

CHAPTER-5

WATER TECHNOLOGY

71 percentage of earth surface is covered by water only. But, only 3 percentage of water is usable for human beings, the rest of 97 percentage is salt water, which is present in the seas and oceans.

OBJECTIVES

After studying this chapter, students will be able to

- Define soft and hard water, differentiate the temporary and permanent hardness in terms of chemical compounds.
- Know the disadvantages of hard water.
- Find the degree of hardness in different units.
- Describe the softening methods : i.e. : Permutit and ion exchange methods.
- Know the essential qualities of drinking water.
- Explain municipal water treatment process.
- Get the knowledge of Osmosis, reverse osmosis and advantages of reverse osmosis.
- Discuss about desalination of sea water by electro dialysis.
- Discuss about municipal water treatment.

5.0 INTRODUCTION

Water is nature's most wonderful, abundant and useful compound. It is essential to all forms of life. Water is not only essential for the animals and plants, but also occupies a unique position in industries. No industry can be established or run without adequate supply of water. The most important use of water in the industries is in the steam generation. Water is widely used in power and chemical plants, production of steel, rayon, paper, atomic energy, textiles and for air-conditioning etc.

5.1 SOURCES OF WATER

The following are the important sources of water.

1. Surface Water :

- (i) **Rain Water** : It is the purest form of water.
- (ii) **River Water** : Rivers are fed by rain and spring waters. This water contains considerable amount of dissolved as well as suspended impurities.
- (iii) **Lake Water** : It has a constant chemical composition and contains large amounts of organic matter.
- (iv) **Sea Water** : It is the most impure form of water and its use is very limited.

2. Ground Water : It occurs in the form of spring water and well water. It contains most of the dissolved salts. Hence it has more hardness.

5.2 SOFT WATER AND HARD WATER

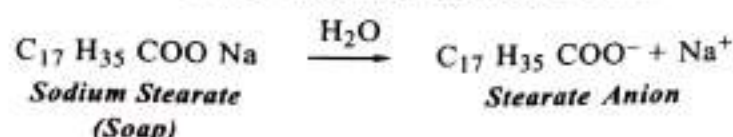
The water is classified into 2 types based on its action with soap. These are :

1. Soft water.
2. Hard water.

(Jan. 2022)

1. **Soft Water** : The water which produces lather easily with soap is called **soft water**.

Soap is a sodium or potassium salt of fatty acids like stearic acid, palmitic acid and oleic acid. Whenever, soap is added to soft water, it ionises into anion of fatty acid and Na^+ . This anion involves in the cleaning action. So lather forms easily.



2. **Hard Water** : The water which does not produce lather easily with soap is called **hard water**.

5.3 HARDNESS OF WATER

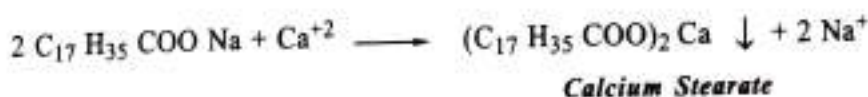
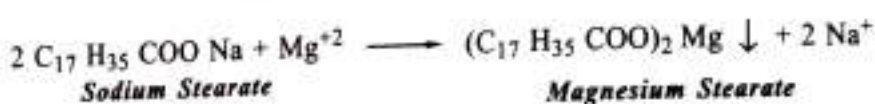
The lather preventing property of water with soap is called **hardness**.

The hardness of water is mainly caused by dissolved minerals, particularly calcium and magnesium ions. Here are the main chemicals responsible for the hardness of water :

1. **Calcium bicarbonate ($\text{Ca}(\text{HCO}_3)_2$)** : Calcium bicarbonate is a common source of hardness in water. It can dissolve in water and forms calcium ion (Ca^{2+}) and bicarbonate ion (HCO_3^-).
2. **Magnesium bicarbonate ($\text{Mg}(\text{HCO}_3)_2$)** : Similar to Calcium bicarbonate, magnesium bicarbonate can dissolve in water to produce magnesium ion (Mg^{2+}) and bicarbonate ion (HCO_3^-).
3. **Calcium Sulfate (CaSO_4)** : Calcium sulfate, commonly known as gypsum, can dissolve in water to release calcium ion (Ca^{2+}) and sulfate ion (SO_4^{2-}).
4. **Magnesium Sulfate (MgSO_4)** : Magnesium sulfate, also known as Epsom salt, can dissolve in water to produce magnesium ion (Mg^{2+}) and sulfate ion (SO_4^{2-}).

5. **Calcium Chloride (CaCl_2)** : Calcium chloride can dissolve in water to release calcium ion (Ca^{2+}) and chloride ion (Cl^-).
6. **Magnesium Chloride (MgCl_2)**: Magnesium chloride can dissolve in water to produce magnesium ion (Mg^{2+}) and chloride ion (Cl^-).
7. **Other Minerals**: In addition to calcium and magnesium compounds, other minerals like iron, manganese and zinc are also contribute to water hardness, but they present in lower concentrations compared to calcium and magnesium.

When soap is treated with hard water, it forms insoluble calcium or magnesium salt of fatty acid. It is precipitated as a white curdy substance.



Soap does not produce lather until all the Ca^{+2} and Mg^{+2} ions have been precipitated. Hence, the salts should be removed from the hard water before its use.

Types of Hardness : Hardness of water is 2 types. They are.

1. Temporary hardness.
2. Permanent hardness.

5.4 TEMPORARY AND PERMANENT HARDNESS

1. **Temporary Hardness (or) Carbonate Hardness** : The hardness causes due to the presence of dissolved bicarbonates of calcium and magnesium is called **temporary hardness**. The formula of these compounds is $\text{Ca}(\text{HCO}_3)_2$, $\text{Mg}(\text{HCO}_3)_2$. Temporary hardness can be removed by boiling.

2. **Permanent Hardness (or) Non-carbonate Hardness** : The hardness causes due to the presence of chlorides and sulphates of calcium and magnesium is called **Permanent Hardness**.

(The formula of these compounds are CaCl_2 , MgCl_2 , CaSO_4 , MgSO_4). Permanent hardness can't be removed by boiling.

5.5 DISADVANTAGES OF USING HARD WATER IN INDUSTRIES

Hard water is not suitable for domestic and industrial use. Following are the disadvantages of using hard water.

1. **Laundry** : Hard water, when used for washing purpose, does not produce lather easily. This causes the wastage of soap and clothes do not become quite clean.
2. **Textile Industry** : When hard water is used in textile industry, precipitates of calcium and magnesium salts adhere to the fabrics and prevent the formation of exact shades of colours in dyeing.
3. **Paper Industry** : If hard water is used in paper industry, it spoils the quality of paper.
4. **Sugar Industry** : If hard water is used in sugar refining, causes difficulty in the crystallisation of sugar. Further, the sugar so produced may be deliquescent.
5. **Boilers** : For steam generation, in industries, boilers are invariably employed. If the hard water is used in the boilers, the disadvantages which arise are :
 - (a) Wastage of fuel.
 - (b) Scale and sludge formation.
 - (c) Corrosion of boiler.
 - (d) Priming and foaming.
 - (e) Caustic embrittlement.
 - (f) Decreases the efficiency of boiler.

6. **Concrete Making :** Hard water if used for concrete making, it effects the hydration of cement and final strength of the hardened concrete.
7. **Pharmaceutical Industry :** Hard water if used in the preparation of drugs, injections, etc., may produce certain undesirable products.

5.6 DEGREE OF HARDNESS AND UNIT OF HARDNESS

5.6.1 Degree of Hardness

The amount of hardness producing salts present in definite quantity of water is called **degree of hardness**.

Degree of hardness of water is expressed in terms of equivalents of calcium carbonate. Calcium carbonate is chosen as the standard for calculating hardness due to the ease of calculations, as its molecular weight is 100.

$$\text{Hardness of water in terms of } \text{CaCO}_3 \text{ equivalents} = \frac{\text{Wt of the salt} \times 100}{\text{GMW of the salt}}$$

$$100 \text{ parts by weight of CaCO}_3 = 162 \text{ Parts by weight of Ca (HCO}_3)_2$$

$$100 \text{ Parts by weight of CaCO}_3 = 146 \text{ Parts by weight of Mg (HCO}_3)_2$$

$$100 \text{ Parts by weight of CaCO}_3 = 111 \text{ Parts by weight of CaCl}_2$$

$$100 \text{ Parts by weight of CaCO}_3 = 95 \text{ Parts by weight of MgCl}_2$$

$$100 \text{ Parts by weight of CaCO}_3 = 136 \text{ Parts by weight of CaSO}_4$$

$$100 \text{ Parts by weight of CaCO}_3 = 120 \text{ Parts by weight of MgSO}_4$$

5.6.2 Units of Hardness

The degree of hardness is expressed by the following units.

1. **Parts Per Million (ppm) :** The number of parts by weight of CaCO_3 equivalents present in one million (10^6) parts by weight of water is called parts per million. i.e., $\text{ppm} = 1 \text{ part of CaCO}_3 \text{ equivalent in } 10^6 \text{ parts of water.}$

2. **Milligrams Perlitre (mg/lit)** : The number of milligrams of CaCO_3 equivalents present in one lit of water is called *milligrams per litre*.

1 mg/lit = 1 mg of CaCO_3 equivalents of hardness in 1 lit of water.

But, 1 lit of water weighs = 1 kg = 1000 g
 = $1000 \times 1000 \text{ mg} = 10^6 \text{ mg}$

3. **Clark degree ($^\circ\text{Clark}$)** : The number of parts by weight of CaCO_3 equivalents present in 70,000 parts of water.

It is also called as *English degree ($^\circ\text{E}$)*.

4. **French degree ($^\circ\text{F}$)** : The number of parts by weight of CaCO_3 equivalents present in 10^5 parts of water.

\therefore Here,

$$\begin{aligned} 1 \text{ mg/lit} &= 1 \text{ mg of } \text{CaCO}_3 \text{ equivalent per } 10^6 \text{ mg of water} \\ &= 1 \text{ Part of } \text{CaCO}_3 \text{ eq. per } 10^6 \text{ part of water} \\ &= 1 \text{ ppm} \end{aligned}$$

i.e., **1 mg/lit = 1 ppm**

NUMERICAL PROBLEMS

PROBLEM-1

Calculate the hardness of sample water containing 16.2 mg of CaSO_4 per litre?

Solution :

Wt. of salt (CaSO_4) = 16.2 mg

GMW of salt (CaSO_4) = 136 g

Hardness of water due to CaSO_4

Terms of CaCO_3 equivalents

$$= \frac{\text{Wt. of salt} \times 100}{\text{GMW of salt}} = \frac{16.2 \times 100}{136} = 11.91 \text{ mg/lit (or) ppm.}$$

PROBLEM-2

A sample of water contains the following salts

(a) 23 mg/lit of $\text{Mg}(\text{HCO}_3)_2$

(b) 33.3 mg/lit of CaCl_2

(c) 30 mg/lit of MgSO_4

Calculate the temporary and permanent hardness.

