

MODULE-1

ELECTROCHEMISTRY & ENERGY STORAGE SYSTEMS

Free energy:

For a reversible cell, the standard free energy (G) of the cell reaction, can be equated to the standard emf E^0 , it is defined as the amount of internal energy of a thermodynamic system that is available to perform work.

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

On such occasions using van't Hoff isotherm we can write

$$\Delta G = \Delta G^0 + RT \cdot \ln K_c$$

Entropy: Entropy is the degree of disorder in the movement of molecules making up a thermodynamic system. The higher the disorder, the higher is the system's entropy. For example, the entropy of a gas is higher than the entropy of a crystal at the same temperature and pressure.

Entropy is denoted by S (unit: JK^{-1}). For its total differential dS we

write $dS =$ [reversible process]

$dS >$ [irreversible process]

Electrochemical cells: "An electrochemical cell is a device which converts chemical energy into electrical energy or electrical energy into chemical energy".

Single electrode potential or Cell potential (E):

It can be defined as "the potential developed at the interface between the metal and solution when it is in contact with a solution of its own ions"

OR

"Single electrode potential is a measure of tendency of a given half cell reaction to occur as reduction when it is in equilibrium with the other half cell"

STANDARD ELECTRODE POTENTIAL (E^0):

"Standard electrode potential is the electrode potential when the electrode is in contact with a solution of unit concentration; at 298K. If the electrode involves a gas then the gas at one-atmosphere pressure".

EMF OF THE CELL:

"Emf is the potential difference between the two electrodes of a galvanic cell which causes the flow of current from one electrode to other",

$$\text{EMF} = E_{\text{Cathode}} - E_{\text{Anode}}$$

Nernst equation for single electrode potential:

Nernst equation gives a relationship between single electrode potential and standard electrode potential through concentration of metal ions at a particular temperature.

The decrease free energy ($-\Delta G$) represents the maximum amount of work that can be obtained from a chemical cell reaction.

$$-\Delta G = W_{\text{max}} \dots \dots \dots (1)$$

$$W_{\text{max}} = nFE \dots \dots \dots (2)$$

Where, n = No of electrons, E = Electrode potential & F = Faraday constant.

$$\therefore -\Delta G = nFE \dots \dots \dots (3)$$

Under standard condition

$$-\Delta G^{\circ} = nFE^{\circ} \dots \dots \dots (4)$$

Where, $-\Delta G^{\circ}$ = Decrease free energy under standard condition, E° = Standard electrode potential

Consider a reversible electrode reaction



According to Vanthoff's reaction isotherm

$$\Delta G = \Delta G^{\circ} + RT \cdot \ln K_c \dots \dots \dots (6)$$

Where, K_c = Equilibrium constant

Substitute the value of K_c , we have

$$\Delta G = \Delta G^{\circ} + RT \cdot \ln \frac{[M]}{[M^{n+}]} \dots \dots \dots (7)$$

Divide the equation (6) by $-nF$

From equation (3) and (4)

$$E = E^{\circ} - \frac{RT}{nF} \cdot \ln \frac{[M]}{[M^{n+}]} \dots \dots \dots (8)$$

For a solid metal concentration is unity, so that $[M] = 1$

Then, we have

$$E = E^{\circ} - \frac{RT}{nF} \cdot \ln \frac{1}{[M^{n+}]} \dots \dots \dots (9)$$

$$E = E^{\circ} + \frac{RT}{nF} \cdot \ln [M^{n+}] \dots \dots \dots (10)$$

$$E = E^{\circ} + \frac{2.303RT}{nF} \cdot \log [M^{n+}] \dots \dots \dots (11)$$

Substitute the value of $R=8.314\text{J/K/mol}$, $T=298\text{K}$, $F=96500\text{C/mol}$ to the eq. (11)

$$E = E^{\circ} + \frac{0.0591}{n} \cdot \log [M^{n+}] \dots \dots \dots (12)$$

Eq.n (12) is the Nernst equation for a single electrode.

