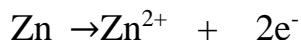


Module II

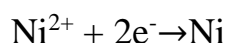
ELECTROCHEMISTRY AND CORROSION

Electronic concept oxidation reduction and redox reactions

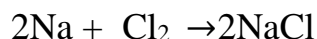
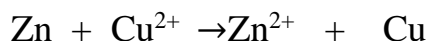
Oxidation: Loss of electrons by any species (ion/ atom)



Reduction: Gain of electrons by any species (ion/ atom)



Redox reaction: The chemical reactions in which the oxidation and reduction reactions occur simultaneously is called **redox reactions**.



i) Classification of materials based on conduction

Conductors

The materials which allow the passage of electricity are called **conductors**.

Eg. Metals (copper, aluminum, gold)

Electrolytes (HCl, NaOH, NaCl)

Insulators

The materials which do not allow the passage of electricity are called **insulators**.

Eg. Rubber, plastic, wood

Semiconductors

The materials having conductivity intermediate between that of conductors and insulators are called **semiconductors**. The conductivity of semiconductors can be increased by doping or by increasing temperature.

Eg. Germanium, Silicon

ii) Types of conductors

<i>Metallic Conductors (Electronic Conductors)</i>	<i>Electrolytic Conductors (Ionic Conductors)</i>
1. Conduction is due to the movement of electrons.	1. Conduction is due to the movement of ions.
2. No chemical change due to conduction.	2. Chemical change due to conduction.
3. No material transfer due to conduction	3. Material transfer due to conduction.
4. Conductance decreases with temperature	4. Conductance increases with temperature.

iii) Electrolytes and Nonelectrolytes

The materials which conduct electricity in molten or dissolved state are called ***electrolytes***.

Eg. HCl, NaOH, KCl

The materials which do not conduct electricity in molten or dissolved state are called ***nonelectrolytes***.

Eg. Urea, sugar

Iv Strong Electrolytes and Weak Electrolytes

The electrolytes which ionize completely in water are called ***strong electrolytes***. They have high conductance.

Eg. HCl, NaOH, NaCl, KCl

The electrolytes which ionize partially in water are called ***weak electrolytes***. They have low conductance.

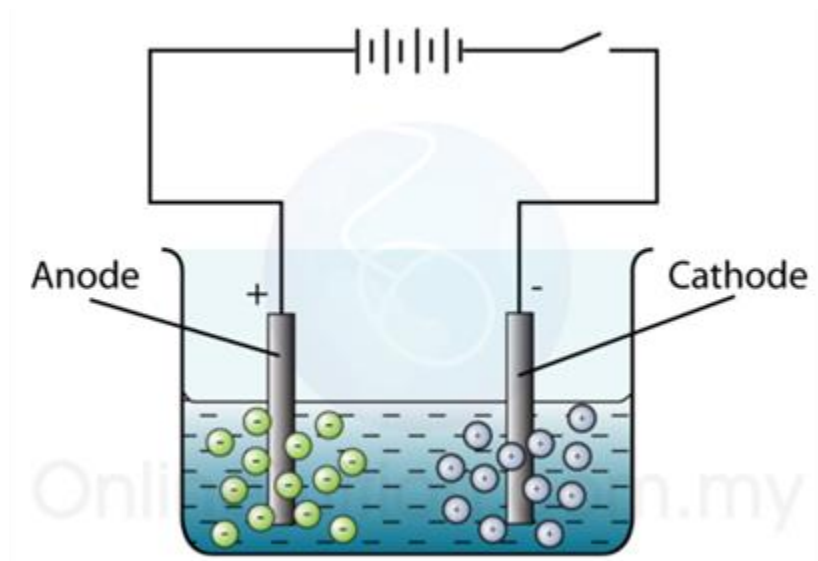
Eg. Acetic acid, oxalic acid, NH_4OH

Electrolysis

The process of decomposition of electrolytes by the passage electricity is called ***electrolysis***.