Solution :

Temporary hardness due to $\text{Mg}(\text{HCO}_3)_2$ and permanent hardness due to CaCl_2 and MgSO_4

(a) Wt. of $\text{Mg}(\text{HCO}_3)_2 = 23 \text{ mg}$

GMW of $\text{Mg}(\text{HCO}_3)_2 = 146 \text{ g}$

Temporary hardness

$$\begin{aligned} \text{Interms of } \text{CaCO}_3 \text{ equivalents} &= \frac{\text{wt. of salt}}{\text{GMW of salt}} \times 100 \\ &= \frac{23 \times 100}{146} = 15.75 \text{ mg/lit} \end{aligned}$$

(b) Wt of $\text{CaCl}_2 = 33.3 \text{ mg/lit}$

GMW of $\text{CaCl}_2 = 111 \text{ g}$

Hardness due to CaCl_2

$$\text{Interms of } \text{CaCO}_3 \text{ equivalents} = \frac{33.3 \times 100}{111} = 30 \text{ mg/lit}$$

(c) Wt of $\text{MgSO}_4 = 30 \text{ mg/lit}$

GMW of $\text{MgSO}_4 = 120 \text{ g}$

Hardness due to MgSO_4

$$\text{Interms of } \text{CaCO}_3 \text{ equivalents} = \frac{30 \times 100}{120} = 25 \text{ mg/lit}$$

Temporary hardness = 15.75 mg/lit

Permanent hardness = 30 + 25 = 55 mg/lit

PROBLEM-3

Calculate the temporary and permanent hardness of water containing the following salts per litre.

$$(i) \text{ Ca (HCO}_3)_2 = 32.4 \text{ mg} \quad (\text{Jan. 2022})$$

$$(ii) \text{ Mg(HCO}_3)_2 = 29.2 \text{ mg.} \quad (\text{Jan. 2022})$$

$$(iii) \text{ CaSO}_4 = 13.6 \text{ mg}$$

$$(iv) \text{ MgCl}_2 = 19 \text{ mg.}$$

Solution :

Temporary hardness is due to $\text{Ca(HCO}_3)_2$ and $\text{Mg(HCO}_3)_2$
 permanent hardness is due to CaSO_4 and MgCl_2

$$(a) \text{ Wt. of Ca (HCO}_3)_2 = 32.4 \text{ mg}$$

$$\text{GMW of Ca (HCO}_3)_2 = 162 \text{ g}$$

$$\text{Wt. of Mg (HCO}_3)_2 = 29.2 \text{ mg}$$

$$\text{GMW of Mg (HCO}_3)_2 = 146 \text{ g}$$

Hardness is due to $\text{Ca (HCO}_3)_2$

interms of Ca CO_3 equivalents

$$= \frac{\text{Wt. of salt}}{\text{GMW of salt}} \times 100 = \frac{32.4 \times 100}{162} = 20 \text{ mg/lit.}$$

Hardness due to $\text{Mg(HCO}_3)_2$ interms of CaCO_3 equivalents

$$= \frac{29.2 \times 100}{146} = 20 \text{ mg/lit.}$$

So, Temporary hardness = $20 + 20 = 40 \text{ mg/lit (or) ppm.}$

$$(b) \text{ Wt. of CaSO}_4 = 13.6 \text{ g}$$

$$\text{GMW of CaSO}_4 = 136 \text{ g}$$

$$\text{Wt of MgCl}_2 = 19 \text{ mg}$$

GMW of $\text{MgCl}_2 = 95 \text{ g}$

Hardness due to CaSO_4 in terms of CaCO_3 equivalents

$$= \frac{136 \times 100}{136} = 10 \text{ mg/lit.}$$

Hardness due to MgCl_2 in terms of CaCO_3 equivalents

$$= \frac{19 \times 100}{95} = 20 \text{ mg/lit.}$$

So, permanent hardness = $10 + 20 = 30 \text{ mg/lit (or) ppm.}$

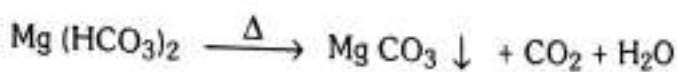
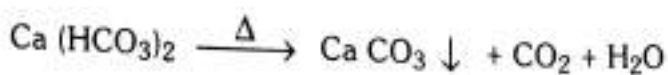
5.7 SOFTENING METHODS OF HARD WATER

The process of removing of hardness producing salts from the water is called **softening**. The method of softening of hard water depends upon the fact whether the hardness is temporary or permanent.

5.7.1 Removal of Temporary Hardness

It is removed by the following methods.

1. **By Boiling** : Whenever, water is boiled, the bicarbonates of calcium and magnesium decompose to form insoluble carbonate (precipitate), which are removed by filtration method.



2. **Clark's Method** : In this method, calculated amount of slaked lime (calcium hydroxide) is added to hard water. The bicarbonates of Ca and Mg react with lime and form insoluble carbonates, which are removed by filtration method.



5.7.2 Removal of Permanent Hardness of Water

The permanent hardness of water can be removed by the following methods.

1. PERMUTIT PROCESS (OR) ZEOLITE PROCESS

The naturally occurring aluminium ortho silicate ($Al_2 Si_2 O_8 \times H_2O$) is called **zeolite**. Permutit is an artificial zeolite. It is obtained by fusing soda ash ($Na_2 CO_3$), silica ($Si O_2$) and alumina (Al_2O_3). Permutit or sodium zeolite is denoted by Na_2Z , where $Z = Al_2 Si_2 O_8 \times H_2O$.

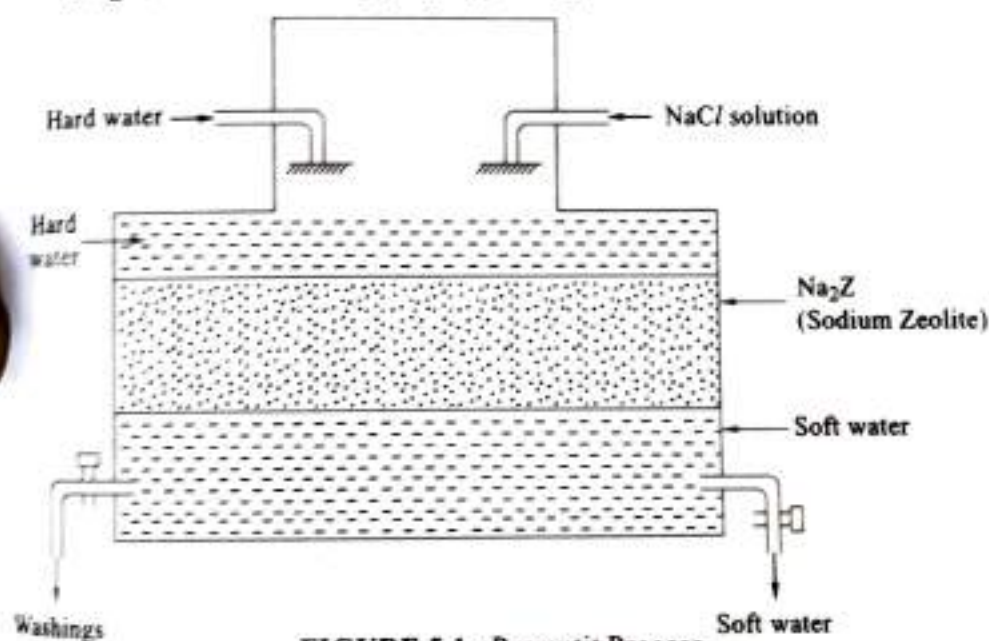


FIGURE 5.1 : Permutit Process

Permutit is packed in a suitable container and hard water is passed through it. Calcium and magnesium ions of hard water are replaced by sodium ions, which do not cause hardness. Thus, water is softened. The soft water is taken out through the outlet. The reactions are.



Once, Na_2Z is completely converted to CaZ or MgZ , it is said to be exhausted. It is necessary to regenerate. Regeneration is carried out by passing 10% brine ($NaCl$) solution.

The reactions during the regeneration are :



2. ION-EXCHANGE PROCESS (DEMINERALIZATION PROCESS)

Among all the available water softening methods the ion-exchange process is the best and the most modern method. All the cations and anions present in the water are removed in this process. The water so obtained is demineralized water.

In this method, ion-exchange resins are used. The resins are cross-linked organic polymers with micro-porous structure. The functional groups attached to the resins are responsible for the exchange of ions. The resins containing $-\text{COOH}$ or $-\text{SO}_3\text{H}$ group (acidic resin) can capable of exchange their H^+ with other cations. They are called **cation exchange resins**. The resins containing $-\text{OH}^-$ or $-\text{NH}_2$ group (basic resin) can capable of exchange their OH^- or NH_2 with other anions. These are called an **ion exchange resins**.

The ion-exchanger consists of two columns, namely cation exchanger and anion exchanger. The cation exchanger is filled with an acidic resin ($\text{R} - \text{COOH}$) and anion exchanger is filled with a basic resin ($\text{R} - \text{OH}$). The hardwater is first sent through the cation exchanger. Here the acidic resin exchanges its H^+ with Mg^{+2} and Ca^{+2} ions of water.



The water is then passed through the anion exchanger. Here, basic resin exchanges its OH^- with Cl^- , HCO_3^- and SO_4^{2-} of water.



The H^+ and OH^- ions combine and form water.

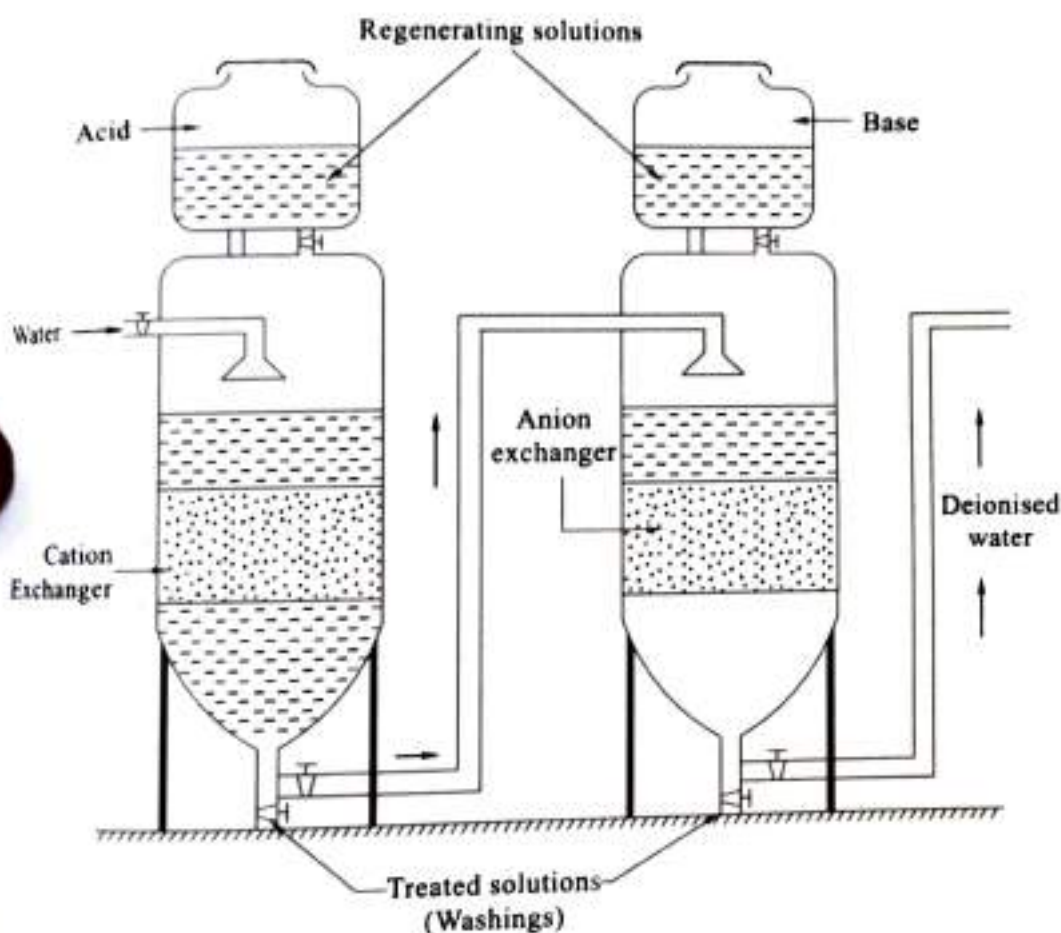
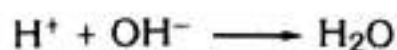


FIGURE 5.2 :

Regeneration of Resins : After some time, the resins are exhausted. The exhausted acidic resin is regenerated by passing an acid like HCl or H_2SO_4 .



The basic exhausted resin is regenerated by passing alkali like $NaOH$.



After regeneration, the resins are ready for softening.

5.8 DESALINATION OF WATER

Desalination is the process of removing salts and other impurities from seawater or brackish water to produce fresh water. This process is essential in regions where fresh water sources are limited or where the available water is too saline for direct use.

5.9 OSMOSIS AND REVERSE OSMOSIS

5.9.1 Osmosis

The process of transfer of solvent from *dilute* solution to a concentrated solution *through* a semi-permeable membrane is called **osmosis**.

Osmosis is a physical process and spontaneous.

A membrane that allows only solvent molecules to pass through it (while leaving behind the solute molecules) is called a semipermeable membrane.

Ex : Thin film of Cellulose acetate, polymethyl acrylate, copper Ferro cyanide or polyamide polymer.