Then, **Nernst equation for emf of cell** is given by

$$E_{cell} = E^{\circ}_{cell} + \frac{0.0591}{n} \cdot \log \left[\frac{\text{Species.at.Cathode}}{\text{Species.at.Anode}} \right]$$

Problems

1. Calculate the potential of Ag-Zn cell at 298 K, if the concentration of Ag^+ and Zn^{+2} are 5.2×10^{-6} M and 1.3×10^{-3} M respectively. E^0 of the cell at 298K is 1.5V given: $T=298\text{K}$; $E^0_{\text{cell}} = 1.5\text{V}$.

$$[\text{Ag}^+] = 5.2 \times 10^{-6} \text{M}$$

$$[\text{Zn}^{+2}] = 1.3 \times 10^{-3} \text{M}$$

Ans:

$$E_{\text{cell}} = E_{\text{cell}}^0 + \frac{0.0591}{n} \log \frac{[\text{Ag}^+]^2}{[\text{Zn}^{+2}]}$$

$$E_{\text{cell}} = 1.5 + \frac{0.0591}{2} \log \frac{(5.2 \times 10^{-6})^2}{1.3 \times 10^{-3}}$$

$$E_{\text{cell}} = 1.27 \text{ V}$$

2. An electrochemical cell consists of iron electrode dipped in 0.1M FeSO_4 and silver electrode in 0.05M AgNO_3 . Write the cell representation cell reaction and calculate the emf of the cell at 298K. (The standard reduction potentials of iron and silver are -0.44V and 0.8V respectively).

Given: $T=298\text{K}$; $E^0_{\text{Fe}} = -0.44\text{V}$; $E^0_{\text{Ag}} = 0.8\text{V}$

$$[\text{Fe}^{+2}] = 0.1\text{M}$$

$$[\text{Ag}^+] = 0.05\text{M}$$

cell representation: $\text{Fe(s)} | \text{FeSO}_4(0.1\text{M}) || \text{AgNO}_3(0.05\text{M}) | \text{Ag(s)}$

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

$$E_{\text{cell}} = E^0_{\text{cathode}} + \frac{0.0591}{n} \log [\text{Ag}^+] - E^0_{\text{anode}} - \frac{0.0591}{n} \log [\text{Fe}^{2+}]$$

$$E_{\text{cell}} = E^0_{\text{cathode}} - E^0_{\text{anode}} + \frac{0.0591}{n} \log \frac{[\text{Ag}^+]^2}{[\text{Fe}^{2+}]}$$

$$E_{\text{cell}} = 0.8 - (-0.44) + \frac{0.0591}{2} \log \frac{[0.05]^2}{[0.1]}$$

$$E_{\text{cell}} = 1.19 \text{ V.}$$

3. Calculate the voltage of the cell $\text{Mg(s)} | \text{Mg}^{+2} (1\text{M}) || \text{Cd}^{+2} (7 \times 10^{-11}\text{M}) | \text{Cd(s)}$, where $E^0_{\text{cell}} = 1.97\text{V}$.

Given: $E^0_{\text{cell}} = 1.97\text{V}$

$$[\text{Mg}^{+2}] = 1\text{M}$$

$$[\text{Cd}^{+2}] = 7 \times 10^{-11}\text{M}$$

Ans:

$$E_{\text{cell}} = E_{\text{cell}}^0 + \frac{0.0591}{n} \log \frac{[\text{Cd}^{+2}]}{[\text{Mg}^{+2}]}$$

