

Electrochemical cells

Electrochemistry is a branch of science, which studies conversion of chemical energy into electrical energy and vice versa or It is a branch of chemistry that studies chemical reactions which take place in solution at the interface of an electron conductor (a metal or semiconductor) and an ionic conductor (electrolyte) and which involve electron transfer between the electrode and the electrolyte or species in solution. The inter conversions of energies takes place through redox reactions form the basis of electrochemical cells.

Terminology used in electrochemical cell

Anode- is the electrode at which oxidation occurs.

Cathode - is the electrode at which electrons are received from the outer circuit. It has a positive charge and is known as (+) in the cell diagrams.

Oxidation- is the loss of electrons or an increase in oxidation state by a molecule, atom or ion

Reduction - is the gain of electrons or a decrease in oxidation state by a molecule, atom, or ion.

Oxidation occurs at the anode and reduction occurs at the cathode.

The half-cell reaction at the anode is oxidation, while the half-cell reaction at the cathode is reduction.

Q-What are Electrochemical cells: Explain different types of electrochemical cells

The device, which converts chemical energy into electrical energy or electrical energy into chemical energy

There are two kinds of electrochemical cells, they are -

1. Galvanic cell or Voltaic cell: It is an electrochemical cell that produces electricity as a result of spontaneous redox reaction due conversion of chemical energy into electrical energy. Ex: Daniel Cell.

2. Electrolytic cell: It is an electrochemical cell in which non-spontaneous reaction is driven by an external source of current is called an Electrolytic cell (conversion of electrical energy into chemical energy)

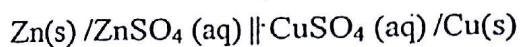
Ex: Electro plating cell

Q- Describe the construction and working of Galvanic cell or Voltaic cell

Galvanic cell consists of two electrodes dipped in two electrolyte solutions which are separated by a porous diaphragm or connected through a salt bridge. The Daniel cell is a typical example for the Galvanic cell (Fig. 1.1). This cell can be constructed by placing zinc rod in zinc sulphate solution and copper rod in copper sulphate solution. Electrical contact is provided between the two electrodes through salt bridge and externally connected by a wire through an ammeter or voltmeter. In this cell zinc rod is found to be negative (anode) and copper rod becomes positive (cathode). The electrons are sent out from the zinc rod to the copper rod. The potential arising for anode is due to oxidation and it is referred as oxidation potential ($E_{Zn/Zn^{2+}}$). Similarly the

potential arising at cathode (copper) is due to reduction potential ($E_{Cu^{2+}/Cu}$)

Daniel cell can be represented as:



Cell reactions: When the zinc and the copper electrodes are connected externally connected, the following reactions take place.

At anode or negative electrode (left electrode): Zinc goes into the solution as Zn^{2+} ions by liberation of electrons

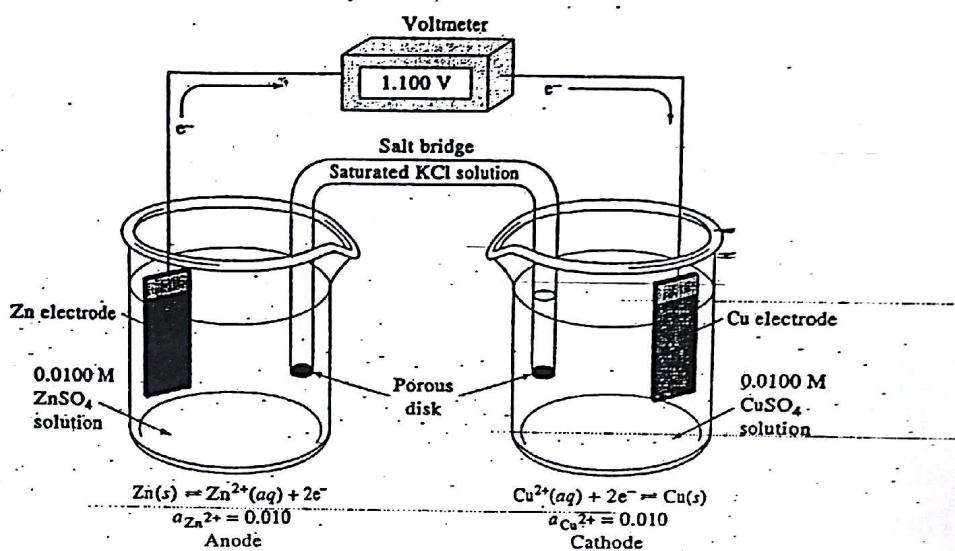
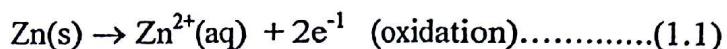
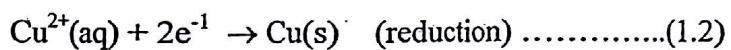
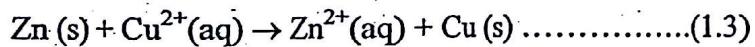


Fig. 1.1

At cathode or positive electrode (right electrode): Reduction of Cu^{2+} ions take place with deposition of metallic copper on copper by consuming electrons



Addition of equation (1.1) and (1.2) gives redox or net chemical cell reaction is



For the above cell the *emf* is found to be 1.1 V at 25°C. The reaction is found to proceed spontaneously from left to right i.e., electrode on the left forces the electrons into the external circuit and electrode on the right withdraws them. Therefore the *emf* of the cell is positive.

In Galvanic cell, *emf* can be expressed as the difference between two single electrode potential

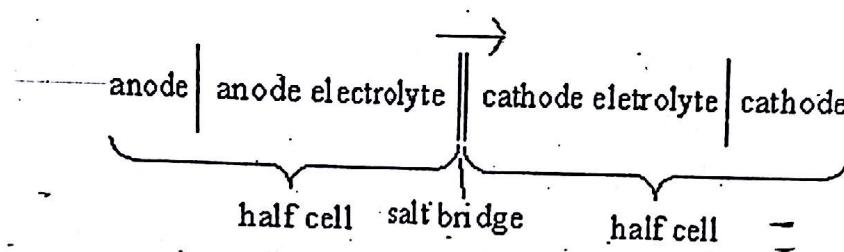
$$\text{The cell emf, } E_{\text{cell}} = E_{\text{cathode}} - E_{\text{anode}} \dots \dots \dots (1.4)$$

When two electrodes are coupled to form a cell, the one with lower reduction potential value acts as anode and

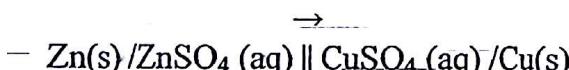
widgoes oxidation, the one with higher reduction potential value acts as cathode and under go reduc For example in Daniel cell Zn-electrode has lower reduction potential value; hence it behaves as anode undergoes oxidation. Where as Cu-electrode has higher reduction potential value, hence it behaves as cat and undergoes reduction. In Zn-Hydrogen cell, Zn acts as anode, Hydrogen electrode acts as cathode. In Fe cell Fe -acts as anode, Cu- electrode acts as cathode.