Exo-Osmosis : The outward flow of solvent molecules from a cell to more dilute solution. This process occurs until equilibrium is reached between the concentrations of solute on both sides of the membrane.

Endo-Osmosis : The inward flow of solvent molecules into the cell from outside solution. Endosmosis continues until equilibrium is reached

Examples :

- (i) Plants absorb water from soil through their roots.
- (ii) Osmosis plays a vital role in the kidneys' ability to regulate water and electrolyte balance in the body.
- (iii) Osmosis is used in food preservation techniques such as pickling. When vegetables or meat are placed in a hypertonic solution (e.g., salt water), water is drawn out of the cells of microorganisms through osmosis, causing them to shrink and die.
- (iv) Revival of wilted flowers upon sprinkling with water.

Osmotic Pressure : The minimum pressure that must be applied on a solution of high concentration just to halt the movement of solvent molecules through semi permeable membrane.

5.9.2 Reverse Osmosis

This is opposite process of osmosis. *"The process of transfer of solvent from a solution of higher concentration to a solution of lower concentration through a semi-permeable membrane by applying the pressure more than the osmotic pressure is called reverse osmosis"*.

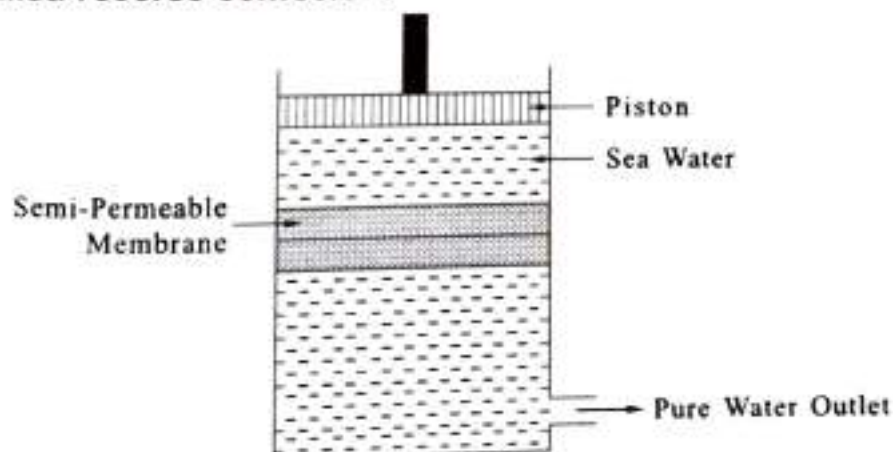


FIGURE 5.3 : Reverse Osmosis Cell

In Fig 5.3 two solutions of different concentrations are separated by a semi-permeable membrane and a high

pressure (i.e., excess of osmotic pressure) is applied on the concentration side. Then, the solvent flows from concentrated solution to dilute solution through the semi-permeable membrane. By using reverse osmosis, water is separated from its contaminants or impurities. This is a type of filtration method. It is called as **super-filtration** or **hyper filtration**.

5.10 PROCESS OF CONVERSION OF SEA WATER INTO DRINKING WATER BY REVERSE OSMOSIS

The conversion of sea water into drinking water, also known as desalination

The detailed explanation of the process are :

1. **Pre-Treatment** : Sea water is pre-treated to remove larger particles, floating matter and organic matter. This step helps protect the reverse osmosis membranes from damage. Pre-treatment may involve screening, sedimentation, coagulation and filtration processes. Chemicals like chlorine may also be added to control biological growth.
2. **Pressurization** : The pre-treated sea water is then pressurized using high-pressure pumps. This pressure is necessary to overcome the osmotic pressure of seawater and to pass it through the semi-permeable membranes.
3. **Passing through Reverse Osmosis Membrane** : The pressurized seawater moves through the reverse osmosis membrane module. The RO membrane is a semi-permeable barrier that allows water molecules to pass through it and rejects dissolved salts, minerals and other impurities.
4. **Separation of Freshwater and Brine** : The freshwater and brine is collected separately and typically undergoes further treatment to adjust its pH, mineral content and disinfection.

5.11 APPLICATIONS AND ADVANTAGES OF REVERSE OSMOSIS**Applications :**

1. Reverse osmosis is used in the production of various beverages, including soft drinks, juices, and alcoholic beverages.
2. Reverse osmosis plays a role in waste water treatment processes, particularly in recycling and reusing waste water in industries.
3. Reverse osmosis is commonly used in aquariums to produce high-quality water for fish and other aquatic organisms.
4. Reverse osmosis used in the desalination process.
5. Reverse osmosis technique used in dialysis process

Advantages :

1. This method removes all impurities like ionic, non-ionic, colloidal, organic and other impurities.
2. This process is cheap and easily carried out.
3. The semipermeable membrane can be replaced with in few minutes and it's life time is nearly two years
4. This process does not involve any heating process, hence, fuels are not required.
5. It can be used in the treatment of polluted water and decreases the pollutants.

5.12 DESALINATION OF SEA WATER BY ELECTRODIALYSIS

This method is commonly used to partially or completely demineralize highly saline waters such as seawater (with 35,000 ppm of dissolved salts) or brackish waters. The ion exchange process is not applicable to desalinating seawater.

In this electrodialysis method, sea water is passed through ion-exchange membranes under the influence of an electric field.

In this method, a series of closely spaced cation exchange membranes and anion exchange membranes are arranged. When a direct current of electricity is passed through sea water, cations pass through the cation exchange membranes and anions pass through the anion exchange membranes. As a result of the movement of cations and anions, the salinity decreases in one space and increases in the next space. The water containing more salt is discarded, while the water containing less salt may be recirculated to obtain demineralized water. However, complete demineralization is not achieved by this method. This method reduces the salinity of seawater or brackish water to make it suitable for drinking and general use.

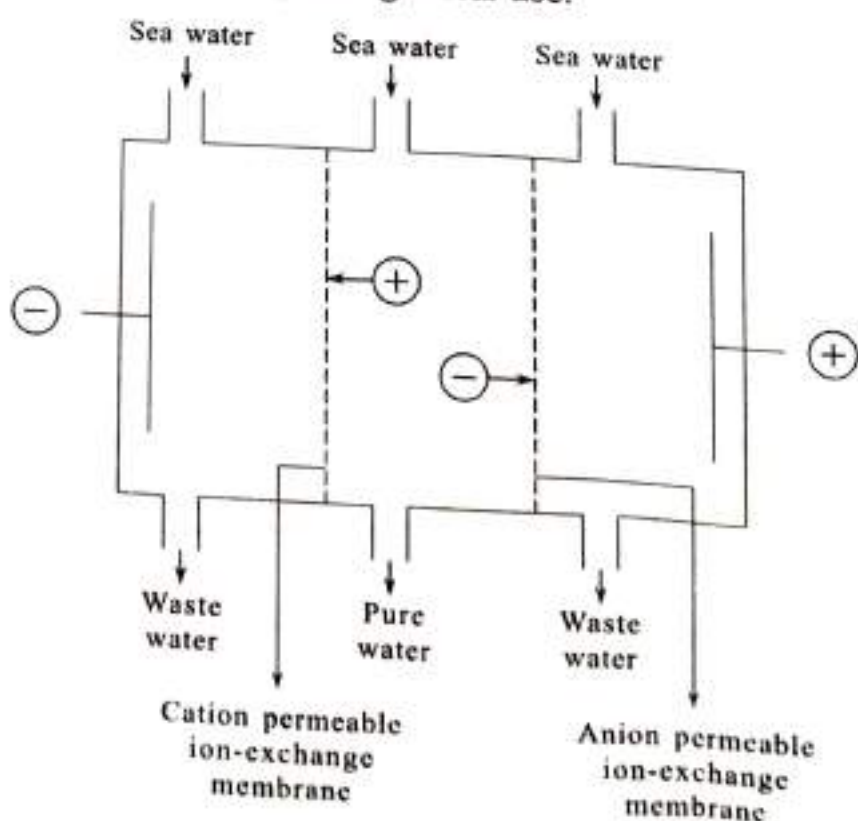


FIG 5.4 : Electrodialysis Method

5.13 ESSENTIAL QUALITIES OF DRINKING WATER

Potable or Drinking Water : The water which is used for drinking purpose is called as Potable or Drinking Water.

Essential Qualities of Drinking Water

1. It should be colour less and odourless.
2. It should be free from colloidal or suspended impurities like mud.
3. It should have pleasant taste.
4. It should not have harmful micro organisms like bacteria, virus, fungi etc.
5. Its hould not have harmful dissolved gases like H_2S .
6. It should not have toxic elements like mercury, arsenic, lead etc.
7. Turbidity of the water should be less than 10 ppm.
8. pH of water should be between 7 and 8.
9. It should not have fluoride more than 2 ppm.

5.14 METHOD OF MUNICIPAL WATER TREATMENT

The water used for drinking purpose usually obtained from natural sources like rivers, deep wells, ponds and lakes etc. This water does not have the minimum required characteristics. Hence, water should be treated by the municipal water treatment method, before using it for drinking purpose.

The following steps involved in municipal water treatment.

- (i) Removal of suspended impurities.
 - (ii) Removal of microorganisms (sterilization).
1. Removal of suspended impurities is carried out in following steps.
 - (a) Screening
 - (b) Sedimentation.
 - (c) Coagulation or flocculation
 - (d) Filtration

- (a) **Screening** : The removal of floating material from the water is called as screening.
- (b) **Sedimentation** : The water after screening pumped into sedimentation tanks and is allowed to stand undisturbed for few hours. The suspended impurities which are bigger in size slowly settle down at the bottom due to the force of gravity. This process of settling down the suspended impurities is called **sedimentation**. To improve the process of sedimentation. Coagulants are added to the water.
- (c) **Coagulation** : Coagulation is a process used to remove small suspended particles, colloids and other impurities from water by causing them to group together and form larger particles called flocs. These flocs can then more easily removed through sedimentation or filtration. The chemicals used for the coagulation process are called coagulants.

EX : Alum [$K_2SO_4Al_2(SO_4)_3 \cdot 24H_2O$], ferrous sulphate [$FeSO_4 \cdot 7H_2O$].

- (c) **Filtration** : The water from the sedimentation tanks is passed over the filter beds. The filter beds are made up of layers of coke, fine sand and gravel. Coke adsorbs the organic gases which are responsible for colours and odours. Sand and gravel act as filter and remove the remaining suspended impurities.

2. **Removal of Micro Organisms (Sterilization)** : The process of killing of harmful micro-organisms is called **sterilization or disinfection**. The sterilization is generally carried out by chlorination and also with aeration etc.,

- (i) Chlorine in the form of bleaching powder [$CaOCl_2$] or in gaseous state [Cl_2] is used in the sterilization. Chlorine reacts with water and form HCl and $HOCl$ (Hypochlorous

acid). HOCl releases nascent oxygen, which kills micro-organisms by oxidation.



- (ii) **Aeration** : Water is sprinkled into air by using fountain pumps. Then it is exposed to O_2 and U.V rays of the sun. Hence, micro organisms are killed.

