 0.51 V and $\text{Ni} | \text{Ni}^{++}(\text{a}=1) || \text{SCE}$ is 0.49 V. Given, $E^\circ_{\text{SCE}} = 0.24 \text{ V}$.

Solution:

- i) **To calculate $E_{\text{Ni}^{++}/\text{Ni}}$**

Consider the cell $\text{Ni} | \text{Ni}^{++}(\text{a}=1) || \text{SCE}$

$$\begin{aligned} E_{\text{cell}} &= E_{\text{cathode}} - E_{\text{anode}} \\ &= E_{\text{SCE}} - E_{\text{Ni}^{++}/\text{Ni}} \end{aligned}$$

$$\begin{aligned} \therefore E_{\text{Ni}^{++}/\text{Ni}} &= E_{\text{SCE}} - E_{\text{cell}} \\ &= 0.24 - 0.49 \\ &= -0.25 \text{ V} \end{aligned}$$

- ii) **To calculate $E_{\text{Zn}^{++}/\text{Zn}}$**

Consider the cell $\text{Zn} | \text{Zn}^{++}(\text{a}=1) || \text{Ni}^{++}(\text{a}=1) | \text{Ni}$

$$\begin{aligned} E_{\text{cell}} &= E_{\text{cathode}} - E_{\text{anode}} \\ &= E_{\text{Ni}^{++}/\text{Ni}} - E_{\text{Zn}^{++}/\text{Zn}} \end{aligned}$$

$$\begin{aligned} \therefore E_{\text{Zn}^{++}/\text{Zn}} &= E_{\text{Ni}^{++}/\text{Ni}} - E_{\text{cell}} \\ &= -0.25 - 0.51 \\ &= -0.76 \text{ V} \end{aligned}$$

- 8) Calculate the emf of a Daniel cell at 298 K, if the free energy change of the cell reaction is $-212.3 \text{ kJmol}^{-1}$ (or $-212300 \text{ Jmol}^{-1}$). Faraday constant, $F = 96.5 \text{ kJ/volt/mol}$.

Solution:

$$\begin{aligned} \Delta G &= -nFE_{\text{cell}} \\ \therefore E_{\text{cell}} &= \frac{\Delta G}{-nF} \\ &= \frac{-212.3 \text{ kJmol}^{-1}}{-(2 \times 96.5 \text{ kJ/volt/mol})} \\ &= 1.10 \text{ V} \end{aligned}$$

9) Calculate the electrode potential of $\text{Cu}^{++} | \text{Cu}$ electrode, when the free energy change for the reaction, $\text{Cu}^{++} + 2 \text{e}^- \rightarrow \text{Cu}$, is $-62.755 \text{ kJmol}^{-1}$.

Solution:

$$\begin{aligned}\Delta G &= -nFE \\ \therefore E_{\text{Cu}^{++}/\text{Cu}} &= \frac{\Delta G}{-nF} \\ &= \frac{-62.755 \text{ kJmol}^{-1}}{-(2 \times 96.5 \text{ kJ/volt/mol})} \\ &= 0.325 \text{ V}\end{aligned}$$

10) What voltage will be generated by a cell that consists of a rod of iron immersed in a 1.0M solution of FeSO_4 and a rod of manganese immersed in a 0.1M solution of MnSO_4 at 25°C . Given: $E^\circ_{\text{Fe}^{++}/\text{Fe}} = -0.44 \text{ V}$ and $E^\circ_{\text{Mn}^{++}/\text{Mn}} = -1.18 \text{ V}$.

Solution:

$$\begin{aligned}E_{\text{cell}} &= E^\circ_{\text{cell}} + \frac{0.0591}{n} \log \frac{[\text{Fe}^{++}]}{[\text{Mn}^{++}]} \\ &= E^\circ_{\text{Fe}^{++}/\text{Fe}} - E^\circ_{\text{Mn}^{++}/\text{Mn}} + \frac{0.0591}{n} \log \frac{[\text{Fe}^{++}]}{[\text{Mn}^{++}]} \\ E_{\text{cell}} &= -0.44 - (-1.18) + \frac{0.0591}{2} \log \frac{1.0}{0.1} \\ &= -0.44 + 1.18 + 0.02955 \log 10 \\ &= 0.74 + 0.02955 \times 1 = 0.76955 \text{ V}\end{aligned}$$

11) A voltaic cell consists of a rod of copper immersed in a 10.0M solution of CuSO_4 and a rod of iron immersed in a 0.1M solution of FeSO_4 . Calculate the voltage for the cell. Given: $E^\circ_{\text{Cu}^{++}/\text{Cu}} = 0.34 \text{ V}$ and $E^\circ_{\text{Fe}^{++}/\text{Fe}} = -0.44 \text{ V}$.