$$E_{\text{cell}} = 1.97 + \frac{0.0591}{2} \log 7 \times 10^{-11}$$

$$E_{\text{cell}} = 1.97 - 0.3001$$

$$E_{\text{cell}} = 1.6699 \text{ V.}$$

4. Write the half cell and net cell reactions for the cell

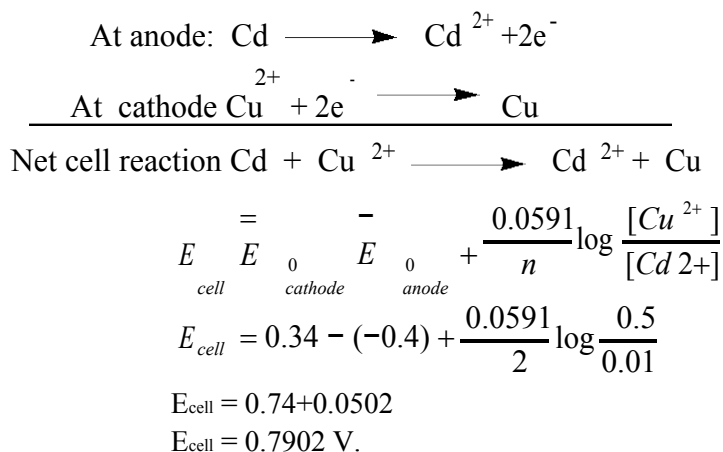


The standard reduction potentials of Cd and Cu are -0.4V and 0.34V respectively. Calculate the emf of the cell.

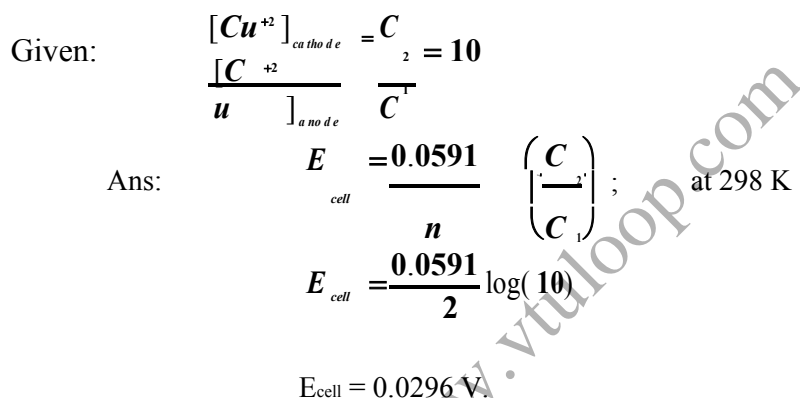
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Given: $E_{\text{Cd}}^0 = -0.4\text{V}$; $E_{\text{Cu}}^0 = 0.34\text{V}$; $[\text{Cd}^{2+}] = 0.01\text{M}$; $[\text{Cu}^{2+}] = 0.5\text{M}$

Ans:



5. Calculate the emf of Copper concentration cell at 25°C , where the copper ions ratio in the cell is 10.



Reference electrodes: "Reference electrodes are the electrode with reference to those, the electrode potential of any electrode can be measured". The Primary reference electrode used for cell potential measurement is the SHE, whose potential is Zero. The secondary reference electrodes are Calomel and Silver-Silver chloride electrode.

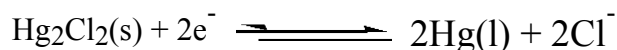
Calomel electrode:

Calomel electrode is a metal-metal salt ion electrode. It consists of mercury, mercurous Chloride and a solution of KCl. Mercury is placed at the bottom of a glass tube.

A paste of mercury and mercurous chloride is placed above the mercury. The space above the paste is filled with a KCl solution of known concentration. A platinum wire is kept immersed into the mercury to obtain an electrical contact. Calomel electrode can be represented as, $\text{Hg} | \text{Hg}_2\text{Cl}_2 | \text{Cl}^-$.

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

The net cell reversible electrode reaction is,



The Nernst equation is given by,

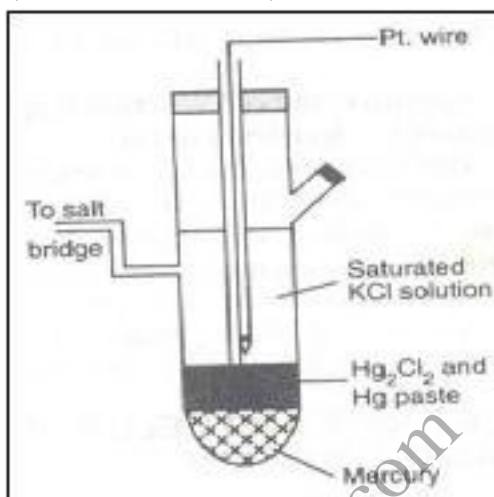
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$$E = E^0 - \frac{2.303RT}{2F} \log[\text{Cl}^-]^2$$

$$E = E^0 - \frac{2.303RT}{F} \log[\text{Cl}^-]$$

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

The electrode potential of calomel electrode is depending upon the concentration of KCl used, 0.1N KCL → 0.334V, 1N KCL → 0.281V, Sat.KCL → 0.2422V.



