Applied Chemistry

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Preface

Applied Chemistry aims to address the needs of the first-year BE/ BTech engineering students. This book deals with the essential and basic concepts of chemistry, as outlined in the first-year syllabi of an engineering course. Written in a very simple and easily understandable manner, it helps even the average student grasp the subject matter very easily.

The unique features of this book are the following:

- Complete syllabus coverage
- Relevant and important topical examples in each unit
- Easy understandable diagrams, equations and problems
- Rich pedagogy
    - 75 Exercise Questions
    - 81 Illustrations
    - 90 Short-Answer Questions

The content is spread over five units.

- **Unit 1** covers Water. It contains topics on Sources of Water, Impurities in Water, Types of Water, Water-Quality Standards, Water-Quality Parameters, Hardness of Water, Boilers, Boiler Troubles Due to Hard Water, Water-Softening Methods, External Treatment, Internal Conditioning (or) Internal Treatment (or) Boiler Compounds, Desalination of Brackish Water, and Drinking Water (or) Potable Water (or) Domestic Water Treatment.
- **Unit 2** presents **Electrochemistry.** It deals with Cells, Representation of a Galvanic Cell, Reversible and Irreversible Cells, Emf of an Electrochemical Cell, Weston Standard Cadmium Cell, Electrode Potential, Determination of Electrode Potential—Nernst Equation, Reference Electrodes, Types of Electrodes, Electrochemical Series or Emf Series—Importance of Electrode Potential, Potentiometric Titration, Conductometric Titrations, Batteries, Lead Accumulator or Acid Storage Cell, Nickel–Cadmium Batteries (NICAD), Lithium Battery, Fuel Cells, and Solar Energy.

- **Unit 3** covers **Corrosion and its Control Methods.** It presents the topics of Classification of Corrosion, Types of Electrochemical Corrosion, Galvanic Series, Factors Influencing Rate of Corrosion, Corrosion-Control Methods, Protective Coatings, Pre-Treatment of Metal Surface or Preparation of Material for Coating, Electroplating or Electrodeposition, Electroless Plating, Surface-Conversion Coating, Anodized Coating, Hot Dipping, and Paints.
- **Unit 4** deals with **Fuels.** It outlines Classification of Fuels, Combustion, Theoretical Calculation of Minimum Air Required for Combustion, Flue-Gas Analysis [Orsat's Method], Important Terms Related to Combustion, Solid Fuels, Metallurgical Coke, Liquid Fuels, Gaseous Fuels, and Determination of Calorific Value by Bomb Calorimeter.
- **Unit 5** presents **High Polymers.** It covers Polymerization, Nomenclature of Polymers, Functionality, Types of Polymerization, Effect of Polymer Structure on Properties, Plastics, Individual Polymers, Conducting Polymers, Polymer Blends and Alloys, Compounding of Plastics, Fabrication of Plastics, Foamed Plastics, Rubber or Elastomers, and Composites.

Apart from these, to help students perform better in examinations, a collection of two-mark and ten-mark important questions is given towards the end. We encourage the student community and the teaching fraternity associated with the contents of this book to make use of it and benefit themselves.

Suggestions and criticisms from the reader will always be welcome.

P N Palanisamy
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Publisher's Note

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Contents

UNIT 1

Water

1.1 INTRODUCTION

Water is one of the abundant available substances in nature. It is essential for the survival and maintenance of all forms of life on earth and consists of forms about 80% of the matter on earth's crust. It also enjoys a unique position in industries.

Although water is plenty on earth, the world's total supply of fresh water is only 2.5% of the total amount, the rest being in the form of oceans. Thus, water available for drinking and other useful purposes is limited. This limited amount of water is further polluted to a great deal by human activities. For drinking and industrial purposes, we need water that is free from undesirable impurities.

1.2 SOURCES OF WATER

The main sources of water are

- Surface water
- Underground water

1.2.1 Surface Water

Surface water exists as rain water, river water, sea water and lake water.

(a) Rain Water It is the main source of water obtained as a result of evaporation of sea water. Rain water may be the purest form of water. It is made impure by pollution in the atmosphere. It contains a considerable amount of industrial gases (like CO_2, SO_2, NO_2, etc.) and suspended solid particles, both of organic and inorganic origin.

(b) River Water It is the water that flows over the surface of the land. It starts from spring water and is fed by rain water. It flows through different kinds/of terrain and dissolves the soluble minerals of the soil. Chlorides, sulphates, bicarbonates of sodium, calcium, magnesium and iron are some of the major mineral salts present in river water. River water also contains organic matter, produced by the decomposition of plants and small particles of sand and rock suspension.

(c) Sea Water This is the most impure form of natural water. Continuous evaporation of water makes it continuously richer in dissolved impurities. It contains sodium chloride, sulphates of sodium, bicarbonates of potassium, calcium, magnesium and a number of other compounds.

(d) Lake Water It contains fewer amounts of dissolved materials.

1.2.2 Underground Water

A part of rain water which falls on the earth's surface percolates into the earth and continues it's journey till it meets a hard rock where it may be stored or come in the form of a spring. During its downward journey, it dissolves a number of salts. Example: Wells and Springs.

From the point of view of industrial applications, it is not usually feasible to use rain water and sea water. Rain water is irregular in supply and generally expensive to collect. Sea water is too saline for most of the industrial uses except cooling.

So river water, lake water and underground water is normally used for industrial and domestic purposes. Each industry has its own specifications for water and so the treatment of water depends on the purpose for which it is to be used.

From the requisites of water for various industries, it is thus seen that water is to be treated to remove all the undesirable substances to suit a particular industry. The process of removing all the types of impurities from water and making it useful for domestic or industrial purposes is called *water treatment*. Before treating water, one must know the nature as well as the amount of impurities present in a given sample.

1.3 IMPURITIES IN WATER

The main impurities present in water are classified into three types.

- Physical impurities

- Chemical impurities
- Bacteriological impurities

Physical Impurities These include suspended and colloidal impurities.

(a) Suspended Impurities Clay, sand, decayed vegetable and animal matter. These make the water turbid.

(b) Colloidal Impurities Finely divided clay and silica, colouring matter,waste products, complex proteins, amines, etc. These impart colour, odour and taste.

Chemical Impurities include dissolved salts and dissolved gases.

(a) Dissolved Salts Chlorides, sulphates, bicarbonates, carbonates of Ca, Mg, Na, etc.

(i) $CaCl_2$, $CaSO_4$, $Ca(HCO_3)_2$, $MgCl_2$, $MgSO_4$, $Mg(HCO_3)_2$ make the water hard.

(ii) $Mg(HCO_3)_2$, $Ca(HCO_3)_2$, Na_2CO_3, $NaHCO_3$, etc.,make the water alkaline.

(b) Dissolved Gases Oxygen, carbon dioxide, hydrogen sulphide, etc.

(i) Oxygen accelerates the rate of corrosion.

(ii) CO_2 and H_2S make the water acidic and corrosive.

Bacteriological Impurities These include pathogenic microorganism like bacteria, which spread various diseases like typhoid, dysentery, hepatitis, etc.

1.4 TYPES OF WATER

Water is classified into two types based on the property of it forming lather with soap solution.

(a) Soft Water Soft water is one that gives good lather readily with soap solution.

$$2RCOONa + \underset{\text{Soft water}}{H_2O} \longrightarrow 2RCOOH + 2\,NaOH$$

(b) Hard Water Water that does not produce lather with soap readily but forms an insoluble precipitate-like white scum is known as hard water.

$$2RCOONa + \underset{\substack{\text{Hard water}\\ \text{(water with } CaCl_2\\ \text{or other impurities)}}}{H_2O} \longrightarrow \underset{\text{Insoluble soap}}{(RCOO)_2Ca} + 2\,NaCl$$

Here, R = long chain fatty acid like palmitic, oleic and stearic acid.

When water with such hardness is used for washing, a large amount of soap is consumed. Thus hardness of water can be defined as the soap-consuming capacity of water.

Common hardness-producing salts present in water are chlorides, sulphates and bicarbonates of calcium and magnesium, i.e. $CaCl_2$, $CaSO_4$, $MgCl_2$, $MgSO_4$,$Ca(HCO_3)_2$ and $Mg(HCO_3)_2$ .Their quantity decides the extent of hardness of water.

1.5 WATER-QUALITY STANDARDS

Water used for drinking purposes should meet certain quality criteria with respect to appearance (turbidity, colour), potability (taste, odour), health (bacteria, nitrates, chlorides, etc.) and toxicity (metals, organics). These criteria are established by health or other regulating agencies to ensure that the water quality in a resource is suitable for drinking purposes.

The following table summarises several quality criteria and their standards for drinking water as suggested by the following agencies.

1. Indian Council of Medical Research (ICMR)
2. World Health Organization (WHO)

Table 1.1 *Standards for drinking water*

S.No	***Parameter***	***Name of Agencies***			
		ICMR		***WHO***	
		A	***B***	***A***	***B***
1.	Colour (units)	5	25	5	50
2.	Turbidity (units)	5	25	5	25
3.	Total dissolved solids	–	–	500	1500
4.	pH	7-8.5	–	7-8.5	–
5.	Total hardness as $CaCO_3$ equivalents	125	350	125	350
6.	Iron	0.3	1.0	0.3	1.0
7.	Manganese	0.1	0.5	0.1	0.5
8.	Nitrate	20	50	–	50-100
9.	Chloride	–	–	–	250
10.	Fluoride	1.0	2.0	0.5	1.0-1.5
11.	Sulphate	200	400	200	400
12.	Pathogenic micro-organisms (Coliform)	–	1 coliform per 100 mL	–	1 coliform per 100 mL

A ⟶ Recommended concentration (mg/L); B ⟶ Maximum permissible concentration (mg/L)

1.6 WATER-QUALITY PARAMETERS

The water-quality parameters are roughly divided into three categories.

1. Physical parameters
2. Chemical parameters
3. Biological parameters

Table 1.2 *Various water-quality parameters*

Physical Parameters	*Chemical Parameters*	*Biological Parameters*
1. Colour	1. Hardness	Pathogenic
2. Turbidity	2. Acidity	microorganisms
3. Taste and odour	3. Alkalinity	
4. Total Dissolved Solids (TDS)	4. Dissolved oxygen	
	5. pH	
	6. Biological Oxygen Demand (BOD)	
	7. Chemical Oxygen Demand (COD)	

Some of the important water-quality parameters are discussed below.

1.6.1 Turbidity

(a) Definition

- Turbidity is a cloudiness or haziness of water caused by individual particles (suspended solids) that are generally invisible to the naked eye, similar to smoke in air.
- Water is said to be turbid if light cannot penetrate through it. The suspended matter in water that prevents the penetration of light inside water is called turbidity.
- Turbidity is usually expressed in Jackson Turbidity Unit (JTU), Nephelometric Turbidity Unit (NTU), Formazin Turbidity Unit (FTU) and milligrams/litre in silica scale.
- The recommended concentration of turbidity in drinking water should not exceed 5 units.

(b) Sources

Presence of finely divided, insoluble impurities which remain suspended in water reduce its clarity. These suspended impurities may be inorganic in nature (clay, silt, silica, ferric hydroxide, $CaCO_3$, S, etc.)

or organic (finely divided vegetable or animal matter, oil, fats, greases, microorganisms etc.).

(c) Sanitary Significance

Turbidity in drinking water causes possible water pollution and health hazards may occur, when used.

(d) Problems Caused by Turbidity

- Objectionable in boilers and in cooling water systems
- Interference in water-softening processes
- Reduction in the disinfection efficiency
- Causes stains on clothes, baths, sinks, porcelain, etc.

(e) Turbidity Removal Methods

Sedimentation followed by

- Coagulation and filtration
- Coagulation and settling
- Coagulation, settling and filtration
- Centrifugation

(f) Turbidity Measurements

- Turbidimeter, nephelometer are instruments used for the determination of turbidity in water.
- Turbidity in water may be measured on a standard silica scale (turbidity is produced by 1 part of finely divided silica in a million parts of distilled water).

1.6.2 Colour

(a) Definition

- Pure water should be absolutely colourless. But the fact is, even water samples obtained from natural resources have some colour ranging from straw-yellow to dark brown.
- The colour of water may also be attributed to the dissolved and suspended solids in water. Colour which is caused by suspended matter is called *apparent colour* and the colour which is contributed by dissolved solids that remains even after the removal of suspended matter is known as *true colour*.
- Colour is usually expressed in milligrams/litre in platinum–cobalt scale or Hazen units.
- The recommended concentration of colour in drinking water should be less than 5 units.

(b) Sources

Colour is due to the presence of dissolved or colloidal dispersed organic matter or of mineral origin.

Examples

- *Mineral origin*: Iron, copper, manganese, dyes
- *Organic origin*: Tannin, peat, humus, algae
- Mainly industries are the basic source of pollution, e.g. dyeing, laundering, textiles, etc.

The ***major sources*** which contribute colour to water are the following:

- The end products from the degradation of organic matter are picked up by water streams and are transported to the water resources that impart colour.
- Colour is also imparted by algal growth. ***Chlamydomonous moecouse*** growing in many surface water bodies excretes a yellowish substances into the water.
- Divalent ions like Fe^{2+} and Mn^{2+} impart colour to the ground water as well as to the surface water.
- Untreated discharge from textile, dyeing, wood pulp, leather and paper industries also impart colour to both surface and ground water.

(c) Sanitary Significance

- It indicates the presence of metal ions and organic matter which affects health, e.g.

  Yellow—Organic matter or chromium

  Yellowish red—Iron

  Red brown—Peat
- Colour in water is usually repulsive.

(d) Problems Caused by Colour

- Organic compounds which contribute true colour to the water exert a high chlorine demand, and hence more quantity of chlorine is necessary for disinfection.
- The colour of water also restricts the penetration of sunlight, which subsequently retards the photochemical reactions, which affects the reoxygenation capacity of water.

(e) Colour Measurements

- The colour of a sample is usually measured with a *tintometer*.

- Colour is measured by comparison with known standards. Potassium chloroplatinate with cobalt chloride is usually prepared as a standard to measure the colour of water. The stock solution of 500 Hazen units and then a series of working standards are prepared from it by dilution. The intensity of colour in water is measured against these standards by direct visual comparison.
- Colour determination is done on the day of collection itself, otherwise Fe^{3+} ion precipitates as $Fe(OH)_3$, which may contribute colour to the sample. Carbonates may also precipitate and exhibit colour.

(f) Methods of Removal of Colour

Coagulation, absorption, filtration and super chlorination

1.6.3 Acidity

(a) Definition

- Acidity is the measure of the ability of water to neutralise bases or it is the tendency of water to donate H^+ ions in order to neutralise the basic anions (HCO_3^-, CO_3^{2-}, OH^-).
- Acidity is usually expressed in terms of pH.

(b) Sources

Acidity is classified into two types.

1. Mineral acidity
2. CO_2 acidity

- ***Mineral acidity*** is due to the presence of mineral acids like HCl, H_2SO_4, HNO_3 and other strong acids in water. This type of acidity is usually introduced into the water resource by metallurgical industries, chemical industries, drainage from abandoned mines, and from many other industrial sewage.
- ***Carbon dioxide acidity*** is due to the presence of free CO_2 in ground and surface waters. CO_2 is released into the water resource due to the oxidation of organic matter by bacteria.
- Humic, fulvic and other organic acids produced by decomposing vegetation also make the water acidic.

(c) Sanitary Significance

- Presence of carbonic acid and other organic acids in water does not have any deleterious effects on health point of view (for example, presence of CO_2 in malt and carbonated beverages has no adverse effects on human beings).

- However, acidic water corrodes concrete pipes and causes dissolution of metals such as Cu, Zn, etc.

(d) Acidity Measurements

- Acidity may be determined by using a pH meter or titrimetry using different acid–base indicators.
- Out of these methods, determination of various types and amounts of acidity is easily carried out by titration with a standard solution of alkaline reagents using methyl orange indicator.

(e) Method of Removal of Acidity

To remove the acidity, a small quantity of sodium hydroxide or sodium carbonate may be added in the water with acidity.

1.6.4 Alkalinity

(a) Definition

- Alkalinity is a measure of the ability of water to neutralise the acid or it is the tendency of water to accept H^+ ions in order to neutralise it with the supply of OH^- ions.
- It is usually expressed in terms of pOH.

(b) Sources

- Alkalinity in water is due to the presence of bicarbonates, carbonates and hydroxides of Ca, Mg, Na and K.
- This type of alkalinity is usually introduced into the water resource by metallurgical industries, chemical industries, drainage from abandoned mines and from many other industrial sewage.

(c) Alkalinity in Water Analysis

In water analysis, it is often desirable to know the kinds and amounts of the various forms of alkalinity present in water.

The alkalinity of water is due to the presence of a wide variety of salts of weak acids such as carbonates, bicarbonates, phosphates, etc., and also due to the presence of weak and strong bases (due to contamination with industrial wastes). The major portion of alkalinity in natural water is caused by the presence of bicarbonates that are formed when water containing free carbon dioxide percolates through soils containing calcium carbonate and magnesium carbonate.

$$CaCO_3 + CO_2 + H_2O \longrightarrow Ca(HCO_3)_2$$

The alkalinity of natural water may be taken as an indication of the concentration of hydroxides, carbonates and bicarbonates.

(d) Classification

1. Bicarbonate alkalinity
2. Carbonate alkalinity
3. Hydroxide alkalinity

(e) Sanitary Significance

High alkalinity in natural water favours the growth of algae and phytoplanktons. Usage of this alkaline water may cause harmful effects on human beings.