Solution:

I method -
$$\begin{aligned}E_{\text{cell}} &= E_{\text{cathode}} - E_{\text{anode}} \\ &= E_{\text{Cu}^{++}/\text{Cu}} - E_{\text{Fe}^{++}/\text{Fe}}\end{aligned}$$

$$\begin{aligned}E_{\text{Cu}^{++}/\text{Cu}} &= E^\circ_{\text{Cu}^{++}/\text{Cu}} + \frac{0.0591}{n} \log_{10} [\text{Cu}^{++}] \\ &= 0.34 + \frac{0.0591}{2} \log_{10}(10) \\ &= 0.34 + 0.02955 (1) \\ &= 0.36955 \text{ V} \\ E_{\text{Fe}^{++}/\text{Fe}} &= E^\circ_{\text{Fe}^{++}/\text{Fe}} + \frac{0.0591}{n} \log_{10} [\text{Fe}^{++}] \\ &= -0.44 + \frac{0.0591}{2} \log_{10}(0.1) \\ &= -0.44 + 0.02955 (-1) \\ &= -0.46955 \text{ V} \\ \therefore E_{\text{cell}} &= E_{\text{Cu}^{++}/\text{Cu}} - E_{\text{Fe}^{++}/\text{Fe}} \\ &= 0.36955 - (-0.46955) \\ &= 0.8391 \text{ V}\end{aligned}$$

II method -
$$E_{\text{cell}} = E^0_{\text{cell}} + \frac{0.0591}{n} \log_{10} \frac{[\text{oxidised form}]}{[\text{reduced form}]}$$

OR
$$E_{\text{cell}} = E^0_{\text{cell}} + \frac{0.0591}{n} \log_{10} \frac{[\text{Cathode}]}{[\text{Anode}]}$$

$$= (E^0_{\text{Cu}^{++}/\text{Cu}} - E^0_{\text{Fe}^{++}/\text{Fe}}) + \frac{0.0591}{n} \log_{10} \frac{[\text{Cu}^{++}]}{[\text{Fe}^{++}]}$$

$$= [0.34 - (-0.44)] + \frac{0.0591}{2} \log_{10} \frac{[10.0]}{[0.1]}$$

$$= 0.78 + 0.02955 \log_{10} 100$$

$$= 0.78 + 0.02955 \times 2 = 0.8391 \text{ V}$$

12) A zinc rod is placed in 0.1M solution of ZnSO_4 at 25°C . Assuming that the salt is dissociated to the extent of 95% at this dilution, calculate the $E_{\text{Zn}^{++}/\text{Zn}}$ at this temperature.

Given: $E^0_{\text{Zn}^{++}/\text{Zn}} = -0.76 \text{ V}$.

Solution:

Concentration of $\text{ZnSO}_4 = 0.1\text{M}$

Percentage dissociation of $\text{ZnSO}_4 = 95$

$$\therefore \text{Concentration of } \text{Zn}^{++} \text{ in solution} = \frac{0.1 \times 95}{100}$$

$$= 0.095\text{M}$$

$$E = E^0 + \frac{0.0591}{n} \log_{10} [\text{M}^{n+}]$$

$$E_{\text{Zn}^{++}/\text{Zn}} = E^0_{\text{Zn}^{++}/\text{Zn}} + \frac{0.0591}{n} \log_{10} [\text{Zn}^{++}]$$

$$= -0.76 + \frac{0.0591}{2} \log_{10} [0.095]$$

$$= -0.76 + 0.02955 (-1.0223)$$

$$= -0.76 - 0.03061$$

$$= -0.79061 \text{ V}$$

13) Calculate the voltage of the cell, $\text{Mg} \mid \text{Mg}^{++}(\text{aq}) \parallel \text{Cd}^{++}(\text{aq}) \mid \text{Cd}$ at 25°C , when $[\text{Cd}^{++}] = 7.0 \times 10^{-11}\text{M}$, $[\text{Mg}^{++}] = 1.0\text{M}$ and $E^0_{\text{cell}} = 1.97 \text{ V}$.

