

Unit-I

ELECTROCHEMISTRY & BATTERY TECHNOLOGY

Corrosion:

Any process of deterioration and consequent loss of a solid metallic material through unwanted chemical or electrochemical attack by its environment, starting at its surface is called corrosion. Thus, corrosion is a process "reverse of extraction of metals".

The most familiar example of corrosion is rusting of iron, when exposed to the atmospheric conditions. During this, a layer of reddish scale of hydrated ferric oxide is formed on the surface of iron.

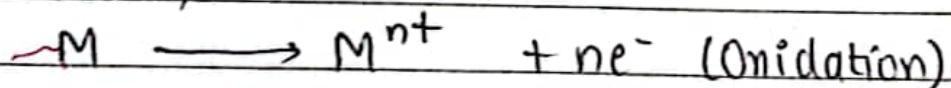
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Mechanism of electrochemical corrosion or wet corrosion:

It takes place mostly under wet or moist conditions through the formation of short circuited galvanic cells. Wet corrosion is more common than dry corrosion. Electrochemical corrosion occurs only on heterogeneous metal surface.

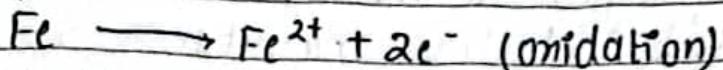
At anode,



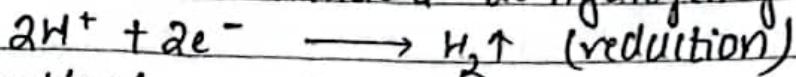
On the other hand, cathodic reaction consumes electrons either by the evolution of hydrogen or by the absorption of oxygen, depending on the nature of the corrosive environment.

a) Evolution of hydrogen type corrosion occur in acidic environment, considering the metal like iron.

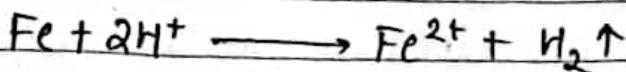
At anode,



These electrons flow from anode to cathode where H^+ ions of acidic solution are eliminated as hydrogen gas.

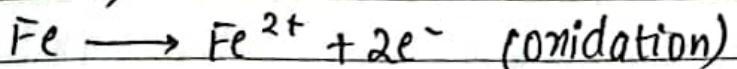


Overall reaction:

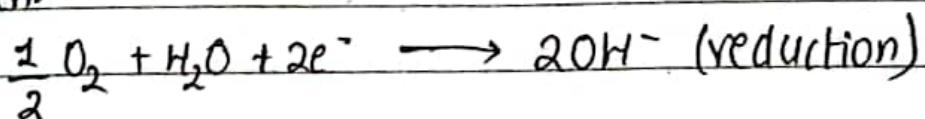


b) Rusting of iron in neutral aqueous soln of electrolyte in the presence of atmospheric oxygen is a common example of absorption of oxygen type corrosion.

At anode,



The liberated electron flow from anodic to cathodic area through iron metals where electrons are intercepted by the dissolved oxygen.

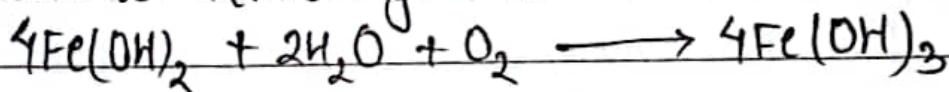


When Fe^{2+} ions at anode and OH^- ions at cathode, diffuse, they meet and Ferrous Hydroxide $\{\text{Fe}(\text{OH})_2\}$ is precipitated.



Ferrous hydroxide

If the enough oxygen is present, ferrous hydroxide is easily oxidised to Ferric hydroxide.



This product is yellow rust and actually corresponds to
 $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$

If the supply of oxygen is limited, the corrosion product maybe even black anhydrous magnetite, Fe_3O_4 .

(cap) # corrosion control methods or protection against corrosion

1) By coating the metal with more active metal like zinc i.e Galvanization of steel with zinc

2) By connecting a metal directly to sacrificial anode

3) By applying a protective coating of paint or enamel on the surface of metal.

4) Use of corrosion inhibitors also help to control corrosion.

For e.g. Iron can be treated with certain solution like potassium chromate, phosphoric acid etc. which inhibit corrosion.

5) Impurities in a metal cause heterogeneity which decreases corrosion resistance of ~~the~~ metal. Thus, the corrosion resistance of a given metal maybe improved by increasing its purity

- Q) Define corrosion. write the mechanism of electrochemical corrosion and mention corrosion control method. (7 marks)
- Q) Write short note on corrosion. (5 marks)

ELECTROCHEMICAL CELLS

It is an assembly of two metallic electrodes dipping into the solution of the same or different electrolytes which is capable of converting either electrical energy into chemical energy or chemical energy into electrical energy.

Electrochemical cells are of two types:

- a) Electrolytic cell
- b) Galvanic cell

a) Electrolytic cell

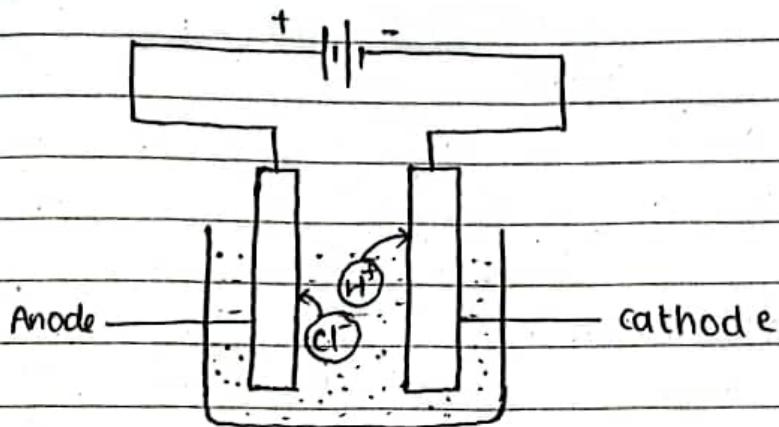


Fig. Electrolysis of an aqueous solution of HCl

An electrolytic cell is a device in which the external supply of electrical energy is necessary in order to bring about the physical or chemical change in the cell.

For example: Electrolysis of an aqueous soln of HCl into H_2 & Cl_2

The electrode which is connected to positive terminal of the battery is called anode and the electrode connected to negative terminal of battery is known as cathode.

Applications: electroplating, electrorefining, electrowinning

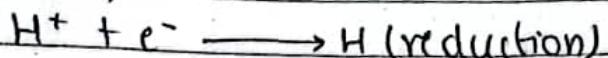
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When the electric current is supplied, dissociation of electrolyte takes place. As a result, cation moves towards cathode and gets reduced, whereas anion moves towards anode and gets oxidised.