(f) Alkalinity Measurements

- Alkalinity may be determined by the potentiometric method or by using pH meter or titrimetry using different acid–base indicators.
- Out of these methods, determination of various types and amounts of alkalinity is easily carried out by titration with standard hydrochloric acid employing phenolphthalein and methyl orange as an indicator separately or in succession.

(g) Experimental Determination of Alkalinity

(i) Principle

The type and extent of alkalinity present in a water sample may be determined by titrating the water with a standard acid to phenolphthalein end point (P) and continuing the titration to methyl orange end point (M). The following reactions may take place.

$$OH^- + H^+ \longrightarrow H_2O \tag{1.1}$$

$$CO_3^{2-} + H^+ \longrightarrow HCO_3^- \tag{1.2}$$

$$HCO_3^- + H^+ \longrightarrow H_2O + CO_2 \tag{1.3}$$

The volume of the acid used up to phenolphthalein end point (P) corresponds to the completion of equations (1.1) and (1.2), while the volume of the acid used after (P) corresponds to the completion of the equation (1.3). The total amount of the acid used from beginning of the experiment corresponds to the total alkalinity present which represents the completion of equations (1.1)–(1.3).

The results are summarised in Table 1.3 from which the amount of hydroxides, carbonates and bicarbonates present in the water sample can be calculated.

Highly alkaline water may lead to caustic embrittlement and also may cause deposition of precipitates and sludges in boiler tubes and pipes.

Table 1.3 *Calculation of hydroxides, carbonates and bicarbonates*

Alkalinity	OH^- (ppm)	CO_3^{2-} (ppm)	HCO_3^- (ppm)
$P = O$	0	0	M
$P = ½ M$	0	$2P$	0
$P < ½ M$	0	$2P$	$(M - 2P)$
$P > ½ M$	$(2P - M)$	$2(M - P)$	0
$P = M$	M	0	0

(P = Phenolphthalein alkalinity; M = Methyl orange alkalinity)

(ii) Procedure

About 20 mL of the given water sample is pipetted out into a clean conical flask. A drop of phenolphthalein indicator is added. Now the water sample becomes pink in colour and this solution is titrated against standard sulphuric acid taken in the burette. The end point is the colour change from pink to colourless. The volume of acid consumed is taken as V_1 mL. To the same water sample, a drop of methyl orange indicator is added and the sample is again titrated against sulphuric acid taken in the burette. The end point is the colour change from yellow to reddish orange. The additional volume of acid consumed is taken as V_2 mL.

(iii) Calculation

Volume of acid used up to phenolphthalein end point = V_1 mL

Normality of acid = N_1

Phenolphthalein alkalinity (P) in terms of calcium carbonate equivalent

$$= \frac{V_1 \times N_1}{20} \times 50 \times 1000 \text{ mg/litre}$$

Additional volume of acid used up to methyl orange end point = V_2 mL

Normality of acid = N_1

Methyl orange alkalinity (M) in terms of calcium carbonate equivalent

$$= \frac{(V_1 + V_2) \times N_1}{20} \times 50 \times 1000 \text{ mg/litre}$$

Then the calculation of hydroxides, carbonates and bicarbonates is made with the help of Table 1.3.

Thus, determination of alkalinity is of importance in

1. Water softening
2. Chemical treatment of waste water
3. Corrosion control

4. Removal of ammonia by air stripping
5. Internal conditioning of boiler feedwater

1.6.5 Nitrogen

(a) Definition

- The nitrogen present in the saline constituents is known as ammoniacal nitrogen and in organic constituents, albuminoid nitrogen. Nitrogen is an inert gas and it is never determined in the water analysis.
- The concentration of nitrogen is expressed in milligrams/litre.
- The normal permissible level of nitrogen compound concentration is 10 mg/L of NO_3^- nitrogen.

(b) Sources

- Nitrogen compounds are also released from proteins and also by the nitrogen–fixing bacteria.
- Certain microbial reactions also contribute to the release of nitrogen. Ions like NO_2^-, NO_3^- are highly mobile in nature and nitrites are easily converted into nitrates through microbial conversion.

Thus, ammoniacal nitrogen can be in the form of ammonia, nitrates and nitrites.

(i) Ammonia

Source: Free ammonia is formed as an initial product of decomposition of nitrogenous organic matter.

Significance: The presence of ammonia indicates that the decomposition has taken place recently.

Permissible Limit: Not greater than 0.15 ppm

Determination Method: Using Nessler's reagent

(ii) Nitrite

Source: Nitrites are the products obtained by oxidation of ammonia.

Significance: Presence of nitrate in water indicates that organic matter is not fully oxidised. It has no corrosive effects on metal.

Limit: Should not be present.

(iii) Nitrate

Source:

- Nitrates are the end products of decomposition of organic matter.

- These are produced by the aerobic stabilisation of organic nitrogen.
- Wastes from chemical fertiliser.

Significance:

- Presence indicates that the organic matter is fully oxidised.
- Greater than 50 mg/L causes methemoglobinemia in children.

Limit:

Permissible: 10 mg/L
Admissible: 50 mg/L

Determination Method: Separation of ammoniacal and albuminoid nitrogen followed by estimation of the nitrogen.

1. Separation of Ammoniacal and Albuminoid Nitrogen

Ammoniacal Nitrogen: The water sample is distilled after adding phosphate buffer. The distillate contains ammoniacal nitrogen.

Albuminoid Nitrogen: The distillation is continued after removal of ammoniacal nitrogen with addition of alkaline $KMnO_4$ and the distillate contains albuminoid nitrogen.

2. Estimation Method of Ammoniacal and Albuminoid Nitrogen

The above distillates are subjected with Nessler's reagent for estimation of nitrogen.

Total Nitrogen: This is estimated by Kjeldhal's method.

Nitrates: By spectrophotometric method by using phenol-disulphonic acid and KOH as reagents.

Nitrites: By spectrophotometric method, by producing a reddish purple dye by diazotisation reaction, using N-(1-naphthyl ethylene diamine) dihydrochloride at pH 2.0 to 2.5.

Sanitary Significance

The presence of nitrogen compounds in water increases the growth of algal and aquatic weeds. Hence an optimum level should always be maintained in order to ensure the safety of the drinking water.

1.6.6 Fluoride

(a) Definition

- When water resources come into contact with the fluoride containing rocks, a large amount of soluble fluorides are released.
- Fluorides are usually expressed in milligrams/litre.

- The normal permissible level of fluoride concentration is 1 mg/L.

(b) Sources

- The general sources are
    1. From geological minerals
    2. Chemical wastes from industries
- The principal sources of fluoride to the physiology of man are ***water*** and ***food***.

(c) Sanitary Significance

- Fluoride, in small doses, has a remarkable influence by strengthening the dental system by inhibiting dental cavities. In high dosages, it may cause dental and skeletal fluorosis.
- The normal permissible level of fluoride concentration is 1 mg/L above which it causes various destructive physiological effects.
- Again deficiency of fluorides may lead to the underdevelopment of bones and may prevent the formation of dental enamel.

(d) Determination Method

Using zirconium–alizarin reagent in Nessler's tube.

Method of Removal of Fluoride

1. By adsorption on activated carbon
2. Precipitation using aluminium salts
3. By using strongly basic anion-exchange resin

1.7 HARDNESS OF WATER

Hardness is the characteristic of water which does not give good lather with soap. This property of water is due to the presence of bicarbonates, chlorides and sulphates of calcium, magnesium and other salts.

1.7.1 Classification of Hardness of Water

Hardness of water can be classified into two categories.

(a) Temporary hardness (or) carbonate hardness
(b) Permanent hardness (or) non-carbonate hardness.

(a) Temporary (or) Carbonate Hardness

This is caused by the presence of dissolved bicarbonates of calcium and magnesium. Temporary hardness is mostly destroyed by mere boiling of water.

During boiling, the bicarbonates are decomposed and form insoluble precipitates. Carbonates and hydroxides can be removed by filtration, while CO_2 escapes out.

$$Ca(HCO_3)_2 \longrightarrow \underset{\text{Insoluble}}{CaCO_3} \downarrow + H_2O + CO_2 \uparrow$$

$$Mg(HCO_3)_2 \longrightarrow \underset{\text{Insoluble}}{Mg(OH)_2} \downarrow + 2CO_2 \uparrow$$

(b) Permanent (or) Non-carbonate Hardness

This is due to the presence of dissolved chlorides and sulphates of calcium and magnesium. Unlike temporary hardness, permanent hardness is not destroyed on boiling.

Total Hardness of Water = Carbonate Hardness + Non-carbonate Hardness

(or)

= *Temporary Hardness* + *Permanent Hardness*

1.7.2 Units of Hardness

The following are the common units used in hardness measurements.

(a) Parts per million (ppm) It is defined as the number of parts by weight of $CaCO_3$ present in million parts by weight of water.

1 ppm = 1 part of $CaCO_3$ equivalent hardness in 10^6 parts of water.

(b) Milligram per Litre (mg/L) It is defined as the number of milligrams of $CaCO_3$ present in one litre of water.

1 mg/L = 1 mg of $CaCO_3$ equivalent hardness in 1 litre of water.

Relationship between ppm and mg/L

$$\begin{aligned}\text{Weight of 1 litre of water} &= 1\text{ kg}\\ &= 1000\text{ g}\\ &= 1000 \times 1000\text{ mg}\\ &= 10^6\text{ mg}\end{aligned}$$

We know that,

$$\begin{aligned}1\text{ mg/L} &= 1\text{ mg of } CaCO_3 \text{ in 1 litre of water}\\ &= 1\text{ mg of } CaCO_3 \text{ in } 10^6 \text{ mg of water.}\\ &= 1\text{ part of } CaCO_3 \text{ per } 10^6 \text{ parts of water.}\\ &= 1\text{ ppm}\end{aligned}$$

Hence 1 mg/litre = 1 ppm

Thus, mathematically both units are equal.

1.7.3 Expression of Hardness

Hardness of water is expressed in terms of number of parts of $CaCO_3$ (or) its equivalent present in a particular quantity of water because

(i) $CaCO_3$ is the most insoluble salt which can be precipitated in water treatment

(ii) Molecular weight of $CaCO_3$ is 100 and its equivalent weight is 50 which is easy for calculations

Calcium Carbonate Equivalent

Thus, hardness is expressed in terms of $CaCO_3$ (or) its equivalent. If water contains $CaCO_3$ alone, the hardness is a measure of number of parts of $CaCO_3$. Usually, water contains some other salts. Hence, all the hardness–causing impurities are first converted in terms of their respective weights equivalent to $CaCO_3$ by using the relation

$$\begin{matrix}CaCO_3\\ \text{equivalent}\end{matrix} = \frac{\text{Weight of hardness producing salt}}{\text{Molecular weight of the salt}} \times \begin{matrix}\text{Molecular weight}\\ \text{of } CaCO_3\end{matrix}$$

or

$$\begin{matrix}CaCO_3\\ \text{equivalent}\end{matrix} = \frac{\text{Weight of hardness producing salt}}{\text{Equivalent weight of the salt}} \times \begin{matrix}\text{Equivalent weight}\\ \text{of } CaCO_3\end{matrix}$$

Table 1.4 *Molecular weights of some hardness-producing salts*

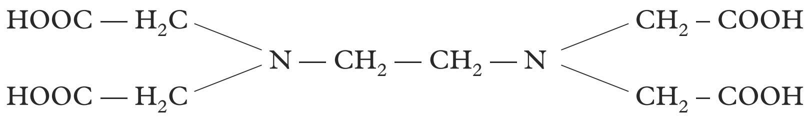
S.No	***Molecular Formula of Salt***	***Molecular Weight***
1	$Mg(HCO_3)_2$	146
2	$Ca\ (HCO_3)_2$	162
3	$CaCO_3$	100
4	$MgCO_3$	84
5	$CaSO_4$	136
6	$MgSO_4$	120
7	$CaCl_2$	111
8	$MgCl_2$	95
9	Ca^{2+}	40
10	Mg^{2+}	24
11	$Ca(NO_3)_2$	164
12	$Mg(NO_3)_2$	148

1.7.4 Estimation of Hardness of Water by EDTA Method

The hardness of water can be estimated by EDTA method. This is a reliable method because of its greater accuracy.

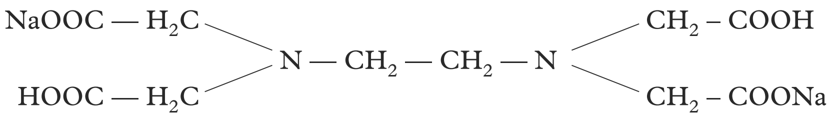
(a) EDTA EDTA is Ethylene Diamine Tetra Acetic acid.

(b) Molecular Structure of EDTA



EDTA is insoluble in water, and its disodium salt is used as a complexing reagent. In this complexometric method, disodium salt of ethylene diamine tetra acetic acid is actually used.

(c) Structure of Disodium Salt of EDTA



(d) Principle

Estimation of hardness by EDTA method is based on the principle that EDTA forms metal complexes with hardness-producing metal ions in water. These complexes are stable when the pH is maintained between 8 and 10. In order to maintain the pH, a buffer solution (NH_4Cl-NH_4OH mixture)is added. The completion of the complexation reaction is indicated by Eriochrome Black-T indicator. When this indicator is added to the sample water, it forms indicator–metal complexes of wine-red colour.

$$Ca^{2+}/Mg^{2+} + \underset{\substack{\text{Indicator}\\\text{(blue colour)}}}{\text{EBT}} \longrightarrow \underset{\substack{\text{Unstable complex}\\\text{(wine-red)}}}{[\text{Ca/Mg-EBT}]}$$

This wine-red solution is titrated against EDTA, and EDTA replaces EBT indicator from [Ca/Mg-EBT] complex. The colour of the solution changes from wine-red to steel-blue at the end point.The total hardness is thus determined.

$$\underset{\substack{\text{Unstable complex}\\\text{(wine-red)}}}{[\text{Ca/Mg-EBT}]} + \text{EDTA} \longrightarrow \underset{\substack{\text{Stable complex}\\\text{(colorless)}}}{[\text{Ca/Mg – EDTA}]} + \underset{\text{(Steel-blue)}}{\text{EBT}}$$

The temporary hardness is removed by boiling and after the removal of precipitate by filtration, the permanent hardness in the filtrate is determined by titration with EDTA as before.Therefore,

Total hardness – Permanent hardness = Temporary hardness

(e) Experimental Procedures

(i) Standardisation of EDTA Solution:

20 ml of standard hard water is taken in a conical flask. 5 ml of buffer solution and a few drop of EBT indicator are added. The solution is titrated against EDTA taken in a burette. The end point is the colour change from wine-red to steel-blue colour. Let the volume of EDTA consumed be V_1 ml.

Calculation

V_1 ml of EDTA consumes 20 ml of std. hard water

$$= 20 \times 1 \text{ mg of } CaCO_3 \text{ eq. hardness}$$

$$1 \text{ ml of EDTA consumes} = \frac{20}{V_1} \text{ mg of } CaCO_3 \text{ eq. hardness}$$

(since 1ml of std. hard water = 1mg of $CaCO_3$)

(ii) Estimation of Total Hardness:

20 ml of sample hard water is pipetted out into a conical flask and titrated against EDTA taken in a burette by adding the buffer and the indicator to get the end point. Let the volume of EDTA consumed be V_2 ml.

Calculation

V_2 ml of EDTA consumes 20 ml of sample hard water

We know

$$1 \text{ ml of EDTA consumes} = \frac{20}{V_1} \text{ mg of } CaCO_3 \text{ eq. hardness}$$

$$V_2 \text{ ml of EDTA consumes} = \frac{20}{V_1} \times V_2 \text{ mg of } CaCO_3 \text{ eq. hardness}$$

$$20 \text{ ml of sample hard water} = \frac{20}{V_1} \times V_2 \text{ mg of } CaCO_3 \text{ eq. hardness}$$

∴ 1000 ml of sample hard water contains,

$$= V_2 \times \frac{20}{V_1} \times \frac{1000}{20} \text{ mg of } CaCO_3 \text{ equivalent hardness}$$

$$\boxed{\textit{Total hardness} = 1000 \times \frac{V_2}{V_1} \textit{ mg/litre (or) ppm}}$$

(iii) Estimation of Permanent Hardness:

250 ml of water sample is boiled off to a volume of 50 ml in a beaker to remove temporary hardness. The temporary hard salts settle down. Filter and wash thoroughly and make up the solution again to 250 ml.

From this, 20 ml of the solution is titrated against the EDTA as done before. Let the volume of EDTA consumed be V_3 ml.

Calculation

V_3 ml of EDTA consumes 20 ml of boiled sample hard water

We know

$$1 \text{ ml of EDTA consumes} = \frac{20}{V_1} \text{ mg of CaCO}_3 \text{ eq. hardness}$$

$$V_3 \text{ ml of EDTA consumes} = V_3 \times \frac{20}{V_1} \text{ mg of CaCO}_3 \text{ eq. hardness}$$

20 ml of boiled sample hard water

$$= V_3 \times \frac{20}{V_1} \text{ mg of CaCO}_3 \text{ eq. hardness}$$

∴ 1000 ml of boiled sample hard water contains

$$= V_3 \times \frac{20}{V_1} \times \frac{1000}{20} \text{ mg of CaCO}_3 \text{ equivalent hardness}$$

$$= 1000 \times \frac{V_3}{V_1} \text{ mg/litre (or) ppm}$$

$$\boxed{\textit{Permanent hardness} = 1000 \times \frac{V_3}{V_1} \textit{ mg/litre (or) ppm}}$$

(iv) Estimation of Temporary Hardness:

This can be calculated by using the following methods.