Q - Write a note on *cell notation or cell representation*

In order to make it easier to describe a given electrochemical cell, a special symbolic notation has been adopt If two electrodes are combined to form a cell, then the cell is represented by writing the electrode convention side by side with the anode on the left and cathode on the right.



The half-cell in which oxidation occurs (anode) is always written on the left. The half-cell in which reduction occurs (cathode) is always written on the right. The vertical line indicates the phase boundary between the metal and solution. The two vertical lines represent salt bridge. An arrow indicates the flow of electrons from anode to cathode (Spontaneous reaction). The electrolyte may be represented by the formula of the whole compound or by ionic species by its concentration in bracket. By placing an ammeter in the external circuit, we can measure the amount of electric charge that passes through the electrodes, and thus the number of moles of reactants that get transformed into products in the cell reaction. Based on the above guidelines Daniel cell can be represented as:



Q- What is salt bridge? Explain its function

Salt bridge is used to connect the oxidation and reduction half cells of a galvanic cell. Salt bridge is U-shaped glass tube filled with a relatively saturated inert electrolyte, usually potassium chloride or sodium chloride. Agar is used for jellification. The conductivity of the glass tube bridges depends on the concentration of the electrolyte solution. An increase in concentration below saturation increases the conductivity. Beyond saturated electrolyte content and narrow tube diameter are lower the conductivity.

Function of salt bridge:

- To avoid liquid junction potential.
- Bring about internal contact between the electrodes
- It keeps the solutions in two half-cells electrically neutral
- It connects the solutions of two half-cells and completes the cell circuit
- It prevents transference or diffusion of the solutions from one half-cell to the other

Q-Define the terms: electromotive force (*emf*) of the cell, standard electrode potential and single electrode potential (Reduction potential) or half-cell potential

Electromotive force (*emf*) of the cell : The difference in potential between the two electrodes of a galvanic cell which causes the flow of current from one electrode (higher potential) to the other (lower potential) as a result of spontaneous redox reaction is called *emf* of the cell or the cell potential and it is denoted by E_{cell}

$$\text{The } emf \text{ of the cell, } E_{cell} = E_{\text{cathode}} - E_{\text{anode}} \quad \text{or} \quad E_{cell} = E_{\text{right}} - E_{\text{left}} \quad (1.5)$$

Standard electrode potential: 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 298 K is called standard electrode potential In case of gas electrode the gas at 1 atm. pressure, it is denoted by E°_{cell} .

Single electrode potential (Reduction potential) or half-cell potential: 'The potential that is developed at the interface between the metal and the solution, when it is in contact with a solution of its ions'. Or 'it is a measure of tendency of a given half-reaction to occur as reduction when it is in equilibrium with the other half cell'. It is denoted by E_M^{n+}/M

For example the reduction potential of zinc electrode is $E_{Zn^{2+}/Zn} = -0.76\text{ V}$

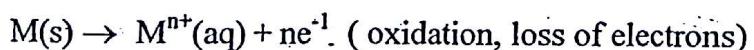
Oxidation potential of zinc electrode is $E_{Zn/Zn^{2+}} = 0.76\text{ V}$

Q: Discuss the origin of single electrode potential.

Origin of electrode potential: 'The potential developed at the interface between the metal and the solution, when it is in contact with a solution of its ions'. When an electrode is in contact with a solution of its ions, such as in a half-cell, a potential arises due to the interaction between the two phases i.e. metal ion – metal electrode.

If a metal M dipped in a solution containing its ions M^{n+} , following two reactions are possible.

- The metal shows the tendency to go into the solution as metal ions by losing electrons.



- The metal ions in the solution show a tendency to get deposited as metal atoms.



Depending upon the nature of the metal, either the dissolution of the metal or the deposition of metal is

faster in the beginning or the other one is slower. But after some time, the reaction will reach a stat equilibrium. $M^{n+}(aq) + n e \leftrightarrow M(s)$

In this reaction the number of metal atoms dissolving is equal to the number of atoms getting deposited.

If the dissolution is faster than the deposition reaction, at equilibrium, the net change is a few m atoms have dissolved in the solution, liberating electrons. $[M(s) \rightarrow M^{n+}(aq) + ne^{-}]$ (oxidation, loss electrons). These electrons accumulate on the electrode surface. Making it negatively charged [Fig. 1(a)]. negatively charged electrode surface attracts a layer of positively charged ions at the interface, developing electrical double layer called **Helmholtz Electric double layer (HDL)** across this double layer the poten develops and this potential is called single electrode potential.

Similarly, if the deposition reaction is faster than the dissolution, at equilibrium, the net change is deposition few metal ions as metal atoms by consuming electrons $[M^{n+}(aq) + ne^{-} \rightarrow M(s)]$ (reduction, gain of electrons As a result the electrode surface develops a layer of positive charge which attracts a layer of negatively charg ions at the interface [Fig. 1 (b)], again HDL is formed and develops single electrode potential. HDL practically indistinguishable from the metal plane and may be visualized as parallel plane capacitor.

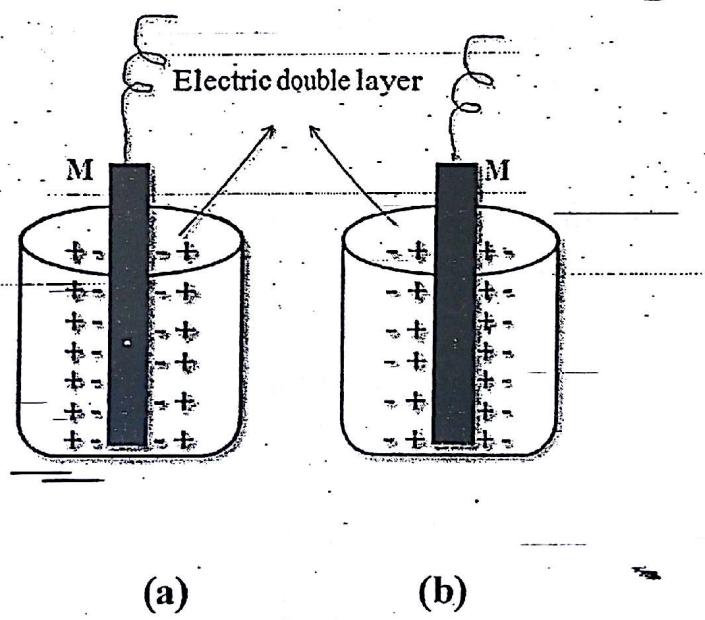


Fig. 1

Q- What is the importance of electrochemical series (electrode potential?)