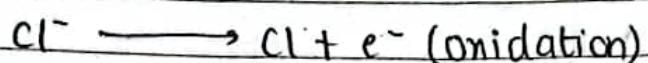
In aqueous soln, HCl ionizes as



At cathode,



At anode,



Overall redox reaction is,



b) Galvanic cell (Voltaic cell)

The devices in which the electrical energy is produced from chemical reactions are called galvanic cell or voltaic cells

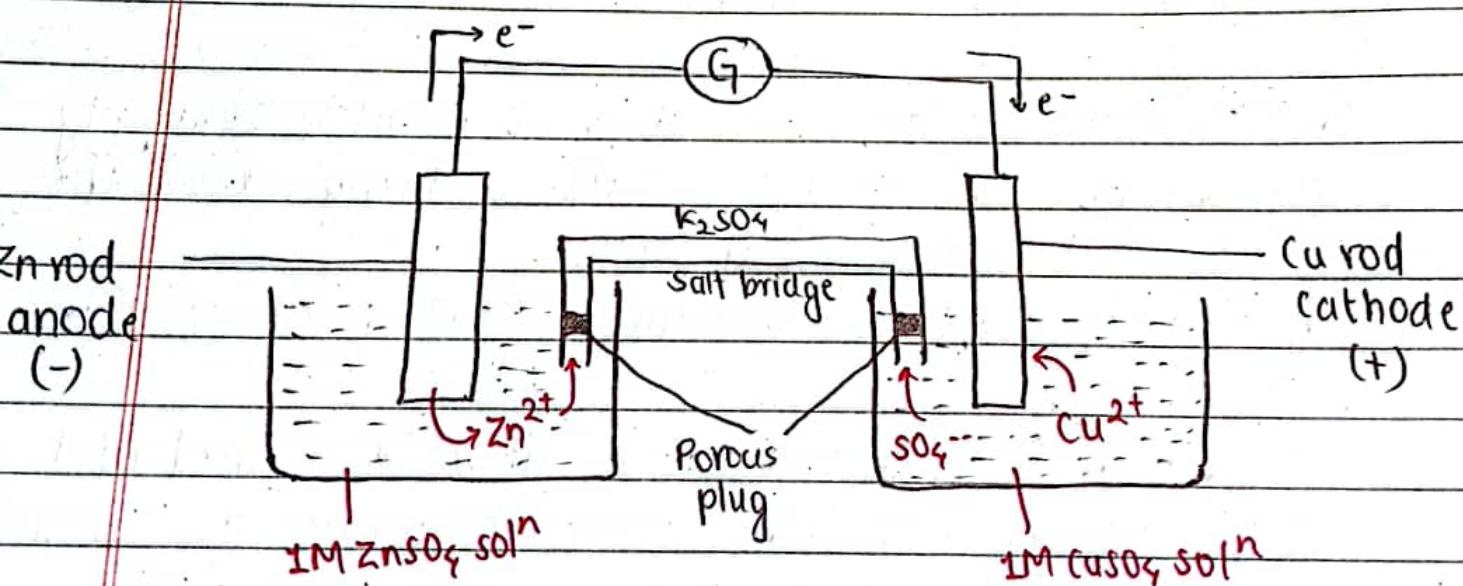
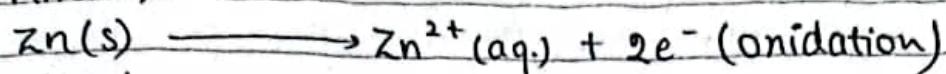
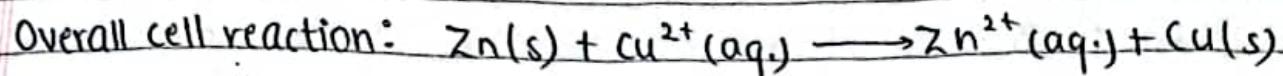
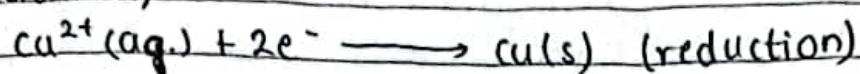


Fig. A simple galvanic or Voltaic cell (Daniell's cell)

At Anode,



At cathode,



A Daniell's cell is a practical galvanic cell. A Daniell's cell can be setup easily by taking two beakers, one of which contains a zinc rod placed in 1M ZnSO_4 solution and the other contains a copper rod placed in 1M CuSO_4 solution. The metallic rods in two beakers are connected to a galvanometer by means of an insulated wire. The solutions in the two beakers are connected by an inverted U-tube known as salt bridge. Salt bridge consists an electrolyte such as KCl , KNO_3 , K_2SO_4 or NH_4NO_3 which doesn't undergo a chemical change during the process. Gelatin or agar-agar is used to make semi-solid mass.

Functions of salt bridge

1. Salt bridge avoids or minimizes the liquid-liquid junction potential.
2. Salt bridge helps to complete the internal circuit of galvanic cell.
3. Salt bridge maintains electrical neutrality without direct mixing of electrolyte solution.
4. Salt bridge avoids the crowding of ions around electrodes.

- In this cell, following observations are made:
1. Zinc rod gradually loses its weight as it gets oxidised and the concentration of Zn^{2+} ions in solution increases.
 2. Cu^{2+} ions of copper sulphate solution get reduced and copper metal gets deposited on copper electrode.
 3. There is a flow of electrons in the external circuit from zinc rod to copper rod.

As the electrons move from zinc rod to the copper rod, zinc rod is regarded as the negative terminal while the copper rod is regarded as the positive terminal.

Applications of Daniell cell

Daniell cells are used to generate electricity or to store electric energy. Daniell cells are used in battery development and electrical telegraphy.

5 marks

(Q) Differentiate bet'n Electrolytic cell & Daniell cell

Electrolytic

1. In Electrolytic cell, chemical reaction is carried out by passing electric current.

2. Anode is positive part of the cell and cathode is negative part of the cell.

Galvanic

1. In Galvanic cell, electric current is produced due to chemical energy.

2. Anode is negative part of the cell and cathode is positive part of the cell.

3. There is no salt bridge.

3. The two electrolytic solution are connected by a salt bridge.

4. The redox reaction occurring at the electrodes are non-spontaneous, and takes place only when electrical energy is supplied.

4. The redox reaction occurring at the electrodes are spontaneous.

5. Electrolytic cell cannot be represented by cell notation.

5. Galvanic cell can be represented by cell notation.

Q) What are the criteria of the electrolytes to be used in the salt bridge?

→ There are following criteria for the electrolytes to be used in the salt bridge.

1. The electrolytes used in the salt bridge should be inert i.e they do not undergo a chemical change during the process.

2. Only those electrolytes for which cations and anions have nearly same ionic mobilities are used as electrolytes in the salt bridge. Thus, KCl , KNO_3 , K_2SO_4 or NH_4NO_3 are preferred as electrolytes in the salt bridge.

Q) Write applications of electrolytic cells & galvanic cells.



Applications of electrolytic cells:

1. It is used for electroplating.

2. It is used for the purification of copper.

3. It is used for the manufacture of caustic soda by Solvay-Kellner process.
4. It is used in electrorefining, electrotyping and electrowinning of several non-ferrous metals.

Applications of galvanic cell:

1. Galvanic cells are used for the generation of portable electrical energy.
2. Galvanic cells are used for the generation of primary and secondary cells.
3. Galvanic cells are used for the construction of fuel cells.

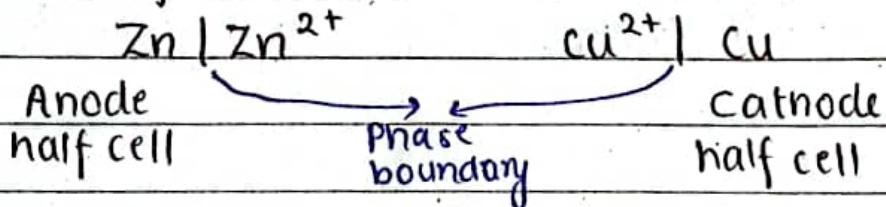
Cell notation or

Symbolic Representation of galvanic cell

short note
5 marks

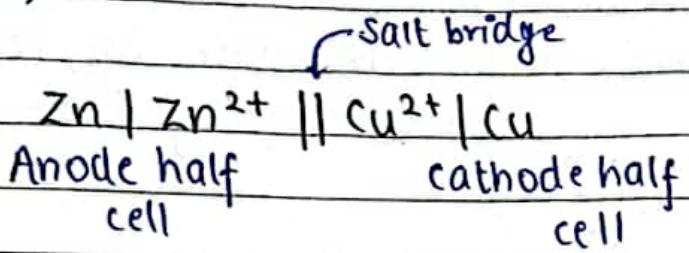
In 1953, IUPAC recommended the following conventions for writing cell diagrams.