Temporary Hardness = Total hardness – Permanent hardness

(or)

$$\textit{Temporary Hardness} = 1000 \times \left[\frac{(V_2 - V_3)}{V_1}\right] \textit{ mg/litre (or) ppm}$$

Note: NH_4Cl–NH_4OH buffer is used in the titration in order to maintain a pH of 8–10. At this pH only, the complexation of Ca^{2+} and Mg^{2+} ions with EBT and EDTA takes place.

(f) Advantages of EDTA Method

1. This method is more accurate in the estimation of hardness of water than other methods.
2. It is a convenient and more rapid process.

Example 1 *If a sample of water contains 72 mg of Mg^{2+} ions per litre, calculate its hardness in terms of calcium carbonate equivalent.*

Solution Given

$$\text{The amount of } Mg^{2+} \text{ ions} = 72 \text{ mg/L}$$

$$\text{Atomic weight of magnesium} = 24$$

$$\text{Amount equivalent to } CaCO_3 = \frac{72}{24} \times 100$$

$$= 300 \text{ mg/L}$$

Example 2 *If a sample of water contains 80 mg of Ca^{2+} ions per litre, calculate its hardness in terms of $CaCO_3$ equivalent.*

Solution Given

$$\text{The amount of } Ca^{2+}\text{ions} = 80 \text{ mg/L}$$

$$\text{Atomic weight of magnesium} = 40$$

$$\text{Amount equivalent to } CaCO_3 = \frac{80}{40} \times 100$$

$$= 200 \text{ mg/L}$$

Example 3 *A sample of water contains 240 mg of $MgSO_4$ per litre. Calculate the hardness in terms of $CaCO_3$ equivalents.*

Solution Given

$$\text{The amount of } MgSO_4 = 240 \text{ mg/L}$$

$$\underset{\text{equivalent}}{CaCO_3} = \frac{\begin{array}{c}\text{Weight of hardness-}\\ \text{producing salt}\end{array}}{\begin{array}{c}\text{Molecular weight}\\ \text{of the salt}\end{array}} \times \begin{array}{c}\text{Molecular weight}\\ \text{of } CaCO_3\end{array}$$

We know that the molecular weight of $MgSO_4$ =120.

Thus amount equivalent to $CaCO_3 = \frac{240}{120} \times 100 = 200$ mg/L

Example 4 *The analysis of three samples of water gives the following results. Sample 1 contains 20 mg/L of calcium sulphate, Sample 2 contains 20 mg/L of magnesium bicarbonate and Sample 3 contains 20 mg/L of magnesium sulphate. Find which sample is more hard.*

Solution Sample 1

The amount of calcium sulphate = 20 mg/litre

$$\text{Amount equivalent to } CaCO_3 = \frac{20}{136} \times 100$$
$$= 14.70 \text{ mg/L}$$

Sample 2

The amount of magnesium bicarbonate = 20 mg/L

$$\text{Amount equivalent to } CaCO_3 = \frac{20}{146} \times 100$$
$$= 13.70 \text{ mg/L}$$

Sample 3

The amount of magnesium sulphate = 20 mg/L

$$\text{Amount equivalent to } CaCO_3 = \frac{20}{120} \times 100$$
$$= 16.67 \text{ mg/L}$$

Hence, Sample **3** is hardest.

Example 5 *If a sample of water contains 70 mg of Ca^{2+} ions per litre, calculate its hardness in terms of $CaCO_3$ equivalent.*

Solution Given

The amount of Ca^{2+} ions	= 70 mg/L
We know that, the molecular weight of calcium	= 40

$$\text{Amount equivalent to } CaCO_3 = \frac{70}{40} \times 100 = 175 \text{ mg/L}$$

Example 6 *A sample of water on analysis contains 27.2 mg/L of calcium sulphate, 29.2 mg/L of magnesium bicarbonate, and 24 mg/L of magnesium sulphate. Calculate the total hardness of the sample.*

Solution In order to calculate the total hardness of the sample, these salts have to be converted into their equivalents of $CaCO_3$.

Molecular Formula of Salt	***Molecular Weight***	***Quantity Present***	***Equivalent of $CaCO_3$***
$CaSO_4$	136	27.2	$\frac{27.2 \times 100}{136} = 20$
$Mg(HCO_3)_2$	146	29.2	$\frac{29.2 \times 100}{146} = 20$
$MgSO_4$	120	24	$\frac{24 \times 100}{120} = 20$

Temporary hardness = 20 mg/L [$Mg(HCO_3)_2$ alone]

Permanent hardness = 20+20 = 40 mg/L ($CaSO_4$ + $MgSO_4$)

Total hardness = (Temporary + Permanent) hardness

= 20 + 40 = 60 mg/L (or) ppm

Example 7 *Calculate the temporary and permanent hardness of a water sample having the following data:* $Mg(HCO_3)_2$ *: 292 mg/L,* $Ca(HCO_3)_2$ *: 162 mg/L,* $CaSO_4$ *: 136 mg/L,* $MgCl_2$ *: 190 mg/L,* $CaCl_2$ *: 222 mg/L*

Solution

Salt	*Mol. Wt.*	*Quantity Present*	*$CaCO_3$ Equivalent*
$Mg(HCO_3)_2$	146	292	$\frac{292}{146}$ x 100 = 200 mg/l
$Ca(HCO_3)_2$	162	162	$\frac{162}{162}$ x 100 = 100 mg/l
$CaSO_4$	136	136	$\frac{136}{136}$ x 100 = 100 mg/l
$MgCl_2$	95	190	$\frac{190}{95}$ x 100 = 200 mg/l
$CaCl_2$	111	222	$\frac{222}{111}$ x 100 = 200 mg/l

Temporary hardness: Due to bicarbonates of Mg and Ca

$$Mg(HCO_3)_2 + Ca(HCO_3)_2 = 200 + 100 = 300 \text{ mg/L (or) ppm}$$

Permanent hardness: Due to $CaSO_4$, $MgCl_2$ and $CaCl_2$

$$= 100 + 200 + 200$$

$$= 500 \text{ mg/L (or) ppm}$$

Example 8 *Calculate carbonate and noncarbonate hardness of a sample of water containing dissolved solids as follows:* $Mg(HCO_3)_2$ *: 9.3 mg/L,* $Ca(HCO_3)_2$ *: 20.50mg/L,* $CaSO_4$ *: 26 mg/L,* $MgCl_2$ *: 10 mg/L and NaCl : 60 mg/L*

Solution

Salt	*Mol. Wt.*	*Quantity Present*	*$CaCO_3$ Equivalent*
$Mg(HCO_3)_2$	146	9.3	$\frac{9.3}{146}$ x 100 = 5 mg/L
$Ca(HCO_3)_2$	162	20.50	$\frac{20.50}{162}$ x 100 = 25 mg/L
$CaSO_4$	136	26	$\frac{26}{136}$ x 100 = 10 mg/L
$MgCl_2$	95	10	$\frac{10}{95}$ x 100 = 22.9 mg/L

NaCl does not produce any hardness of water.

Carbonate hardness: Due to presence of bicarbonates of Ca and Mg

$$Mg(HCO_3)_2 + Ca\ (HCO_3)_2 = 6.4 + 12.7 = 19.1 \text{mg/l (or) ppm}$$

Noncarbonate hardness: Due to $CaSO_4$, and $MgCl_2$

$$= 19.1 + 10.5$$

$$= 29.6 \text{ mg/L (or) ppm}$$

Example 9 *A water sample contains 408 mg of* $CaSO_4$ *and 73 mg of* $Mg(HCO_3)_2$ *per litre. What is the total hardness in terms of* $CaCO_3$ *equivalent?*

Solution

Salt	*Mol. Wt.*	*Quantity Present*	$CaCO_3$ *Equivalent*
$CaSO_4$	136	408	$\frac{408}{136} \times 100 = 300$ mg/l
$Mg(HCO_3)_2$	146	73	$\frac{73}{146} \times 100 = 50$ mg/l

Temporary hardness: Due to $Mg(HCO_3)_2 = 50$ mg/L

Permanent hardness: Due to $CaSO_4 = 300$ mg/L

$$\text{Total hardness} = 50 + 300$$
$$= 350 \text{ mg/L(or) ppm}$$

Example 10 *Sample water of 100 mL has a hardness equivalent to 25 mL of 0.16 N* $MgSO_4$*. What is the hardness of water?*

Solution

100 mL of sample of water = 25 mL of 0.16 N $MgSO_4$

$$N_{\text{hardness}} = \frac{25 \times 0.16}{100}$$

Hardness in terms of $CaCO_3$ equivalent

$$= \frac{25 \times 0.16}{100} \times 50 \times 1000$$
$$= 2000 \text{ mg/L or ppm}$$

Example 11 *Hard water of 100 mL required 30 ml of EDTA solution for titration (1 mL of EDTA = 1 mg of* $CaCO_3$*). Calculate the hardness of the sample of water.*

Solution

1 mL of EDTA = 1 mg of $CaCO_3$ equivalent

30 mL of EDTA = 30 mg of $CaCO_3$ equivalent

This amount of hardness is present in 100 mL of hard water. So

$$\text{Hardness present in 1 litre} = \frac{30}{100} \times 1000$$
$$= 300 \text{ ppm}$$

Example 12 *Sample water of 100 mL on EDTA titration with Eriochrome Black-T as indicator consumed 16 mL of 0.024 M EDTA till end point is reached. Calculate the hardness of water.*

Solution

$$1 \text{ ml of } 0.01 \text{ M EDTA} = 1 \text{ mg of } CaCO_3 \text{ equivalent}$$

$$16 \text{ ml of } 0.024 \text{ M EDTA} = \frac{1 \times 16 \times 0.024}{1 \times 0.01}$$

$$= 38.4 \text{ mg of } CaCO_3$$

This amount of hardness is present in 100 mL of water sample.

$$\text{So, hardness present in 1 litre} = \frac{38.4}{100} \times 1000$$

$$= 384 \text{ ppm}$$

Example 13 *Sample of water of 200 mL required 40 mL of 0.01M EDTA for the titration with Eriochrome Black-T indicator. 100 mL of the same sample after boiling and filtering required 20 mL of 0.01M EDTA. Calculate the total carbonate (temporary) and noncarbonate (permanent) hardness of the sample.*

Solution **Total hardness:**

$$1 \text{ mL of } 0.01 \text{ M EDTA} = 1 \text{ mg of } CaCO_3 \text{ equivalent}$$

$$40 \text{ mL of } 0.01 \text{ M EDTA} = 40 \text{ mg of } CaCO_3 \text{ equivalent}$$

This amount of hardness is present in 200 mL of the sample water.

$$\text{So, total hardness present in 1 litre} = \frac{40}{200} \times 1000$$

$$= 200 \text{ ppm}$$

Permanent or noncarbonate hardness:

$$1 \text{ mL of } 0.01\text{M EDTA} = 1 \text{ mg of } CaCO_3 \text{ equivalent}$$

$$20 \text{ mL of } 0.01\text{M EDTA} = 20 \text{ mg of } CaCO_3 \text{ equivalent}$$

This amount of hardness is present in 200 mL of the water sample.

$$\text{So, permanent hardness present in 1 litre} = \frac{20}{200} \times 1000$$

$$= 100 \text{ ppm}$$

Carbonate or temporary hardness:

$$\text{Carbonate hardness} = \text{Total hardness} - \text{noncarbonate hardness}$$

$$= 200 - 100$$

$$= 100 \text{ ppm}$$

Example 14 *Calcium carbonate of 0.5 g was dissolved in dil. HCl and diluted to 500 mL. 50 mL of this solution required 48 mL of EDTA solution for titration. 50 mL of a hard-water sample required 15 mL of the same EDTA solution for titration. Calculate the total hardness of water.*

Solution 500 mL of $CaCl_2$ solution = 0.5 g of $CaCO_3$

= 0.5 × 1000 mg of $CaCO_3$

= 500 mg of $CaCO_3$

Standardisation of EDTA:

1 mL of $CaCl_2$ solution = 1 mg of $CaCO_3$

50 mL of $CaCl_2$ solution = 50 mg of $CaCO_3$

48 mL of $CaCl_2$ solution = 50 mg of $CaCO_3$

$$1 \text{ ml of } CaCl_2 \text{ solution} = \frac{50}{48} \times 1$$

= 1.04 mg of $CaCO_3$

Total hardness:

1 mL of $CaCl_2$ solution = 1.04 mg of $CaCO_3$

15 mL of $CaCl_2$ solution = 1.04 × 15

= 15.6 mg of $CaCO_3$

This amount of hardness is present in 50 mL of the water sample.

$$\text{So, total hardness present in 1 litre} = \frac{15.6}{50} \times 1000$$

= 312 ppm.

Example 15 *Calcium carbonate of 0.25 g was dissolved in dil. HCl and diluted to 250 mL. 100 mL of this solution required 20 mL of EDTA solution for titration. 100 mL of a hard-water sample required 30 mL of the same EDTA solution for titration. 100 mL of the same water sample on boiling, filtering required 10 mL of EDTA. Calculate the total permanent and temporary hardness.*

Solution

250 mL of $CaCl_2$ solution = 0.25 g of $CaCO_3$

= 0.25 × 1000 mg of $CaCO_3$

= 250 mg of $CaCO_3$

1 mL of $CaCl_2$ solution = 1 mg of $CaCO_3$

Standardisation of EDTA:

100 mL of $CaCl_2$ solution = 100 mg of $CaCO_3$

20 mL of $CaCl_2$ solution = 100 mg of $CaCO_3$

$$1 \text{ mL of } CaCl_2 \text{ solution} = \frac{100}{20} \times 1$$

$$= 5 \text{ mg of } CaCO_3$$

Total hardness:

$$30 \text{ mL of } CaCl_2 \text{ solution} = 30 \times 5$$

$$= 150 \text{ mg of } CaCO_3$$

This amount of hardness is present in 100 mL of the water sample.

$$\text{So, total hardness present in 1 litre} = \frac{150}{100} \times 1000$$

$$= 1500 \text{ ppm}$$

Permanent hardness:

$$10 \text{ ml of EDTA solution} = 5 \times 10$$

$$= 50 \text{ mg of } CaCO_3$$

This is present in 100 mL of hard water.

$$\text{So, permanent hardness present in 1 litre} = \frac{50}{100} \times 1000$$

$$= 500 \text{ ppm.}$$

$$\text{Temporary hardness} = \text{Total hardness} - \text{Permanent hardness}$$

$$= 1500 - 500$$

$$= 1000 \text{ ppm}$$

1.7.5 Disadvantages of Hard Water

Some important disadvantages of hard water are the following

1. Hard water is not useful for various domestic purposes, viz. washing, bathing, drinking, etc. The ions responsible for the hardness convert soluble soaps to insoluble precipitates. This causes wastage of soap in washing and bathing. Also, presence of iron salts may result in staining of cloth.
2. Hard water is harmful for many industries such as textile, sugar, paper, laundry, etc. Dissolved calcium, magnesium and iron salts may react and affect the following properties:
    (a) May cause coloured spots on fabrics in textile industry
    (b) May cause difficulties in the crystallisation of sugar in sugar industry
    (c) May cause wastage of lot of soap in laundry
    (d) Giving a smooth and glossy finish to paper in paper industry

3. Hard water is also not suitable in steam generation in boilers since there arise many troubles like scales and sludge formation, corrosion, priming and foaming and caustic embrittlement.
4. Hard water is not suitable in laboratory analysis also because the hardness-producing ions interfere in various reactions.

1.8 BOILERS

Most of the water used in industry and powerhouses is in the form of steam. For steam generation, boilers are almost invariably employed.

1.8.1 Classification of Boilers

Boilers are generally classified according to their pressures into three categories.

(i) Low-pressure boilers: Up to 15 kg/cm^2
(ii) Medium-pressure boilers: 15 to 30 kg/cm^2
(iii) High-pressure boilers: Over 30 kg/cm^2

1.8.2 Boiler Feedwater

The water fed into the boiler for the production of steam is called boiler feedwater.

Requisites (or) Specification of Boiler Feedwater

Water used in boilers should be free from dissolved calcium and magnesium salts and dissolved gases such as oxygen (O_2) and carbon dioxide (CO_2).

Any natural source of water does not supply a perfectly suitable boiler feedwater. The boiler feedwater must have the following requirements.

Table 1.5 *Suggested limits of tolerance for boiler feedwater*

S. No	Parameter	Amount
1	Hardness for 0–10 kg/cm^2 boiler 10–15 kg/cm^2 boiler 15–30 kg/cm^2 boiler Above 30 kg/cm^2	 80 ppm (max) 40 ppm (max) 10 ppm (max) 2 ppm (max)
2	pH	7.0
3	Colour	Colourless
4	Odour	Nil
5	Dissolved gases like O_2 and CO_2	0 ppm

1.9 BOILER TROUBLES DUE TO HARD WATER

If the boiler feedwater contains impurities (or) if the hard water obtained from natural sources is fed directly to the boilers, the following troubles may arise:

1. Scale and sludge formation
2. Boiler corrosion
3. Caustic embrittlement
4. Priming and foaming (carry over)

1.9.1 Scale and Sludge Formation in Boilers

In boilers, water evaporates continuously and the concentration of the dissolved salts increases progressively. When the salt concentrations reach their saturation points, they are thrown out of water in the form of precipitates on the inner walls of the boiler.

If the precipitated matter is soft and slimy, it is called ***sludge***. When the precipitate forms an adherent coating on the inner walls of the boiler, it is called ***scale***.