Electrolytic cell

The device used to carry out electrolysis is called electrolytic cell.



Electrolytic cell consists of two metal electrodes dipped in the electrolyte connected to a battery.

The negative electrode is called cathode. The positive electrode called anode.

The positive ions (Cations) move towards cathode and get reduced.

The negatively charged ions (Anions) move towards anode and get discharged by oxidation.

Reduction: Addition of electrons

Oxidation: Removal of electrons

Faraday's Laws of Electrolysis

Faraday's First Law of Electrolysis

The amount of substance liberated or deposited at the electrode is directly propotional to the quantity of electricity passed through the electrolyte.

That is,

$$W \propto Q$$

W: weight of substance deposited at electrode

Q: Quantity of electricity

$W = ZQ$ Z : a constant called electrochemical equivalent.

$Q = It$ I : Current in amperes; t : time in seconds

$W = ZIt$

When 1C electricity passed through the electrolyte, $W=Z$, Electrochemical equivalent

The mass of substance liberated or deposited at the electrode by the passage of 1C of electricity through the electrolyte is called **Electrochemical Equivalent**.

Faraday's Second Law of Electrolysis

When the same quantity of electricity is passed through solutions of different electrolytes connected in series, the masses of substances deposited at respective electrodes are proportional to their equivalent masses.

$W_A \propto E_A$ $W_B \propto E_B$; $W_A/W_B = E_A/E_B$

W_A : Weight of substance A deposited at electrode

E_A : Equivalent Weight of substance A

W_B : Weight of substance B deposited at electrode

E_B : Equivalent Weight of substance B

Applications of electrolysis

- Electroplating
- Anodizing
- Refining metals like Cu, Ag, Sn etc.
- Extraction of highly reactive metals like Na, K, Ca, Mg etc.
- Manufacture of chemicals like NaOH, Cl_2 , H_2 , O_2 etc.
- Determination of equivalent weight using Faraday's second law.

Electroplating

The process of making a metal coating over another metal by electrolysis is called **Electroplating**.

Purpose of electroplating

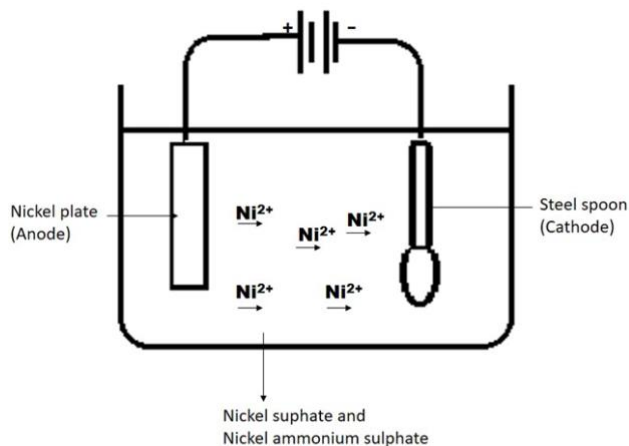
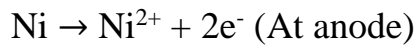
- To protect the highly reactive metal

- To protect the metal from chemical attack
- To improve physical appearance
- To modify hardness
- To repair the damaged parts of machinery
- To obtain conducting surfaces

Electroplating of Nickel on mild steel

In the electrolytic cell a nickel plate is taken as anode and steel as the cathode.

The electrolyte is a solution of nickel sulphate containing some nickel ammonium sulphate. On passing electricity the nickel from anode dissolves and get deposited on the spoon.



Electrolytic refining

Electrolytic refining of copper

Anode: Impure copper

Cathode: pure copper strip

Electrolyte : Acidified copper sulphate solution

Anode reaction : $\text{Cu} \rightarrow \text{Cu}^{2+} + 2\text{e}^-$ (At anode)

Cathode reaction: $\text{Cu}^{2+} + 2\text{e}^- \rightarrow \text{Cu}$ (At cathode)

Pure copper transferred to cathode and impurity deposit as anode mud.