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

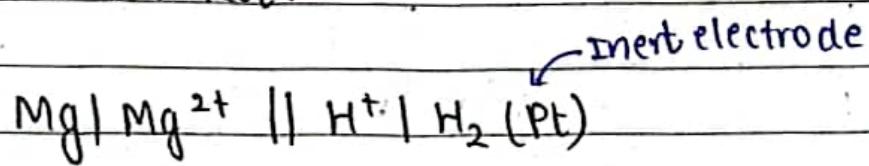


It may be noted that the metal electrode in anode half cell is on the left, while in cathode half cell, it is on the right of the metal ion.

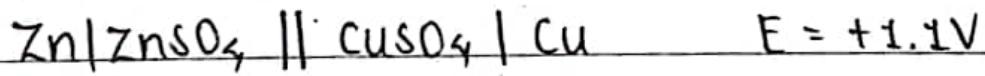
2. A double vertical line represents the salt bridge, porous partition or any other means of permitting ion flow while preventing the electrolyte from mixing.
3. Anode half cell is written on the left and cathode half cell on the right.
4. In the complete cell diagram, the two half cells are separated by a double vertical line. The zinc-copper cell can now be written as,



5. The symbol for an inert electrode like platinum is often enclosed in a bracket.



6. The value of emf of a cell is written on the right of the cell diagram notation.



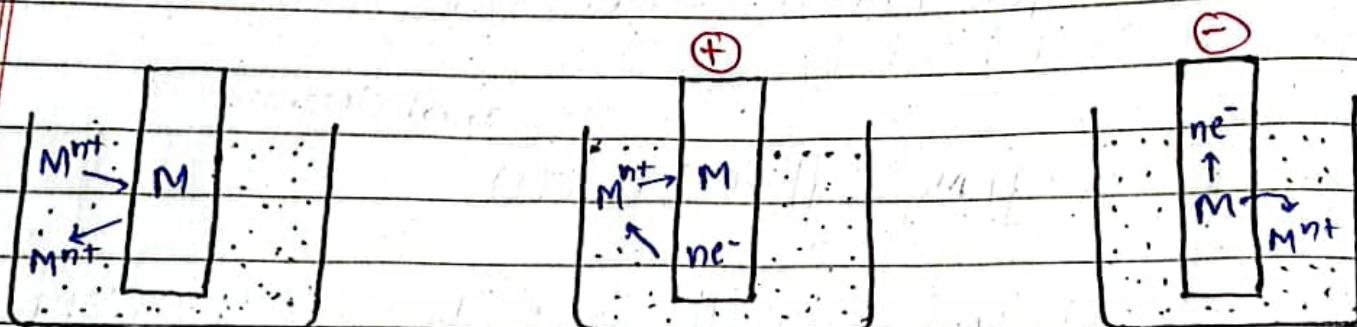
(4 marks)

† Single Electrode Potential

The potential of a single electrode in a half cell is called single electrode potential.

When the electrode is dipped into electrolyte solution of its soluble salt. Then, either the metal atom loses electrons and positive ions dive into the electrolyte solution or the ions of electrolyte accept electrons and deposit on the electrode. During this process, there is separation of charge on the electrode and electrolyte interface. Potential difference exists in this double layer of charge.

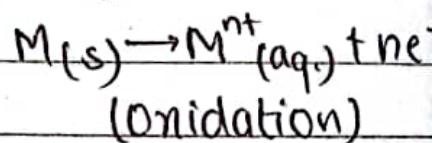
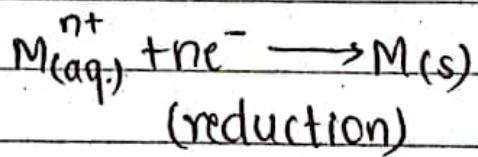
Thus, electrode potential is a measure of tendency of an electrode in a half cell to gain or lose electrons.



a) No charge on
electrode

b) Positive charge
on electrode

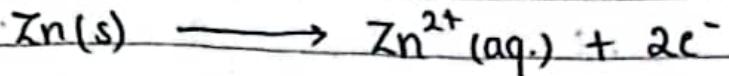
c) Negative charge
on electrode



Types of Electrode Potential

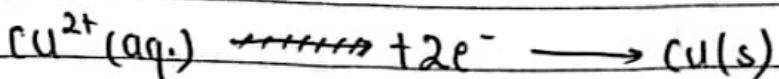
a) Oxidation Potential

The tendency of an electrode to lose electrons or to get oxidised is called oxidation potential.



b) Reduction Potential

The tendency of an electrode to gain electrons or to get reduced is called reduction potential.



Emf of cell or cell potential

It is defined as the force which causes flow of electrons from one electrode to another and thus results in the flow of current.

Mathematically,

$$\begin{aligned} E_{\text{cell}} &= E_{\text{red}}(\text{cathode}) - E_{\text{red}}(\text{anode}) \\ &= E_{\text{red}}(\text{Right}) - E_{\text{red}}(\text{Left}) \end{aligned}$$

Standard Hydrogen Electrode (SHE) or Normal Hydrogen Electrode (NHE)

It is a reference electrode whose potential is arbitrarily taken as zero and the electrode potential of other electrode is determined with respect to it.

It consists of a platinum wire shield in a glass tube and has a platinum foil attached to it. The foil is coated with finely divided platinum black which helps in the adsorption of hydrogen gas on the electrode. The platinum foil is dipped into an acid solution containing H^+ ions in 1M concentration. Pure hydrogen gas at 1 atm. pressure is constantly bubbled into solution at constant temperature of 25°C. The surface of coil acts as a site of reaction.

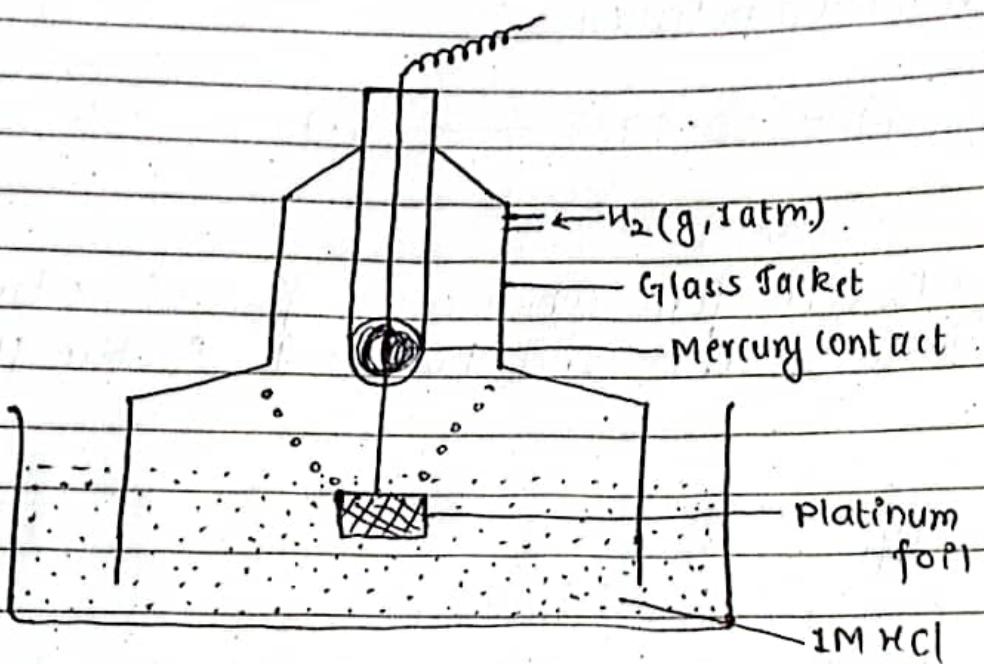
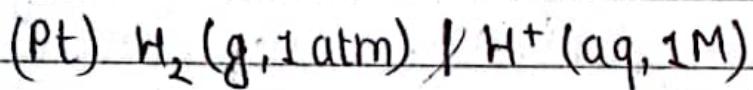
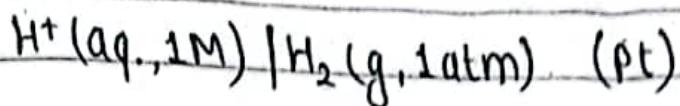


Fig. Standard Hydrogen Electrode
(SHE)

If the combination of SHE is anode, then the following half cell notation is given:



If the combination of SHE is cathode, then the following half cell notation is given,



Q) Define standard electrode potential.