When elements are arranged in increasing order of their standard electrode potential values form a series called electrochemical series, called electrochemical series. Standard electrode potential values of some elements are given below.

M^{n+}/M	E° (V)	M^{n+}/M	E° (V)	M^{n+}/M	E° (V)
Li^{+}/ Li	-3.05	Al^{+3}/ Al	-1.66	H^{+}/ H_2	0.0
K^{+}/ K	-2.93	Zn^{+2}/ Zn	-0.76	Cu^{+2}/ Cu	0.34
Ba^{+2}/ Ba	-2.90	Fe^{+2}/ Fe	-0.44	Ag^{+}/ Ag	0.80

$\epsilon_{\text{Ca}^{+2}/\text{Ca}}$	-2.87	Cd^{+2}/Cd	-0.40	Hg^{+2}/Hg	0.8
Na^{+}/Na	-2.71	Sn^{+2}/Sn	-0.14	Pt^{+2}/Pt	1.20
Mg^{+2}/Mg	-2.37	Pb^{+2}/Pb	-0.13	Au^{+3}/Au	1.38

Electrochemical series gives the following valuable information.

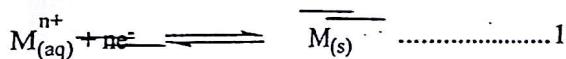
1. A negative value indicates oxidation tendency and a positive value indicates reduction tendency with respect to hydrogen.
 2. The metal with lower electrode potential is more reactive and as the electrode potential increases, the reactivity decreases and the metal with higher electrode potentials are nobler.
 3. Metals with lower electrode potentials have the tendency to replace metals with higher potential from their solutions.
 4. Metals with negative electrode potentials can liberate hydrogen from acidic solutions.

Q- Derive Nernst equation for a single electrode (Thermodynamic concept of cell potential/electrode potential)

In 1889 WALTHER NERNST derived a thermodynamic equation, which equation relates the reduction potential of a half-cell (or the total voltage, i.e. the electromotive force, of the cell) at any point in time to the standard electrode potential (E°), temperature (T), concentration of metal ion (M^{n+}) in solution and reaction quotient of the underlying reactions and species used. It is named after the German physical chemist WALTHER NERNST (1864-1941) who first formulated it. He received the Nobel prize in 1920 "in recognition of his work in thermochemistry". His contribution to chemical thermodynamics led to the well-known equation correlating chemical energy and the electric potential of a galvanic cell or battery.

In order derive this equation, free energy concept is used

Consider the following reversible electrode reaction



The free decrease energy change ($-\Delta G$) in a spontaneous reaction is equal to the energy available to do work.

$$(-\Delta G) = W_{max}$$

Where, W_{\max} is the maximum amount work that can be done and equal to the product of number of coulombs and energy available per coulomb and it is given by

$$W_{max} = nFE$$

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

where n = the number of electrons involved in reaction; F = Faraday constant

The free energy change is also related to equilibrium constant (K). For a reversible reaction, the change in

free energy (ΔG) are inter related as

$$\Delta G = \Delta G^{\circ} + RT \ln K \quad (1.7)$$

Where R = Gas constant

T = Absolute temperature

ΔG° = Standard free energy change ($\Delta G^{\circ} = -nFE^{\circ}$)

From equation (1.6) and (1.7)

$$-nFE = \Delta G^{\circ} + RT \ln K$$

$$-nFE = \Delta G^{\circ} + RT \ln [\text{Product}] / [\text{Reactant}]$$

$$-nFE = \Delta G^{\circ} + RT \ln [M] / [M^{n+}] \quad \text{since } K = [M] / [M^{n+}]$$

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

$$= E^{\circ} - RT/nF \ln [1] / [M^{n+}] \quad \text{since } [M] = 1 \quad (1.8)$$

Equation (1.8) is basic Nernst equation. By substituting R ($8.314 \text{ J K}^{-1} \text{ mol}^{-1}$) Faraday constant F ($96500 \text{ J V}^{-1} \text{ mol}^{-1}$) and absolute temperature, T (298 K) and converting ln to \log_{10} , the above equation further reduced to

$$E = E^{\circ} + 0.0591/n \log [M^{n+}]$$

The Nernst equation for a cell: The Nernst equation can also be applied for calculation of *emf* of a cell.

For Daniel cell: $\text{Zn(s)}/\text{ZnSO}_4(\text{aq}) \parallel \text{CuSO}_4(\text{aq})/\text{Cu(s)}$

$$E_{\text{cell}} = \{E_{\text{Cu}}^{\circ 2+}/\text{Cu} + 0.0591/n \log [\text{Cu}^{2+}]\} - \{E_{\text{Zn}}^{\circ 2+}/\text{Zn} + 0.0591/n \log [\text{Zn}^{2+}]\}$$

$$E_{\text{cell}} = [E_{\text{Cu}}^{\circ 2+}/\text{Cu} - E_{\text{Zn}}^{\circ 2+}/\text{Zn}] + 0.0591 \log [\text{Cu}^{2+}/\text{Zn}^{2+}]$$

$$E_{\text{cell}} = E_{\text{cell}}^{\circ} + 0.0591/2 \log [\text{Cu}^{2+}] / [\text{Zn}^{2+}] \quad (1.9)$$

In general-

$$E_{\text{cell}} = E_{\text{cell}}^{\circ} + \frac{0.0591}{n} \log \frac{[\text{Concentration of ionic species in cathode half cell}]}{[\text{Concentration of ionic species in anode half cell}]}$$

Q- Discuss different types of Electrodes

Types of Electrodes: In electrochemical work, the various electrodes are used depending upon the purpose

1. Metal – metal ion electrode: This type of electrodes consists of a metal dipped in a solution containing its own ions. Ex: Zn/Zn^{2+} , Cu/Cu^{2+}

The electrode reaction can be written as $\text{M}^{n+}(\text{aq}) + n\text{e}^- \rightarrow \text{M(s)}$

2. Metal – metal salt ion electrode (Metal – insoluble salt electrode): These electrodes consist of a metal

in contact with a sparingly soluble salt of the same metal which is in contact with solution containing anion of the salt. Ex: Calomel electrode ($\text{Hg}/\text{Hg}_2\text{Cl}_2/\text{KCl}$), Silver - Silver chloride electrode ($\text{Ag}/\text{AgCl}/\text{KCl}$) and Lead - lead sulphate electrode ($\text{Pb}^{+2}/\text{PbSO}_4/\text{SO}_4^{2-}$)

3. Gas electrode: Gas electrodes consist of a gas bubbling about an inert metal wire or foil, immersed in ionic solution of the gas molecule.

Ex: H_2 - gas electrode ($\text{Pt}/\text{H}_2/\text{H}^+$)

Chlorine - gas electrode ($\text{Pt}/\text{Cl}_2/\text{Cl}^-$)

4. Ion selective electrode (Membrane electrode): In this type of electrodes, a membrane is in contact with a solution, with which it can exchange ions.