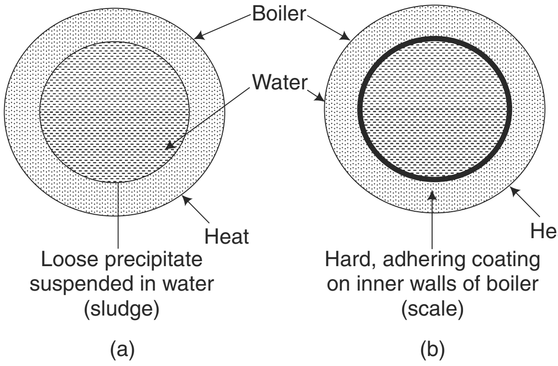


Fig. 1.1 *(a) Sludge formation in boilers; (b) Scale formation in boilers*

(a) Sludge Formation

1. Sludge is a soft, loose and slimy precipitate which forms inside the boiler during steam generation.
2. The main sludge-forming substances in water are $MgCO_3$, $MgCl_2$, $MgSO_4$, $CaCl_2$, etc.
3. Sludges are generally formed at cooler portions of the boiler.
4. Sludges can be easily scrapped off with a wire brush.

Disadvantages of Sludge Formation

1. Sludges are poor conductors of heat, so they waste a portion of heat generated.
2. Excess of sludge formation decreases the efficiency of a boiler.
3. If sludges are formed along with scales then both will be deposited on inner walls of boiler as scales, and then it cannot be removed easily.

Prevention of Sludge Formation

Sludge formation in boilers can be prevented by the following methods:

1. By using well-softened water.
2. By frequent blow-down operation a process in which a portion of concentrated water containing large amount of dissolved salts is replaced with fresh water frequently, during steam making)
3. It can be easily scrapped off with a wire brush

(b) Scale Formation

1. Scale is a hard, adherent coating which forms on the inner walls of the boiler during steam generation.
2. In a low-pressure boiler, the main scale-forming substances are $Ca(HCO_3)_2$ and $MgCl_2$.
3. In a high-pressure boiler, the scale-forming substances are mainly $CaSO_4$ and Silica.

1.9.2 Scale-formation Reactions

(a) In Low-pressure Boilers

(i) Decomposition of $Ca(HCO_3)_2$

$$Ca\,(HCO_3)_2 \xrightarrow{\Delta} \underset{\substack{\text{Soft scale}\\ \text{(Insoluble)}}}{CaCO_3} \downarrow + H_2O + CO_2 \uparrow$$

However, scale composed chiefly of calcium carbonate is soft and is the main cause of scale formation in low-pressure boilers. But in high-pressure boilers, $CaCO_3$ is soluble.

$$CaCO_3 + H_2O \longrightarrow \underset{\text{Soluble}}{Ca(OH)_2} + CO_2 \uparrow$$

(ii) Hydrolysis of Magnesium Salts

Dissolved magnesium salts undergo hydrolysis, forming magnesium hydroxide precipitate.

$$MgCl_2 + 2H_2O \longrightarrow \underset{\substack{\text{Soft scale}\\\text{(precipitate)}}}{Mg(OH)_2 \downarrow} + 2HCl$$

(b) In High-pressure Boilers

(i) Deposition of $CaSO_4$

The solubility of calcium sulphate in water decreases with rise of temperature. Thus, solubility of $CaSO_4$ is 3200 ppm at 15°C and it reduces to 55 ppm at 230°C and 27 ppm at 320°C. In other words, $CaSO_4$ is soluble in cold water, but almost completely insoluble in superheated water. Consequently, $CaSO_4$ gets precipitated as hard scale on the heated portion of the boiler. This is the main cause of scales in high-pressure boilers.

Note: Calcium sulphate is quite adherent and difficult to remove, even with the help of a hammer and chisel.

(ii) Presence of SiO_2 (Silica)

SiO_2 present in water, even in small quantities, deposits as $CaSiO_3$ and $MgSiO_3$. These deposits stick very firmly to the inner side of the boiler surface and are very difficult to remove. One important source of silica in water is the sand filter.

1.9.3 Disadvantages of Scale Formation

(a) High Consumption of Fuel

Scale is a poor conductor of heat and thus it decreases the evaporative capacity of the boiler. So, the consumption of fuel is much more than usual.

(b) Danger of Explosion

Since the scale acts as a heat insulator, the boiler metal is overheated. Due to over heating, the metal expands until the scale on it cracks. When thick scales crack ,the water suddenly comes in contact with overheated boiler metal. This results in the development of high pressure inside the boiler which may lead to a dangerous explosion.

(c) Low Effiency

Due to scale formation, heat available to water is reduced and hence more heat is required to produce steam. This causes overheating of boiler plates and tubes and thus their life is reduced.

1.9.4 Prevention of Scale Formation

Scale formation in boilers can be prevented by the following methods:

(a) External Treatment

This method involves the removal of scale-forming impurities from water before feeding to the boiler, for example

- Lime soda process
- Zeolite process
- Demineralisation process

(b) Internal Treatment

This method involves the addition of chemicals directly to the water in boilers to remove the scale-forming substances which were not completely removed during external treatment, for example

- Colloidal conditioning
- Carbonate conditioning
- Calgon conditioning
- Phosphate conditioning

Table 1.6 *Differences between sludges and scales*

S.No	*Sludges*	*Scales*
1.	Sludges are soft and non-adherent deposits.	Scales are hard deposits which stick very firmly to the inner surface of boiler during steam generation.
2.	Sludges can be removed easily.	Scales are very difficult to remove.
3.	*Disadvantages:* Sludges can transfer heat to some extent and are less dangerous. Excess of sludge formation decreases the efficiency of boiler.	*Disadvantages:* Scales are bad conductors of heat and are more dangerous. Scale formation also decreases the efficiency of a bolier. Any crack developed on the scale leads to an explosion.
4.	*Formation:* Sludges are formed by substances like $MgCl_2$, $CaCl_2$, etc.	*Formation:* Scales are formed by substances like $CaSO_4$, $Mg(OH)_2$.
5.	*Prevention:* It is prevented by either using well softened water or by frequent blow down operation. (Blow down operation is a process in which a portion of concentrated water containing large amount of dissolved salts and replace it by fresh water frequently during steam making)	*Prevention:* It is prevented by (a) *External treatment*-removal of scale formation impurities from water before feeding into the boiler(using Lime-Soda process, Demineralisation process) and (b) *Internal treatment*- involves the removal of scale forming substances which were not completely removed in the external treatment by adding chemicals directly in the boiler during evaporation itself.

1.9.5 Boiler Corrosion

The decay of boiler material by its environment is termed as boiler corrosion. Corrosion in boilers is due to the presence of

(i) Dissolved oxygen
(ii) Dissolved carbon dioxide
(iii) Dissolved salts

(a) Dissolved Oxygen

The presence of dissolved oxygen in water is the main cause of boiler corrosion. When water containing dissolved oxygen is heated in the boiler, the dissolved oxygen gets liberated and attacks the boiler material as follows:

$$2Fe + O_2 + 2H_2O \longrightarrow 2Fe(OH)_2 \downarrow$$

$$\underset{\text{Ferrous hydroxide}}{4Fe(OH)_2 \downarrow} + O_2 \longrightarrow \underset{\text{Rust}}{2[Fe_2O_3.2H_2O] \downarrow}$$

Removal of Dissolved Oxygen

Dissolved oxygen can be removed by chemical (or) mechanical methods.

- **Chemical Method** Sodium sulphite, hydrazine (or) sodium sulphide are some of the chemicals used for removing oxygen.

$$\underset{\text{Sodium sulphite}}{2\,Na_2SO_3} + O_2 \longrightarrow \underset{\text{Sodium sulphate}}{2\,Na_2SO_4}$$

$$\underset{\text{Hydrazine}}{N_2H_4} + O_2 \longrightarrow N_2 + 2\,H_2O$$

$$Na_2S + 2O_2 \longrightarrow Na_2SO_4$$

- **Mechanical Method** Dissolved oxygen can also be removed from water by mechanical de-aeration.
- **Mechanical De-aeration** It is one of the method, used to remove dissolved gases such as O_2 and CO_2.

In this process, water is allowed to fall slowly on the perforated plates fitted inside the tower.

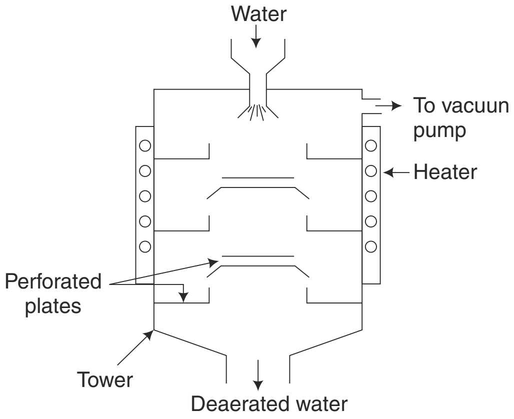


Fig. 1.2 *Mechanical de-aerator*

To reduce pressure inside the chamber, the de-aerator is connected to a vacuum pump. The sides of the tower are heated. The water flowing down through perforated plates undergoes deaeration at high temperature and low pressure. [(High temperature, low pressure, and large exposed surface (provided by perforated plates) reduces the dissolved oxygen in water.]

This is because the solubility of a gas in water is directly proportional to pressure and inversely proportional to temperature (Dalton's law + Henry's law).

(b) Dissolved Carbon Dioxide

Dissolved carbon dioxide in water produces carbonic acid, which is acidic.

$$CO_2 + H_2O \longrightarrow \underset{\text{Carbonic acid}}{H_2CO_3}$$

Carbon dioxide is also released inside the boiler if water used for steam generation contains bicarbonates of calcium and magnesium.

$$Ca(HCO_3)_2 \longrightarrow CaCO_3 \downarrow + H_2O + CO_2 \uparrow$$

$$Mg(HCO_3)_2 \xrightarrow{\Delta} Mg(OH)_2 + 2CO_2 \uparrow$$

Removal of dissolved carbon dioxide

- Carbon dioxide may be removed by adding calculated amount of NH_4OH into water.

  $$2NH_4OH + CO_2 \longrightarrow (NH_4)_2CO_3 + H_2O$$

- Carbon dioxide along with oxygen in water can be removed by mechanical de-aeration.

(c) Dissolved Salts

If water used for steam generation contains dissolved magnesium salts, they liberate acids on hydrolysis.

$$MgCl_2 + 2H_2O \longrightarrow Mg(OH)_2 \downarrow + 2HCl$$

The liberated acid reacts with iron material of the boiler in a chain like reaction producing HCl again and again.

$$Fe + 2HCl \longrightarrow FeCl_2 + H_2 \uparrow$$

$$FeCl_2 + 2H_2O \longrightarrow Fe(OH)_2 \downarrow + 2HCl$$

Thus, presence of even a small amount of $MgCl_2$ will cause corrosion of iron to a large extent.

1.9.6 Caustic Embrittlement

Caustic embrittlement is a type of boiler corrosion caused by using highly alkaline water in the boiler. It means the inter crystalline cracking of boiler metal.

Boiler water usually contains a certain proportion of sodium carbonate, added for water-softening purposes. In high-pressure boilers, Na_2CO_3 decomposes to give sodium hydroxide and carbon dioxide, and this makes the boiler water caustic.

$$Na_2CO_3 + H_2O \longrightarrow 2NaOH + CO_2$$

This NaOH containing water flows into the minute hair cracking usually present on the boiler material by capillary action. Here, water evaporates and the dissolved caustic soda concentration increases progressively. This caustic soda attacks the surrounding area, thereby dissolving iron of the boiler as sodium ferroate.

$$Fe + 2NaOH \longrightarrow \underset{\text{Sodium ferroate}}{Na_2FeO_2} + H_2 \uparrow$$

This causes embrittlement of boiler parts, particularly stressed parts like bends, joints, rivets, etc., causing even failure of the boiler.

Caustic cracking can be explained by considering the following concentration cell;

$$\left| \begin{array}{c|c|c|c} \text{Iron at riverts,} & \text{Concentrated} & \text{Dilute} & \text{Iron at plane} \\ \text{bends, joints, etc.} & \text{NaOH} & \text{NaOH} & \text{surfaces} \end{array} \right|$$

The iron surrounded by the dilute NaOH becomes the cathodic side;while the iron in contact with rather concentrated NaOH becomes the anodic part,which is consequently dissolved or corroded.

Prevention

It can be prevented by

1. Adding sodium sulphate (or) sodium phosphate as softening reagent instead of sodium carbonate
2. Adding tannin, lignin to the boiler water which blocks the hair cracks
3. Adjusting the pH of the feedwater between 8 and 9

1.9.7 Priming and Foaming (Carry-over Process)

Steam sometimes may be associated with small droplets of water. Such steam-containing liquid water is called *wet steam*. These droplets of water may carry with them some dissolved salts and sludge materials present in water. This phenomenon is called *carry over process*. This occurs mainly due to priming and foaming. Priming and Foaming, usually occur together.

(a) Priming It refers to the formation of wet steam by rapid boiling of water at the heating surface.

Causes:

Priming may be caused by

(i) High steam velocity
(ii) Very high water level in the boiler
(iii) Improper boiler design
(iv) Sudden boiling of water

Prevention:

Priming can be controlled by

(i) Controlling the velocity of steam
(ii) Keeping the water level lower
(iii) Good boiler design

(b) Foaming The formation of stable bubbles above the surface of water is called foaming. These bubbles are carried along with steam leading to excessive priming.

Causes:

Foaming may be caused by presence of oil, grease in water and finely divided sludge particles.

Prevention:

Foaming can be prevented by

1. Adding coagulants like sodium aluminate, aluminium hydroxide, ferrous sulphate etc.
2. Adding antifoaming chemicals such as castor oil and synthetic polyamides

1.10 WATER-SOFTENING METHODS

1.10.1 Softening of Water

Water used for industrial purposes should be pure, i.e. it should be free from hardness, scale forming substances and corrosive agents like dissolved O_2, etc. The process of removing hardness-producing salts from water is known as *softening of water*.

Softening of water can be done by the following two ways

(a) **External Treatment or External Conditioning**

Treatment of water before feeding to the boiler is known as external treatment.

(b) **Internal Treatment or Internal Conditioning**

Treating the raw water inside the boiler is known as internal treatment.

Table 1.7 *Differences between external and internal treatment*

S.No	*External Treatment*	*Internal Treatment*
1.	The external treatment of water is carried out before its entry into the boiler.	The internal treatment of water is carried out in the boiler itself.
2.	It includes limesoda process,permutit process and ion-exchange process.	It includes colloidal conditioning, carbonate conditioning, phosphate conditioning, calgon conditioning, etc.
3.	High-pressure boilers require external treatment.	Low-pressure boilers require internal treatment.
4.	It is a preventive method.	It is a corrective method.

1.11 EXTERNAL TREATMENT

It involves the removal of hardness producing salts from the water before feeding into the boiler. The external treatment can be done by the following methods.

(a) Lime soda process (precipitation method)

(b) Zeolite (or) Permutit process (ion-exchange method)

(c) Demineralisation (or) De-ionisation (ion-exchange method)

The above processes are the examples of water softening.

In an ion-exchange process, a reversible exchange of ions taking place between a stationary solid phase and an external liquid mobile phase.

1.11.1 Lime Soda Process

The lime soda process is a very important method used for the softening of water.

(a) Principle

The lime soda process involves the chemical conversion of all the soluble hardness-causing salts by the addition of soda and lime into insoluble precipitates which could easily be removed by settling and filtration.

In this process, water to be softened is treated with calculated amounts of lime $Ca(OH)_2$ and soda Na_2CO_3. For quick completion of reactions, the reagents may be used in 10 % excess. The functions of lime and soda are as follows.

(i) Functions of Lime

Lime removes

1. Temporary hardness
2. Permanent magnesium hardness
3. Dissolved iron and aluminium salts
4. Dissolved CO_2 and H_2S gases
5. Free mineral acids present in water

The reactions involved are as follows:

1. *Removal of temporary calcium and magnesium hardness*
   $Ca(HCO_3)_2 + Ca(OH)_2 \longrightarrow 2CaCO_3 \downarrow + 2H_2O$
   $Mg(HCO_3)_2 + 2Ca(OH)_2 \longrightarrow 2CaCO_3 \downarrow + Mg(OH)_2 \downarrow + 2H_2O$
2. *Removal of permanent magnesium hardness*
   $MgCl_2 + Ca(OH)_2 \longrightarrow Mg(OH)_2 \downarrow + CaCl_2$
   $MgSO_4 + Ca(OH)_2 \longrightarrow Mg(OH)_2 \downarrow + CaSO_4$
3. *Removal of dissolved iron and aluminium salts*
   $Al_2(SO_4)_3 + 3\,Ca(OH)_2 \longrightarrow 2Al(OH)_3 \downarrow + 3CaSO_4$
   $FeSO_4 + Ca(OH)_2 \longrightarrow Fe(OH)_2 \downarrow + CaSO_4$
   $2Fe(OH)_2 + H_2O + 1/2\,O_2 \longrightarrow 2Fe(OH)_3 \downarrow$
4. *Removal of dissolved CO_2 and H_2S*
   $CO_2 + Ca(OH)_2 \longrightarrow CaCO_3 \downarrow + H_2O$
   $H_2S + Ca(OH)_2 \longrightarrow CaS \downarrow + 2H_2O$
5. *Removal of free mineral acid*
   $2HCl + Ca(OH)_2 \longrightarrow CaCl_2 + 2H_2O$
   $H_2SO_4 + Ca(OH)_2 \longrightarrow CaSO_4 + 2H_2O$

(ii) Functions of Soda

During the removal of Mg^{2+}, Fe^{2+}, Al^{3+}, HCl and H_2SO_4 by lime, permanent calcium hardness is introduced in the water due to formation of calcium salts. The permanent calcium hardness, thus introduced on account of the treatment of water with lime and the permanent calcium hardness already present in water before lime treatment, are removed by soda. The reactions involved are as follows:

$$CaCl_2 + Na_2CO_3 \longrightarrow CaCO_3 \downarrow + 2NaCl$$

$$CaSO_4 + Na_2CO_3 \longrightarrow CaCO_3 \downarrow + Na_2SO_4$$

The chemical reactions involved in the lime soda process are quite slow. Moreover, the precipitates formed [particularly of $CaCO_3$ and

$Mg(OH)_2$] are fine and have a tendency to form super-saturated solutions. This results in *after deposition* of these precipitates later in the pipes and boiler tubes leading to their clogging and corrosion. These drawbacks of the process can be overcome by

(a) thorough mixing of chemicals and water,
(b) allowing proper time for the completion of reactions,
(c) the use of accelerators such as active charcoal, and
(d) the use of coagulants such as alum or $NaAlO_2$.