→ Standard Electrode potential is the electrode potential of an electrode under standard conditions (25°C , 1M concn of ions) with reference to standard hydrogen electrode, whose electrode potential is taken is zero. It is denoted by E° .

Measurement of single electrode potential of zinc Electrode:

For the measurement of standard single electrode potential of zinc electrode, we have to make a complete galvanic cell with SHE at standard conditions. In this combination, zinc electrode becomes anode and SHE acts as cathode. If we make a combination as shown in the diagram, then the voltmeter reading is 0.76V .

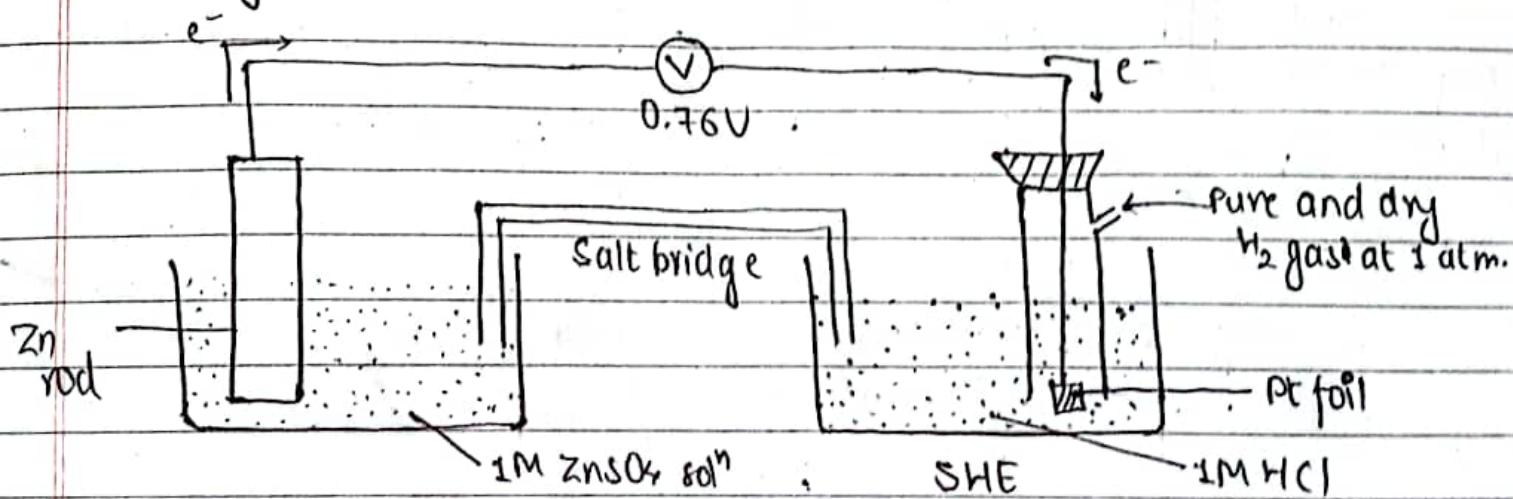


Fig. Measurement of single electrode potential of zinc electrode

We have,

$$E_{\text{cell}}^{\circ} = E_{\text{red}}^{\circ}(\text{cathode}) - E_{\text{red}}^{\circ}(\text{anode})$$

$$\text{Or}, 0.76 \text{V} = 0 - E_{\text{red}}^{\circ}(\text{anode})$$

$$\therefore E_{\text{red}}^{\circ}(\text{anode}) = -0.76 \text{V}$$

Hence, the standard reduction potential of Zn = -0.76 V

In other words,

the standard oxidation potential of Zn = +0.76 V

Measurement of single electrode potential of Cu electrode

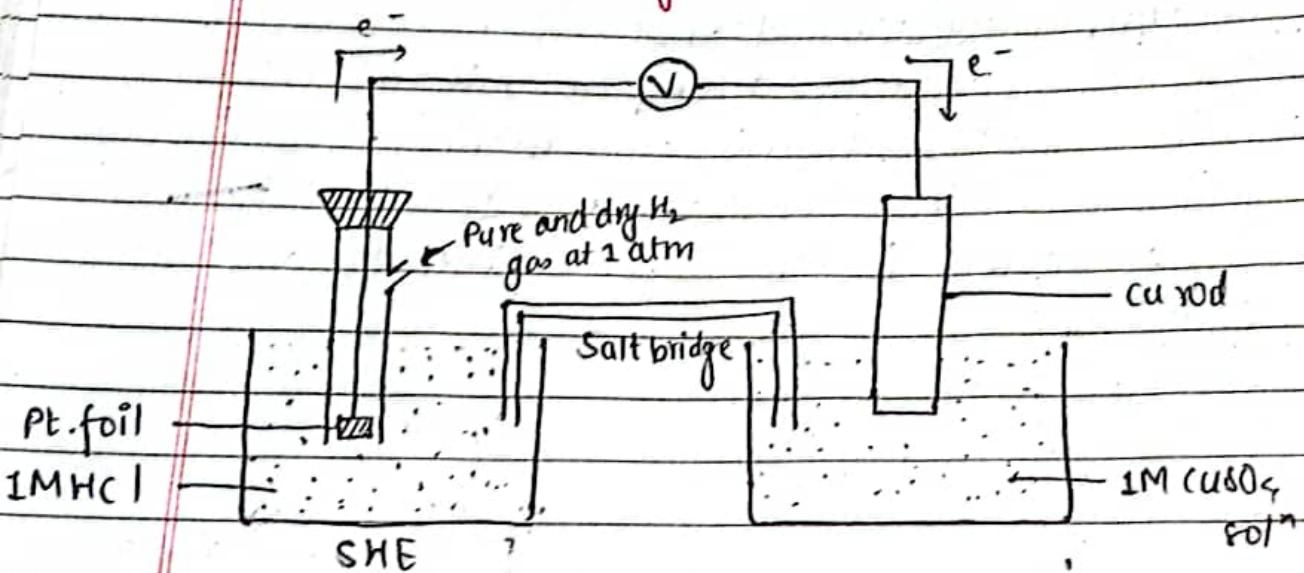


Fig. Measurement of single electrode potential
of Cu electrode

For the measurement of standard single electrode potential of Cu electrode, we have to make a complete galvanic cell with SHE at standard condition.

In this combination, SHE becomes anode and Cu electrode becomes cathode, if we make a combination as shown in the diagram, then the voltmeter reading is 0.34V.