Ex: Glass electrode (exchanges H^+ ions with the solution), various metal ions selective electrodes, which exchange metal ions with the solution.

Q- What are Reference Electrodes? Explain difference types of reference electrodes

Reference electrodes are those electrodes which have constant reduction potential and which are used to determine the electrode potential of other electrode

There are two types of reference electrodes. They are -

1. Primary reference electrode
2. Secondary reference electrode

1. Primary reference electrode: The primary reference electrode used for cell potential measurements. The best primary standard reference electrode is *standard hydrogen electrode* (SHE), whose potential is taken as zero at all temperatures. However, it is not convenient for potential measurements. Because of that

- i. Construction and working is difficult on account of difficulties involved in maintaining concentration of H^+ ions at unity and in keeping the pressure of H_2 -gas uniformly at 1 atm.
- ii. The electrodes become inactive in the presence impurity gases present in hydrogen.
- iii. It cannot be used in solution containing strong oxidizing agents-(salts of MnO_4^- , $\text{Cr}_2\text{O}_7^{2-}$).
- iv. In the presence of reducible ions or substances having positive electrodes, it cannot be used.

2. Secondary reference electrodes: Because of the difficulties involved in SHE as a reference electrode, some other electrodes of constant potential are used as reference electrode and these electrodes are called secondary reference electrodes, important potential are employed secondary reference electrodes are (i) Calomel electrode (ii) Silver - silver chloride electrode.

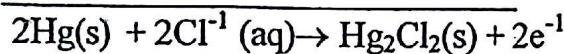
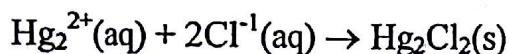
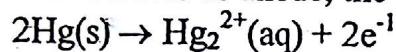
(i) Calomel electrode: Calomel electrode is a commonly used electrode containing of mercury and sparingly soluble mercurous chloride along with potassium chloride solution.

Construction: It is a metal-metal insoluble salt electrode, it consists of a glass tube with a side tube. Mercury placed at the bottom of the tube. A paste of mercurous chloride and mercury is placed over the pool of mercury. The remaining part of the tube is filled with KCl solution. Platinum wire is dipped into the mercury layer for electrical contact. The side tube filled with KCl solution functions as a salt-bridge (Fig. 1.3).

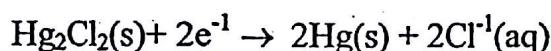
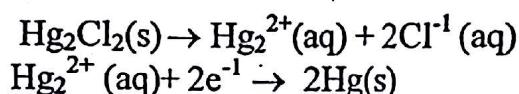
Notation of electrode: Calomel electrode can be represented as $\text{Hg(l)}/\text{Hg}_2\text{Cl}_2;\text{KCl(sat)}$

Electrode reactions: The calomel electrode can act as anode or cathode depending on the nature of the electrode.

As Anode: when it acts as anode, the electrode reaction is



As Cathode: When it acts as cathode, the electrode reaction is



The net reversible reaction is

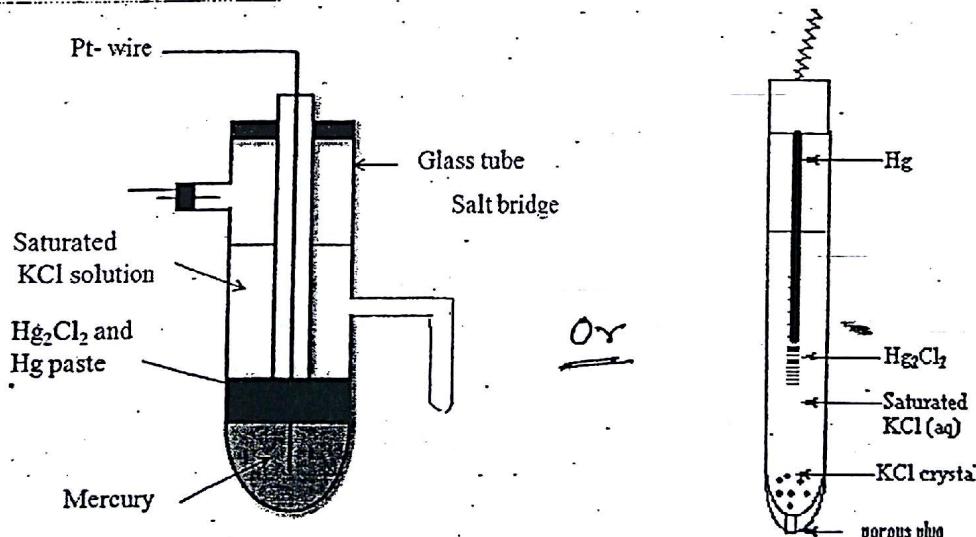
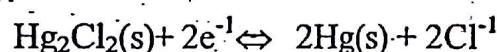


Fig. 1.3

Reduction electrode potential E for a given KCl solution is given by the equation

$$E = E^0 - 0.0591/n \log K$$

$$E = E^0 - 0.0591/n \log [[Hg]^2Cl^{-1}]^2/[Hg_2Cl_2]$$

$$E = E^0 - 0.0591/2 \log [Cl^{-1}]^2 \quad \dots \dots \quad (1.11) \quad \text{since } [Hg] = [Hg_2Cl_2] = 1$$

Since the electrode is reversible with respect to chloride ion, the electrode-potential depends on the concentration of KCl solution. The potential of the calomel electrode is found to depend on the concentration of KCl solution used in the half cell.

Concentration of the KCl solution

E_{calomel} at 298K

0.1 N

0.3334 V

1.0 N

0.2810 V

Saturated

0.2422 V

Advantages of calomel electrode:

1. It is very simple to construction.
2. Potential is reproducible and stable
3. Electrode potential doesn't vary with temperature

Applications:

- (i) Commonly used as reference electrode in all potentiometric determinations
- (ii) Used as a secondary reference electrode in the measurement of single electrode potential
- (iii) It is useful as a reference electrode in measurement of corrosion rate
- (iv) Used as reference electrode in measurement of pH of solution

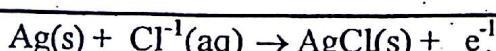
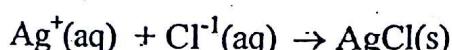
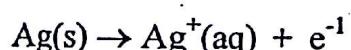
(ii) Silver-Silver chloride electrode:

It is another metal-metal salt electrode used in analytical instrumentations. It is a secondary reference electrode consisting of silver electrode coated with sparingly soluble silver chloride and is immersed in solution containing potassium chloride or hydrochloric acid solution.