Advantages:-

1. Simple to Construct.
2. Cell potential does not vary with temperature.
3. The cell potential is reproducible and constant over a long period.

Applications:

1. It is used as a secondary reference electrode in the measurement of a single electrode.
2. It is used as a reference electrode in all potentiometer determinations.

Ion-selective electrode: “Ion-selective electrode is one which selectively responds to specific ions in a mixture and the potential developed at the electrode is a function of the concentration of those ions in the solution”.

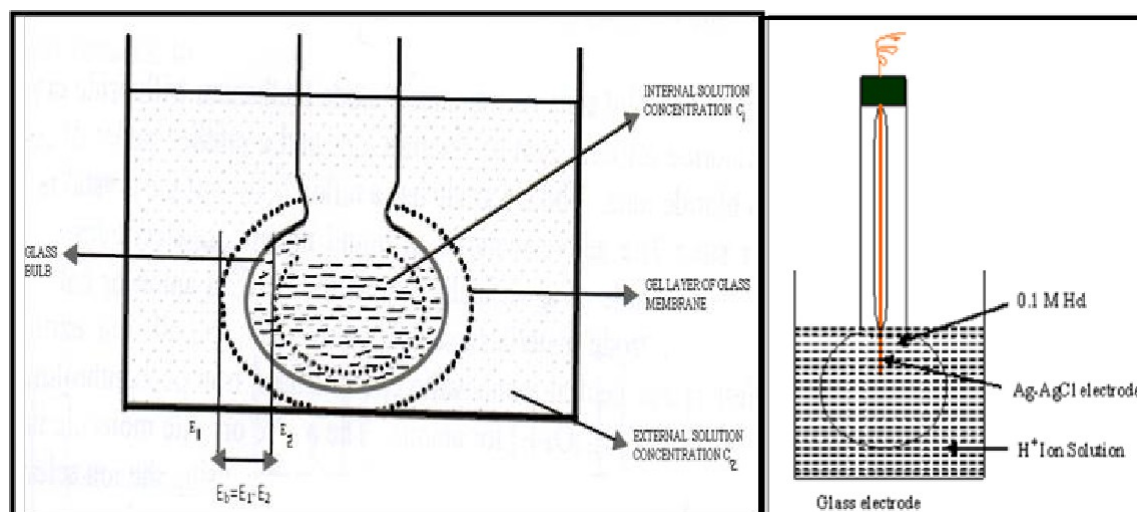
To determine the concentration of a number of cations and anions such as H^+ , Li^+ , Na^+ , K^+ , Pb^{2+} , Cu^{2+} , Mg^{2+} , CN^- , NO_3^- , F^- etc.

There are Four types of membranes, They are

- 1) Glass membranes
- 2) Heterogeneous membranes
- 3) Solid State membranes
- 4) Liquid membranes

Glass electrode:

Principle: - A thin-walled glass bulb containing an acid is immersed in another solution a potential is developed across the glass membrane. The potential difference, E_b at the interface is referred to as boundary potential is the difference in potential ($E_1 - E_2$) developed across the layer of the glass membrane b/w the two liquids.