(b) Process

The lime-soda process can be carried out both at room temperature as well as at higher temperatures. The process carried out at room temperature is called ***cold lime soda process*** and that carried out at 94°–100°C is called ***hot lime soda process.***

(i) Cold Lime Soda Process

In this method, water to be softened is treated with calculated quantities of lime and soda at room temperature. Small amounts of a coagulant such as alum, aluminium sulphate, sodium aluminate, etc., are also added. The coagulant helps the finely divided precipitate formed in the process to flocculate. Sodium aluminate also helps in the removal of silica and oil present in water.

Method: The mixture of water, calculated quantities of lime and soda and a small amount of a coagulant is fed from the top into the inner chamber of a vertical circular tank (Fig. 1.3). The chamber is provided with a vertical rotating shaft carrying a number of paddles to ensure vigorous stirring and continuous mixing of water with the chemicals added.

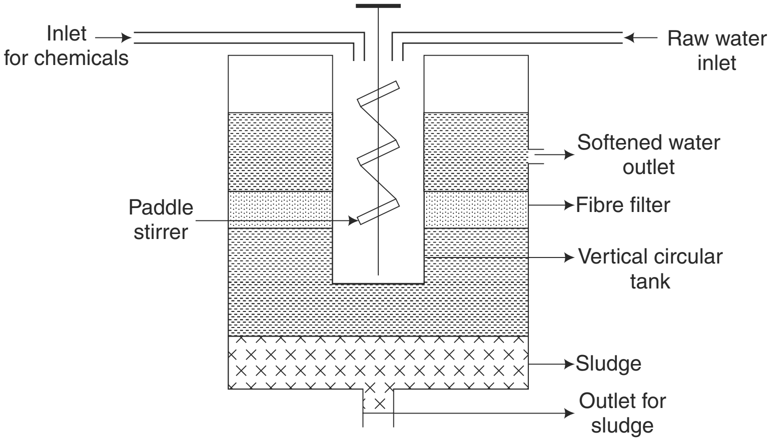


Fig. 1.3 *Cold lime soda process*

The chemical reactions take place and the hardness-producing salts get converted into insoluble precipitates which accumulate in the form of a *heavy sludge*. As the softened water reaches the outer coaxial chamber, it rises upwards and is filtered by a wood-fibre filter and finally taken out from an outlet provided at the top of the outer cylinder. The heavy sludge settles down at the bottom of the outer chamber and is taken out through an outlet.

The softened water obtained from this process contains a residual hardness of about 50–60 ppm.

(ii) Hot Lime Soda Process

In this process, water is treated with the softening chemicals at a temperature of 94°–100°C. Since the process is carried out at a temperature close to the boiling point of the solution, the reaction proceeds faster and the softening capacity of the process increases several times.

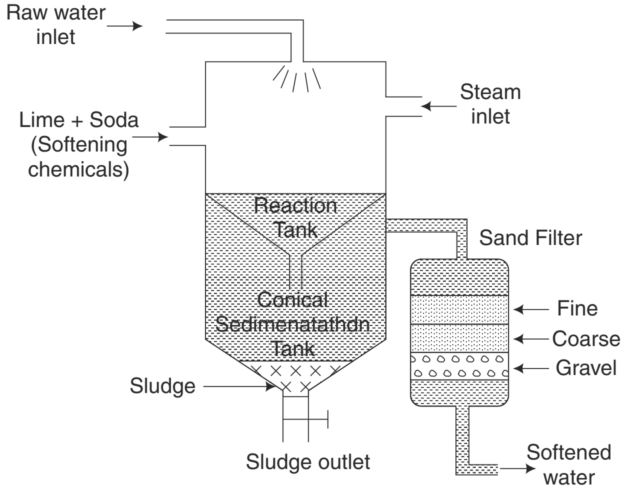


Fig. 1.4 *Hot lime soda process*

At this temperature, the viscosity of water is much less than that at room temperature. Hence, rate of aggregation of particles increases and there is hardly any need of adding any coagulant. Moreover, the dissolved gases also escape to some extent at the temperature of the process.

Method: A typical hot lime soda water softening plant is shown in Fig. 1.4. It consists of

(i) A reaction tank
(ii) A conical sedimentation vessel
(iii) A sand filter

Raw water is fed from the top into the reaction tank where it is thoroughly mixed with calculated quantities of softening chemicals and is agitated with superheated steam. The reactions take place and water gets softened. The softened water containing sludge then enters into the sedimentation vessel where the sludge settles down. The softened water rises up in the vessel, while precipitated sludge is taken out through an outlet provided at the bottom of the vessel. The softened water is then taken to a sand filter which ensures the complete removal of the sludge from softened water.

The softened water obtained from this process contains a residual hardness of 15–30 ppm.

Advantages of the Process

The hot lime soda process has the following advantages.

1. The process is much faster as compared to the cold soda lime process.
2. It is very economical.
3. Lesser amounts of coagulants are needed.
4. The process increases the pH value of the treated water, thereby reducing the corrosion of distribution pipes.
5. To a certain extent, iron and manganese are also removed from water.
6. Much of dissolved gases in water are also removed.
7. Due to an increase in the pH, the amount of pathogenic bacteria in treated water also gets reduced.

Disadvantages of the Process

The hot lime soda process has the following disadvantages.

1. Disposal of large amounts of sludge formed in the process poses problems.
2. The treated water obtained by this process is not completely softened. It still contains a residual hardness of about 15–30 ppm, which is not good for boilers.

Table 1.8 *Difference between cold and hot lime soda process*

S.No	Cold L-S Process	Hot L-S Process
1.	Done at room temperature.	Done near the boiling point of water.
2.	Reactions are slow and takes hours to complete.	Fast and takes only 15 minutes.
3.	Precipitate is finely divided and therefore coagulants are needed.	Coarse precipitate coagulants not needed.
4.	Tank size is large.	Small and compact.
5.	Residual hardness 50 to 60 ppm.	15 to 30 ppm.
6.	Chemicals are consumed by dissolved gas, CO_2 etc.	CO_2 and temporary hardness are automatically removed.

(c) Numerical Calculation

We have already seen that the lime-soda process involves the conversion of soluble hardness-producing salts into insoluble substances which could easily be removed. Besides the removal of hardness causing substances, the process also removes Fe^{2+} and Al^{2+} salts, free mineral acids such as HCl, H_2SO_4 and dissolved gases such as CO_2 and H_2S. From the chemical reaction involved in the process it is clear that:

(i) One equivalent of temporary calcium hardness requires one equivalent of lime

(ii) One equivalent of temporary magnesium hardness requires two equivalents of lime

(iii) One equivalent of permanent magnesium hardness requires one equivalent of lime

(iv) One equivalent each of Fe^{2+}, Al^{2+}, CO_2, H_2S, and H_2SO_4 requires one equivalent of lime

(v) One equivalent of permanent magnesium hardness requires one equivalent of soda

(vi) Soda not only removes permanent calcium hardness already present in water but also removes permanent calcium hardness introduced during the removal of permanent magnesium hardness, Fe^{2+}, Al^{2+}, HCl and H_2SO_4 by lime.

Hence for the calculation of the amounts of lime and soda required for the treatment of a given sample of water, it would be convenient to convert the amounts of all the substances present in the sample in terms of $CaCO_3$ equivalent. As we have already seen, $CaCO_3$ equivalent is given by

$$CaCO_3 \text{ equivalent} = \frac{W \times 50}{E}$$

where

W = mass of the impurity and

E = equivalent mass of the impurity

The lime and soda requirements can be calculated as follows:

(i) Lime Requirement

100 parts by mass of $CaCO_3$ are equivalent to 74 parts by mass of $Ca(OH)_2$. Hence if the amounts of impurities are expressed in terms of their $CaCO_3$ equivalents, the amount of lime required to soften a given sample of water is given by

Lime required for softening

$$= \frac{74}{100} \times [\text{Temp. calcium hardness} + 2 \times \text{Temp. magnesium hardness}$$
$$+ \text{Perm. magnesium hardness} + CO_2 + HCl + H_2SO_4 + Fe^{2+} + Al^{3+}$$
$$+ HCO_3^- - NaAlO_2\text{; all expressed in terms of } CaCO_3]$$

(ii) Soda Requirement

Soda required for softening

$= \frac{106}{100} \times$ [Perm. Calcium hardness + Perm. Magnesium Hardness

+ HCl + H_2SO_4 + Fe^{2+} + Al^{3+} – HCO_3^- – $NaAlO_2$; all expressed in terms of $CaCO_3$ equivalents]

The following points are important to be noted

- 1 equivalent HCO_3^- requires 1 equivalent of lime which simultaneously produces 1 equivalent of CO_3^{2-}.

  $$\underset{\text{2 equivalents}}{Ca(OH)_2} + \underset{\text{2 equivalents}}{2HCO_3^-} \longrightarrow CaCO_3 + \underset{\text{2 equivalents}}{CO_3^{2-}} + H_2O$$

  1 equivalent of CO_3^{2-} ions thus produced may be regarded as equivalent to 1 equivalent of soda. This is why corresponding quantity of HCO_3^- in equivalent has been subtracted in the calculation of soda requirement.

- $NaAlO_2$ requires neither lime nor soda. However, 1 equivalent of $NaAlO_2$ undergoes hydrolysis to produce 1 equivalent of OH^- which may be regarded as equivalent to 1 equivalent of lime.

  $$\underset{\text{1 equivalent}}{NaAlO_2} + 2H_2O \longrightarrow \underset{\text{1 equivalent}}{NaOH} + Al(OH)_3$$

  This is why corresponding quantity of $NaAlO_2$ in equivalent has been subtracted in the calculations of both lime and soda requirements mentioned above.

Example 16 *A sample of water contains following impurities; $Mg(HCO_3)$ = 146 mg/L, $CaCl_2$ = 111 mg/L, $MgSO_4$ = 60 mg/L, and $Ca(NO_3)$ = 82 mg/L. Calculate the quantity of lime (85% pure) and soda (90% pure) needed for softening of 10,000 litres of water.*

Solution:

(i) Calculation of $CaCO_3$ equivalents of hardness-producing substances:

Substance	*Mass of the Substance*	*Equivalent mass of Substance (E)*	*$CaCO_3$ equivalent* $\frac{W \times 50}{E}$
$Mg(HCO_3)_2$	146 mg/L	73	$\frac{146}{73} \times 50 = 100$ mg/L
$CaCl_2$	111 mg/L	55.5	$\frac{111}{55.5} \times 50 = 100$ mg/L
$MgSO_4$	60 mg/L	60	$\frac{60}{60} \times 50 = 50$ mg/L
$Ca(NO_3)_2$	82 mg/L	82	$\frac{82}{82} \times 50 = 50$ mg/L

(ii) Calculation of lime requirement:

Since lime is 85% pure, purity factor = $\frac{100}{85}$

Lime is required for $Mg(HCO_3)_2$ and $MgSO_4$. Hence, 85% pure lime required for the treatment of 10,000 litres of water

$$= \frac{74}{100} \times [2 \times Mg(HCO_3)_2 + MgSO_4 \text{ as } CaCO_3 \text{ equivalents}]$$

$$\times \text{ purity factor} \times \text{volume of water}$$

$$= \frac{74}{101} \times [2 \times 100 + 50] \times \frac{100}{85} \times 10{,}000$$

$$= \frac{74}{100} \times 250 \times \frac{100}{85} \times 10{,}000$$

$$= 2176470.58 \text{ mg}$$

$$= 2.176 \text{ kg}$$

(iii) Calculation of soda requirement:

Since soda is 90% pure, purity factor = $\frac{100}{90}$

Soda is required for $CaCl_2$ and $Ca(NO_3)_2$ and $CaSO_4$ generated as a result of reaction of lime with $MgSO_4$.

Hence, 90% pure soda required for softening of 10,000 litres of water

$$= \frac{106}{100} \times [CaCl_2 + Ca(NO_3)_2 + MgSO_4 \text{ as } CaCO_3 \text{ equi.}]$$

$$\times \text{ purity factor} \times \text{volume of water}$$

$$= \frac{106}{100} \times [100 + 50 + 50] \times \frac{100}{90} \times 10{,}000$$

$$= \frac{106}{100} \times 200 \times \frac{100}{90} \times 10{,}000$$

$$= 2355555.5556 \text{ mg}$$

$$= 2.355 \text{ kg}$$

Example 17 *A water sample gave the following constituents on analysis:* $Ca(HCO_3)_2 = 20$ *ppm,* $Mg(HCO_3) = 18$ *ppm,* $CaSO_4 = 17$ *ppm,* $MgCl_2 = 24$ *ppm* $MgSO_4 = 3$ *ppm and NaCl = 2.5 ppm. Calculate the amount of lime (95% pure) and soda (90% pure) needed for the trearment of 20,000 litres of water. Also calculate the cost of chemicals if costs per 100 kg each of lime and soda are Rs.80 and Rs. 2550 respectively.*

Solution

(i) Calculation of $CaCO_3$ equivalents of impurities:

Substance	***Mass of Substance (W)***	***Equivalent mass of Substance (E)***	***$CaCO_3$ Equivalent $\frac{W \times 50}{E}$***
$Ca(HCO_3)_2$	20 ppm	81	$\frac{20}{91} \times 50 = 12.3$ ppm (or) mg/L
$Mg(HCO_3)_2$	18 ppm	73	$\frac{18}{73} \times 50 = 12.3$ ppm (or) mg/L
$CaSO_4$	17 ppm	68	$\frac{17}{68} \times 50 = 12.5$ ppm (or) mg/L
$MgCl_2$	24 ppm	47.5	$\frac{24}{47.5} \times 50 = 25.3$ ppm (or)mg/L
$MgSO_4$	3 ppm	60	$\frac{3}{60} \times 50 = 2.5$ ppm (or) mg/L
NaCl	2.5 ppm	Ignored as it does not produce hardness	

(ii) Calculation of lime requirement:

Since lime is 95% pure, purity factor = $\frac{100}{95}$

Lime is required for $Ca(HCO_3)_2$ and $MgCl_2$ and $MgSO_4$.

Hence, 95% pure lime required for the treatment of 20,000 litres of water

$$= \frac{74}{100} \times [Ca(HCO_3)_2 + 2 \times Mg(HCO_3)_2 + MgCl_2 + MgSO_4 \text{ as } CaCO_3 \text{ equi.}] \times \text{purity factor} \times \text{volume of water}$$

$$= \frac{74}{100} \times [12.3 + 2 \times 12.3 + 25.3 + 2.5] \times \frac{100}{95} \times 20{,}000$$

$$= \frac{74}{100} \times 64.7 \times \frac{100}{95} \times 20{,}000$$

$$= 1007957.8947 \text{ mg}$$

$$= 1.0079 \text{ kg}$$

(iii) Calculation of soda requirement:

Since soda is 90% pure purity factor = $\frac{100}{90}$

Soda is required for $CaSO_4$ and the calcium hardness generated as a result of reaction of lime with $MgCl_2$ and $MgSO_4$

Hence, 90% pure soda required for softening of 20,000 litres of water

$= \frac{106}{100} \times [CaSO_4 + MgCl_2 + MgSO_4 \text{ as } CaCO_3 \text{ equi}] \times \text{purity factor}$

$\times$ volume of water

$= \frac{106}{100} \times [12.5 + 25.3 + 2.5] \times \frac{100}{90} \times 20{,}000$

$= \frac{106}{100} \times 40.3 \times \frac{100}{90} \times 20{,}000$

= 949288.88 mg

= 0.949 kg

Cost of chemicals:

Given that the cost of lime $= \frac{80}{100}$ = Rs 0.80 per kg

The cost of soda $= \frac{2550}{100}$ = Rs 25.50 per kg

Hence, the cost of lime and soda required for the treatment of the sample of water under consideration

$= 1.0079 \times 0.80 + 0.949 \times 25.50$

= Rs 0.806 + Rs 24.19

= Rs 24.99

1.11.2 Zeolite (or) Permutit Process

Zeolites are naturally occuring hydrated sodium alumino silicate minerals:

$Na_2O.Al_2O_3. \times SiO_2\ yH_2O$ where $x = 2$ to 10 and $y = 2$ to 6.

Natural zeolites are nonporous. The synthetic form of zeolite is known as ***permutit***. Synthetic zeolite is represented by Na_2Ze. Synthetic zeolites are porous and have a jelly structure. They are prepared by heating together china clay, feldspar and soda ash. These zeolites have higher exchange capacity per unit weight than natural zeolites.

In this synthetic zeolite process, the hard water is allowed to percolate through sodium zeolite. The sodium ions which are loosely held in Na_2Ze are replaced by Ca^{2+} and Mg^{2+} ions present in the water.

(a) Process

In this process, the hard water is passed through a bed of sodium zeolite (Na_2Ze).