Construction: It consists of a glass tube, one end of which is plugged saturated agar. Over this layer solid KCl is placed followed by a saturated KCl solution. A silver wire coated with AgCl is immersed in KCl solution (Fig. 1.4). Notation of Electrode: Ag - AgCl electrode can be represented as Ag(s) / AgCl(s)/ KCl.

Electrode reaction:

As Anode: when it act as anode, the electrode reaction is oxidation



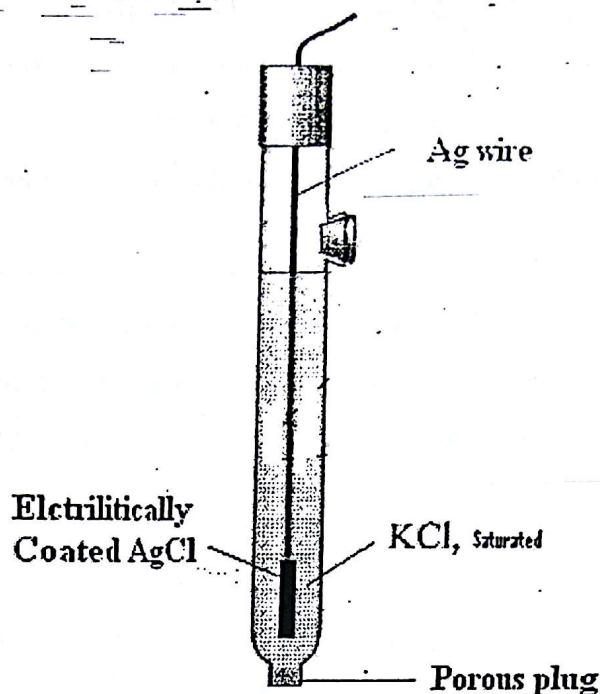
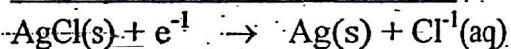
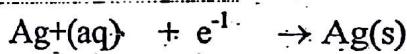
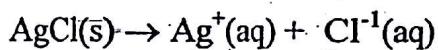


Fig. 1.4

As Cathode: When it act as cathode, the electrode reaction is reduction —



The electrode potential value of Ag-AgCl is also depends on the concentration of chloride ions, for 0.1 M KC solution electrode potential is 0.2901 V, 1.0 M KCl solution electrode potential is 0.233 V, for saturated KC solution the potential is 0.199 V

The electrode potential can be given by the equation

$$E_{\text{Ag}-\text{AgCl}} = E_{\text{Ag}-\text{AgCl}}^0 - 0.0591 \log [\text{Cl}^{-1}] \text{ at } 298 \text{ K} \quad \dots \dots \dots (1.12)$$

Applications:

1. Ag - AgCl electrode is used as internal reference electrode (in glass electrode).

2. It is also used as reference electrode in determination of single electrode

Q - Discuss determination of single electrode potential using secondary reference electrode (SCE/Ag-AgCl electrode)

Principle: It is impossible to measure the absolute value of a single electrode potential experimentally. Only the difference in electrode potential between any two electrodes can be measured as *emf* of the cell formed by the combination of the electrodes. Hence electrode potential value are assigned for different electrodes with respect

to the standard hydrogen electrode $[H^+ (1M) / Pt, H_2 (1atm)]$ whose potential is arbitrary taken as zero at temperatures. The single electrode potential of an unknown can also be determined by using secondary reference electrodes like calomel or Ag-AgCl electrode.

Determination of Single electrode potential using calomel electrode:

The potential of a given electrode is measured using saturated calomel electrode (SCE) whose potential is accurately known. The electrode whose potential to be determined is coupled with calomel electrode as shown in fig. The *emf* of the cell is determined using an electronic voltmeter (Fig.1.5), Ex: Zn electrode is coupled with a standard hydrogen electrode through salt bridge. The cell assembly can be represented as

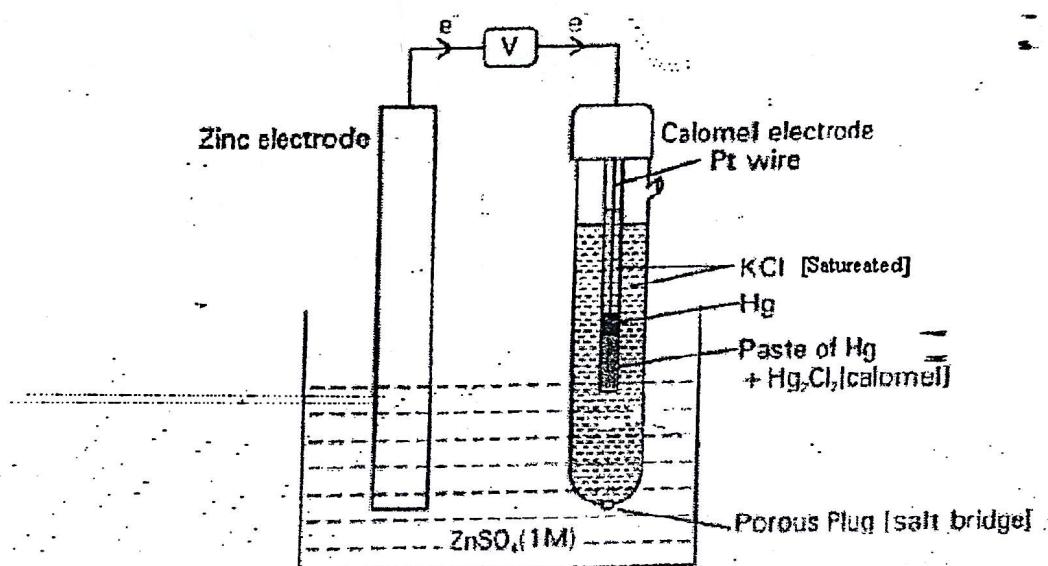
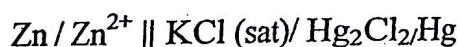


Fig. 1.5



$$\begin{aligned} \text{Calculation of } E_{\text{cell}} &= E_{\text{cathode}} - E_{\text{anode}} \\ &= E_{\text{SCE}} - E_{Zn^{2+}/Zn} \\ &= 0.241 - E_{Zn^{2+}/Zn} \end{aligned}$$

Therefore, $E_{Zn^{2+}/Zn} = 0.241 - E_{\text{cell}}$

Determination of Single electrode potential using Ag-AgCl electrode:

Write similar to calomel

Q: What is ion-selective or membrane electrode? Explain principle, construction and working of glass electrode.