ELECTROCHEMICAL CELL

The device used to convert the chemical energy to electrical energy is called electrochemical cell/galvanic cell or voltaic cell.

In this cell the chemical energy produced during the redox reaction is converted to electrical energy.

It consists of two half cells.

The electrode at which the oxidation takes place is called anode. (Oxidation: release of electrons).

The electrode at which reduction takes place is called cathode. (Reduction: Accepting electrons)

The electrons flow from anode to cathode.

The salt bridge completes the circuit.

Salt Bridge and its significance

A salt bridge is a U-shaped tube containing inert salt like KCl, KNO₃, K₂SO₄ etc in gel form with agar-agar or gelatin.

Functions of Salt Bridge

1. It maintains electrical neutrality of the two solutions.
2. It completes the circuit.
3. It prevents the intermixing of the two solutions.
4. It avoids liquid junction potential between the two solutions.

Daniel cell

Daniel cell is a typical galvanic cell.

In this cell,

Zinc rod dipped in zinc sulphate solution acting as anode.

Copper electrode dipped in copper sulphate solution acting as cathode.

The zinc and copper electrodes are connected by metal wire.

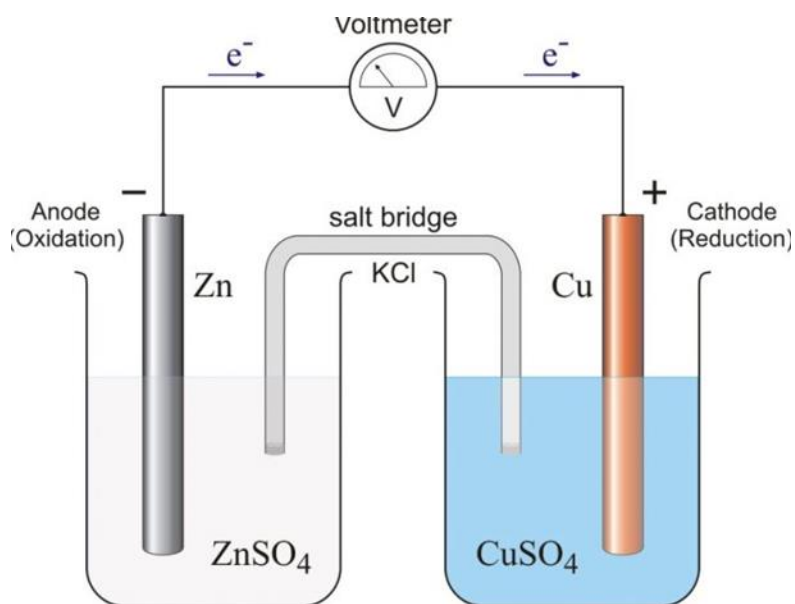
The two half cells are joined by salt bridge.

Reaction taking place are:

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

At cathode: Reduction of copper: $\text{Cu}^{2+} + 2\text{e}^- \rightarrow \text{Cu}$

Net reaction is: $\text{Zn} + \text{Cu}^{2+} \rightarrow \text{Zn}^{2+} + \text{Cu}$



The Zn rod get thinner due to lose of Zn as Zn^{2+} and Cu rod get thicker due deposition of Cu by the reduction of Cu^{2+} ions from CuSO_4 .

Cell representation

Anode metal/ Anode metal ion// cathode metal ion/ cathode metal

$\text{Zn} / \text{Zn}^{2+} // \text{Cu}^{2+} / \text{Cu}$ (Daniel Cell)

Primary Cells

The cell in which the redox reactions are not reversible are called primary cells. These cells are not rechargeable.

Eg: Daniel cell, dry cell, mercury cell

Secondary Cells

The cell in which the redox reactions are reversible are called primary cells. These cells are rechargeable and can be used again and again.