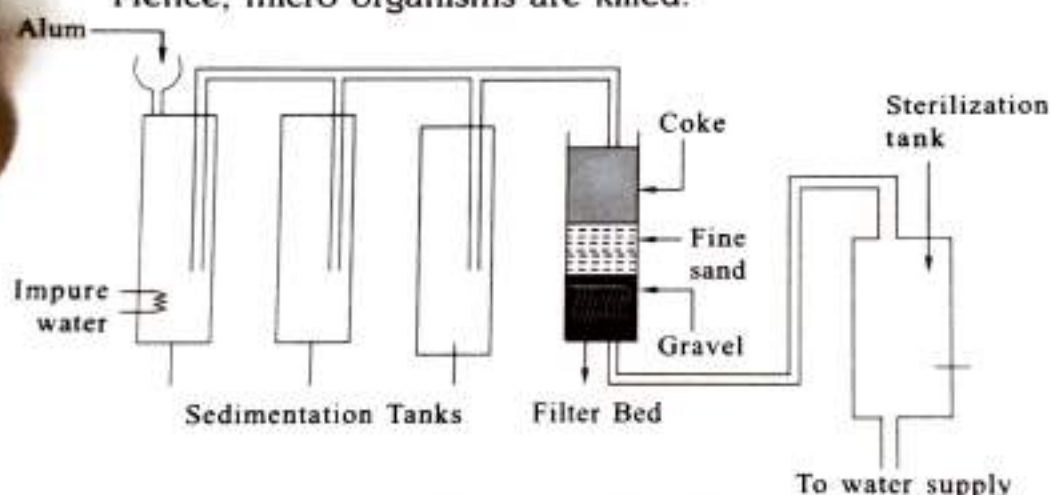


FIGURE 5.5: Schematic Diagram of Municipal Water Treatment

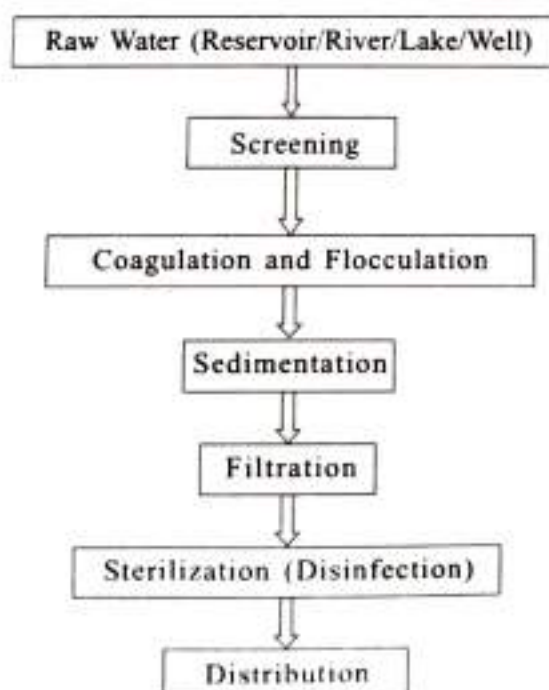


FIGURE 5.6 : Flow Chart of Municipal Water Treatment

SYNOPSIS

1. Natural water from different sources can be classified into surface water and underground water.
2. The common impurities present in the water are :
 - (a) Suspended impurities.
 - (b) Dissolved gases.
 - (c) Dissolved Mineral Salts.
 - (d) Micro scopic matter.
3. Water which does not give lather easily with soap is called **hard water**.
4. Water which gives lather easily with soap is called soft water.
5. Temporary hardness of water is due to bicarbonates of calcium and magnesium. Permanent hardness of water is due to sulphates and chlorides of calcium and magnesium.
6. Degree of hardness of water is expressed interms of CaCO_3 equivalents.

Hardness interms of CaCO_3 equivalents

$$= \frac{\text{wt. of the salt}}{\text{GMW of the salt}} \times 100$$

7. Degree of hardness is expressed in ppm, mg/lit, clarke's degree ($^\circ\text{C}$) and French degree ($^\circ\text{Fr}$)

$$1 \text{ ppm} = 1 \text{ mg/lit} = 0.1^\circ\text{Fr} = 0.07^\circ\text{C}$$

8. Temporary hardness can be removed by boiling of water (or) by adding of lime.
9. Total hardness is removed by
 - (a) Permutit process.
 - (b) Ion-exchange process.
 - (c) Lime - soda process

10. In Lime-soda process, calculated quantities of lime $[\text{Ca}(\text{OH})_2]$ and soda $[\text{Na}_2\text{CO}_3]$ are added to the water. The precipitates formed settled down as sludge and it is then filtered off.
11. In permutit (or) Zeolite process, the Ca^{+2} , Mg^{+2} ions are exchange with Na^+ ions. Water containing sodium salts which do not cause hardness is obtained.
12. In ion-exchange process, the cations (Mg^{+2} , Ca^{+2}) and anions (Cl^- , HCO_3^- , SO_4^{+2}) of water are exchanged with H^+ and OH^- of resins respectively. By this process demineralized water is obtained.
13. Potable water should be free from suspended impurities, colourless, odour less and free from micro organisms.
14. Purification of water is carried out in 3 steps.
 - (a) Sedimentation
 - (b) Filtration
 - (c) Sterilization.
15. Impurities can be removed by sedimentation and filtration. Microorganisms can be removed by sterilization.
16. Sterilization is carried out by chlorination.
17. The process of transfer of solvent from lower concentration to higher concentration through a semi permeable membrane is called **osmosis**.
18. The process of transfer of solvent from higher concentration to lower concentration through a semi permeable membrane is called **reverse osmosis**.

CHAPTER-6

ELECTRO CHEMISTRY

Electrolytic cell and galvanic cell application are the most significant in the development of chemistry in our day-to-day life.

OBJECTIVES

After studying this chapter, students will be able to

- Know the conductor, insulator, electrolyte and non-electrolytes and types of electrolytes.
- Differentiate between metallic and electrolytic conductors
- Explain the Arrhenius theory of electrolytic dissociation.
- Describe electrolysis of fused and aqueous NaCl
- Get concept of electroplating and electrolytic refining
- Understand the Faraday's laws of electrolysis
- Define chemical equivalent, electro chemical equivalent and relation between them
- Calculate the problems on Farady's laws of electrolysis

6.0 INTRODUCTION

Electrochemistry is a branch of chemistry which deals with the relationship between electricity and chemical changes. It is a well known fact that during electrolysis of copper sulphate solution, Cu deposits over the cathode. This shows that electrical energy produces chemical reactions. Electrochemistry has a great engineering and industrial importance, since the laws of electro chemistry are used for the development of important technical processes like,

- (a) Extraction and refining of metals.
- (b) Synthesis of organic and inorganic compounds.
- (c) Electro plating, electro typing and electro printing etc.
- (d) Electro chemical machinery.
- (e) Electro analysis of trace elements.
- (f) Construction of electro chemical cell etc.

In this chapter, various aspects of electrochemistry will be studied.

6.1 CONDUCTORS, INSULATORS, ELECTROLYTE AND NON-ELECTROLYTE

Electric current is considered as flow of electrons or flow of electric charges through a conducting medium.

1. **Conductors** : The substances which permit the passage of electric current through them are called **conductors**. These substances may be solid materials, metals or fused salts or aqueous solutions.
2. **Insulators** : The substances which do not permit the passage of electric current through them are called **insulators** (or) **non-conductors**.

Example : Non-metals (except graphite), wood, glass, rubber, wax etc.

Types of Conductors : The electric conductors are classified into two categories based on the mechanism of flow of current. They are :

- (i) Metallic (or) Electronic conductors.
- (ii) Electrolytic (or) Ionic conductors.

Metallic (or) Electronic Conductors : The conductors which permit flow of electric current through them due to the movement of electrons are called **metallic conductors**. In metallic conductors, flow of electrons takes place from high potential region to low potential region. No chemical changes occur in these conductors due to the flow of electricity. Hence, no transfer of matter. The conductivity decreases with the increase of temperature in these conductors.

Example : Metals, alloys, graphite etc.

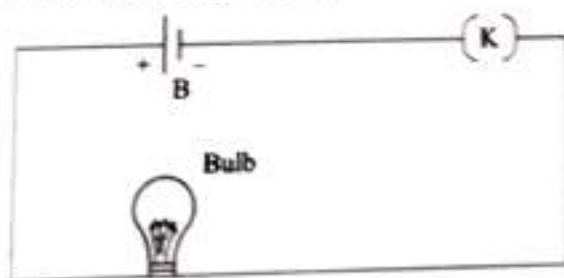


FIGURE 6.1 : Metallic Conduction

3. **Electrolytic (or) Ionic Conductors (or) Electrolytes :** The conductors which permit flow of electric current in the fused state (molten state) or in aqueous solution are called **electrolytic conductors or electrolytes**.

Electrolytes conduct current due to the movement of ions towards the oppositely charged electrodes. Chemical reactions take place in electrolytes due to the flow of electricity. Hence, mass of electrolytes decreases. The conductivity of electrolytes increases with the increasing of temperature.

Example : Acids, bases and metal salts.

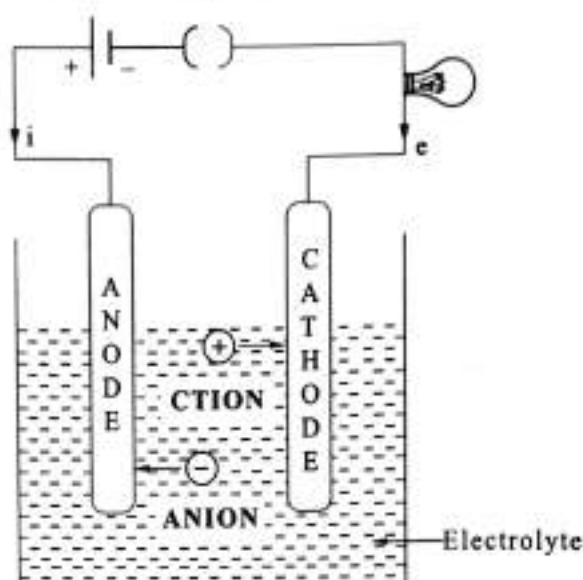


FIGURE 6.2 : Electrolytic Conduction

4. **Non-Electrolytes** : The substances which do not permit flow of electric current in the molten state (or) in aqueous solution are called *non-electrolytes*.

Example : Sugar, Urea, Glucose, Alcohol, Benzene etc.

6.2 TYPES OF ELECTROLYTES

Based on the extent of ionisation, the electrolytes are divided into two types. They are :

- (a) Strong electrolytes.
- (b) Weak electrolytes.

1. **Strong Electrolytes** : The electrolytes which ionise almost completely even at moderate concentrations are called strong electrolytes. The conductivity of strong electrolytes is high due to containing of more ions.

Example : Strong acids like HCl , HNO_3 , H_2SO_4 etc.

Strong bases like KOH , NaOH , $\text{Ba}(\text{OH})_2$ etc.

Salts like NaCl , KNO_3 , CuSO_4 etc.

2. **Weak Electrolytes** : The electrolytes which ionise partially at moderate concentrations and having low conductivity are called as *weak electrolytes*.

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Examples : Weak acids like CH_3COOH , HCN , H_2CO_3 , H_3BO_3 etc.

Weak bases like NH_4OH , $\text{Mg}(\text{OH})_2$, $\text{Al}(\text{OH})_3$ etc.

Salts like AgCl , BaSO_4 etc.

6.3 COMPARE AND CONTRAST THE METALLIC CONDUCTORS AND ELECTROLYTIC CONDUCTORS

| S.No. | Metallic Conductors | Electrolytic Conductors |
|-------|--|---|
| 1. | The conductors which permit flow of electricity due to the movement of electrons are called <i>metallic conductors</i> . | The conductors which permit flow of electricity in the fused state (or) in solution are called <i>electrolytic conductors</i> . |
| 2. | They conduct the current by the flow of electrons from cathode to anode. | They conduct the current by movement of ions towards oppositely charged electrodes. |
| 3. | No chemical reactions occur due to flow of current. | Chemical reactions take place due to flow of current. |
| 4. | They do not involve the transfer of matter. | They involve transfer of matter. |
| 5. | The conductivity decreases with the increase of temperature. Ex : Metals and alloys. | The conductivity increases with the increase of temperature. Ex : Acids and bases. |

6.4 ARRHENIUS THEORY OF ELECTROLYTIC DISSOCIATION

This theory was proposed by Arrhenius, a Sweden chemist in 1887 to explain the behaviour of electrolytes.

MAIN POSTULATES OF ARRHENIUS THEORY

1. Electrolytes in solution (or) in molten state split into positive and negative ions. The process of splitting of an electrolyte is called **ionisation** (or) **electrolytic dissociation**.
2. The positively charged ions are called **cations** and negatively charged ions are called **anions**.
3. The total positive charge of cations is equal to the total negative charge of anions. So, the electrolyte behaves as electrically neutral.
4. The properties of electrolytes in solution are the properties of the ions produced.

Example : CuSO_4 in aqueous solution shows the properties of Cu^{+2} and SO_4^{-2} ions.

5. The process of ionisation is reversible. The ions and undissociated molecules are in dynamic equilibrium.



6. When electricity is passed through the electrolyte, cations move towards cathode and anions move towards anode.
7. The ions discharge their charges at the electrode, i.e., anions by losing of electrons and cations by gaining of electrons lost their charges. So, oxidation takes place at anode and reduction takes place at cathode.
8. The ratio between the number of molecules dissociated into ions to the total number of molecules taken initially is called degree of Ionisation or dissociation.