We have,

$$\begin{aligned} E_{\text{cell}}^{\circ} &= E_{\text{red(cathode)}}^{\circ} - E_{\text{red(anode)}}^{\circ} \\ \text{or, } 0.34\text{V} &= E_{\text{red(cathode)}}^{\circ} - 0 \\ \therefore E_{\text{red(cathode)}}^{\circ} &= 0.34\text{V} \end{aligned}$$

Hence, the standard reduction potential of Cu = +0.34V

In other words, the standard oxidation potential of Cu = -0.34V

Measurement of single electrode potential of Ag electrode

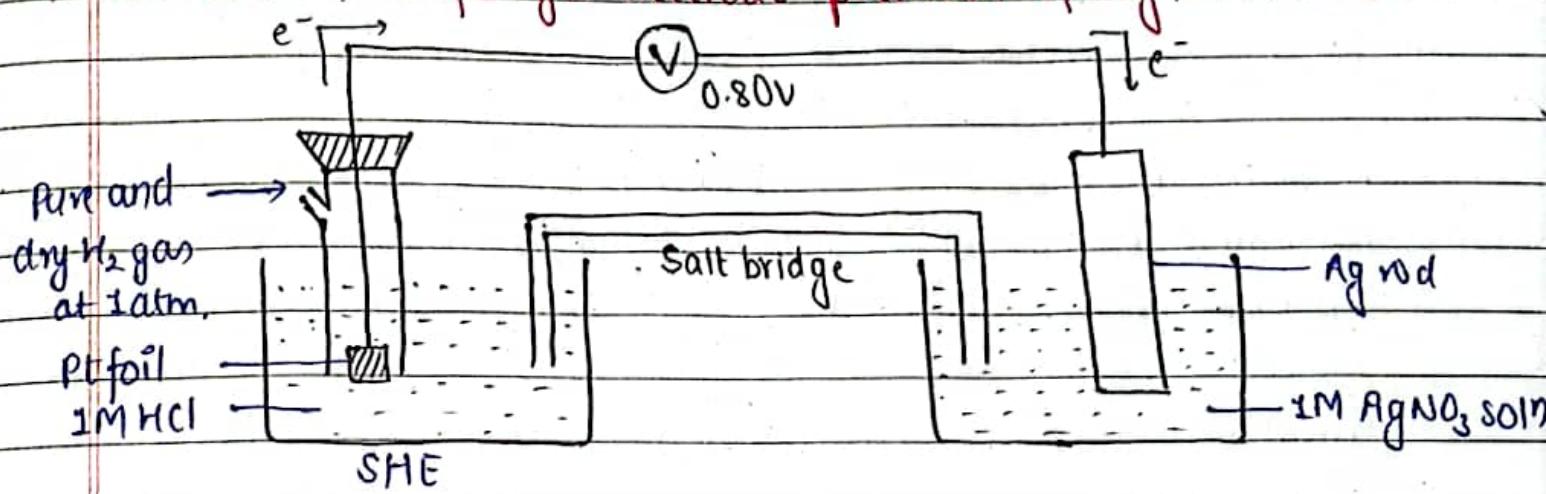


Fig. Measurement of single electrode potential of Ag electrode

For the measurement of standard single electrode potential of Ag electrode, we have to make a complete galvanic cell with SHE at standard condition.

In this combination, SHE becomes anode and Ag electrode becomes cathode. If we make a combination as shown in diagram, then the voltmeter reading is 0.80V.

We have,

$$\begin{aligned} E^\circ_{\text{cell}} &= E^\circ_{\text{red(cathode)}} - E^\circ_{\text{red(anode)}} \\ \text{or, } 0.80\text{V} &= E^\circ_{\text{red(cathode)}} - 0 \\ \therefore E^\circ_{\text{red(cathode)}} &= 0.80\text{V} \end{aligned}$$

Hence, the standard reduction potential of Ag = +0.80V

In other words, the standard oxidation potential of Ag = -0.80V

Electrochemical Series

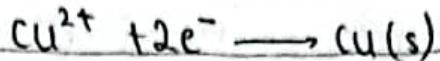
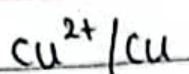
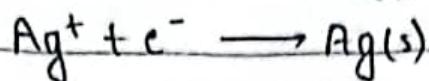
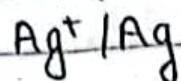
A series in which the standard electrode potential (reduction) of various electrodes have been arranged in the increasing order (downwards) is called electrochemical series.

The standard electrode potential of Hydrogen-electrode is zero.

The electrodes above hydrogen have negative reduction potential while those placed below it have positive reduction potential.

Electrode	Electrode reaction	standard reduction potential in volts
Li^+/Li	$\text{Li}^+ + \text{e}^- \rightarrow \text{Li(s)}$	-3.04
Zn^{2+}/Zn	$\text{Zn}^{2+} + 2\text{e}^- \rightarrow \text{Zn(s)}$	-0.76
$2\text{H}^+/\text{H}_2(\text{Pt})$	$2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2(\text{g, 1 atm.})$	+0.00

↑ Increasing tendency for oxidation

 $+0.34$  $+0.80$

Increasing
tendency for
reduction

Applications of Electrochemical series

1) Prediction of Anode and cathode

An electrode with higher oxidation potential (lower reduction potential) is called anode.

The electrode with lower oxidation potential (higher reduction potential) is called cathode.

2) Displacement of one species by another

The metals with more negative reduction potentials can displace those with lesser negative or positive reduction potential from their solutions.

For e.g.

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

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

When zinc metal is dipped into CuSO_4 solution, copper will be displaced by zinc.



3) Calculation of standard emf of the cell

we have,

$$E^\circ_{\text{cell}} = E^\circ_{\text{red(cathode)}} - E^\circ_{\text{red(anode)}}$$

By using above equation, standard emf of the cell can be determined.

4. Determination of the feasibility of cell reaction
since, in a cell reaction,

$$-\Delta G = nFE$$

$$\text{or, } \Delta G = -nFE$$

In standard state,

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

From above equation, following conclusion may be drawn.

- a) If $\Delta G = -ve$, i.e. $E = +ve$, then reaction will be spontaneous.
- b) If $\Delta G = +ve$, i.e. $E = -ve$, then reaction will be non-spontaneous.

5) Prediction of reaction of Metals with acids to liberate hydrogen

The metals like Zn, Fe etc. lying above Hydrogen electrode react with dil. HCl or dil. H_2SO_4 to give hydrogen while metals like Cu, Ag etc. which lie below hydrogen electrode cannot liberate from dil. HCl.

6) Determination of standard free energy change of reaction

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

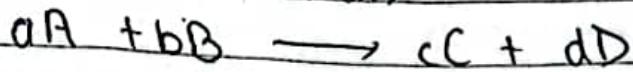
7) Determination of Equilibrium constant of the reaction

$$\Delta G^\circ = -RT \ln K_{eq}$$

NERST EQUATION

In electrochemical cell, the potential of an electrode depends upon the nature of electrolyte, concentration of metal ions and temperature.

consider a redox reaction,



The free energy change in redox reaction at standard condition is given by

$$\Delta G = \Delta G^\circ + RT \ln Q \quad \dots \quad (1)$$

where, ΔG = Free energy change

ΔG° = standard free energy change

R = Universal gas constant

T = Absolute temperature

Q = Ratio of concentration of product and reactants at equilibrium electrode reaction

$$\text{i.e. } Q = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

We have,

$$\Delta G = -nFE$$

At standard conditions

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

Substituting the values of ΔG & ΔG° in eqⁿ (1), we get,

$$-nFE = -nFE^\circ + RT \ln Q$$

$$\text{or, } -nFE = -nFE^\circ + 2.303 RT \log Q$$

Dividing by $-nF$, we get,

$$E = E^\circ - \frac{2.303RT}{nF} \log Q$$

At 25°C ,

$$E = E^\circ - \frac{2.303 \times 8.314 \times (25 + 273)}{n \times 96500} \log Q$$

$$\therefore E = E^\circ - \frac{0.0591}{n} \log Q$$

where, E = Emf of cell at non-standard condition

E° = Emf of cell at standard condition

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

T = Absolute temperature

n = No. of electrons taking part

F = Faraday's constant ($1F = 96500 \text{ coulomb mol}^{-1}$)

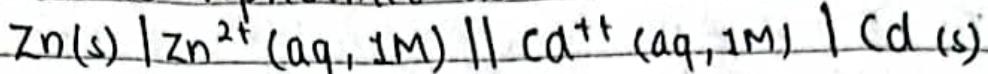
Q = Reaction quotient.