Ion selective or membrane electrode: Ion selective electrode is one which selectively responds to specific ion in a mixture and the potential developed at the electrode is a function of the concentration of that ion in the solution. Ion selective electrodes make use of a kind of membrane which is sensitive to a particular

chemical species. Therefore, these electrodes are also known as membrane electrodes. The electrode generally consists of a thin membrane which is capable of exchanging the specific ion with the solution it is in contact. There are four kinds of membranes. They are-

1. Glass membrane
2. Solid state membrane
3. Heterogeneous membrane
4. Liquid membrane

Glass electrode:

Principle: If solutions of different pH are separated by a thin membrane, the potential develops across membrane. The magnitude of potential depends on the difference in pH of two solutions. If pH of one of them is held constant, the observed glass electrode potential is a linear function of pH of the second solution.

Construction: Glass electrode is an ion selective reference electrode. It consists of a thin walled glass bulb of special type with high electrical conductivity with low melting point. A portion of the bulb is filled with a solution of constant pH (0.1 M HCl). Ag-AgCl electrode is dipped to provide electrical contact (Fig. 1.6).

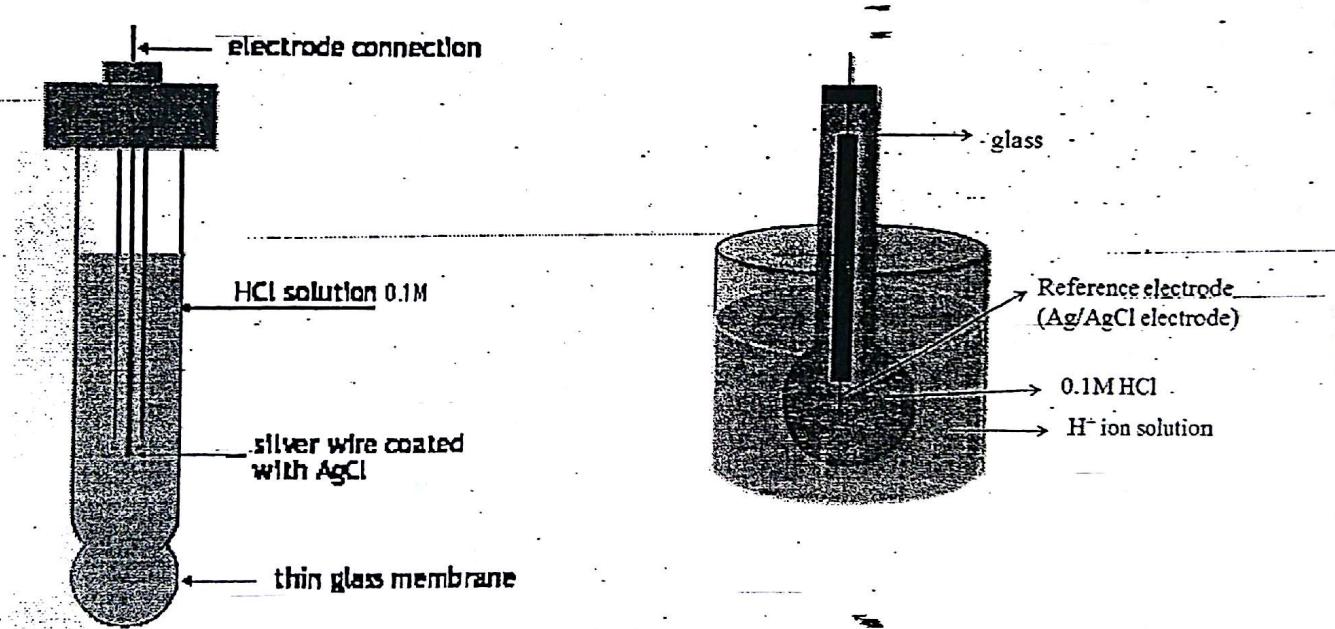


Fig.1.6

Notation of the electrode potential: Glass electrode can be represented as $\text{Ag}/\text{AgCl}(\text{s})/0.1 \text{ M HCl}/\text{glass}$

When glass membrane ($\text{SiO}_2 - \text{CaO} - \text{Na}_2\text{O}$) is dipped in a solution of unknown pH, glass membrane exchanges its cations which are bound on silica network with H^+ ions



Electrode potential of Glass electrode: The potential of the glass electrode E_G has three components

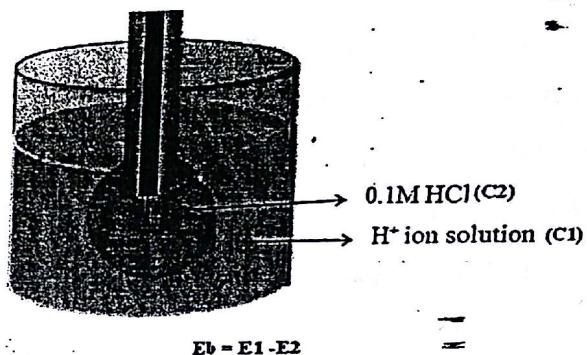
1. The boundary potential (E_b)

2. The potential of the internal Ag/AgCl reference electrode (E_{ref})

3. A small asymmetry potential (E_{asy})

$$E_G = E_b + E_{ref} + E_{asy} \quad \dots \dots \dots (1.13)$$

When the glass electrode is placed in a test solution, a potential is developed across the membrane. Potential difference at the interface E_b is the result of the difference in potential $E_1 - E_2$ across the membrane between the two liquids.



$$E_1 = J_1 - 0.0591 / n \log C_1 \text{ and } E_2 = J_2 - 0.0591 / n \log C_2$$

Where J_1 and J_2 are constants, C_1 and C_2 are concentration of H^+ ions at the external and internal surfaces of the glass membrane. Since the glass at inner and outer solutions is identical $J_1 = J_2$. Then $E_b = E_1 - E_2$, where E_b is the boundary potential

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

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

Since the concentration of inner solution is constant C_2 is constant. So that above equation becomes

$$E_b = L^1 + 0.0591 \log C_1$$

$$= L^1 + 0.0591 \log [H^+] \quad \dots \dots \dots (1.13)$$

Where $L^1 = -0.0591 \log C_2$

Substitute E_b in equation $E_G = E_b + E_{ref} + E_{asy}$

$$= L^1 + 0.0591 \log [H^+] + E_{ref} + E_{asy}$$

$$E_G = E_G^0 - 0.0591 \text{ pH} \quad \text{where } E_G^0 = L^1 + E_{ref} + E_{asy}$$

E_G^0 is specific to a particular glass electrode.

Q What are the advantages and disadvantages of glass electrode?

Advantages: (1) It is simple and can easily be operated.

(2) Equilibrium is rapidly achieved

(3) Accurate results are obtained between pH 1-9 ranges.

(4) It is does not easily poisoned

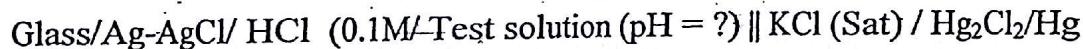
(5) It can be used in oxidizing and reducing environments.

Disadvantages: (1) It can be used for solutions with pH range only from 0 to 10. Above pH 10, solut electrode becomes sensitive to Na^+ ions and leads to *alkaline error*.