Degree of Ionisation (α)

$$= \frac{\text{No. of molecules dissociated into ions}}{\text{Total no. of molecules taken initially}}$$

9. The degree of ionisation increases with dilution and at infinite dilution it approaches unity, i.e., dissociation is complete. Further, the ionisation of electrolyte depends on nature of solute, nature of solvent and temperature.

6.5 ELECTROLYSIS

The process of decomposition of an electrolyte by the passage of electricity is called **electrolysis**. In the electrolysis, electrical energy is converted into chemical energy, i.e., chemical reactions take place due to the passage of electricity.

Electrolysis is carried out in a vessel known as electrolytic cell. The electrolyte is taken in the cell in the form of solution or in molten state. Two platinum wires or rods are placed in the electrolyte, which act as electrodes. The electrodes are connected with the help of Cu wires to the two poles or terminals of a battery. (+ ve and - ve poles). When electricity is passed through the electrolyte, the ions move towards oppositely charged electrodes. Chemical reactions occur at the electrodes with the electrolyte and formation of decomposition of products and the current flows through the solution.

Ionisation of Electrolyte : $MA \rightarrow M^{+n} + A^{-n}$

at cathode : $M^{+n} + ne^{-} \rightarrow M$ (Reduction)

at anode : $A^{-n} \rightarrow A + ne^{-}$ (Oxidation)

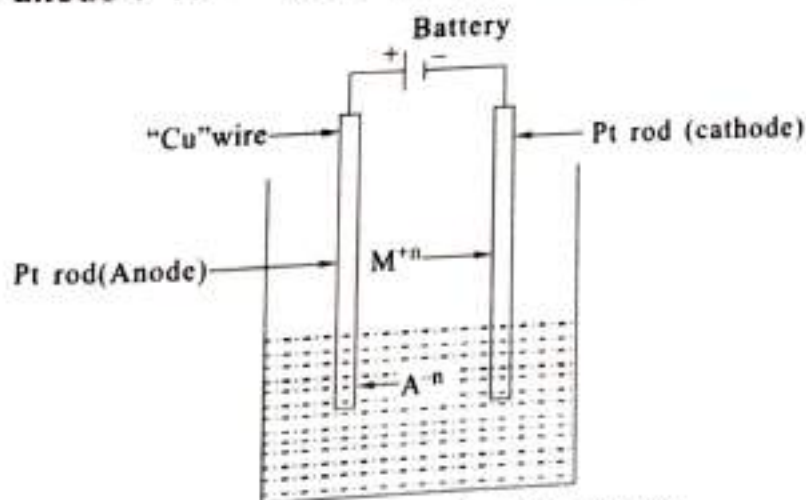


FIGURE 6.2 : Electrolytic Conduction

6.6 FARADAY'S LAWS OF ELECTROLYSIS

The relation between the quantity of electricity passing through an electrolyte and the amount of substance produced at the electrode was studied by Michael Faraday. The results were expressed in the form of two laws known as **Faraday's laws of electrolysis**.

Faraday's I-Law : It is defined as : "*The mass of the substance liberated (or) dissolved (or) deposited at an electrode is directly proportional to the quantity of electricity passing through the electrolyte*".

This is expressed mathematically,

$$w \propto Q$$

$$(or) \quad w = eQ \quad \dots\dots\dots (1)$$

where, w = Mass or weight of element deposited (or) liberated at electrode

e = Electro chemical equivalent

Q = Quantity of electricity in coulombs.

But $Q = ct$

So, the equation (1) may be written as

$$w = ect \quad \dots\dots\dots (2)$$

where, c = current strength in amperes

t = time in seconds.

Faraday's II-Law : It is defined as : "*If the same quantity of electricity is passed through different electrolytes, the mass of different elements deposited or liberated at the electrodes are proportional to their chemical equivalent (E)*".

$$w \propto E$$

$$(or) \quad \frac{W}{E} = \text{constant.}$$

$$(or) \quad \frac{w_1}{E_1} = \frac{w_2}{E_2}$$

$$(or) \quad \frac{w_1}{w_2} = \frac{E_1}{E_2} \quad \dots\dots\dots (3)$$

where, w_1 = wt. or mass of 1st element

E_1 = Chemical equivalent of 1st element

w_2 = wt. or mass of 2nd element

E_2 = Chemical equivalent of 2nd element

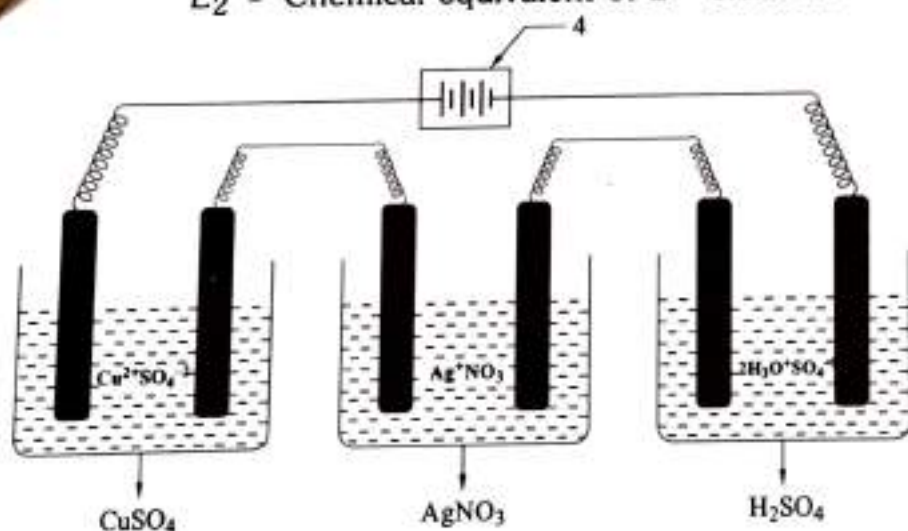


FIGURE 6.3 :

Explanation of II-law : If Q coulombs of electricity is passing through three electrolytic cells connected in series containing aqueous solutions of CuSO_4 , AgNO_3 and H_2SO_4 as electrolytes, the masses of Cu , Ag and H_2 produced at the cathode in 3 cells are in the ratio of their chemical equivalents.

$$\begin{aligned} W_{\text{Cu}} : W_{\text{Ag}} : W_{\text{H}} \\ &= E_{\text{Cu}} : E_{\text{Ag}} : E_{\text{H}} \\ &= 31.75 : 108 : 1 \end{aligned}$$

6.7 CHEMICAL EQUIVALENT AND ELECTROCHEMICAL EQUIVALENT

1. **Electro Chemical Equivalent (ECE)** : The mass of a substance deposited or liberated or dissolved at an electrode by passing 1 coulomb of electricity is called **electro chemical equivalent**.

From Faraday's I-law :

$$w = eQ \quad (\text{or}) \quad e = \frac{w}{Q} \quad (\text{or}) \quad e = \frac{w}{ct}$$

If $c = 1 \text{ amp}$, $t = 1 \text{ sec}$, i.e., 1 coulomb of electricity is passed through the electrolyte, then

$$e = w$$

The unit of e.c.e. is $\text{grams coulombs}^{-1}$ (or) $\text{grams amp}^{-1} \text{ sec}^{-1}$.

2. **Chemical Equivalent (E)** : The mass or weight of a substance deposited (or) liberated (or) dissolved at an electrode by the passage of one faraday (F) of electricity during the electrolysis is called **chemical equivalent (E)**.

Chemical Equivalent of an element or ion is calculated by the following equation.

Chemical equivalent of an element or ion

$$= \frac{\text{Atomic weight}}{\text{Valency of element (or) Ion}}$$

Chemical Equivalent (or) Equivalent weight of some important elements.

| S.No. | Element | Atomic Wt | Valency | Equivalent Weight |
|-------|-----------|-----------|---------|-------------------|
| 1. | Sodium | 23 | 1 | $23/1 = 23$ |
| 2. | Magnesium | 24 | 2 | $24/2 = 12$ |
| 3. | Aluminium | 27 | 3 | $27/3 = 9$ |
| 4. | Hydrogen | 1 | 1 | $1/1 = 1$ |

| | | | | |
|-----|----------|------|---|------------------|
| 5. | Oxygen | 16 | 2 | $16/2 = 8$ |
| 6. | Copper | 63.5 | 2 | $63.5/2 = 31.75$ |
| 7. | Zinc | 65.4 | 2 | $65.4/2 = 32.7$ |
| 8. | Silver | 108 | 1 | $108/1 = 108$ |
| 9. | Ferrous | 56 | 2 | $56/2 = 28$ |
| 10. | Ferric | 56 | 3 | $56/3 = 18.66$ |
| 11. | Chlorine | 35.5 | 1 | $35.5/1 = 35.5$ |
| 12. | Calcium | 40 | 2 | $40/2 = 20$ |

3. **Faraday (F)** : Faraday is the quantity of electric current carried by one mole of electrons (i.e., 6.023×10^{23} electrons).

$$F = N \times e \Rightarrow 6.023 \times 10^{23} \times 1.602 \times 10^{-19} \text{ coulomb} \\ = 96,500 \text{ coulombs.}$$

N = Mole value

e = Charge of electron

6.7.1 *Relation Between Chemical Equivalent (E) and Electro Chemical Equivalent (e)*

1 Faraday = 96500 coulombs of electricity produces E gm. of element

1 coulomb of electricity produces $\frac{E}{F}$ grams of element.

i.e.,
$$e = \frac{E}{F}$$

By substituting 'e' value in Faraday's 1st law equation,

$$w = \frac{Ect}{F} \quad (\text{or}) \\ w = \frac{EQ}{F}$$

6.8 SOLVED PROBLEMS ON FARADAY'S LAW**PROBLEM-1**

0.4 amperes of current is passing through a metal salt solution for 100 seconds. If 0.05 grams of metal deposited, what is its electro chemical equivalent.

Solution :

Current (c) = 0.4 amperes

Time (t) = 100 seconds

w.t. of metal = 0.5 g

$$e = ? ; w = ect$$

$$(or) \quad e = \frac{w}{ct} = \frac{0.05}{0.4 \times 100} = 0.00125 \text{ gram/coulomb.}$$

PROBLEM-2

The electro chemical equivalent of a metal is 0.00028 grams/coulomb. Calculate the weight of metal deposited by the passage of 10 amperes of current for 10 minutes ?

Solution :

$$e = 0.00028 \text{ g/col.}$$

$$c = 10 \text{ amperes}$$

$$t = 10 \times 60 = 600 \text{ seconds.}$$

$$w = ?$$

$$w = ect = 0.00028 \times 10 \times 600 \text{ grams} \\ = 1.68 \text{ grams}$$

PROBLEM-3

A current of 0.5 amp. is passed through molten $AlCl_3$ for 96.5 seconds. Calculate the mass of Al deposited on the cathode ?

Solution :

$$\text{Current (c)} = 0.5 \text{ amp}$$

$$\text{time (t)} = 96.5 \text{ seconds}$$

$$\text{Atomic weight of Al} = 27$$

$$\begin{aligned}
 \text{Valency of Al} &= 3 \\
 \text{Equivalent weight of Al} &= \frac{27}{3} = 9 \\
 \text{Faraday (F)} &= 96500 \text{ coulombs} \\
 w &= ?
 \end{aligned}$$

The equation to calculate weight is

$$\begin{aligned}
 w &= \frac{Ect}{F} \Rightarrow \frac{9 \times 0.5 \times 96.5}{96500} \\
 &= 4.5 \times 10^{-3} \text{ g}
 \end{aligned}$$

PROBLEM-4

A current of 0.5 amperes is sent through a solution of CuSO_4 for 20 minutes using pt electrodes. Calculate the weight of Cu deposited?

Solution :

$$\text{Current (c)} = 0.5 \text{ amp}$$

$$\text{Time (t)} = 20 \times 60 = 1200 \text{ seconds}$$

$$\text{At. wt of Cu} = 63.5$$

$$\text{Valency of Cu} = 2$$

$$\text{Equivalent wt of Cu} = \frac{63.5}{2} = 31.75$$

$$F = 96500 \text{ coulombs.}$$

$$w = ?$$

$$\begin{aligned}
 w &= \frac{Ect}{F} = \frac{31.75 \times 0.5 \times 1200}{96500} \text{ g} \\
 &= \frac{3175 \times 0.5 \times 12}{96500} \text{ g} = 0.1976 \text{ g}
 \end{aligned}$$

PROBLEM-5

0.5 grams of Ag was deposited by passing certain amount of current during the electrolysis of AgNO_3 ? Find the amount of current?