Application of Nernst Equation

1. To calculate the potential of a galvanic cell at non-standard condition
2. To determine the unknown concentration in galvanic cell
3. To calculate the temperature of the system.

Numerical:

1) A galvanic cell is represented as



calculate the standard emf of cell. Given that,

$$E^\circ_{\text{Zn}^{2+}/\text{Zn}} = -0.76\text{V} \quad \text{and} \quad E^\circ_{\text{Cd}^{2+}/\text{Cd}} = -0.40\text{V}$$

Also, predict the spontaneity of the reaction.

Soln:

It is clear from the cell representation that zinc electrode acts as anode and cadmium electrode (cd) acts as cathode.

We have,

$$\begin{aligned} E^\circ_{\text{cell}} &= E^\circ_{\text{red(cathode)}} - E^\circ_{\text{red(anode)}} \\ &= [-0.40 - (-0.76)] \\ &= +0.36\text{V} \end{aligned}$$

since the standard emf of cell is positive, the reaction is spontaneous.

2) calculate the standard emf of cell.

Given that, $E^\circ_{\text{Zn}/\text{Zn}^{2+}} = +0.76\text{V}$, $E^\circ_{\text{Ag}/\text{Ag}^+} = -0.80\text{V}$

Soln: Here, $E^\circ_{\text{Zn}/\text{Zn}^{2+}} = +0.76\text{V}$

so, $E^\circ_{\text{Zn}^{2+}/\text{Zn}} = -0.76\text{V}$

Similarly, $E^\circ_{\text{Ag}/\text{Ag}^+} = -0.80\text{V}$

so, $E^\circ_{\text{Ag}^+/\text{Ag}} = +0.80\text{V}$

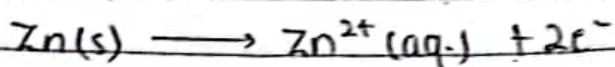
We have, $E^\circ_{\text{cell}} = E^\circ_{\text{red(cathode)}} - E^\circ_{\text{red(anode)}}$
 $= 0.80 - (-0.76)$
 $= +1.56\text{V}$,

3) A galvanic cell consists of two electrodes zinc and lead. Zinc electrode is immersed in 0.1M zinc ion solution and lead electrode in 0.02M lead ion solution. Calculate the emf of cell at 298K write the equations of electrode process and represent cell schematically.
 Given that, $E^\circ_{Zn^{2+}/Zn} = -0.76V$ and $E^\circ_{Pb^{2+}/Pb} = -0.13V$.

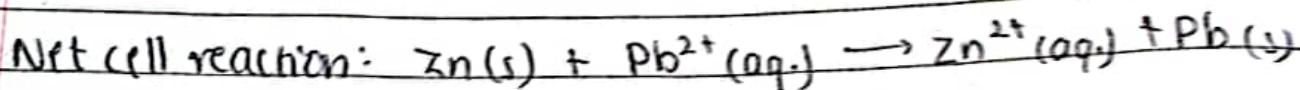
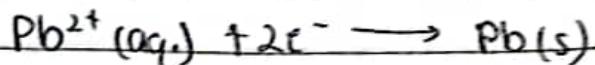
sol?

Here, Zinc electrode acts as anode and lead electrode acts as cathode.

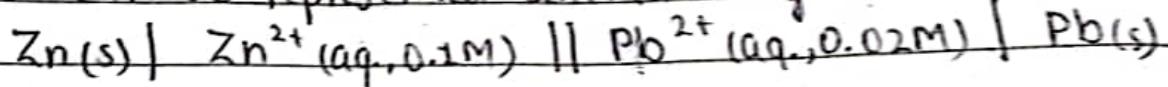
At anode,



At cathode,



The cell can be represented schematically as,



We have,

$$\begin{aligned} E^\circ_{cell} &= E^\circ_{red(cathode)} - E^\circ_{red(anode)} \\ &= -0.13 - (-0.76) \\ &= +0.63V \end{aligned}$$

Using Nernst equation at 298K,

$$E = E^\circ - \frac{0.0591}{\eta} \log Q$$

$$= 0.63 - \frac{0.0591}{2} \log \frac{[Zn^{2+}][Pb]}{[Zn]^2[Pb^{2+}]}$$

$$= 0.63 - \frac{0.0591}{2} \log \frac{0.1 \times 1}{1 \times 0.02}$$

$$= 0.609 \text{ V}_{\text{Am}}$$

Q) calculate the emf of cell at 30°C when the given electrodes are coupled together.

$$E^\circ_{\text{Ni}|\text{Ni}^{2+}} = 0.25 \text{ V}, E^\circ_{\text{Cd}|\text{Cd}^{2+}} = 0.40 \text{ V}$$

$$R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}, [\text{Ni}^{2+}] = 0.01 \text{ M}, [\text{Cd}^{2+}] = 0.1 \text{ M}$$

Soln

$$\text{Here, } E^\circ_{\text{Ni}|\text{Ni}^{2+}} = 0.25 \text{ V}$$

$$\text{So, } E^\circ_{\text{Ni}^{2+}|\text{Ni}} = -0.25 \text{ V}$$

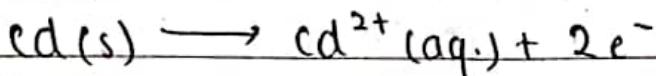
$$\text{Now, } E^\circ_{\text{Cd}|\text{Cd}^{2+}} = 0.40 \text{ V}$$

$$\text{So, } E^\circ_{\text{Cd}^{2+}|\text{Cd}} = -0.40 \text{ V}$$

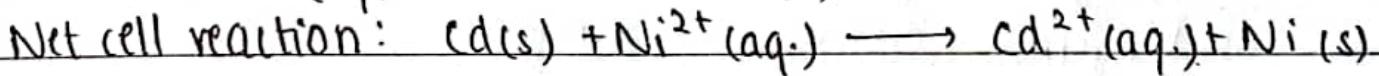
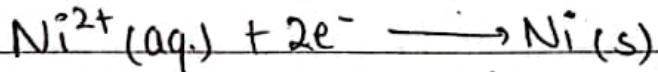
$$\text{We have, } E^\circ_{\text{cell}} = E^\circ_{\text{red cath}} - E^\circ_{\text{red anode}}$$

As seen from the reduction potential, Cd acts as anode and Ni acts as cathode.

At anode,



At cathode,



We have,

$$E^\circ = RY + \frac{RT}{4F}$$

$$E^\circ_{\text{cell}} = E^\circ_{\text{red (cathode)}} - E^\circ_{\text{red (anode)}}$$

$$= -0.25 - (-0.40)$$

$$= +0.15 \text{ V}$$

We have,

$$E = E^\circ - \frac{2.303 RT}{nF} \log Q$$

$$= 0.15 - \frac{2.303 \times 8.314 \times 303}{2 \times 96500} \log \frac{[Cd^{2+}][Ni]}{[Cd][Ni^{2+}]}$$

$$= 0.15 - \frac{2.303 \times 8.314 \times 303}{2 \times 96500} \log \frac{0.1 \times 1}{1 \times 0.01}$$

$$= 0.119 V$$

- (Q) From the following data at 35°C, write electrode reaction, cell reaction, emf of cell, cell notation and also predict the spontaneity of the rxn.