The potential of glass electrode E_G is given by

$$E_G = E_1 - E_2 \quad \dots\dots\dots 1 \quad \text{Where, } E_1 \& E_2 \text{ are the electrode potential of outer \& inner membrane}$$

$$E_G = [E^0 + 0.0591 \log [C_2]] - [E^0 + 0.0591 \log [C_1]] \quad \dots\dots\dots 2 \quad \text{Where } C_1 \& C_2 \text{ are the concentration inner \& outer acid solutions.}$$

$$E_G = 0.0591 \cdot \log \frac{[C_2]}{[C_1]} \quad \dots\dots\dots 3 \quad \text{Or} \quad E_G = 0.0591 \cdot \log \frac{[C_2]}{[C_1]}$$

$$E_G = -0.0591 \cdot \log [C_1] + 0.0591 \cdot \log [C_2] \quad \dots\dots\dots 4$$

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

$$E_G = \text{Constant} + 0.0591 \cdot \log [C_2] \quad \dots\dots\dots 5$$

$$E_G = \text{Constant} + 0.0591 \cdot \log [H^+] \quad \dots\dots\dots 6 \quad \text{Since, } C_2 = [H^+]$$

$$E_G = \text{Constant} - 0.0591 \cdot \text{pH} \quad \dots\dots\dots 7 \quad \text{Where } \text{pH} = -\log [H^+]$$

A glass electrode is an ion selective electrode where potential depends on upon the pH of the medium. The glass electrode consists of a glass bulb made up of a special type of glass (22%Na₂O, 6%CaO, and 72%SiO₂) which has low melting point and relatively high electrical conductivity. The glass bulb is filled with a solution of constant pH (0.1MHCl) and inserts with an Ag-AgCl electrode, which is the Internal reference electrode and also serves as the external electrical contact. The electrode dipped in a solution containing H^+ ions. The electrode representation is,



Advantages

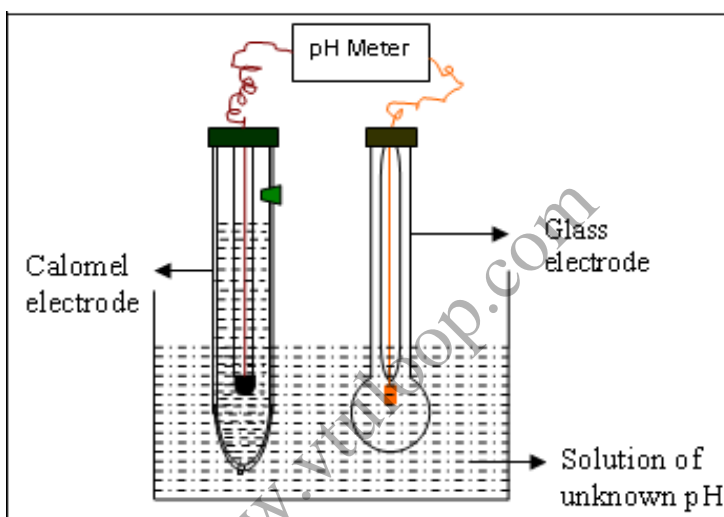
1. This electrode can be used to determine pH in the range 0-9, with a special type of glass even up to 12 can be calculated.
2. It can be used even in the case of strong oxidizing agents.
3. The equilibrium is reached quickly.
4. It is simple to operate, hence extensively used in various laboratories.

Limitations

1. The glass membrane though it is very thin, it offers high resistance. Therefore ordinary potentiometers cannot be used; hence it is necessary to use electronic potentiometers.
2. This electrode cannot be used to determine the pH above 12.

Determination of pH using glass electrode:

Principle: When a thin glass membrane is placed between two solutions of different pH values, a potential difference arises across the membrane. The potential difference varies as the pH of these solutions varies. In practice, pH of one of these solutions is kept constant and therefore the electrode potential depends on pH of the other solution i.e. Experimental solution.