WARNING

IF ANYBODY CAUGHT WILL BE PROSECUTED

Solution:

$$w = 0.5 \text{ g.}$$

$$\text{At. wt. of Ag} = 108$$

$$\text{Valency of Ag} = 1$$

$$\text{Eq. wt. of Ag (E)} = \frac{108}{1} = 108$$

$$\text{Faraday (F)} = 96500 \text{ col.}$$

$$Q = ?$$

$$w = \frac{EQ}{F} \quad (\text{or})$$

$$Q = \frac{wF}{E} \Rightarrow \frac{0.5 \times 96500}{108} = \frac{48250}{108} = 446.2 \text{ col}$$

PROBLEM-6

On passing electricity for 30 minutes, through HCl solution, 1 gram of hydrogen is liberated. Calculate the current strength?

Solution :

$$\begin{aligned} \text{Time (t)} &= 30 \times 60 \text{ seconds} \\ &= 1800 \text{ seconds} \end{aligned}$$

$$\text{At. wt. of hydrogen} = 1$$

$$\text{Valency of hydrogen} = 1$$

$$\text{Eq. wt of Hydrogen (E)} = \frac{1}{1} = 1$$

$$\text{Current (c)} = ?$$

$$\text{Faraday (F)} = 96500 \text{ coulombs}$$

$$w = \frac{Ect}{F} \quad (\text{or})$$

$$c = \frac{wF}{Et} \Rightarrow \frac{1 \times 96500}{1 \times 1800} \text{ amp} = 53.6 \text{ amp.}$$

PROBLEM-7

Calculate the no. of Faradays of electricity required to deposit 60 grams of magnesium?

Solution :

$$\text{wt. of Mg} = 60 \text{ grams}$$

$$\text{At. wt of Mg} = 24$$

$$\text{Valency of Mg} = 2$$

$$\text{Eq. wt. of Mg(E)} = \frac{24}{2} = 12$$

$$\text{no. of Faradays} = ?$$

12 grams of Mg (1 GEW) is deposited by 1F

60 grams of Mg is deposited by how many Faradays ?

$$\text{no. of Faradays required} = \frac{60 \times 1}{12} = 5 \text{ F}$$

PROBLEM-8

In the electrolysis of molten NaCl, 6.023×10^{22} electrons are transferred from anode to cathode. Calculate the weight of chlorine liberated at anode?

Solution :

$$\text{At. wt of Cl} = 35.5$$

$$\text{Valency of Cl} = 1$$

$$\text{Eq. wt. (E)} = \frac{35.5}{1} = 35.5$$

$$1\text{F} = 96500 \text{ col} = 6.023 \times 10^{23} \text{ electrons}$$

$$6.023 \times 10^{22} \text{ electrons} = 9650 \text{ coulomb}$$

$$\text{i.e., } Q = 9650 \text{ coulombs}$$

$$\text{w.t of Cl (w)} = ?$$

$$w = \frac{EQ}{F} \Rightarrow \frac{35.5 \times 9650}{96500} = 3.55 \text{ grams.}$$

PROBLEM-9

A 100 watt, 110 volt incandescent lamp is connected in series with an electrolytic cell containing ZnSO_4 solution. What mass of Zn is deposited by the current flowing for 10 hours?

Solution :

$$\text{Current in amperes (c)} = \frac{100 \text{ w}}{110 \text{ v}} = \frac{10}{11} \text{ amp}$$

$$\begin{aligned} \text{Time} &= 10 \text{ hrs.} = 10 \times 60 \times 60 \\ &= 36000 \text{ seconds} \end{aligned}$$

$$\text{At. wt. on Zn} = 65.4$$

$$\text{Valency of Zn} = 2$$

$$\text{Eq. wt. of Zn (E)} = \frac{65.4}{2} = 32.7$$

$$\text{Wt of Zn (w)} = ?$$

$$w = \frac{Ect}{F} \Rightarrow \frac{32.7 \times 10 \times 36000}{11 \times 96500}$$

$$= \frac{327 \times 360}{11 \times 965} = 11.08 \text{ g}$$

PROBLEM-10

During the electrolysis of an aqueous solution of NaCl, 10.3 g of Cl_2 is liberated at anode. Calculate the weight of H_2 liberated from acidulated water, if same quantity of electricity used in the electrolysis of NaCl was passed?

Solution :

If the same quantity of electricity was passed, as per Faraday's II-law

$$\frac{W_1}{E_1} = \frac{W_2}{E_2}$$

Eq. Wt of 1st element

$$\text{i.e., } Cl (E_1) = \frac{35.5}{1} = 35.5$$

W.t of chlorine (W_1) = 10.3 g

Eq. Wt of 2nd element

$$\text{i.e., } H (E_2) = \frac{1}{1} = 1$$

w.t of 2nd element

$$\text{i.e. } H (W_2) = ?$$

$$\frac{W_1}{E_1} = \frac{W_2}{E_2} \Rightarrow \frac{10.3}{35.5} = \frac{W_2}{1}$$

$$\text{(or) } W_2 = 0.29 \text{ g}$$

Wt of H_2 liberated = 0.29 grams

PROBLEM-11

*The cost of electricity need to deposit 1 g of Mg is 2 rupees.
What is the cost to deposit 45 g of Aluminium?*

Solution :

$$\text{Eq. wt of Mg} = \frac{24}{2} = 12$$

$$\text{Eq. wt of Al} = \frac{27}{3} = 9$$

Cost to deposit 1 g of Mg = 2 rupees

Cost to deposit 12 g of Mg (1 GEW) = $12 \times 2 = 24$ Rs.

i.e., To deposit 1 GEW Mg, 24 rupees is required.

No. of gram equivalents of Al in 45 grams = $\frac{45}{9} = 5$

So, cost to deposit 45 grams of Al (i.e., 5 GEW Al) of

$$= 5 \times 24 = 110 \text{ rupees.}$$

6.9 ELECTROLYSIS OF FUSED NaCl/ AND AQUEOUS NaCl/

1. **Electrolysis of Molten (Fused) Sodium Chloride :** Fused sodium chloride is taken as an electrolyte in the electrolyte cell. Two platinum rods are dipped in it, which act as electrodes. They are connected to the two terminals of a battery. The electrode connected to the positive terminal is called anode and the electrode connected to the negative terminal is called **cathode**. On passing electricity through it, the Na^+ ions move towards cathode and Cl^- ions move towards anode. Cl^- ions lose electrons and converted into Cl atoms (i.e., Oxidation takes place at anode). Two chlorine atoms combine and liberated as Cl_2 gas. Sodium ions are converted into atoms by gaining of electrons. These Na atoms are deposited at cathode (i.e., reduction takes place at cathode). Reactions in the cell.

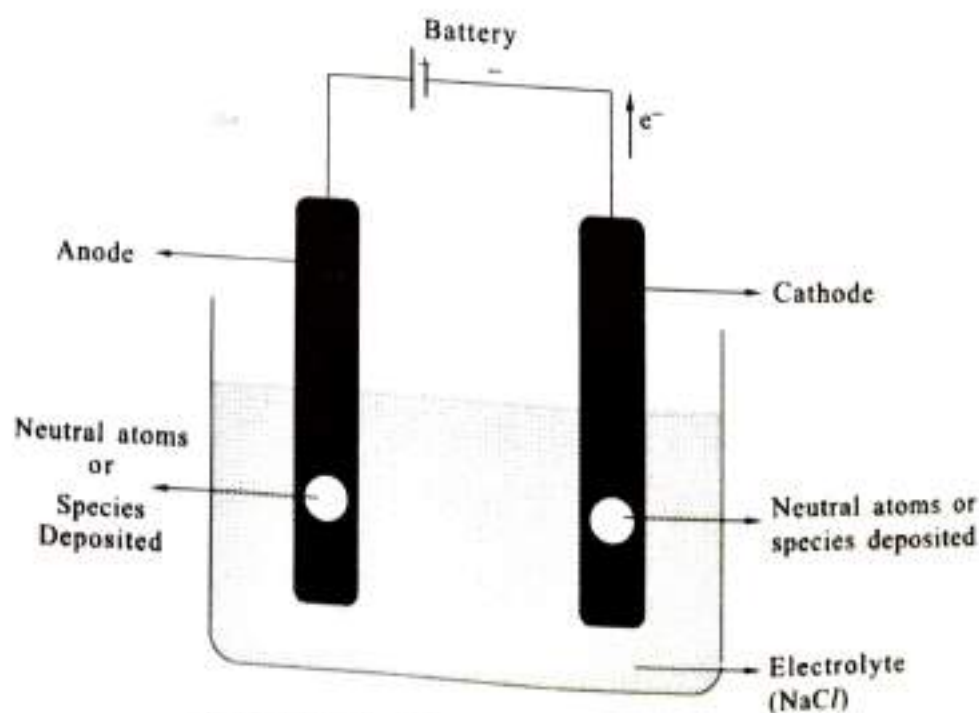
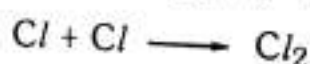
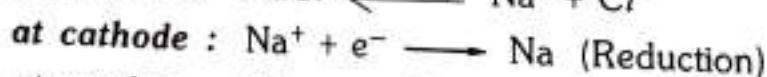
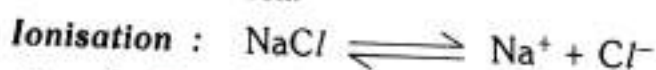
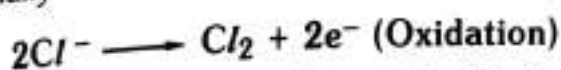
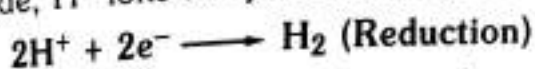


FIGURE 6.4 : Electrolysis of Fused NaCl

2. **Electrolysis of Aqueous NaCl Solution :** Aqueous NaCl solution is electrolysed by nelson cell. A perforated U-shaped iron container is used as electrolytic cell. This also acts as cathode. A graphite rod is suspended in the cell, which acts as anode. The solution contains Na^+ and Cl^- ions and due to slight dissociation of water, very small amounts of H^+ and OH^- ions are also present. When electricity is passed, Na^+ and H^+ move towards the cathode and Cl^- and OH^- move towards anode. At anode, Cl^- ions are preferentially discharged due to its smaller discharge potential.



At cathode, H^+ ions are preferentially discharged



In solution Na^+ and OH^- combine to form NaOH.

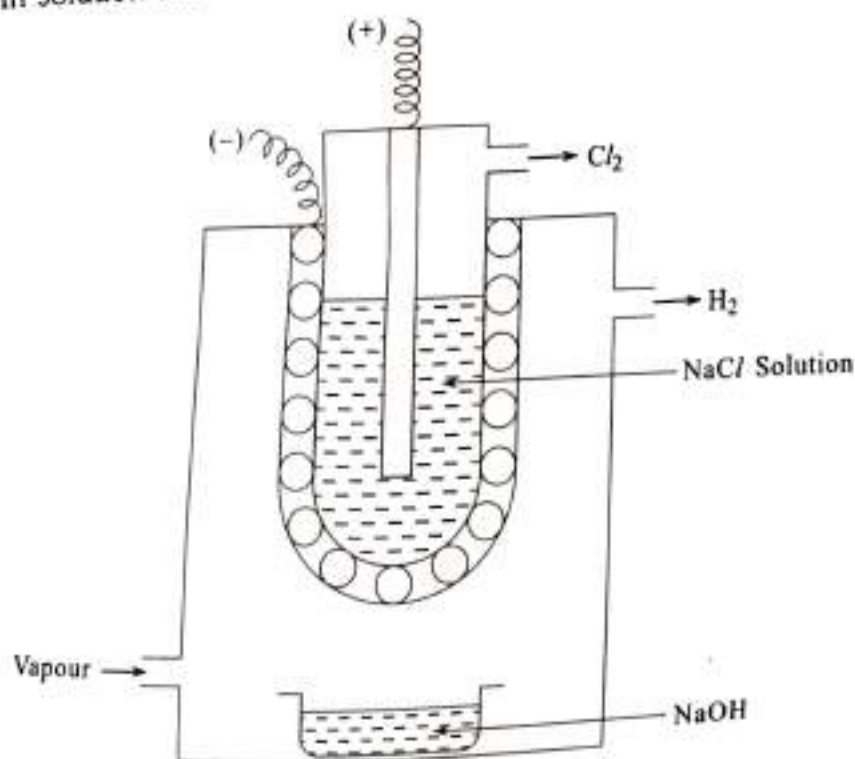


FIG 6.5 : Nelson Cell

6.10 ELECTRO PLATING AND ELECTROLYTIC REFINING

1. **Electroplating :** Electroplating is process in which a metal is deposited on another metal by passing a direct current through an electrolytic solution by means of electrolysis.