Solution:

$$E_{\text{cell}} = E^0_{\text{cell}} + \frac{0.0591}{n} \log_{10} \frac{[\text{oxidised form}]}{[\text{reduced form}]}$$

$$E_{\text{cell}} = E^0_{\text{cell}} + \frac{0.0591}{n} \log_{10} \frac{[\text{Cd}^{++}]}{[\text{Mg}^{++}]}$$

$$E_{\text{cell}} = 1.97 + \frac{0.0591}{2} \log_{10} \frac{(7.0 \times 10^{-11})}{1.0}$$

$$= 1.97 + 0.02955 (-10.1549)$$

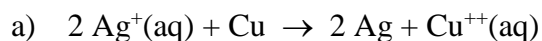
$$= 1.97 - 0.2998$$

$$= 1.6702 \text{ V}$$

14) Compute the cell potential of $\text{Ag}^+ | \text{Ag}$ couple with respect to $\text{Cu} | \text{Cu}^{++}$ couple if the concentration of Ag^+ and Cu^{++} are $4.2 \times 10^{-6}\text{M}$ and $1.3 \times 10^{-3}\text{M}$ respectively.

$E_{\text{cell}}^0 = 0.46 \text{ V}$. What is the value of ΔG for the reduction of 1.0 mol of Ag^+ by Cu^{++} at the indicated ion concentrations?

Solution:



$$E_{\text{cell}} = E_{\text{cell}}^0 + \frac{0.0591}{n} \log_{10} \frac{[\text{oxidised form}]}{[\text{reduced form}]}$$

$$= E_{\text{cell}}^0 + \frac{0.0591}{2} \log_{10} \frac{[\text{Ag}^+]^2}{[\text{Cu}^{++}]}$$

$$= 0.46 + 0.02955 \log_{10} \frac{[4.2 \times 10^{-6}]^2}{1.3 \times 10^{-3}}$$

$$= 0.46 + 0.02955 \log_{10}(13.56 \times 10^{-9})$$

$$= 0.23 \text{ V}$$

- b) For the reduction of 2 mol of Ag^+ ions, 2 electrons are required
For the reduction of 1 mol of Ag^+ ions, 1 electron are required

$$\Delta G = -n F E_{\text{cell}}$$

$$= -1 \times 96.5 \text{ kJ volt}^{-1} \text{ mol}^{-1} \times 0.23 \text{ volt}$$

$$= -22 \text{ kJ mol}^{-1}$$

15) (a) What is the potential of the cell containing $\text{Zn} | \text{Zn}^{++}$ and $\text{Cu}^{++} | \text{Cu}$ couples, if the Zn^{++} and Cu^{++} concentrations are 0.1M and $1.0 \times 10^{-9}\text{M}$ respectively at 25°C ?

(b) What is ΔG for the reduction of 1.0 mol of Cu^{++} by Zn at the indicated concentrations of the ions, and what is ΔG^0 for the reaction both at 25°C ?

Solution:

(a) The cell reaction is, $\text{Zn} + \text{Cu}^{++} \rightarrow \text{Zn}^{++} + \text{Cu}$; $n=2$

$$E_{\text{cell}} = E_{\text{cell}}^0 + \frac{0.0591}{n} \log_{10} \frac{[\text{oxidised form}]}{[\text{reduced form}]}$$

$$= E_{\text{cell}}^0 + \frac{0.0591}{2} \log_{10} \frac{[\text{Cu}^{++}]}{[\text{Zn}^{++}]}$$

$$= 1.1 + \frac{0.0591}{2} \log_{10} \frac{(1.0 \times 10^{-9})}{(0.1)}$$

$$= 1.1 + 0.02955 \log 10^{-8}$$

$$= 1.1 + 0.02955 (-8.0)$$

$$= 0.8636 \text{ V}$$

(b) $\Delta G = -nFE_{\text{cell}}$

$$= -2 \times 96.5 \text{ kJmol}^{-1}\text{V}^{-1} \times 0.8636 \text{ V}$$

$$= -166.67 \text{ kJ mol}^{-1}$$

$$\Delta G^0 = -nFE_{\text{cell}}^0$$

$$= -2 \times 96.5 \text{ kJ mol}^{-1} \text{V}^{-1} \times 1.1 \text{ V} = -212.3 \text{ kJ mol}^{-1}$$

16) Calculate the emf of a cadmium-copper cell in which Cd is in contact with 0.002M CdSO₄ and Cu in contact with 0.02M CuSO₄ solution. The standard emf of the cell is 0.74 V at 298K.