Given,

$$E^\circ_{Fe/Fe^{2+}} = 0.44 V$$

$$E^\circ_{Ag|Ag^+} = -0.80 V$$

$$[Fe^{2+}] = 0.5 M$$

$$[Ag^+] = 0.2 M$$

$$\text{Hence, } E^\circ_{Fe/Fe^{2+}} = 0.44 V$$

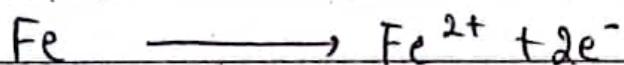
$$\text{So, } E^\circ_{Fe^{2+}/Fe} = -0.44 V \quad (\text{Anode})$$

$$E^\circ_{Ag|Ag^+} = -0.80 V$$

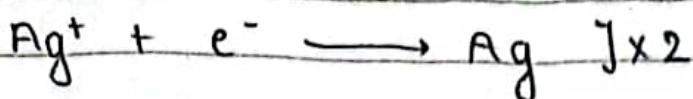
$$\text{So, } E^\circ_{Ag^+/Ag} = 0.80 V \quad (\text{cathode})$$

So, Fe acts as anode & Ag acts as cathode.

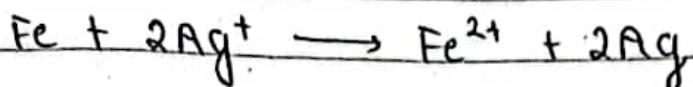
At anode,



At cathode,



Net cell rxn:

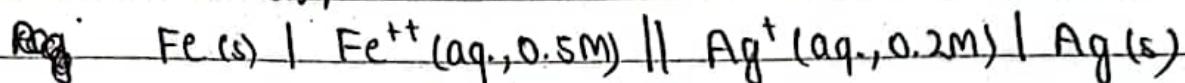


Here,

$$\begin{aligned} E^\circ_{\text{cell}} &= E^\circ_{\text{red(cathode)}} - E^\circ_{\text{red(anode)}} \\ &= 0.80 - (-0.44) \\ &= 1.24 \text{ V} \end{aligned}$$

Since, the standard emf of cell is positive, the rxn is spontaneous.

The cell notation is as,



The emf of cell at 35°C is,

$$\begin{aligned} E &= E^\circ - \frac{RT \times 2.303}{nF} \log \frac{[\text{Fe}^{2+}][\text{Ag}]^2}{[\text{Fe}][\text{Ag}^+]^2} \\ &= 1.24 - \frac{2.303 \times 8.314 \times 308}{2 \times 96500} \log \left(\frac{0.5 \times 1^2}{1 \times 0.2^2} \right) \\ &= 1.24 - 0.0335 \\ &= 1.206 \text{ V} \end{aligned}$$

Q) calculate the Emf of cell at 27°C

Zn

Batteries

One of the main uses of galvanic cells is the generation of portable electrical energy. The term battery is generally used for two or more galvanic cells connected in series. Thus, a battery is an arrangement of electrochemical cells used as an energy source.

Classification of Batteries

1) Primary cells

In these cells, the electrode rxn cannot be reversed by an external energy. In these cells, rxn occurs only once and after use they become dead. Therefore, they are not rechargeable. Some common examples are dry cells, memory cells etc.

- Dry cells are used in toys, flashlight, radio etc.
- ~~Button~~ cells are used in electronic watches, calculators etc.

Leclanche dry cell:

It consists of zinc cylinder which acts as an anode. Zinc cylinder is filled with a paste of NH_4Cl and litter of zinc chloride (ZnCl_2), in the form of paste in water which acts as electrolyte. The cathode is graphite rod (carbon). The carbon rod is surrounded by a black paste of MnO_2 and carbon powder. A porous paper separates the electrolyte and zinc container.

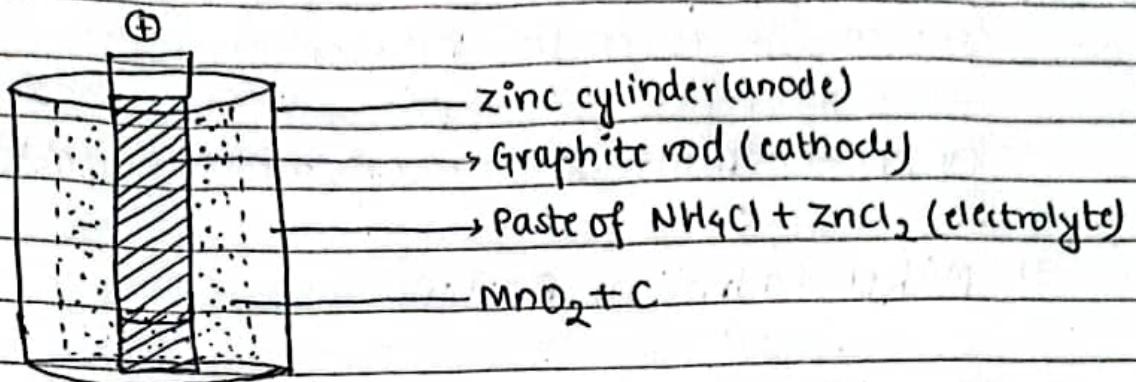
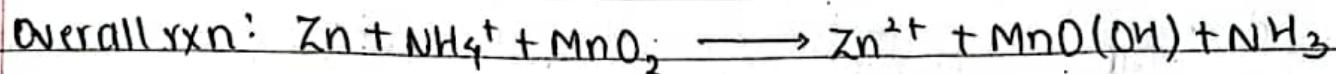
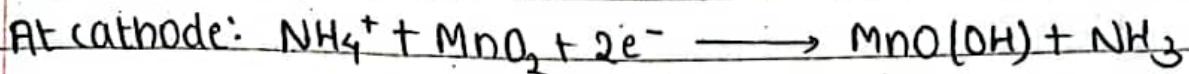
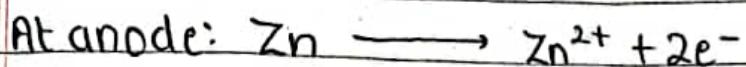
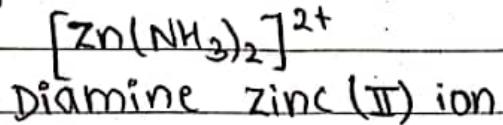


Fig. Dry cell



Here, Ammonia is not liberated as a gas, but combines with sum of the Zn^{2+} produced from Anode to form complex ion having formula.



It gives voltage of approximately 1.2 to 1.5V.

2) Secondary Cells

In the secondary cells, the reaction can be reversed by an external electric source.

Therefore, these cells can be recharged by passing electric current and used again and again.

These cells are also called storage cells.

For an example: Lead storage batteries are used in automobile
i.e. cars, buses, motorbike etc.

Nickel - cadmium batteries are used in portable electronic equipment

Nickel - cadmium Batteries :

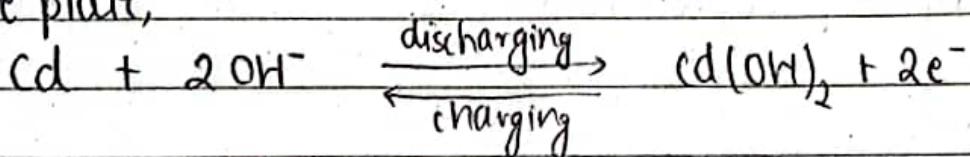
The Nickel cadmium battery is a type of rechargeable battery.
It has high power and energy density. It has also high efficiency of charge and discharge.

construction:

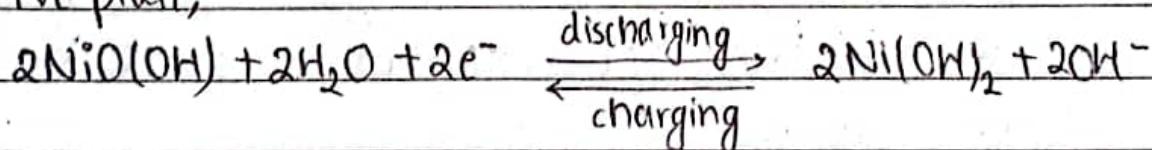
- Cd is used as negative electrode plate (anode)
- Nickel ^(III) oxide ^{hydroxide} is used as positive electrode (cathode)
- A separator soaked in moist NaOH / KOH
- An alkaline electrolyte potassium hydroxide (KOH)

Working:

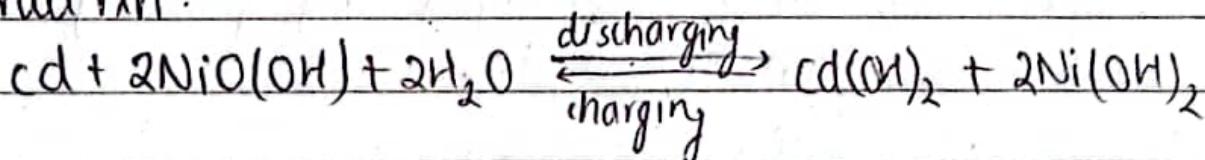
At -ve plate,



At +ve plate,



Overall rxn :



- The nickel cadmium battery has nominal voltage of 1.2V /cell.
- The primary demerit of Nickel -cadmium batteries is a relatively high cost because the manufacturing process is expensive.
- Cadmium is toxic.
- Ni-Cd batteries also suffer from "memory effect" where batteries only take a full charge after series of full discharges.