(2) Membrane of glass though very thin renders high resistance which cannot be measured by ordin potentiometers. Therefore it is necessary to use electronic potentiometers.

Q- Explain determination of pH of an unknown solution using glass electrode.

Glass electrode is used as the internal reference electrode for determining the pH of solution especially color solution containing oxidizing or reducing agents. Calomel electrode is used as the secondary referen electrode. To determine the pH of the given solution, the glass electrode is placed in the test solution and th half cell is coupled with saturated calomel electrode (Fig. 1.7). The glass electrode acts as anode calom electrode behaves as cathode. The cell assembly is represented as-



The *emf* of the cell is determined potentiometrically (pH meter)

$$\begin{aligned} E_{\text{cell}} &= E_{\text{cathode}} - E_{\text{anode}} \\ &= E_{\text{calomel}} - E_{\text{Glass}} \\ &= E_{\text{calomel}} - [E_G^0 - 0.0591 \text{ pH}] \quad [\text{since } E_G = E_G^0 - 0.0591 \text{ pH}] \end{aligned}$$

$$0.0591 \text{ pH} = E_{\text{cell}} - E_{\text{calomel}} + E_G^0$$

$$\text{Or} \quad \text{pH} = E_{\text{cell}} - 0.241 + E_G^0 / 0.0591$$

[since Electrode potential of saturated calomel is -0.241 V]

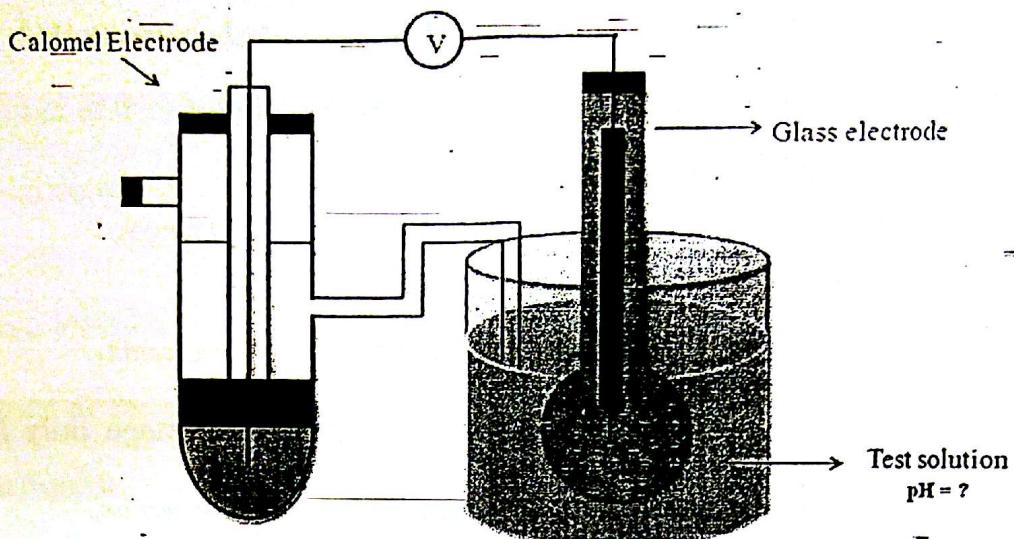


Fig. 1.7

E_G^0 value of the glass electrode is evaluated by dipping the glass electrode in a solution of known pH and measuring the *emf* of the cell formed when combined with a calomel electrode.

Q- What are concentration cells? Explain with suitable example

From study of thermodynamics you may recall that the process



is accompanied by a fall in free energy, and therefore is capable of doing work on the surroundings; all that is required is some practical way of capturing this work. One way of doing this is by means of a concentration cell. The electrode potential of a half-cell dependent on the concentration of the electrolyte with which the electrode is in contact. In concentration cell, two similar metal electrodes are in contact the solutions of its own ions at different concentration, resulting in difference in the electrode potential. So, the concentration cell is a type of Galvanic cell, in which electrodes of the same metal are in contact with solutions of its own ions with different concentration. The *emf* arises due to the difference in concentrations of solutions.

For example: $M(s) | M^{n+}(C_1) \parallel M^{n+}(C_2) | M(s)$

where C_1 and C_2 are molar concentration of M^{n+} ions in the two half cells respectively.

The concentration cell reaction is written as



Adding the two half-cell reaction (redox or net cell reaction or overall cell reaction)



The concentration of M^{n+} ions in the anode solution increases and that of the cathode solution decreases until

both electrode solutions attain the equal concentration.

A typical concentration cell is illustrated as follows: $\text{Cu(s)} / \text{Cu}^{2+}(\text{C}_1) \parallel \text{Cu}^{2+}(\text{C}_2) / \text{Cu(s)}$

In this concentration cells, two copper electrodes are immersed in copper sulphate solutions of concentrations C_1 and C_2 (Fig. 1.8). By convention, the left hand electrode is the anode and the right hand electrode is cathode. The following reactions are takes place in the copper concentration cell.

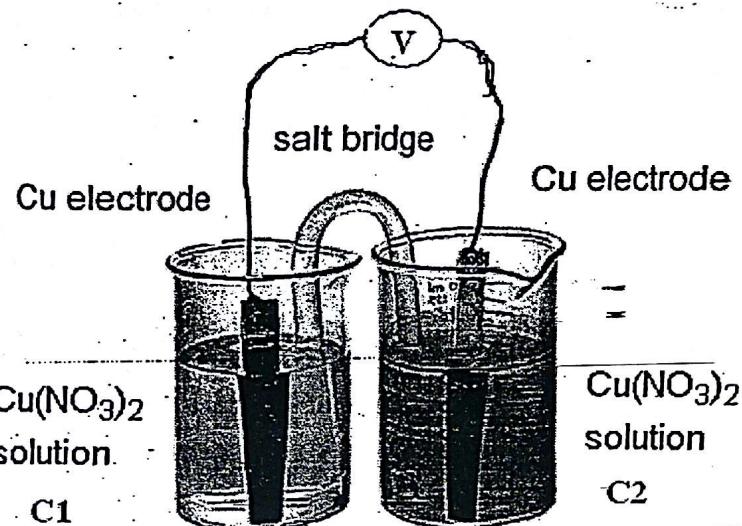


Fig. 1.8

The *emf* of the concentration cell can be represented as

$$E_{cell} = \{E^0 + 0.0591/n \log [C_2]\} - \{E^0 + 0.0591/n \log [C_1]\}$$

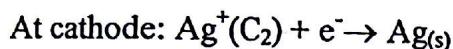
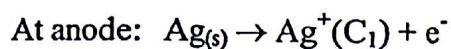
It may be noted that the term E^0 does not appear in the equation since it gets cancelled.