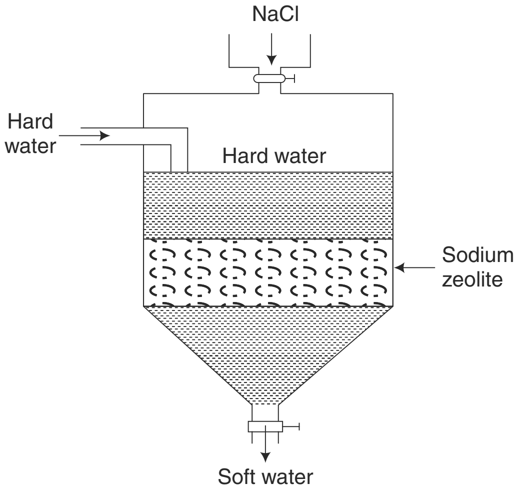


Fig. 1.5 *Zeolite process*

The hardness-causing ions (Ca^{2+}, Mg^{2+}) in hard water is replaced by loosely held sodium ions in zeolite bed (Fig. 1.5). The outgoing soft water contains only sodium ions.

$Na_2Ze + Ca(HCO_3)_2 \longrightarrow CaZe + 2NaHCO_3$

$Na_2Ze + Mg(HCO_3)_2 \longrightarrow MgZe + 2NaHCO_3$

$Na_2Ze + CaCl_2 \longrightarrow CaZe + 2NaCl$

$Na_2Ze + MgCl_2 \longrightarrow MgZe + 2NaCl$

$Na_2Ze + CaSO_4 \longrightarrow CaZe + Na_2SO_4$

$Na_2Ze + MgSO_4 \longrightarrow MgZe + Na_2SO_4$

As sodium ions do not give any hardness to water, the effluent water will be soft.

(b) Regeneration

After the softening process, the zeolite is completely converted into calcium and magnesium zeolites and it gets exhausted. At this stage, the hard-water supply is stopped and the exhausted bed is regenerated by treating with a concentrated 10% brine (NaCl) solution.

$CaZe + 2\,NaCl \longrightarrow Na_2Ze + CaCl_2$

$$\underset{\text{Exhausted zeolite}}{MgZe} + 2\,NaCl \longrightarrow \underset{\text{Regenerated zeolite}}{Na_2Ze} + MgCl_2$$

(c) Limitations of Zeolite Process

1. If the supplied water is turbid, the suspended matter must be removed first by coagulation, filtration, etc. Otherwise, the turbidity will clog the pores of zeolite bed making it inactive.

2. If the water contains coloured ions (Mn^{2+}, Fe^{2+}), these ions should be removed first because these ions produce manganese and iron zeolite, which cannot be regenerated.
3. If any mineral acid present in the water, it will destroy the zeolite bed, therefore it is neutralised first with soda ($Na_2 CO_3$).

(d) Advantages of Zeolite Process

1. Water quality of below 5 ppm hardness is obtained.
2. This equipment is compact and occupies small space.
3. It requires less time for softening.
4. It requires less skill for maintenance and operation.
5. No sludge is formed during this process.
6. Its operation is also easy.

(e) Disadvantages of Zeolite Process

1. This process cannot be used for turbid and acidic water as they will destroy the zeolite bed.
2. This treatment replaces only cations leaving all the anions in the soft water.
3. The zeolite process cannot be used for softening brackish water because brackish water also contains Na^+ ions. So the ion exchange reaction will not take place.

1.11.3 Demineralisation (or) De-ionisation Process (or) Ion-Exchange Process

In this method, ion-exchange resins are used as softening material. In this process, cations like Ca^{2+}, Mg^{2+} and anions like Cl^-, SO_4^{2-} which are responsible for hardness are removed respectively by cation exchange resins and anion exchange resins.

Ion-exchange resins are insoluble, cross-linked, long-chain organic polymers with a microporous structure. The functional groups attached to the chains are responsible for the ion-exchanging properties.

(a) Cation-exchange Resins (RH^+)

Resins containing acidic functional groups (–COOH, $-SO_3H$) are capable of exchanging their H^+ ions with cations of hard water, for example

(i) Sulphonated coals

(ii) Sulphonated polystyrene

$R\text{-}SO_3H$; $R\text{-}COOH \equiv \boldsymbol{RH^+}$

(b) Anion-exchange Resins ($R'OH^-$)

Resins containing basic functional groups ($-NH_2$, $-OH$) are capable of exchanging their OH^- ions with the anions of hard water, for example

(i) Cross-linked quaternary ammonium salts

(ii) Urea-formaldehyde resin

$R\text{-}NR_3OH$; $R\text{-}OH$; $R\text{-}NH_2 \equiv \boldsymbol{R'OH^-}$

(c) Process

The hard water first passed through a cation exchange column (Fig.1.6) which absorbs all the cations like Ca^{2+}, Mg^{2+}, Na^+, K^+, etc., present in the hard water and equivalent amount of H^+ ions are released from this column to water. Thus,

$$2RH^+ + Ca^{2+} \longrightarrow R_2\,Ca^{2+} + 2\,H^+$$

$$2RH^+ + Mg^{2+} \longrightarrow R_2\,Mg^{2+} + 2\,H^+$$

The cation-free water is then passed through an anion-exchange column, which absorbs all the anions like Cl^-, SO_4^{2-} etc., present in the water and equivalent amount of OH^- ions are released from this column to water. Thus,

$$R'(OH)^- + Cl^- \longrightarrow R'\,Cl^- + OH^-$$

$$2R'(OH)^- + SO_4^{2-} \longrightarrow R_2'SO_4^{2-} + 2OH^-$$

$$2R'(OH)^- + CO_3^{2-} \longrightarrow R_2'\,CO_3^{2-} + 2OH^-$$

H^+ and OH^- ions (released from cation-exchange and anion-exchange columns respectively) get combined to produce a water molecule.

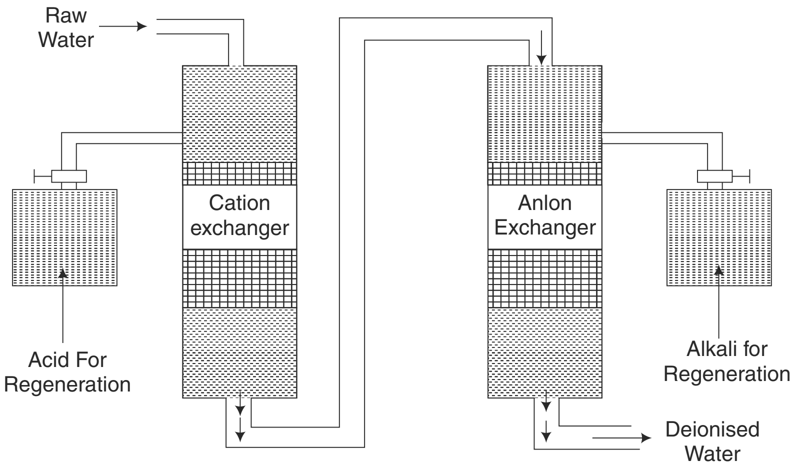


Fig. 1.6 *Demineralization process*

$$H^+ + OH^- \longrightarrow H_2O$$

Thus, the water coming out from the exchanger is free from both cations and anions. This water is known as ion-free water (or) deionised (or) demineralised water.

(d) Regeneration

When the cation-exchange column is exhausted, it can be regenerated by passing a solution of dil. HCl (or) dil. H_2SO_4.

$$R_2\,Ca^{2+} + 2\,H^+ \longrightarrow 2RH^+ + Ca^{2+}$$

$$R_2\,Mg^{2+} + 2\,H^+ \longrightarrow 2RH^+ + Mg^{2+}$$

When the anion-exchange column is exhausted, it can be regenerated by passing a solution of dil. NaOH.

$$R'\,Cl^- + OH^- \longrightarrow R'(OH)^- + Cl^-$$

$$R_2'SO_4^{2-} + 2OH^- \longrightarrow 2R'(OH)^- + SO_4^{2-}$$

$$R_2'\,CO_3^{2-} + 2OH^- \longrightarrow 2R'(OH)^- + CO_3^{2-}$$

(e) Advantages

1. Highly acidic (or) alkaline water can be treated by this process.
2. It generates very low hardness of water(nearly 2 ppm). So such water can be used in high pressure boilers.

(f) Disadvantages

1. The equipment is costly and more expensive chemicals are needed.
2. If the water contains turbidity then the output of the process is reduced.

Table 1.9 *Comparison of zeolite and demineralisation process*

S.No	Zeolite (or) Permutit Process	Demineralisation (or) Deionisation Process
1.	This is an ion-exchange process.	This is also an ion-exchange process.
2.	It exchanges only cations.	Both the cation and anions are exchanged.
3.	Residual hardness is 1–5 ppm.	Residual hardness is 0–2 ppm.
4.	Cost of plant and material is high.	Cost is higher.
5.	Operating expenses are low.	High operating expenses.
6.	Acidic water cannot be treated.	Even highly acidic or highly alkaline water can be treated.
7.	Treated water contains more dissolved solids (sodium salts).	No dissolved solids.

(g) Characteristics of Soft, Deionised and Distilled Water

(i) Hard Water

It contains all hardness-producing ions.

(ii) Soft Water

1. It does not contain hardness-producing ions like Ca^{2+}, Mg^{2+}
2. It may contain Na^+, K^+, SO_4^{2-}, Cl^- ions and micro-organisms.

(iii) De-ionised Water (Mineral Water)

1. It does not contain any ions including hardness-producing cations.
2. It may contain some amount of microorganisms.

(iv) Distilled Water

It does not contain any ions and microorganisms, because it is prepared by condensing the vapour of boiling water.

1.12 INTERNAL CONDITIONING (OR) INTERNAL TREATMENT (OR) BOILER COMPOUNDS

In this process, an ion is prohibited to exhibit its original character by 'complexing' or converting it into other more soluble salts by adding an appropriate reagent. An internal treatment is accomplished by adding a proper chemical to the boiler water either

(a) to precipitate the scale-forming impurities in the form of sludges, which can be removed by blow down operation, or

(b) to convert them into compounds, which will stay in dissolved form in water and thus do not cause any harm.

Note:

1. Blow-down operation is partial removal of hard water through a tap at the bottom of boiler, when extent of hardness in the boiler becomes alarmingly high.
2. 'Make-up' water is addition of fresh softened water to the boiler after blow-down operation.

Internal treatment methods are generally followed by blow-down operation, so that accumulated sludge is removed. Important internal conditioning/treatment methods are the following:

(a) Colloidal Conditioning

Scale formation in boilers is mainly due to crystalline precipitates. When certain chemicals like tannin or agar agar ,kerosene, gelatin and glue are added to water,these substances get coated on the outer surfaces of crystalline precipitates and convert them into colloidal nonsticky and sludge-like precipitates, which can be removed by mechanical methods of blow operation.

(b) Carbonate Conditioning

In low-pressure boilers, scale formation can be avoided by adding Na_2CO_3 to the boiler water. The scale-forming salts like $CaSO_4$ are partially converted to $CaCO_3$.

$$CaSO_4 + Na_2CO_3 \rightleftharpoons CaCO_3 + Na_2SO_4$$

The forward reaction is favoured by increasing the concentration of CO_3^{2-}. Calcium carbonate is precipitated in the boiler as loose sludge which can be scrapped off. For the precipitation of $CaCO_3$, the carbonate ions added should exceed the sulphate ions present in water.

(c) Calgon Conditioning

Calgon is sodium hexa metaphosphate with the composition $Na_2[Na_4(PO_3)_6]$. During the process of softening water, four sodium ions are replaced by double salts containing calcium inside the complex. Since the complex is highly soluble, there is no problem of sludge disposal.

$$\underset{\text{Calgon}}{Na_2[Na_4(PO_3)_6]} \longrightarrow 2Na^+ + [Na_4(PO_3)_6]^{2-}$$

$$2CaSO_4 + [Na_4(PO_3)_6]^{2-} \longrightarrow \underset{\text{Highly soluble complex}}{[Ca_2(PO_3)_6]^{2-}} + 2Na_2SO_4$$

(d) Phosphate Conditioning

In high-pressure boilers, $CaSO_4$ forms hard-type scale. This is because the solubility of $CaSO_4$ decreases with increase of temperature. It can be converted into soft sludge by adding excess of soluble phosphates. The optimum pH for the precipitation of $Ca_3(PO_4)_2$ soft sludge is 9.5–10.5.

$$3CaSO_4 + 2Na_3PO_4 \xrightarrow{pH = 9.5-10.5} \underset{\text{Soft sludge}}{Ca_3(PO_4)_2} + 3Na_2SO_4$$

There are three types of phosphates employed for this purpose

1. Trisodium phosphate — Na_3PO_4 (too alkaline)
2. Disodium hydrogen phosphate — Na_2HPO_4 (weakly alkaline)
3. Monosodium dihydrogen phosphate — NaH_2PO_4 (acidic)

The choice of salt depends upon the alkalinity of the boiler feedwater. Hence, Na_3PO_4 is used for too acidic water, Na_2HPO_4 is used for weakly acidic water, and NaH_2PO_4 is used for alkaline water in boilers.

(e) Treatment with Sodium Aluminate

When sodium aluminate is treated with boiler water, it gets hydrolysed to give sodium hydroxide and a gelatinous precipitate of aluminium hydroxide.

$$NaAlO_2 + 2H_2O \longrightarrow NaOH + Al(OH)_3$$

The formed NaOH reacts with magnesium salts.

$$MgCl_2 + 2NaOH \longrightarrow Mg(OH)_2 + 2NaCl$$

The flocculent precipitates of $Mg(OH)_2$ and $Al(OH)_3$ entrap finely suspended and colloidal impurities like sand and oil drops which are difficult to remove ordinarily. The flocculent precipitates then settle to the bottom and can be removed easily.

1.13 DESALINATION OF BRACKISH WATER

Depending upon the quantity of dissolved solids, water is graded as

1. **Fresh water** contains < 1000 ppm of dissolved solids.
2. **Brackish water** contains > 1000 ppm but < 35000 ppm of dissolved solids.
3. **Sea water** contains > 35,000 ppm of dissolved solids.

Water containing high concentration of dissolved salts/solids is known as brackish water, for example sea water contains about 3.5% salts. Brackish water is unfit for domestic and industrial applications. Hence, it is necessary to remove the high concentration of the salts. The process used for the removal of salts from brackish or saline water is called desalination.

The common method for the desalination of brackish water are

1. Electrodialysis
2. Reverse osmosis
3. Distillation
4. Freezing.

1.13.1 Electrodialysis

Electrodialysis is one of the efficient techniques used for the desalination of saline water.

(a) Principle

Electrodialysis involves the separation of dissolved salts from saline water in the form of ions under the influence of a direct current using particular types of membranes called *ion-selective membranes*.

An ion-selective membrane is permeable for only one kind of ions having specific charge. For example, a *cation-selective membrane* allows the passage of cations only. It does not let anions to pass through it. Similarly, an *anion-selective membrane* is permeable only to anions and checks the passage of cations through it.

When a direct current is passed through saline water enclosed between ion-selective membranes, the cations of the dissolved salt move towards the cathode through the cation-selective membrane, whereas anions of the salts move towards the anode through the anion-selective membrane. This decreases the concentration of ions in saline water and after some time, the saline water turns into fresh water.

(b) Process

The process is carried out in a special type of cell called **electrodialysis cell** shown in Fig. 1.7. It consists of a large number of paired sets of ion-selective membranes. Saline water under a pressure of about 5-6 kg/m^2 is introduced from the top of the cell and is made to pass between membrane pairs.

An electric field is applied perpendicular to the direction of flow of water. The ions start moving towards the oppositely charged electrodes through the membranes. On account of this, the concentration of ions in alternate compartments 2, 4, 6, etc., decreases, while the concentration of ions in alternate compartments 1, 3, 5, 7, etc., goes on increasing.

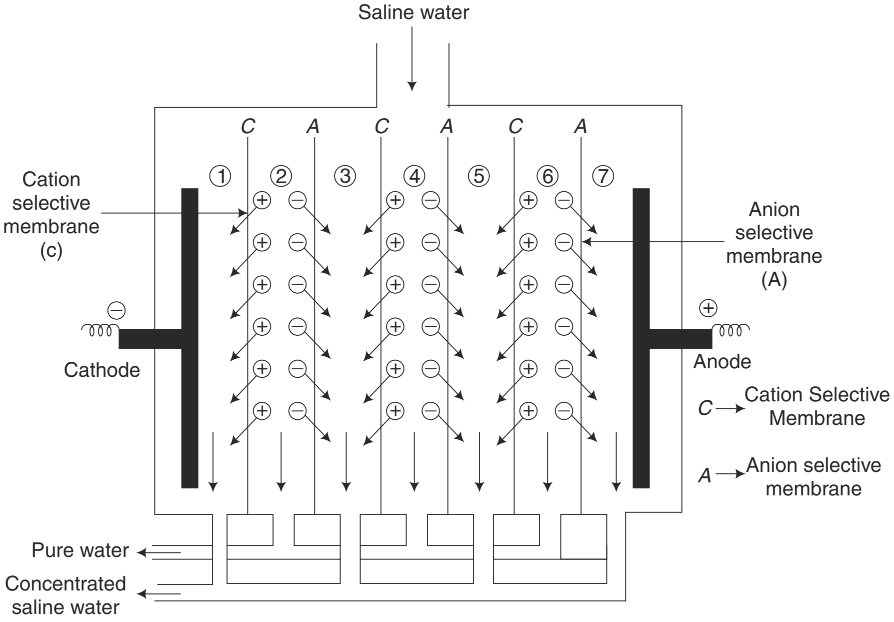


Fig. 1.7 *Electrodialysis of saline water*

Thus, water collected from compartments 2, 4, 6, etc., is pure; while that collected from compartments 1, 3, 5, 7, etc., is more concentrated saline water.