Eg: Lead-storage battery, Nickel- cadmium cell

Fuel Cell

Fuel cells are galvanic cells in which the chemical energy of combustion is converted into electrical energy. The fuels such as H_2 , CO , CH_4 and alcohols can be used to produce electricity.

E.g. Hydrogen-Oxygen Fuel Cell

Fuel + oxygen \rightarrow Oxidation products + Electricity

Advantages of Fuel Cells

1. It converts energy of fuel directly to electrical energy.
2. Do not cause pollution problem.
3. Fuel cell is light and compact
4. Efficiency is very high.
5. Energy supply is continuous
6. It can be connected in series to get high voltage

Uses of fuel cells

As energy source in

(i) Space vehicles (ii) Submarines (iii) Military vehicles (iv) automobiles

Electrode potential

The tendency of the electrode to lose or gain electrons when it is in contact with its own ions in solution is called **electrode potential**.

The tendency of the electrode to **lose electrons** is called **oxidation potential**.

The tendency of the electrode to **gain electrons** is called **reduction potential**.

Standard electrode potential

The electrode potential at 298K, 1atm pressure and 1m concentration of electrolyte is called **standard electrode potential**.

EMF of cell


The difference in potentials of two half cells of a cell is called EMF of cell.

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

Electrochemical Series or Activity series

The arrangement of elements in the increasing order their standard reduction potential is called electrochemical series.

Metal	State	E° (V)
Lithium	1+	- 3.05
Potassium	1+	- 2.93
Calcium	2+	- 2.87
Sodium	1+	- 2.71
Magnesium	2+	- 2.37
Aluminum	3+	- 1.66
Manganese	2+	- 1.18
Zinc	2+	- 0.76
Chromium	3+	- 0.74
Iron (II)	2+	- 0.44
Cadmium	2+	- 0.40
Cobalt	2+	- 0.28
Nickel	2+	- 0.25
Tin (II)	2+	- 0.14
Lead	2+	- 0.13
Hydrogen	1+	0.00
Tin (IV)	4+	0.15
Copper	2+	0.16
Iron (III)	3+	0.77
Silver	1+	0.80
Platinum	2+	1.20
Gold	1+	1.68



Applications of Electrochemical Series

1. It helps to calculate emf of galvanic cell.
2. It helps to predict whether a metal can act as anode or cathode, when a cell is constructed.
3. It helps to compare various properties of metals like reactivity, electro positivity etc.
4. Helps to compare oxidation and reducing power of metals.
5. A metal higher in series will displace lower metal in series from solution.
Eg; we cannot keep coppersulphate in iron or zinc vessel. Because iron and Zn can displace Cu from its solution.
6. The metals above hydrogen can displace hydrogen from acids.

CORROSION

The process of destruction of metal or alloy by the chemical or electrochemical attack by its environments is called corrosion.

1. Dry or chemical corrosion

This occurs by the direct chemical attack of gases or inorganic liquids present in the environment. Oxygen, halogens, H_2S , SO_2 etc causes chemical corrosion. Moisture is not involved in this corrosion.

Eg ; oxide formation on metals like Al, Mg and Ca

2. Wet or electrochemical corrosion

Moisture is required for the corrosion process. This occurs due to the formation of separate anodic and cathodic areas on the surface of the metal.

Eg; rusting of iron.

Factors/ conditions for rusting

Impurities in iron

Presence of oxygen

Presence of moisture

Presence of electrolyte

Presence of chlorine or SO_2 present in atmosphere

Prevention of corrosion

Barrier protection

In this method a physical barrier is creating between the metal and the environment

Eg: painting, plastic coating, rubber coating, non-corrosive metal coating

Sacrificial protection

In this method a more reactive metal is used to make a coating over the metal object. This reactive metal acting as the anode get corroded and the object get protected.