Uses of Electroplating :

- (i) To increase corrosion resistance.
- (ii) To get better appearance or decorative purpose.
- (iii) To increase the hardness.
- (iv) To change the surface properties of metals and non metals.

Process of Electroplating : The cleaned base metal is made as the cathode and the coat metal is taken as the anode. A solution of the coat metal salt is taken as the electrolyte. The electrodes are connected to the battery and current is passed. Now electrolysis takes place and the coat metal is deposited over the base metal.

The nature of coating depends on :

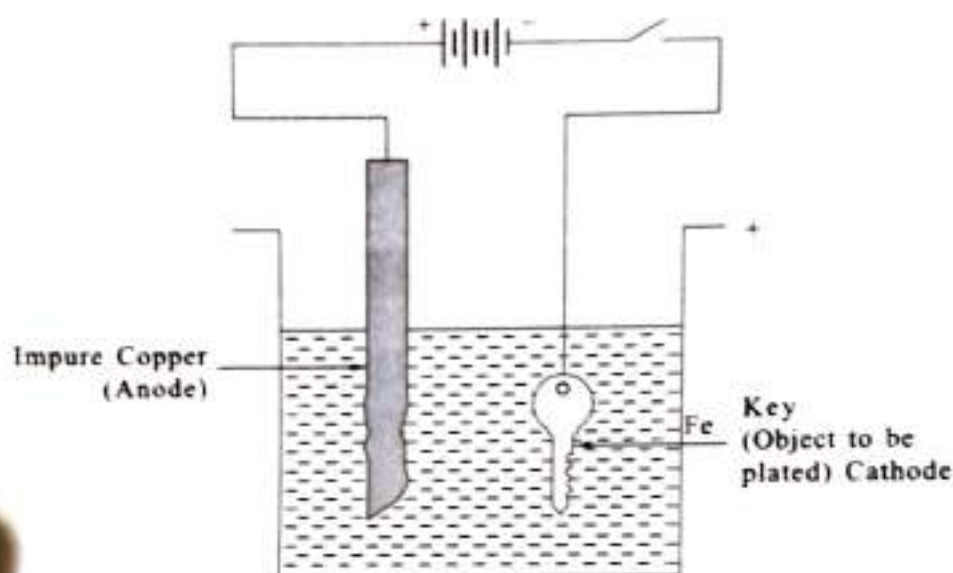
- (i) The current density.
- (ii) Time.
- (iii) Temperature and
- (iv) The concentration of the electrolyte.

For example, to electroplate a key made of iron with copper, the iron key is taken as the cathode. A copper rod is taken as the anode. Copper sulphate solution is the electrolyte. When the electrodes are connected to a source of electricity, copper is deposited over the iron key.

Reactions :

At cathode : $\text{Cu}^{+2} + 2\text{e}^- \longrightarrow \text{Cu}$ (reduction)

At anode : $\text{Cu} \longrightarrow \text{Cu}^{+2} + 2\text{e}^-$ (oxidation)

Electroplating Diagram :**FIG 6.6 :** Electroplating of Iron Key

2. **Electrolytic Refining of Copper (Purification of Copper by Electrolysis) :** Copper is usually mined from its ore known as blister copper. It is about 98 to 99 per cent pure. However, the electro-refining process can easily make it 99.95% pure, which makes it a good product to be used in electrical components.

In this process a block of impure copper is taken as an anode. Acidified Copper sulfate used as electrolyte along with pure copper sheet as a cathode. In this process of electrolysis, copper sulfate divides into a positive ion of copper (Cu^{+2}) and a negative ion of sulfate (SO_4^{-2}). The positive copper ion (Cu^{+2}) or cations travel towards the negative electrode made of pure copper, where it absorbs the electrons from the cathode, then Cu atoms deposits on the cathode. The copper atoms of impure metal oxidized to copper ions in electrolyte. The impurities settle down at anode as anode mud (sludge).

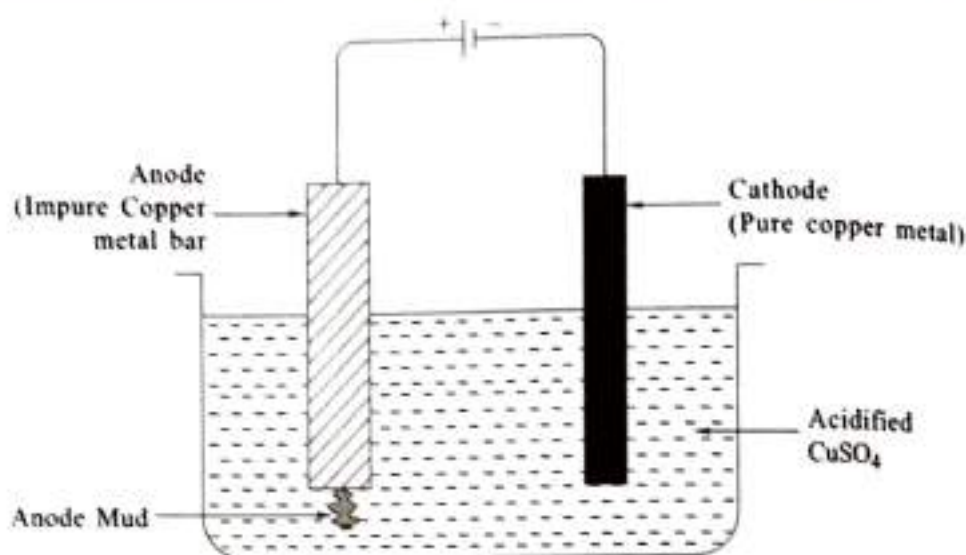
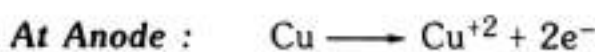
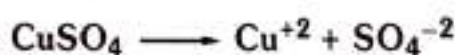


FIG 6.7 : Refining of Copper

Reactions :



SYNOPSIS

1. Electro chemistry deals with the relationship between electricity and chemical changes.
2. The conductors which permit flow of electric current through them due to the movement of electrons are called **metallic** (or) **electronic conductors**.
3. The substances which permit flow of electric current in the fused state or in aqueous solution are called **electrolytes**.
4. The conductivity of electrolytes is due to the ions.
5. A strong electrolyte ionises to a larger extent while a weak electrolyte ionises partially.
6. According to Arrhenius theory of electrolytic dissociation.
 - (a) An electrolyte splits into positive and negative ions in the molten state (or) in solution.

- (b) Dynamic equilibrium exists between the ions and undissociated molecules.
 - (c) When electricity is passed through the electrolyte, the ions are attracted towards the oppositely charged electrode.
 - (d) The ratio of no. of molecules ionised to the total no. of molecules is called degree of ionisation.
 - (e) Degree of ionisation increases with the dilution.
7. The process of decomposition of an electrolyte by the passage of electricity is called **electrolysis**.
8. **Faraday's I-law is defined as** : The mass of the substance liberated or deposited or dissolved at an electrode is directly proportional to the quantity of electricity passing through the electrolyte.
9. The mass of a substance produced by the passage of 1 coulomb of electricity is called **electrochemical equivalent**.
10. **Faraday's II-law is defined as** : if the same quantity of electricity is passed through different electrolytes, the masses of different elements deposited or liberated at the electrodes are proportional to their chemical equivalents.

$$\frac{W_1}{E_1} = \frac{W_2}{E_2}$$

11. Faraday is the quantity of electricity equal to 6.023×10^{23} electrons.
12. 1 F of electricity liberates or deposits 1 gram equivalent of an element.
13. The relation between chemical equivalent and electrochemical equivalent is

$$e = \frac{E}{F} \quad (\text{or})$$

$$E = eF$$

14. Electrolysis is used in the extraction and refining of metals, in electroplating and in electro typing.
15. In electroplating process a metal is deposited on another metal by passing a direct current through an electrolytic solution by means of electrolysis.

OBJECTIVE BITS FOR ECET

1. Which of the following is not a conductor
 - (a) Metal
 - (b) Fused salt
 - (c) Aqueous solution
 - (d) Wax
2. Which of the following is a conductor
 - (a) Wood
 - (b) Graphite
 - (c) Rubber
 - (d) Glass
3. Which of the following is wrong regarding to metallic conductor
 - (a) Current due to movement of ions
 - (b) Graphite is an electronic conductor
 - (c) No chemical change
 - (d) Conductivity decrease with increase of temperature
4. How many Faradays of current required to decompose 45 g of water
 - (a) 1 F
 - (b) 3 F
 - (c) 5 F
 - (d) 7 F
5. The amount of substance deposited at an electrode is directly proportional to
 - (a) Quantity of current passed through electrolytic solution
 - (b) Atomic weight of the substance
 - (c) Both
 - (d) None

6. One Faraday means
- (a) One mole of electrons
 - (b) One gram equivalent of the substance
 - (c) 96500 coulombs
 - (d) All the above
7. Which of the following forms non conducting aqueous solution
- (a) Ethyl alcohol
 - (b) Acetic acid
 - (c) Magnesium chloride
 - (d) Potassium chloride
8. Electrolytic cell converts
- (a) Electrical energy into chemical energy
 - (b) Chemical energy into electrical energy
 - (c) Electrical energy into mechanical energy
 - (d) Electrical energy into heat energy
9. Which of the following is not a strong electrolyte?
- (a) CuSO_4
 - (b) Ba(OH)_2
 - (c) HNO_3
 - (d) AgCl
10. Electrolysis of salt solution results in the formation of
- (a) Oxides
 - (b) Ions
 - (c) Electrons
 - (d) Colloids
11. The metal with maximum conductivity
- (a) Ag
 - (b) Al
 - (c) As
 - (d) Au
12. The unit of electrochemical equivalent
- (a) Gram
 - (b) Coulomb
 - (c) Gram/coulomb
 - (d) Coulomb/gram
13. During the electrolysis
- (a) Oxidation takes place at anode
 - (b) Reduction takes place at cathode
 - (c) a & b
 - (d) None

14. The electrolysis of fused NaCl produces, at anode and cathode respectively
- (a) Na & Cl_2 (b) Cl_2 & H_2
(c) Cl_2 & H_2 (d) H_2 & Cl_2
15. Equivalent weight of Ferric
- (a) 18.66 (b) 28
(c) 31.75 (d) 75.31
16. The electrolysis of aqueous NaCl produces, at anode and cathode respectively
- (a) Na & Cl_2 (b) Cl_2 & Na
(c) Cl_2 & H_2 (d) H_2 & Cl_2
17. In the electrolytic refining of copper
- (a) Impure copper is anode
(b) Pure copper is anode
(c) Both anode and cathode are pure copper
(d) Both anode and cathode are impure copper
18. Which of the following is non-electrolyte ?
- (a) Benzene
(b) Sodium chloride
(c) Ferric chloride
(d) Ferrous sulphate
19. Electrolysis means
- (a) Association of ions (b) Decomposition of electrolyte
(c) Dilution of electrolyte (d) All
20. Ionic conduction is due to
- (a) Electrons (b) Atoms
(c) Ions (d) Molecules

ANSWERS

| | | | | | | | | | |
|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|
| 1.(d) | 2.(b) | 3.(a) | 4.(c) | 5.(a) | 6.(d) | 7.(b) | 8.(a) | 9.(d) | 10.(b) |
| 11.(a) | 12.(c) | 13.(c) | 14.(b) | 15.(a) | 16.(c) | 17.(a) | 18.(a) | 19.(b) | 20.(c) |

SOLVED QUESTION AND ANSWERS

Q. 1. *Point out any 4 differences between electronic and electrolytic conductors ?*

MARCH/APRIL, 2014 [DME] ; APRIL - 2010 ; APRIL/MAY - 2011

Answer :

| S.No. | Electronic Conductor | Electrolytic Conductor |
|-------|--|---|
| 1. | It permits flow current due to movement of electrons. | It conducts current in the molten state due to movement ions. |
| 2. | No chemical reactions occur due to flow of current. | Chemical reactions take place due to flow of current. |
| 3. | They do not involve the transfer of matter. | They involve transfer of matter |
| 4. | Conductivity decreases with the increase of temperature. | Conductivity increases with the increase of temperature. |

Q. 2 *How do you know whether a substance is an electrolyte or not ?*

Answer :

The given substance is taken in a vessel in fused state or in aqueous solution. Two electrodes are placed in it. The electrodes are connected with an ammeter to the battery. If the pointer in ammeter is deflected, the substance is an electrolyte. If the pointer in ammeter is not deflected, the substance is non-electrolyte. If the deflection of the pointer is more, it is a strong electrolyte. If the deflection of the pointer is less, it is a weak electrolyte.