Solution:

The cell reaction is, $\text{Cd} + \text{Cu}^{++} \rightarrow \text{Cd}^{++} + \text{Cu}$

$$E_{\text{cell}} = E_{\text{cell}}^0 + \frac{0.0591}{n} \log_{10} \frac{[\text{oxidised form}]}{[\text{reduced form}]}$$

$$\begin{aligned} &= E_{\text{cell}}^0 + \frac{0.0591}{2} \log_{10} \frac{[\text{Cu}^{++}]}{[\text{Cd}^{++}]} \\ &= 0.74 + \frac{0.0591}{2} \log_{10} \frac{(0.02)}{(0.002)} \\ &= 0.74 + 0.02955 \log 10 \\ &= 0.76955 \text{ V} \end{aligned}$$

17) For the cell, $\text{Fe} | \text{Fe}^{++}(0.01\text{M}) || \text{Ag}^+ (0.1\text{M}) | \text{Ag}$, write the cell reaction and calculate the emf of the cell at 298K, if $E_{\text{Fe}^{2+}|\text{Fe}}^0$ and $E_{\text{Ag}^+|\text{Ag}}^0$ are -0.44V and 0.8V respectively.

Solution:

Half-cell reactions:

At anode : $\text{Fe} \rightarrow \text{Fe}^{2+} + 2\text{e}^-$

At cathode: $[\text{Ag}^+ + \text{e}^- \rightarrow \text{Ag}] \times 2$

Net cell reaction: $\text{Fe} + 2 \text{Ag}^+ \rightarrow \text{Fe}^{2+} + 2 \text{Ag}$

$$\begin{aligned} E_{\text{cell}}^0 &= E_{\text{cathode}}^0 - E_{\text{anode}}^0 \\ &= E_{\text{Ag}^+/\text{Ag}}^0 - E_{\text{Fe}^{2+}/\text{Fe}}^0 \\ &= 0.8 - (-0.44) \\ &= 0.24\text{V} \end{aligned}$$

$$E_{\text{cell}} = E_{\text{cell}}^0 + \frac{0.0591}{n} \log_{10} \frac{[\text{oxidised form}]}{[\text{reduced form}]}$$

$$\begin{aligned} &= E_{\text{cell}}^0 + \frac{0.0591}{2} \log_{10} \frac{[\text{Ag}^+]^2}{[\text{Fe}^{++}]} \\ &= 1.24 + 0.02955 \log \frac{(0.1)^2}{0.01} \\ &= 1.24 + 0.02955 \log 1 \\ &= 1.24 \text{ V} \end{aligned}$$

- 18) Two copper electrodes placed in copper sulphate solutions of equal concentration are connected to form a concentration cell. What is the cell voltage? One of the solutions is diluted until the concentration of Cu^{2+} ions is $1/5^{\text{th}}$ of its original value. What is the cell voltage after dilution?

Solution:

- i) When the concentration of CuSO_4 solutions are equal, the cell voltage will be zero according to, $E_{\text{cell}} = \frac{0.0591}{n} \log \frac{C_2}{C_1}$
- ii) When one of the solutions is diluted to $1/5^{\text{th}}$ of its original value, i.e., $C_2 = 1\text{M}$ and $C_1 = 1/5\text{ M}$

$$E_{\text{cell}} = \frac{0.0591}{n} \log \frac{C_2}{C_1}$$

$$E_{\text{cell}} = \frac{0.0591}{2} \log \frac{1}{1/5}$$

$$E_{\text{cell}} = \frac{0.0591}{2} \log 5 = 0.02955 \times 0.699 = 0.0206\text{ V}$$

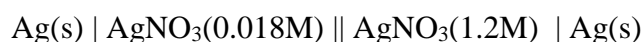
- 19) Two copper rods are placed in 0.1M and 1M CuSO_4 solutions separately to form a cell. Write the representation of the cell. Calculate the emf of the cell.