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



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

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

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

Since E_{SCE} is known EMF of the cell,

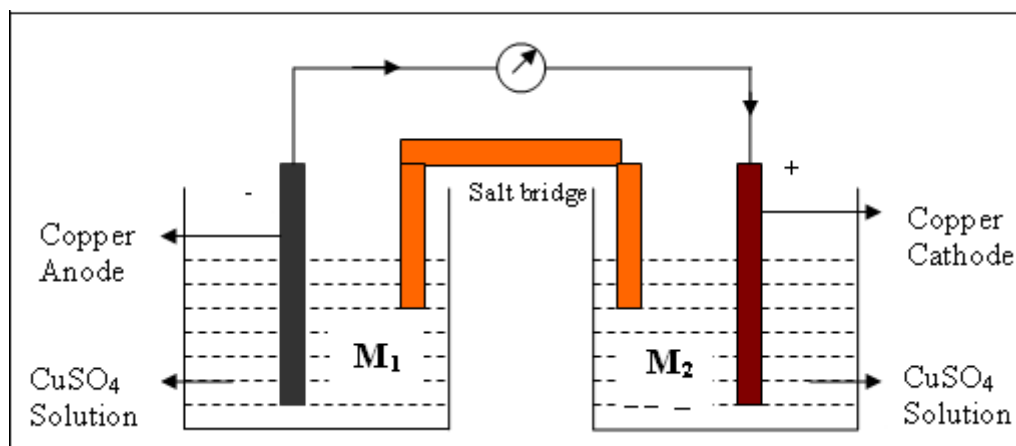
Substitute the value of E_{G} to equation (2)

$$E_{\text{cell}} = \text{Const} t - 0.0591 \cdot \text{pH} - E_{\text{sce}} \dots\dots\dots(3)$$

$$\text{pH} = \frac{\text{Const} t - E_{\text{cell}} - E_{\text{sce}}}{0.0591} \dots\dots\dots(4)$$

Electrolyte Concentration cells:

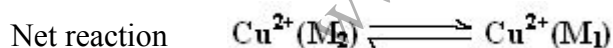
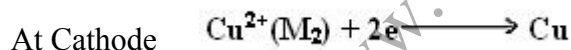
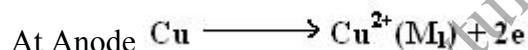
“Electrolyte Concentration cell is an electrochemical cell in which the electrode material and the solution in both the electrodes are composed of the same substances but only the concentrations of the two solutions (electrolyte) are different”. A typical example of Copper concentration cell is shown below.



It consists of two Copper electrodes are immersed in two different concentration of CuSO_4 solutions. These two electrodes are externally connected by metallic wire and internally by a salt bridge. The cell can be represented as,



By convention left-hand electrode is the anode and right-hand electrode is a cathode.



The net cell reaction is merely the change in concentration as a result of current flow.

Emf of concentration cell:

We know that electrode potential depends on the concentration of the electrolyte. By convention, the potential of the cell is

$$E_{\text{cell}} = E_{\text{cathode}} - E_{\text{anode}} \quad \dots\dots\dots 1$$

$$E_{\text{cell}} = \frac{0.0591}{n} \cdot \log [M_2] - \frac{0.0591}{n} \cdot \log [M_1] \quad \dots\dots\dots 2$$

$$E_{\text{cell}} = \frac{0.0591}{n} \log \frac{[M_2]}{[M_1]} \quad \text{at, } 298\text{K} \quad \dots\dots\dots 3$$

From equation (3) following conclusions may be drawn.

1. When the two solutions are the same concentrations, $\log \frac{[M_2]}{[M_1]} = 0$ and no electricity

flows. Hence, $E_{\text{cell}} = 0$

2. When $M_2/M_1 > 1$ i.e $M_2 > M_1$, $\log M_2/M_1$ is positive & electrode potential is positive.

3. Higher the ratio of M_2/M_1 , higher is the value of cell potential.

Problems:

1. Calculate the potential of Daniel cell at 25⁰ C, given the electrode potentials of Cu and Zn are 0.34V and -0.76V respectively.

Given: $E_{Zn}^0 = -0.76V$; $E_{Cu}^0 = 0.34V$

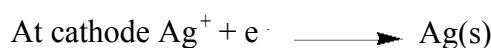
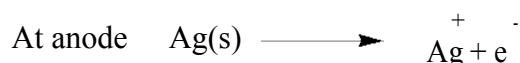
Ans: $E_{cell} = E_{cathode} - E_{anode}$

$$E_{cell} = 0.34 - (-0.76)$$

$$E_{cell} = 1.1 V.$$

2. Write the electrode reactions and Calculate the EMF of the given concentration cell at 298K, $Ag(s) | AgNO_3 (0.018M) || AgNO_3 (1.2M) | Ag(s)$.