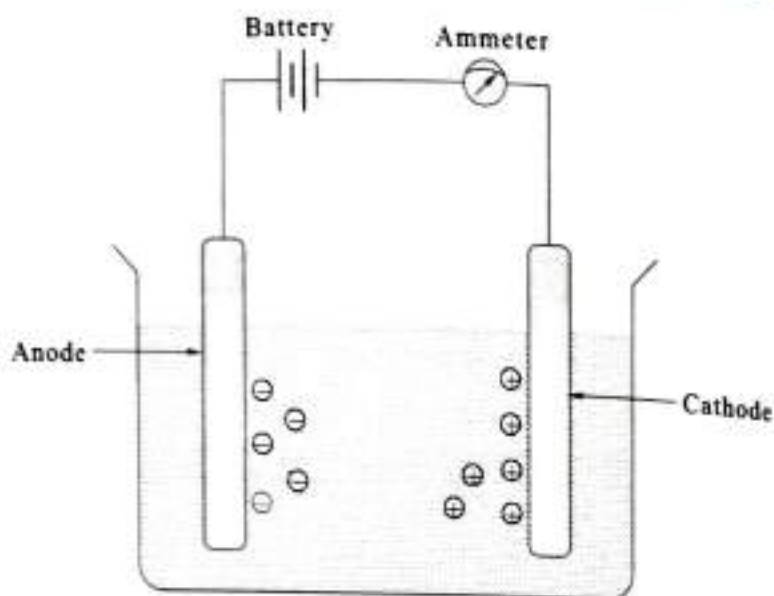


FIGURE :

Q. 3 What is electrolysis ? Explain the mechanism of electrolysis of fused NaCl ?

APRIL, 2014 [EEE] ; 2013 [EEE, ECE] ; 2012 [ECE, EEE] ; 2011 ; 2009

Answer :

The process of decomposition of an electrolyte by the passage of current is called **electrolysis**.

Ex : Electrolysis of NaCl .

Fused sodium chloride is taken as an electrolyte in the electrolytic cell. Two platinum rods are dipped in it, which act as electrodes.

They are connected to the two terminals of a battery. The electrode connected to the positive terminal is called **anode** and the electrode connected to the negative terminal is called **cathode**. If electricity is passed, the Na^+ ions move towards cathode and Cl^- ions move towards anode. Reduction of Na^+ and oxidation of Cl^- occur at the electrodes. Hence, Na is formed at the cathode and Cl_2 is liberated at anode.

Ionisation of NaCl, $\text{NaCl} \rightleftharpoons \text{Na}^+ + \text{Cl}^-$

Reaction at cathode, $\text{Na}^+ + e^- \rightarrow \text{Na}$

Reaction at anode, $2\text{Cl}^- \rightarrow \text{Cl}_2 + 2e^-$

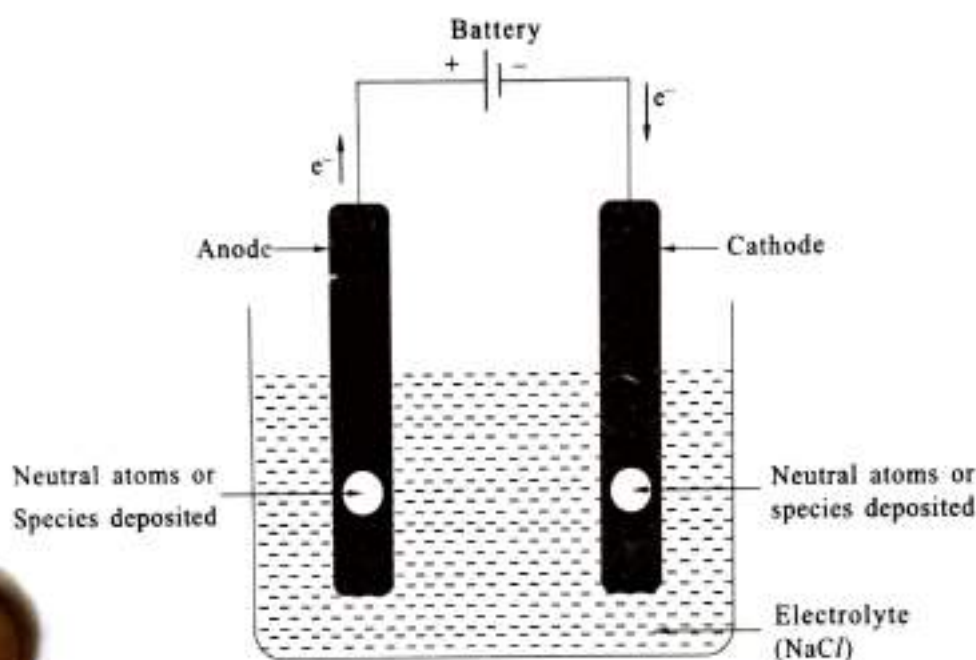


FIGURE :

Q. 4. Explain Faraday's laws of electrolysis ?

APRIL. 2015 [DCE] ; 2013 [DCE, DME, EEE] ;

2012 [ECE, CME, CIVIL, DME] ; 2011 ; 2010, 2009

Answer :

Faraday's I-law is defined as "the mass of the substance liberated (or) dissolved at an electrode is directly proportional to the quantity of electricity passing through the electrolyte".

$$W \propto Q$$

(or) $W = eQ$

W = Mass (or) weight of element

e = Electrochemical equivalent

Q = Quantity of electricity in coulombs

But, $Q = ct,$

So, $W = ect$
 c = current in amperes
 t = time in seconds

Faraday's II-Law is defined as : "If same quantity of electricity is passed through different electrolytes, the masses of different elements deposited or liberated at the electrodes are proportional to their chemical equivalents".

$$W \propto E \text{ (or) } \frac{W}{E} = \text{Constant}$$

$$\text{(or) } \frac{W_1}{E_1} = \frac{W_2}{E_2}$$

Q. 5. What are chemical equivalent and electrochemical equivalent ? How are they related ?

APRIL, 2015 [EEE] ; 2014 [EEE, CME] ; 2013 [EEE] ; 2009, 2010

Answer :

Chemical Equivalent (E) : The mass of a substance deposited (or) liberated at an electrode by the passage of 1 Faraday of current during the electrolysis is called **chemical equivalent : (E)**

The chemical equivalent of an element is ratio of atomic weight to the valency.

$$E = \frac{\text{atomic weight}}{\text{valency}}$$

Electrochemical Equivalent (e) : The mass of an element deposited (or) liberated at an electrode by passing 1 coulomb of electricity is called **electro-chemical equivalent**.

The relation between chemical equivalent (E) and electrochemical equivalent (e) is

$$e = \frac{E}{F} \text{ (or) } E = eF$$

where, F = Faraday. Its value is 96500 coulombs.

PROBLEMS FOR PRACTISE

1. The electro chemical equivalent of a metal is 0.0003296 g/coulomb. Find the amount of metal deposited by a current of 0.2 amp in 50 minutes? [Ans : 0.19776 g]
2. 0.2864 grams of a metal was deposited on passage of a current of 0.5 amperes for 30 minutes through a solution of metal sulphate solution. What is the electro-chemical equivalent of metal? [Ans : 0.00032 g/col]
3. A current of 9.65 amp is passed through an aqueous solution of Ag NO_3 for 10 minutes. Calculate the weight of Ag deposited on the cathode? (at. wt. of Ag = 108)
[Ans : 6.48 g]
4. A current of 0.5 amp is passed through CuSO_4 solution for 45 minutes. Calculate the Wt. of copper deposited? (at. wt. of Cu = 63.5)
[Ans : 0.44 g]
5. A current of 10 amp is passed through molten AlCl_3 for 96.5 seconds. Calculate the wt. of Al metal deposited on the cathode?
[Ans : 0.09 g]
6. Calculate the current required in amperes to deposit 10 g of Ag in 2 hours?
[Ans : 1.242 g]
7. How long a current of 0.5 amp should be passed through molten CuBr_2 to deposit 0.4 g of Br_2 ? (At. wt. of Br = 80)
[Ans : 965 seconds]
8. How much time in hours is required for a current of 2 amp to decompose electrically 18 g of water? [Ans : 26.8 hr]
9. 2 grams of a divalent metal is deposited by the passage of 9650 coulombs of electricity. Find the at. wt. of metal?

(Jan. 2022) [Ans : 40]

10. 3F of electricity is passed through FeCl_3 solution. Calculate the amount of Fe deposited on the cathode? [Ans : 56 g]
11. In the electrolysis of molten NaCl , 4.6 grams of Na is deposited. If same quantity of electricity is passed through MgCl_2 , what weight of Mg is deposited?
[Ans : 2.4]
12. Find the number of electrons passing through a conductor carrying 10^{-2} amperes of current for 10 seconds?
[Ans : 6.22×10^{17} electrons]
13. If 0.5 grams of hydrogen is liberated in the electrolysis of H_2SO_4 what wt of Ag is deposited by passing same amount of electricity through AgNO_3 solution?
14. In the electrolysis AlCl_3 , if 3.0115×10^{24} electrons are transferred from anode to cathode, what weight of Al is deposited at the cathode. [Ans : 45 g]
15. A current of 4 amp passing through AgNO_3 solutions for 10 minutes, deposits 2.686 g of silver. What is the electrochemical equivalent of Ag.
[Ans : 0.00112 g/coulombs]
16. A current of 2 amp passing through NaCl solution for 300 Seconds, deposits 11.5 g of Na. What is the electrochemical equivalent of Na. [Ans : 0.0192 g/coulombs]
17. A current of 3 amp is passed through AlCl_3 solution for 30 minutes, the amount Al deposited is 2.25 g. Calculate the electrochemical equivalent.
[Ans : 0.00042 g/coulombs]
18. Calculate the mass of Cu get deposited on passing of 3 amp of current for 7.5 minutes through CuSO_4 solution.
[Ans : 0.44 g]

19. Calculate the mass of Iron get deposited on passing of 2 amp of current for 15 minutes through Ferric Chloride solution.
[Ans : 0.348 g]
20. 0.197 g of metal is deposited by passing 0.2 amp of current in 25 minutes. What is it's electrochemical equivalent.
[Ans : 0.00065 g/coulombs]
21. The electro chemical equivalent of the metal is 0.00028 gram/coulomb. Calculate the weight of metal deposited by the passage of 5 amp of current for 1 hour.
[Ans : 5.04 g]
22. A current of 5 amps is passed through molten NaCl for 965 Seconds. Calculate the weight of Na deposited at the cathode.
[Ans : 1.15 g]
23. How much of current in coulombs required to deposit 3.175 grams of Cu during the electrolysis of CuSO_4 solution.
[Ans : 9650 coulombs]
24. Calculate the amount of current in coulombs required to deposit 1 mole of Mg.
[Ans : 193000 coulombs]
25. During the electrolysis of an aqueous solution of NaCl, 5.6 litres of Cl_2 is liberated at anode, if the same quantity of electricity is passed through acidulated water. Find the weight of H_2 liberated from cathode.
[Ans : 0.5 g]
26. During the electrolysis of CuCl_2 0.3175 grams of Cu was deposited at cathode. How many moles of Na deposits, if the same quantity of electricity is passed through NaCl solution.
[Ans : 0.001 moles]