Uses:

1. Portable Computers
2. Drills
3. Camcorders (video recording device) & other small battery operated devices

Reserve Batteries

Reserve Battery, also called stand-by battery is a battery where a key component is isolated until the battery needs to be used.

When long storage is required, reserved battery are often used. Since the active chemicals of the cell are segregated until needed, thus reducing self discharge.

Most reserved battery are used only once and then discarded. These batteries are used primarily to deliver high power for relatively short period of time.

Reserve Batteries may be activated by the addition of water, by adding electrolyte, by introducing gas or by heating a solid electrolyte to a temperature at which it becomes conductive.

In missiles, reserve batteries typically use a small container of pressurized air to force the electrolyte from a storage tank into the battery.

Types Of Reserve Batteries:

Some Reserve Batteries are:

a) Aluminium battery, a variant of zinc-air battery where aluminium and air are used

b) Silver-zinc Battery, ~~where~~ often found in old missiles.

c) Thermal Battery, a class of battery in which the battery is in an inert state until the electrolyte melts through heating. This type of battery is common in military applications.

d) Water-activated battery

A class of battery where the electrolyte is water that has to be added such as Hydropak or NoPoPo.

Uses of Reserve Batteries

These batteries are often used in missile, projectiles, radiosondes, bomb fuzes and various weapon systems.

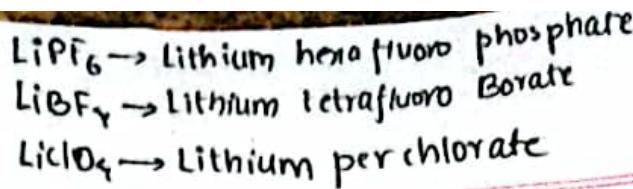
long your
imp.

Q) Write construction, working and applications of lithium-ion battery.

Construction:

A lithium-ion battery is a type of rechargeable battery that uses reversible reductions of lithium ions to store energy.

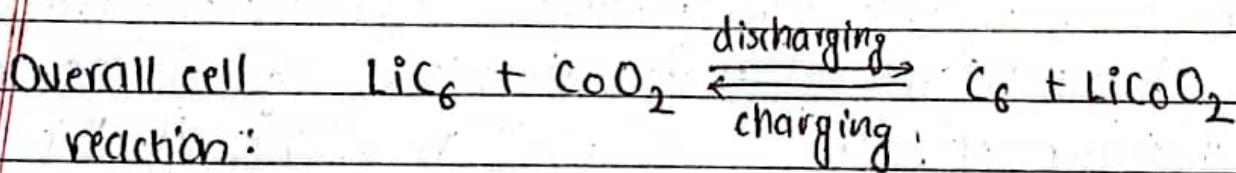
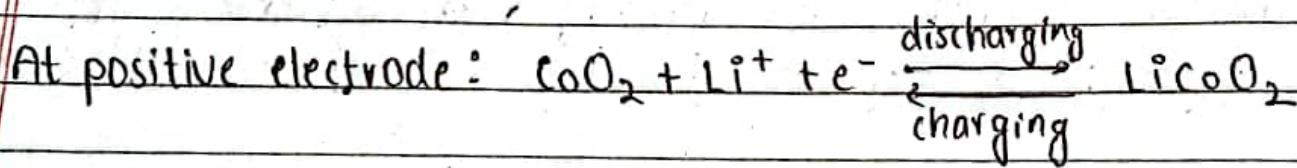
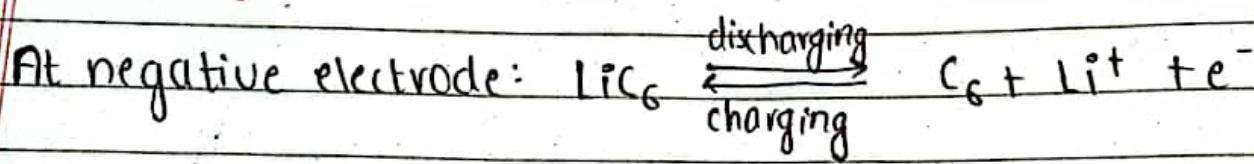
Compared to other rechargeable battery technologies, lithium-ion batteries have high energy densities, low self-discharge and no memory effect (although a small memory effect is reported in poorly made cells).



Date _____
Page _____

- The anode (-ve electrode) of a conventional lithium ion cell is typically graphite made from carbon, which in its fully lithiated state correlates to maximum capacity.
- The cathode (+ve electrode) is lithiated form of a transition metal oxide i.e. LiCoO_2 or LiMn_2O_4
- The electrolyte is Lithium salts such as LiPF_6 , LiBF_4 or LiClO_4 in an organic solvent.
- The separator is generally made of polypropylene (PP), polyethylene (PE) or a laminate of PP and PE.

Working:



The nominal voltage of lithium ion battery is 3.6V/cell.

Uses:

- 1) Used in portable devices such as mobile phones, smart phones, laptops and tablets, digital cameras, camcorders, electronic cigarettes, etc.
 - 2) They are used in power tools such as cordless drills, saws, etc.
 - 3) Used in electric cars, electric motorcycles, electric scooters, electric bicycles, advanced wheelchairs etc.
 - 4) They are also frequently discussed as a potential option for grid energy storage.
- Q) Write construction, working and applications of sodium ion battery.

→

The sodium ion battery is a type of rechargeable battery that uses sodium ion (Na^+) as its charge carriers. Its working principle and cell construction are almost identical with those of Li-ion battery types, but replace lithium with sodium.

They are potential alternative to lithium based battery technologies, largely due to sodium's low cost and greater availability. The environmental impact of sodium ion batteries are also lower.

Construction:

* Anode :

sodium-ion batteries use hard carbon that stores sodium ions at a low potential.

* Cathode :

A layered sodium transition metal oxide such as sodium manganese oxide (NaMnO_2) or sodium transition metal phosphate, sodium iron phosphate (NaFePO_4)
such as

* Electrolyte :

sodium ion batteries use aqueous and non-aqueous electrolytes. The most commonly used non-aqueous electrolyte uses sodium hexafluorophosphate (NaPF_6) as the salt dissolved in a mixture of polar aprotic solvents. These include ethylene carbonate, dimethyl carbonate, diethyl carbonate and propylene carbonate.

* Separator

~~B~~ Polypropylene (PP) microporous separators are generally used.

Working :

During charging, sodium ions move from the cathode to the anode while electrons travel through external circuit. During discharging, the process is reversed.

Uses :

- 1) sodium-ion batteries are used in electric vehicles including electric cars and bikes.
- 2) Grid level application (large energy store)
- 3) Na-ion batteries can utilize maximize asset utilization & minimize operating cost, thus increasing industrial mobility.
- 4) Power backup for data and telecom companies.