(c) Examples for Ion-selective Membranes

- Cation-selective membrane—polystyrene containing sulphonic acid group
- Anion-selective membrane—polystyrene containing tetra ammonium chloride

(d) Advantages of Electrodialysis Process

1. The equipment used in the process is very compact.
2. The cost of installation is economical.
3. The cost of operation of the process largely depends upon the cost of electricity available.

1.13.2 Reverse Osmosis

(a) Process

It is a membrane process by which water is separated from saline water. Osmosis is defined as the spontaneous flow of 'water' from dilute to more concentrated solution through a semipermeable membrane. The driving force in this phenomenon is called *osmotic pressure*.

A semipermeable membrane is one which permits only water molecules to pass through it. Examples of semipermeable membranes are cellulose acetate, polyamide, polymide, etc.

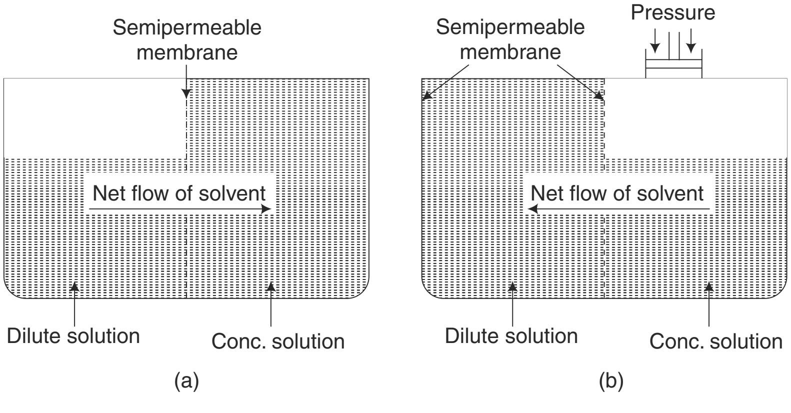


Fig. 1.8 *(a) Osmosis (b) Reverse osmosis*

This natural process can be reversed by applying pressure higher than the osmotic pressure on the concentrated side. Thus the solvent is forced to move from concentrated side to dilute side across the membrane. This principle is known as ***reverse osmosis***.

In the reverse osmosis process (Fig. 1.9), the pure water (free from ions) is separated from the contaminated brine water (salty water). This membrane filtration is also called ***super filtration*** (or) ***hyper filtration***.

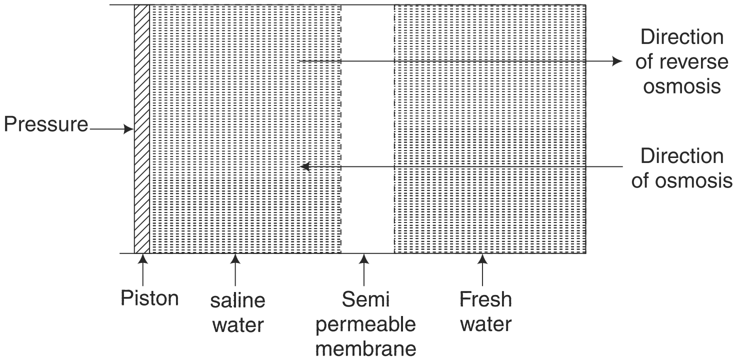


Fig. 1.9 *Desalination of sea water*

(b) Advantages

1. This method has greater advantages of removing ionic, non-ionic, colloidal and high-molecular weight organic matter.
2. The lifetime of the membrane is quite high (2 years).
3. The membrane can be replaced within a few minutes. It provides nearly uninterrupted water supply.
4. Due to low capital cost, low operating cost and high reliability, this method is superior than other methods.

(c) Applications

1. Reverse osmosis plays a major role in providing portable water defined by the WHO criterion of < 500 ppm of total dissolved solids (TDS).
2. Extremely high-quality water required for nuclear power plants can be made from sea water by the reverse-osmosis process.
3. Sugar concentration, waste-water recovery and beverage uses are a few of the current popular applications of the reverse-osmosis process.

1.14 DRINKING WATER (OR) POTABLE WATER (OR) DOMESTIC WATER TREATMENT

Water which is safe to drink and fit for human consumption is called drinking water or potable water.

1.14.1 Specifications for Drinking Water

The common specifications recommended by the US Public Health for drinking water are given below.

(i) Water should be clear and odourless.
(ii) It should be cool.
(iii) It should be pleasant to taste.
(iv) Turbiditiy of water should not exceed 10 ppm.
(v) pH of the water should be in the range of 7.0–8.5.
(vi) Chloride and sulphate contents should be less than 250 ppm.
(vii) Total hardness of the water should be less than 500 ppm.
(viii) Total dissolved solids should be less than 500 ppm.
(ix) Fluoride content of the water should be less than 1.5 ppm.
(x) The water must be free from disease-producing bacteria.
(xi) Water should be free from objectionable dissolved gases like H_2S.
(xii) Water should be free from objectionable minerals such as lead, chromium, manganese and arsenic salts.

1.14.2 Various Stages of Domestic Water Treatment

Natural water from rivers, canals, etc., does not confirm to all the required specifications of drinking water. For removing various types of impurities, the following treatment processes are employed.

Note:

Municipal water treatment does not aim at removing the dissolved salts present. Consequently, municipalities do not, generally, supply softened water.

The various stages in the treatment of water are given below.

(a) Removal of Suspended Impurities

(i) Screening

The raw water is passed through screens, having large number of holes, where floating matter are removed.

(ii) Aeration

Aeration of water involves

- Increasing the content of oxygen in water, make it fresh and promote taste
- Removing unwanted gases like H_2S, CO_2 and other volatile substances causing bad odour
- Removing the salts of iron and manganese.

(iii) Sedimentation

In this process, water is allowed to stand undisturbed in big tanks for 2 to 8 hours. Most of the suspended particles settle down at the bottom due to gravity. In this method, about 75% of the suspended impurities are removed and clean supernatant water is drawn from the tank with the help of pumps.

(iv) Sedimentation with Coagulation

The suspended and colloidal impurities are separated in the sedimentation tank by gravitation. The main principle of sedimentation is to allow water to rest or flow at a very slow velocity so that the heavier particles settle down due to gravity.

However, fine particles take many hours or sometimes days to settle down. So certain chemicals are added to speed up the sedimentation and the process is called coagulation.

The common coagulants (chemicals) used are generally salts of aluminium (alum, sodium aluminate) and salts of iron (ferrous sulphate, ferric sulphate, ferric chloride).

When a congulant is added to the water and mixed thoroughly, a thick gelatinous precipitate is formed which is insoluble in water. This precipitate is called floc.

Some of the chemical coagulants are the following:

1. **Alum** $[K_2SO_4.Al_2(SO_4)_3.24H_2O]$ is the most widely used in water-treatment plants. Alum reacts with water in the presence of alkalinity of water. If natural alkalinity is not present, sufficient lime is also added.

$$\underset{\text{Coagulant}}{Al_2(SO_4)_3} + \underset{\substack{\text{(Ca.bicarbonate}\\\text{present in water)}}}{Ca(HCO_3)_2} \longrightarrow \underset{\substack{\text{(Al. hydroxide}\\\text{Flocculent ppt)}}}{2Al(OH)_3\downarrow} + 3CaSO_4 + 6CO_2$$

2. **Sodium aluminate** ($NaAlO_2$) is obtained from bauxite refineries in the form of a thick solution. This can very easily be used for treating water having no alkalinity (pH less than 7). The pH range for best results is 5.5–8.0

$$NaAlO_2 + 2H_2O \longrightarrow \underset{\text{Gelatinous floc of al. hydroxide}}{Al(OH)_3\downarrow + NaOH}$$

The aluminium hydroxide floc causes sedimentation. The sodium hydroxide thus produced precipitates of magnesium salts as $Ma(OH)_{2.}$

$$MgSO_4 + 2\,NaOH \longrightarrow Mg(OH)_2\downarrow + Na_2SO_4$$

3. Ferrous sulphate ($FeSO_4.7H_2O$) is also commonly used for coagulation purposes. It gives good results above pH values of 8.5(slightly alkaline). Ferrous sulphate reacts with water in the presence of alkalinity. If alkalinity is not present, sufficient lime is also added.

$$\underset{\text{(Coagulant)}}{FeSO_4} + \underset{\substack{\text{(Mg.bicar.}\\ \text{present in water)}}}{Mg(HCO_3)_2} \longrightarrow Fe(OH)_2\downarrow + MgCO_3 + CO_2 + H_2O$$

$$4Fe(OH)_2\downarrow + \underset{\text{Dissolved oxygen}}{O_2} + 2H_2O \longrightarrow \underset{\substack{\text{Ferric hydroxide}\\ \text{(heavy floc)}}}{4\,Fe(OH)_3\downarrow}$$

$Fe(OH)_3$ is in the form of heavy floc, which causes quick sedimentation.

(v) Filtration

It is the process of removal of colloidal and suspended matter (remaining after sedimentation) and bacteria by passing water through a filter bed containing fine sand, coarse sand and gravel.

Generally, filtration is carried out by using sand filters.

(b) Removal of Microorganisms

The process of destroying or killing the disease producing bacteria, microorganisms, etc., from the water and making it safe for use is called *disinfection*. The chemicals or substances, which are added to water for killing the bacteria, etc., are known as *disinfectants*. This can be carried out by the following methods.

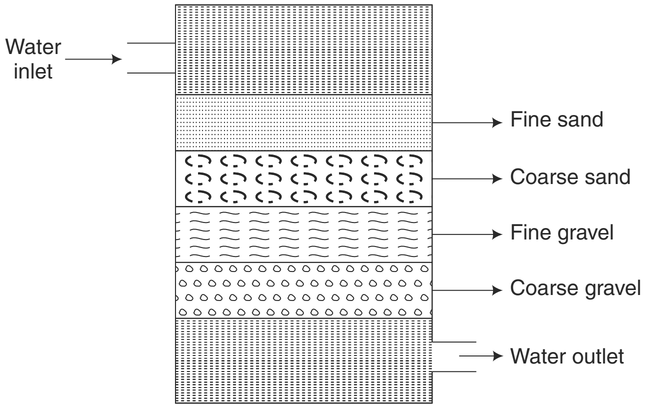


Fig. 1.10 *Sand filter*

(i) By Boiling

The harmful disease-producing bacteria can be killed by boiling the water to 100°C for 10 to 15 minutes.

(ii) Ultraviolet Radiations

UV rays are produced by passing electric current through mercury vapour lamp. This is particularly useful for sterilising water in a swimming pool.This method is found to be costly and it cannot be used for turbid water.

(iii) Sterilisation or Disinfection by Ozone (O_3)

Ozone is a powerful disinfectant and is readily absorbed by water. Ozone is highly unstable and breaks down, liberating nascent oxygen [O] which is capable of destroying the bacteria. It not only kills bacteria but also bleaches, decolorises and deodorizes water and improves the taste of water.

$$\underset{\text{Ozone}}{O_3} \longrightarrow O_2 + \underset{\text{Nascent oxygen}}{[O]}$$

The commonly used dose strength of ozone for sterilisation of water is 2–3 ppm. The method being expensive is generally not used for the sterilisation of municipal water supply.

(iv) Chlorination

The process of adding chlorine to water is called chlorination. Chlorine is a strong oxidising agent, is colourless and the excess of it may easily escape. It is mostly preferred for the disinfection of water. Chlorination can be done by the follwing methods.

- **By adding chlorine gas:** Chlorine (gas or liquid form) produces hypochlorous acid (powerful germicide)

$$Cl_2 + H_2O \longrightarrow HCl + \underset{\text{Hypochlorous acid}}{HOCl}$$

$$HOCl + \text{Bacteria} \longrightarrow \text{Bacteria are killed}$$

Advantages

1. About 0.3–0.5 ppm of chlorine is sufficient to act as ideal disinfectants.
2. It is cheap.
3. For storing it requires minimum space.

Disadvantages

1. Adding excess chlorine leads to unpleasant taste and odour.
2. At higher pH values, it is less effective and at lower pH values, it is more effective.

- **By adding chloramines ($ClNH_2$):** The use of excess of chlorine gas or bleaching powder as disinfectant often produces disagreeable odour and unpleasant taste in water.

The unpleasant taste can be avoided by the use of chloramine which may be obtained by treating chlorine with ammonia in the ratio of 2:1 by volume.

$$NH_3 + Cl_2 \longrightarrow ClNH_2 + HCl$$

Chloramine provides a greater lasting effect than that of chlorine.

$$H_2O + ClNH_2 \longrightarrow HOCl + NH_3$$

$$HOCl + \text{Bacteria} \longrightarrow \text{Bacteria are killed} + HCl + \underset{\text{Nascent oxygen}}{[O]}$$

- **Addition of bleaching powder ($CaOCl_2$):** Bleaching powder has the constitution $Ca(OCl)_2.CaCl_2.Ca(OH)_2$. It is commonly represented as CaOCl2 It contains about 30% available chlorine. It reacts with water to produce hypochlorous acid which is a powerful disinfectant due to its property of liberating nascent oxygen. One kilogram of bleaching powder is sufficient to sterilise one million parts of water.

$$H_2O + \underset{\text{Bleaching powder}}{CaOCl_2} \longrightarrow Ca(OH)_2 + Cl_2$$

$$H_2O + Cl_2 \longrightarrow HCl + \underset{\text{Hypochlorous acid}}{HOCl}$$

$$HOCl + \text{Bacteria} \longrightarrow \text{Bacteria are killed} + HCl + \underset{\text{Nascent oxygen}}{[O]}$$

The nascent oxygen thus liberated kills the pathogens by oxidation.

Drawback

1. Only calculated amount of $CaOCl_2$ should be used, since an excess of it gives bad taste and smell to the treated water.
2. Bleaching powder introduces calcium ions to water which increases water hardness.
3. During storage, the water quality deteriorates, and therefore the water should be analyzed for its effective chlorine content before use.

(c) Break-point Chlorination (or) Free Residual Chlorination

Water contains the following impurities:

(i) Bacteria
(ii) Organic matter
(iii) Reducing substances (Fe^{2+}, H_2S)
(iv) Free ammonia

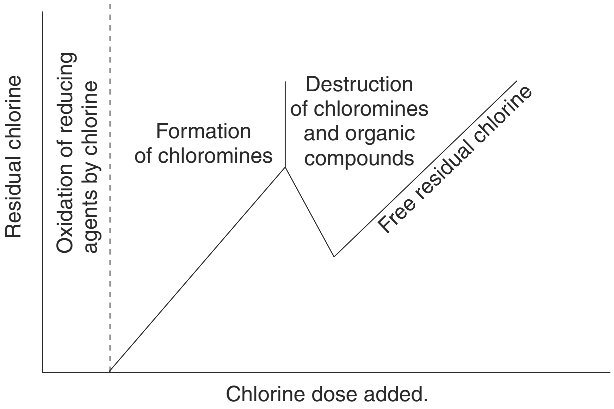


Fig. 1.11 *Break-point chlorination curve*

Chlorine may be added to water directly as a gas or in the form of bleaching powder. When chlorine is applied to water, the results obtained can be depicted graphically as in Fig. 1.14. The graph shows the relationship between the amount of chlorine added to water and the residual chlorine.

It is seen from the graph that initially the applied chlorine is used to kill bacteria and oxidises all the reducing substances present in the water and there is no free residual chlorine.

As the amount of applied chlorine increases, the amount of combined residual chlorine also increases. This is due to the formation of chloramines and other chloro compounds.

At one point, on further chlorination, the oxidation of chloramines and other impurities starts and there is a fall in the combined chlorine content. Thus the combined residual chlorine decreases to a minimum point at which oxidation of chloramines and other impurities complete and free residual chlorine begins to appear. This minimum point is known as **break-point chlorination.**

Thus break-point chlorination eliminates bacterias, reducing substances,organic substances responsible for the bad taste and odour from the water.

(i) Advantages

1. It completely oxidises organic compounds, ammonia and other reducing compounds.
2. It removes colour in water due to the presence of organic matter.
3. It destroys completely 100% of all the disease-producing bacteria.

4. It removes both odour and taste from the water.
5. It prevents the growth of any weeds in water.

(d) De-chlorination

The water treated by break-point chlorination contains decomposition products formed and may also contain excess of chlorine. These objectionable qualities may be removed by filtering the treated water over activated carbon. Over-chlorination of water can also be removed by treating it with SO_2 or Na_2SO_3.

$$SO_2 + Cl_2 + 2H_2O \longrightarrow H_2SO_4 + 2HCl$$

$$Na_2SO_3 + Cl_2 + H_2O \longrightarrow Na_2SO_4 + 2HCl$$

Note:

Ozone is expensive. UV light can also be used as a disinfectant especially for swimming-pool water. $KMnO_4$ is a useful disinfectant for domestic well water.

QUESTIONS

Two-Mark Questions with Answers

1. **Define hard and soft water.**

   Soft water is one that gives good lather readily with soap solution. Water that does not produce lather with soap readily but forms an insoluble precipitate-like white scum is known as hard water.
2. **Mention any two problems caused by turbidity.**
   - Objectionable in boilers and in cooling water systems
   - Interference in water-softening processes
3. **What is meant by apparent colour?**

   Colour which is caused by suspended matter is called ***apparent colour***.
4. **Mention any two sanitary significances of acidity.**
   - Presence of carbonic acid and other organic acids in water does not have any deleterious effects on human health (for example, presence of CO_2 in malt and carbonated beverages has no adverse effects on human beings).
   - However, acidic water corrodes concrete pipes and causes dissolution of metals such as Cu, Zn, etc.