From the above equation, we can conclude the followings

- When two solutions are at the same concentration $\log [C_2] / [C_1] = 0$ and hence no electricity flows.
 - When $C_2 > C_1$ or $[C_2] / [C_1] > 1$, $\log [C_2] / [C_1]$ is positive. So that E is positive. Thus the direction of spontaneous reaction is from the more concentration solution C_2 to less concentration solution C_1 .
 - Higher the ratio of $[C_2] / [C_1]$, higher is the value of cell potential. For ex: If the ratio of $[C_2] / [C_1]$ increases from 0.001 M to 0.01 M (i.e 10 times) the voltage doubles and if the ratio increases 100 times, the voltage becomes three times.
 - When $C_2 < C_1$, $\log [C_2] / [C_1]$ is negative, so that E is negative. Thus the cell reaction is non-spontaneous.

Q-Derivation of Nernst equation for concentration cell (for Example - Ag concentration cell)

- Two silver rods are dipped in silver nitrate solutions of concentrations C_1 and C_2 respectively,
- The cell may be represented as: $\text{Ag}_{(s)} \mid \text{AgNO}_3(C_1) \parallel \text{AgNO}_3(C_2) \mid \text{Ag}_{(s)}$. Where $C_2 > C_1$.
- The electrode reactions are:



- The EMF of the above cell is: $E_{\text{cell}} = E_{\text{cathode}} - E_{\text{anode}}$

$$E_{\text{cell}} = E_{\text{Ag}}^{\circ} + \frac{2.303RT}{nF} \log[\text{Ag}^+]_{\text{cathode}} - E_{\text{Ag}}^{\circ} - \frac{2.303RT}{nF} \log[\text{Ag}^+]_{\text{anode}}$$

$$E_{\text{cell}} = \frac{2.303RT}{nF} \log(C_2) - \frac{2.303RT}{nF} \log(C_1)$$

$$E_{\text{cell}} = \frac{2.303RT}{nF} \log\left(\frac{C_2}{C_1}\right) \quad (\text{or}) \quad E_{\text{cell}} = \frac{0.0591}{n} \log\left(\frac{C_2}{C_1}\right); \text{ at } 298 \text{ K}$$

Where $C_2 > C_1$

Note - E° does not appear in Nernst equation of a concentration cell because it gets cancelled.

REVIEW QUESTIONS

- 1) Explain the terms with examples (i) galvanic cell (ii) half cell.
- 2) What are reactions that occur at the electrodes of a galvanic cell? Explain by taking Daniel cell as an Example.
- 3) How galvanic cell is different from electrolytic cell?
- 4) Define the term single electrode potential. Describe the origin of single electrode potential.
- 5) Why the anode of a galvanic cell is negative and cathode is positive? Write different electrode reactions occur at the electrodes.
- 6) Describe the role of salt bridge in a galvanic cell.
- 7) What is Nernst equation? Derive Nernst equation for single electrode potential
- 8) What are reference electrodes? Describe the construction, working and applications of calomel electrode
- 9) What are secondary reference electrodes? Describe the construction, working and applications of Ag-AgCl electrode.
- 10) Give the principle of glass electrode. Describe its construction. What are the advantages and limitation of glass electrode?
- 11) What are ion selective electrodes? Explain determination of pH of a solution using a glass electrode.
Why glass electrode cannot be used for solution of pH above 9.0?
- 12) What is an ion-selective electrode (membrane)? Derive equation $E = E^{\circ}G - 0.591 \text{ pH}$ for a glass electrode.
- 13) What is standard electrode potential? Explain determination of single electrode potential using Calomel electrode.
- 14) What is standard emf of a cell? Explain determination of single electrode potential using Ag-AgCl electrode.
- 15) What are concentration cells? Derive an expression for the e.m.f. of a concentration cell.
- 16) Define the term: asymmetric potential and boundary potentials.
- 17) Explain how Helmholtz Electrode double layer arises when a metal is in contact with its ionic solution
- 18) Justify the following statements
 - (i) In a galvanic cell anode is -ve and cathode is +ve.
 - (ii) The emf of a cell is always positive.
 - (iii) A salt bridge is used in the construction of a Galvanic cell
 - (iv) Ordinary voltmeter are not used in the voltage measurement of Galvanic cell.
 - (v) In a concentration cell, no electricity flows when the concentration of metal ion is same in both the half cells.
 - (vi) E° does not appear in concentration cell.
 - (vii) Zn reacts with dil. H_2SO_4 to give H_2 , but Ag does not.

Numericals:

- 1) Why no emf is generated in a concentration cell when the concentration of electrolytes are same in both the half cells? A concentration cell was constructed using two iron electrodes in N/50 M and N/10 M

ferric chloride solution. Write the cell representation, cell reaction and calculate e.m.f of the cell.

- 2) What is single electrode potential? Calculate the emf of the cell $\text{Fe}/\text{Fe}^{2+}(0.01) \parallel \text{Ag}^+(0.1)/\text{Ag}$ at 298 K if standard reduction potentials of Fe and Ag electrodes are -0.44 and +0.8 V respectively.
- 3) What is standard electrode potential? A spontaneous galvanic cell -
 $\text{Zn}/\text{Zn ion}(0.1 \text{ M}) \parallel \text{Fe ion}(C_1)/\text{Fe}$ develops an *emf* of 0.3495 V at 25 °C. Given reduction potential of Zn electrode is -0.76 V and reduction potential of Fe electrode is -0.44 V. Calculate C_1 .
- 4) What is single electrode potential? Write cell reactions. Calculate the emf of the cell $\text{Fe}/\text{Fe}^{2+}(0.01) \parallel \text{Ag}^+(0.1)/\text{Ag}$ at 298 K, if standard reduction potentials of Fe and Ag electrodes are 0.44 and 0.8 V respectively.
- 5) Calculate the potential of Ag-Cu cell at 298 K, if the concentration of Ag^+ and Cu^{2+} are 0.01 M and 0.008 M respectively. Standard reduction potential of Cu and silver electrodes are +0.34 and +0.8 volt respectively. Calculate the change in free energy ΔG . 1 Faraday = 96.5 KJ $V^{-1}\text{mole}^{-1}$
- 6) A concentration cell was constructed using two iron electrodes in N/50 M and N/10 M ferric chloride solution. Write the cell representation, cell reaction and calculate e.m.f of the cell.
- 7) A galvanic cell is constructed by dipping zinc rode in 5×10^{-2} M zinc sulphate solution and silver rod in 1.2×10^{-1} M silver sulphate solution. Write the cell representation, cell reactions and calculate the e.m.f of the cell. Given E° values of Zinc and silver metals are -0.76 V and +0.80 V respectively.
- 8) If two Zn electrodes were in contact with Zn ions, emf of the cell was found to be 0.065 V. If concentration of solution at cathode is 0.1 M, calculate concentration of other solution.