Solution:

Cell representation: $\text{Cu(s)} \mid \text{CuSO}_4(0.1\text{M}) \parallel \text{CuSO}_4(1.0\text{M}) \mid \text{Cu(s)}$

$$\begin{aligned} E_{\text{cell}} &= \frac{0.0591}{n} \log \frac{C_2}{C_1} \\ &= \frac{0.0591}{2} \log \frac{1.0}{0.1} \\ &= 0.02955 \log 10 \\ &= 0.02955 \times 1 \\ &= 0.02955\text{ V} \end{aligned}$$

- 20) Calculate the EMF of the given concentration cell at 298 K.



Solution:

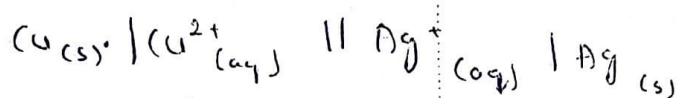
$$\begin{aligned} E_{\text{cell}} &= \frac{0.0591}{n} \log \frac{C_2}{C_1} \\ &= \frac{0.0591}{1} \log \frac{1.2}{0.018} \\ &= 0.0591 \log 66.66 \\ &= 0.0591 \times 1.8239 \\ &= 0.1078\text{ V} \end{aligned}$$

Questions:

1. What is an electrochemical cell? Discuss the classification of an electrochemical cell.
2. What is single electrode potential? Explain the origin of single electrode potential.
3. Derive Nernst equation for the single electrode potential.
4. Discuss the construction of Daniel cell.
5. Discuss the types of electrodes with example.
6. Write a note on sign conventions and cell notations.
7. What are reference electrodes? Describe the construction of Calomel electrode.
8. Describe the construction and working of Ag-AgCl electrode.
9. Discuss the construction and working of glass electrode. Mention the limitations and advantages of glass electrode.
10. What is a concentration cell? Derive an expression for the emf of a concentration cell.
11. What are ion selective electrodes? Describe the experimental method of determination of pH of a given solution using glass electrode.
12. Distinguish between concentration cells with transference and without transference with an example.

A chemist was determining the concentration of copper ions in an effluent sample from an electroplating industry. He used a silver electrode dipped in a 1.00 M solution of AgNO_3 which was connected by means of a salt bridge to a copper electrode dipped in the effluent sample. The cell potential measured was 0.52 V, what is the concentration of Cu^{2+} ions in the water sample.

Given $E^\circ_{\text{Ag}^+/\text{Ag}} = 0.80$ and $E^\circ_{\text{Cu}^{2+}/\text{Cu}} = 0.34$ V.



$$E_{\text{cell}} = E^\circ_{\text{cell}} + \frac{0.0591}{n} \log_{10} \frac{[\text{reactant}]}{[\text{product}]}$$

$$= (E^\circ_{\text{Ag}^+/\text{Ag}} - E^\circ_{\text{Cu}^{2+}/\text{Cu}}) + \frac{0.0591}{2} \log_{10} \frac{[\text{Ag}^+]^2}{[\text{Cu}^{2+}]}$$

$$0.52 = (0.80 - 0.34) + 0.02955 \log_{10} \frac{[1]}{[\text{Cu}^{2+}]}$$

$$0.52 = 0.46 + 0.02955 [\log 1 - \log (\text{Cu}^{2+})]$$

$$0.06 = 0.02955 \{-\log (\text{Cu}^{2+})\}$$

$$\log_{10} (\text{Cu}^{2+}) = \frac{0.06}{0.02955} = -2.030$$

$$[\text{Cu}^{2+}] = 9.33 \times 10^{-3} \text{ M}$$

$\text{Li(s)} | \text{Li}^+ (0.11\text{M}) || \text{Al}^{3+} (0.16\text{M}) | \text{Al}$ at 298 K if the standard reduction potential of lithium electrode is -3.05 V and aluminium electrode is -1.66 V.

$$E = E^{\circ} + \frac{0.0591}{n} \log_{10} \frac{[\text{Cathode}]}{[\text{Anode}]}$$

$$= [-1.66 - (-3.05)] + \frac{0.0591}{3} \log_{10} \frac{[0.16]}{[0.11]^3}$$

$$= 1.39 + 0.0197 \log_{10} [120.2]$$

$$= 1.39 + 0.04097$$

$$E = 1.4309 \text{ V}$$