Ans:



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

$$E_{cell} = 0.0591 \log \left(\frac{1.2}{0.018} \right) \quad (n=1)$$

$$E_{cell} = 0.1078 V.$$

3. Calculate the emf of Copper concentration cell at 25⁰ C, where the copper ions ratio in the cell is 10.

Given: $\frac{[Cu^{+2}]_{cathode}}{[Cu^{+2}]_{anode}} = \frac{C_2}{C_1} = 10$

Ans: $E_{cell} = \frac{0.0591}{n} \log \left(\frac{C_2}{C_1} \right); \quad \text{at 298 K}$

$$E_{cell} = \frac{0.0591}{2} \log(10)$$

$$E_{cell} = 0.0296 V.$$

4. Calculate the electrode potential at a copper electrode dipped in a 0.1M solution of Copper sulphate at 298K, assuming copper sulphate to be completely dissociated. The standard electrode potential of Cu^{+2}/Cu is 0.34V at 298K. Given: $T=298K$; $E_{Cu}^0 = 0.34V$

$$[Cu^{+2}] = 0.1M$$

Ans: $E_{Cu^{+2}/Cu} = E^0 + \frac{0.0591}{n} \log[Cu]$ at 298 K

$$E_{Cu^{+2}/Cu} = 0.34 - \frac{0.0591}{2} \log(0.1)$$

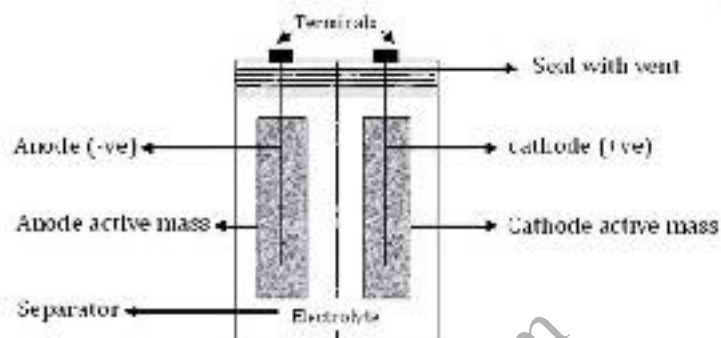
$$E_{Cu^{+2}/Cu} = 0.3105 V.$$

Energy storage systems

Battery: It is a device consisting of two or more galvanic cells connected in series or parallel or both.

Principle components of a battery are:

1. An anode where oxidation occurs.
2. A cathode where reduction occurs.
3. An electrolyte, which is ionically conducting.
4. A separator to separate anode and cathode compartments.



Classification of batteries:

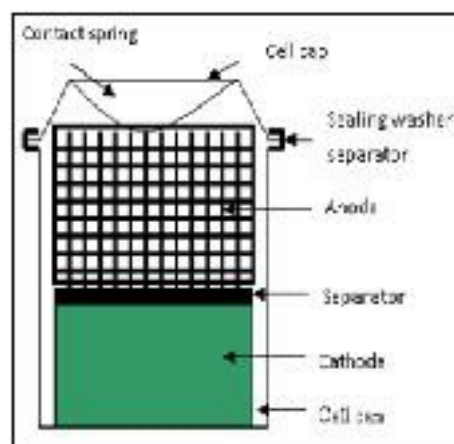
1. **Primary batteries:** In these batteries the cell reaction is not reversible after discharging cannot be rechargeable. e.g. Zn-MnO₂ dry cell.
2. **Secondary batteries:** In this battery the cell reaction is completely reversible after discharging can easily rechargeable. e.g. Lead-acid battery, Ni-MH battery.
3. **Reserve batteries:** In these batteries, one of the active components (e.g. electrolyte) of the battery is separated from the rest of the components. It is assembled just before the use. e.g. Mg-water activated the battery.