Eg: galvanization of iron (Making Zn coating)

Cathodic protection

In this method the metallic object is protected by connecting it to more active metal. The object acting as cathode and get protected. The active metal acting as anode and suffers the damage.

Eg: The underground iron pipes are protected by connecting with active metal like Mg or Zn

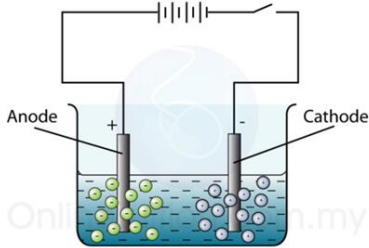
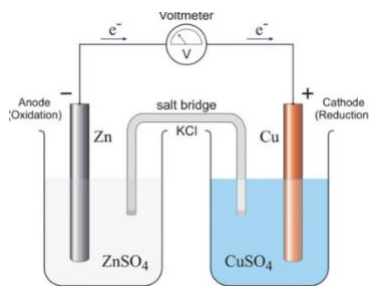
Anti-rust solutions

The alkaline solution of phosphate or chromate of sodium or potassium salt acting as antirust solutions. These solutions can form a protective insoluble coating of iron phosphate or chromate.

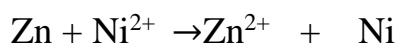
Eg for anti-rust solution: Alkaline solution of sodium phosphate, potassium phosphate, Sodium chromate or potassium chromate



Difference between Electrolytic cell and Electrochemical cell (Galvanic Cell).

Electrolytic Cell	Electrochemical cell (Galvanic Cell)
Electrical energy is converted into chemical energy	Chemical energy is converted into electrical energy
Anode is positive while cathode is negative	Anode is negative while cathode is positive
Oxidation and reduction is carried out in same container	Oxidation and reduction is carried out separately.
Salt bridge is not used.	Salt bridge is generally used.
Cell reaction is non-spontaneous.	Cell reaction is spontaneous.
	

Qn. A galvanic cell reaction is given below



Write cell representation, cell reactions and compute the e.m.f.

(Given $\text{Ni}^{2+}/\text{Ni} = -0.25\text{V}$, $\text{Zn}^{2+}/\text{Zn} = -0.76$)

Answer:

Cell representation: $\text{Zn}/\text{Zn}^{2+} // \text{Ni}^{2+}/\text{Ni}$

Cell Reactions: $\text{Zn} \rightarrow \text{Zn}^{2+} + 2\text{e}^-$ (Anode)

$\text{Ni}^{2+} + 2\text{e}^- \rightarrow \text{Ni}$ (Cathode)

Cell e.m.f. : $E_{\text{cell}} = E_{\text{cathode}} - E_{\text{anode}} = -0.25 - (-0.76) = \underline{\underline{0.51\text{V}}}$

Assignment-I

1. How materials are classified based on conduction?
2. Distinguish between electronic and electrolytic conductors?
3. Distinguish between electrolyte and non-electrolyte?
4. Distinguish between strong and weak electrolyte?
5. Explain the electrolysis process of aqueous and molten NaCl?
6. State Faraday's Laws of electrolysis?
7. Write any five applications of electrolysis.
8. Write any three difference between electroplating and anidising.
9. Explain the process of electroplating of nickel on mild steel.

Assignment-II

1. Explain the working of Daniel cell.
2. What is a salt bridge? What are its functions?
3. What are primary and secondary cell? Give two example for each.
4. Distinguish between electrolytic cell and galvanic cell.
5. What is a fuel cell? What are its advantages?
6. Explain the working of hydrogen-oxygen fuel cell.
7. What is an electrochemical series? Mention any five of its applications.
8. Define corrosion. What are the types of corrosion?
9. Explain electrochemical theory of rusting.
10. What are the conditions of rusting?
11. Write notes on (a) Barrier protection (b) Sacrificial protection (c) Cathodic protection (d) Anti-rust solutions.