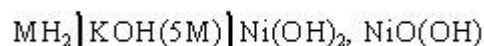
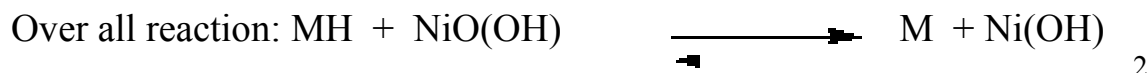
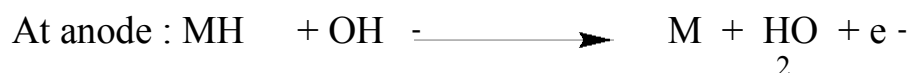
Nickel-metal hydride battery:

Construction: In these batteries, electrodes are made of porous nickel foil or nickel grid, into which the active material is packed. The active material for the anode is a mixture of a metal hydride (such as TiH₂, VH₂, or ZrH₂) and a hydrogen storage alloy (such as LaNi₅ or TiNi). The active material for the cathode is nickel oxyhydroxide, NiO(OH). An aqueous solution of KOH acts as the electrolyte. Polypropylene is used as the separator.

The anode material has (i) a good hydrogen storage capacity capable of adsorbing and desorbing hydrogen as the battery is discharged and charged.

(ii) high resistance to chemical oxidation and corrosion and (iii) high electrochemical reactivity.



Cell representation:**Cell reactions:**

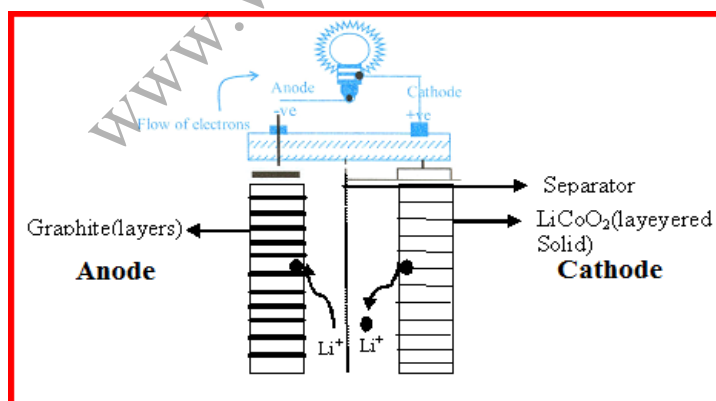
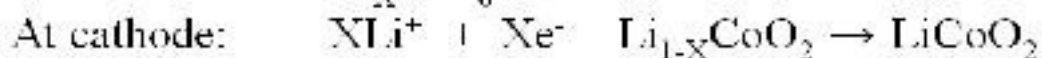
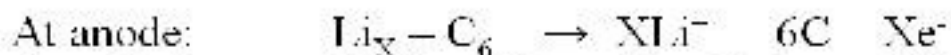
Uses: Used in cellular phones, camcorders and laptop computers.

Lithium batteries: These batteries with high energy density, high energy efficiency, high voltage and long life cycle. Lithium has the following characteristics.

(i) It is light weight. (ii) It has high electrochemical equivalence (3.86 Ah g^{-1}). (iii) It has good electrical conductivity. (iv) It has high standard electrode potential (-3.05V).

Li- ion battery:

A conventional lithium ion battery consists of and a metal oxide such as carbon (graphite) forms the anode and lithium cobalt oxide (LiCoO_2) as a cathode. The electrolyte consists of a lithium salt in an organic solvent. The salts include lithium hexafluorophosphate LiPF_6 , lithium tetrafluoroborate LiBF_4 and lithium perchlorate LiClO_4 . The solvents used are ethylene carbonate, dimethyl carbonate, and diethyl carbonate. The cell delivers an emf of 4V.

**Cell reaction:**

With discharge, the Co is oxidized from Co^{3+} to Co^{4+} . The reverse process (reduction) occurs when the battery is being charged.

Applications: Used in laptops, cell phones and airspace applications.

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