5. **Define carbonate and noncarbonate hardness of water.**

   Carbonate hardness is caused by the presence of dissolved bicarbonates of calcium and magnesium. Temporary hardness is mostly destroyed by mere boiling of water. Noncarbonate hardness is due to the presence of dissolved chlorides and sulphates of calcium and magnesium. Unlike temporary hardness, permanent hardness is not destroyed on boiling.

6. **Define ppm and mg/lit.**

   ppm is defined as the number of parts by weight of $CaCO_3$ present in million parts by weight of water, and mg/lit is defined as the number of milligrams of $CaCO_3$ present in one litre of water.

7. **A sample of water contains 240 mg of $MgSO_4$ per litre. Calculate the hardness in terms of $CaCO_3$ equivalents.**

   Given

   The amount of $MgSO_4$ = 240 mg/lit

$$\begin{array}{c}CaCO_3\\ \text{equivalent}\end{array} = \frac{\text{Weight of hardness producing salt}}{\text{Molecular weight of the salt}} \times \begin{array}{c}\text{Molecular weight}\\ \text{of } CaCO_3\end{array}$$

   We know that the molecular weight of $MgSO_4$ =120.

   Thus amount equivalent to $CaCO_3 = \frac{240}{120} \times 100 = 200$ mg/lit.

8. **Mention any two specification of boiler feedwater.**

   Water used in boilers should be free from dissolved calcium and magnesium salts and dissolved gases such as oxygen (O_2) and carbon dioxide (CO_2).

9. **Give the difference between scale and sludge.**

S.No	Sludge	Scale
1.	Sludges are soft and non-adherent deposits.	Scales are hard deposits which stick very firmly to the inner surface of boiler during steam generation.
2.	Sludges are formed by substances like $MgCl_2$, $CaCl_2$, etc.	Scales are formed by substances like $CaSO_4$, and $Mg(OH)_2$.

10. **Define caustic embrittlement.**

    Caustic embrittlement is a type of boiler corrosion, caused by using highly alkaline water in the boiler. It refers to the inter-crystalline cracking of boiler metal. In high-pressure boilers, Na2CO3 decomposes to give sodium hydroxide and carbon dioxide, and this makes the boiler water *caustic*. This NaOH containing water flows into the minute hair cracking usually present on the boiler material by capillary action. Here water evaporates and the dissolved caustic soda concentration increases progressively. This caustic soda attacks the surrounding area, thereby dissolving iron of the boiler as sodium ferroate.

$$Na_2CO_3 + H_2O \longrightarrow 2NaOH + CO_2$$

$$Fe + 2NaOH \longrightarrow \underset{\text{Sodium ferroate}}{Na_2FeO_2} + H_2 \downarrow$$

11. What are the limitations of zeolite process?

1. If the supplied water is turbid, the suspended matter must be removed first by coagulation, filtration, etc. Otherwise the turbidity will clog the pores of the zeolite bed, making it inactive.
2. If any mineral acid is present in the water, it will destroy the zeolite bed. Therefore it is neutralised first with soda ($Na_2\ CO_3$).

12. What are cationic- and anionic-exchange resins?

Resins containing acidic functional groups (–COOH, $–SO_3H$) are capable of exchanging their H^+ ions with cations of hard water. They are said to be cationic exchange resins, e.g., sulphonated coals, etc.,

Resins containing basic functional groups ($–NH_2$, –OH) are capable of exchanging their OH^- ions with the anions of hard water. They are said to be anionic exchange resins, e.g. cross-linked quaternary ammonium salts, etc.

14. What is reverse osmosis?

If a solvent is forced to move from concentrated side to dilute side across the membrane by applying osmotic pressure, it is known as *reverse osmosis*.

15. Write the reaction of bleaching powder with water.

$$H_2O + \underset{\text{Bleaching powder}}{CaOCl_2} \longrightarrow Ca(OH)_2 + Cl_2$$

$$H_2O + Cl_2 \longrightarrow HCl + \underset{\text{Hypochlorous acid}}{HOCl}$$

$$HOCl + \text{Bacteria} \longrightarrow \text{Bacteria are killed} + HCl + \underset{\text{Nascent oxygen}}{[O]}$$

The nascent oxygen thus liberated kills the pathogens by oxidation.

Ten-Mark Questions

1. Define the term 'desalination', and with a neat diagram describe desalination by 'reverse osmosis' method.
2. What are coagulants? Write the mechanism of coagulation process with a suitable example.
3. What is meant by reverse osmosis? Describe desalination of brackish water by reverse-osmosis method.
4. What are boiler troubles? How are they caused? Suggest steps to minimise boiler troubles.
6. Compare the zeolite process with ion-exchange process in water softening. How will you regenerate the used-up reagents?
7. Describe the process of demineralisation of water using ion-exchange resins and specify its advantages over zeolite process.
8. Explain break-point chlorination.
9. Name eight methods for disinfection of water.
10. With the help of a neat diagram, explain the use of electrodialysis for desalination of water.
11. Define alkalinity. How is it determined?
12. Write short notes on (i) carry-over process, and (ii) lime-soda process.
13. What are the water-quality physical parameters? Explain their significance.
14. What is the principle of the EDTA method? Describe the estimation of hardness of water by the EDTA method.
15. What is meant by sterilisation of water? Explain how sterilisation of water is carried out by using chlorine and ozone.

UNIT 2

Electrochemistry

2.1 INTRODUCTION

Electrochemistry is a branch of chemistry, which deals with the chemical applications of electricity, i.e. chemical reactions produced by passing electric current through an electrolyte or the production of electric current through chemical reaction.

If a chemical reaction is driven by an external applied voltage then it is known as electrolysis, and if a voltage is created by a chemical reaction then the electrical arrangement is called a battery.

2.1.1 History of Electrochemistry

Understanding of electrical matters began in the sixteenth century. During this century, the English scientist William Gilbert spent 17 years experimenting with magnetism and, to a lesser extent, electricity. For his work on magnets, Gilbert became known as the *'father of magnetism.'*

Fig. 2.1 *Swedish chemist Svante* ***Arrhenius*** *portrait circa 1880s*

In 1800, William Nicholson and Johann Wilhelm Ritter succeeded in decomposing water into hydrogen and oxygen by electrolysis.

Svante Arrhenius (Fig. 2.1) published his thesis in 1884 on investigations on the galvanic conductivity of electrolytes. From his results, Arrhenius concluded that electrolytes, when dissolved in water, become to varying degrees split or dissociated into electrically opposite positive and negative ions.

Walther Hermann Nernst (Fig. 2.2) developed the theory of the electromotive force of the voltaic cell in 1888. In 1889, he showed how the characteristics of the current produced could be used to calculate the free energy change in the chemical reaction producing the current. He constructed an equation, now known as **Nernst equation**, which related the voltage of a cell to its properties.

Fig. 2.2 *German scientist Walther **Nernst** portrait in the 1910s*

2.1.2 Types of Conductors

The material which conducts electricity is called a conductor. Conductors are broadly classified into two types.

(a) Metallic conductor (b) Electrolytic conductor

(a) Metallic Conductors Metallic conductors are solid substances which conduct electric current due to the movement of electrons from one electrode to another. The conductance decreases with increase of temperature.

Example: All metals, graphite

(b) Electrolytic Conductors An electrolytic conductor conducts electric current due to the movement of ions in solution or in fused state. The conduction increases with increase of temperature.

Example: HCl, NaOH, NaCl, etc.

Table 2.1 *Difference between metallic conduction and electrolytic conduction*

S. No.	*Metallic Conduction*	*Electrolytic Conduction*
1.	It involves the flow of electrons in a conductor.	It involves the movement of ions in a solution.
2.	It does not involve any transfer of matter.	It involves transfer of electrolyte in the form of ions.
3.	Conduction decreases with increase in temperature.	Conduction increases with increase in temperature.
4.	No change in chemical properties of the conductor.	Chemical reaction occurs at the two electrodes.

2.2 CELLS

A cell is a single arrangement of two electrodes dipping into a solution of electrolyte or electrolytes. Cells may be divided into

(a) Electrolytic cells
(b) Electrochemical cells

(a) Electrolytic Cell

Electrolytic cells are cells in which electrical energy is used to bring about a chemical reaction. The redox reaction in an electrolytic cell is nonspontaneous. Electrical energy is required to induce the electrolysis reaction. An example of an electrolytic cell is shown in Fig. 2.3, in which molten NaCl is electrolyzed to form liquid sodium and chlorine gas. The sodium ions migrate toward the cathode, where they are reduced to sodium metal. Similarly, chloride ions migrate to the anode and are oxidized to form chlorine gas. This type of cell is used to produce sodium and chlorine. The chlorine gas surrounding the cell can be collected. The sodium metal is less dense than the molten salt and is removed as it floats to the top of the reaction container.

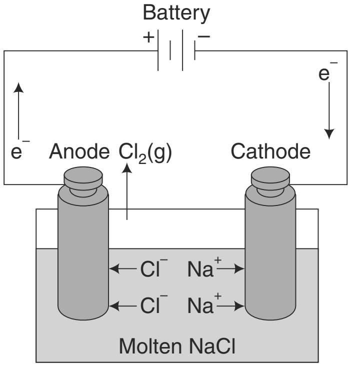


Fig. 2.3 *Electrolytic cell*

At anode

$$2Cl^- \longrightarrow Cl_2 + 2\,e^- \text{ (oxidation)}$$

At cathode

$$Na^+ + e^- \longrightarrow Na \text{ (reduction)}$$

(b) Electrochemical Cell

An electrochemical cell is a device in which a redox reaction is utilized to get electrical energy. An electrochemical cell is also commonly referred to as *voltaic* or *galvanic cell*. The electrode where oxidation occurs is called the *anode*; while the electrode where reduction occurs, is called the *cathode*.

The practical application of an electrochemical or galvanic cell is the *Daniel cell*. It consists of a zinc electrode dipping in $ZnSO_4$ solution (where oxidation takes place) and a copper electrode dipping in $CuSO_4$ solution (where reduction takes place). In other words, each electrode may be regarded as a half-cell. The electrode reactions in a Daniel cell are the following:

At anode

$$Zn \longrightarrow Zn^{2+} + 2\,e^- \quad \text{(oxidation)}$$

At cathode

$$Cu^{2+} + 2\,e^- \longrightarrow Cu \quad \text{(reduction)}$$

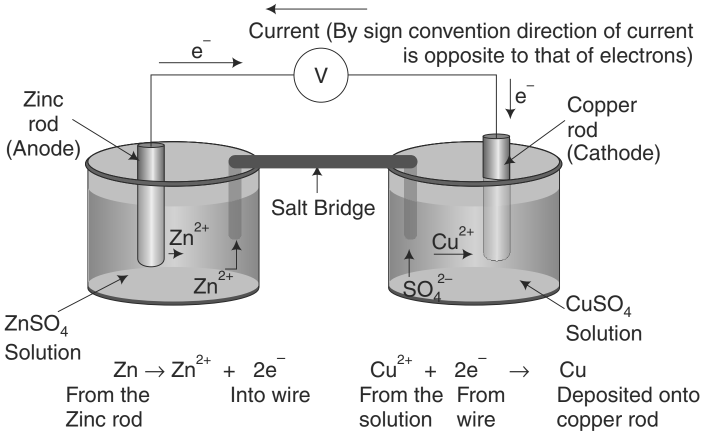


Fig. 2.4 *Daniel cell*

Overall reaction

$$Zn + Cu^{2+} \longrightarrow Zn^{2+} + Cu$$

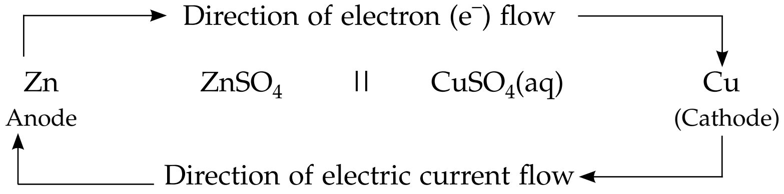


Table 2.2 *Differences between electrolytic cells and electrochemical cells*

Sl. No	*Electrolytic Cells*	*Electrochemical Cells*
1.	Electrolytic cells are cells in which electrical energy is converted to chemical energy. *Example:* Electrolysis	Electrochemical cells are cells in which chemical energy is converted to electrical energy. *Example:* Daniel cell
2.	Sign Convention: The cathode carries negative charge. The anode carries positive charge.	Sign Convention: The cathode carries positive charge. The anode carries negative charge.
3.	Here the electrons are supplied to the cell from the external battery, i.e. electrons move in through the cathode and come out from the anode.	But electrons are drawn from the cell, i.e. electrons move from anode to cathode through the external circuit.
4.	The amount amount of electricity passed during electrolysis is measured by coulometer or ammeter.	The emf produced in the cell is measured by a potentiometer or voltmeter.
5.	The extent of chemical reaction occurring at the electrodes is governed by Faraday's law of electrolysis.	The emf of the cell depends on the concentration of the electrolytes and the chemical nature of the electrode.

Points to Remember

Cell Type	***Reaction Type***	***ΔG***	***E***	***Reduction***	***Oxidation***	***Direction of e-flow***	***Sign at Cathode***	***Sign at Anode***
Electrolysis	Nonspontaneous	+	–	Cathode	Anode	e-flow to cathode	–	+
Galvanic	Spontaneous	–	+	Cathode	Anode	e-flow to cathode	+	–

2.3 REPRESENTATION OF A GALVANIC CELL

According to present conventions, a galvanic cell is represented by keeping in view the following points.

- **Two half-cells:** anodic half-cell and cathodic half-cell each make up galvanic cell.
- The anodic half-cell is also called oxidation half-cell.
- The cathodic half-cell is also called reduction half-cell.

Depending upon the cell, a half-cell can be used both as a cathode or as an anode, i.e. a half-cell may act as an anodic half-cell in one galvanic cell, while the same half-cell may act as a cathodic half-cell in some other galvanic cell.

The two half-cells (or electrodes) of a galvanic cell may be represented as follows:

1. The anodic half-cell is written on the left-hand side while the cathodic half-cell is written on the right-hand side.
2. The anode of the cell is represented by writing the metal first and then the electrolyte, the two separated by a vertical line (|) or slash (/) or semicolon (;).

   The oxidation half-cell is represented as

   $$M(s) \mid M^{n+}(aq) \quad \text{or} \quad M(s) / M^{n+} \quad \text{or} \quad M(s); M^{n+}(aq)$$

   The concentration of the electrolyte is mentioned within the bracket after the cation, e.g.

   $$Zn(s) \mid Zn^{2+}(aq)\ (1M)$$

3. The cathode of the cell is represented by writing the electrolyte and its cation first and then the metal, the two are separated by a vertical line (|) or slash (/) or semicolon (;).

   The reduction half-cell is represented as

   $$M^{n+}(aq) \mid M(s) \quad \text{or} \quad M^{n+}(aq) / M(s) \quad \text{or} \quad M(s); M^{n+}(aq)$$

The small vertical bar (|) or slash (/) drawn between M and M^{n+} (aq) represents an electrode--electrolyte interface, i.e. the plane where the electrode and the electrolyte meet.

4. In certain galvanic cells, the two electrodes are dipped into two different electrolytes. Using a salt bridge develops the electrical contact between the two half-cells. Such a salt bridge between the two solutions is denoted by a double-bar (| |) or a double slash (//) between the two solutions as shown in the cell given below.

$$\mathrm{Zn(s)} \underset{\substack{\text{Electrode–electrolyte}\\ \text{interface}}}{|} \mathrm{Zn^{2+}\,(aq)\,(1M)} \underset{\substack{\text{Salt}\\ \text{bridge}}}{||} \mathrm{Cu^{2+}\,(aq)\,(1M)} \underset{\substack{\text{Electrolyte–electrode}\\ \text{interface}}}{|} \mathrm{Cu(s)}$$

or

$$\mathrm{Zn(s)} \underset{\substack{\text{Electrode–electrolyte}\\ \text{interface}}}{/} \mathrm{Zn^{2+}\,(aq)\,(1M)} \underset{\substack{\text{Salt}\\ \text{bridge}}}{//} \mathrm{Cu^{2+}\,(aq)\,(1M)} \underset{\substack{\text{Electrolyte–electrode}\\ \text{interface}}}{/} \mathrm{Cu(s)}$$

5. Species that are in the same phase (e.g., different ions in the same solution) are separated by a comma (,).

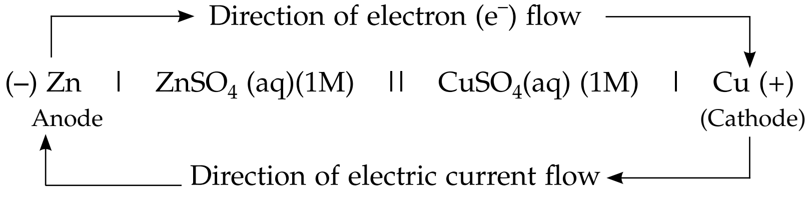
   For example, a solution of HCl containing H^+ and Cl^- is described as H^+ (aq), Cl^- (aq).

   In case of gas electrodes such as hydrogen, the inert metal platinum, (which serves as the electrical contact) is also written while representing the half-cell.

$$\mathrm{Pt,\ H_2\ (1\ atm);\ H^+\ (1M)}$$

6. Sometimes a negative sign is put on the anode and a positive sign on the cathode. The electrons flow from the negative pole (anode) to the positive pole (cathode) in the external circuit. Conventionally, current is said to flow in the opposite direction.

   The complete formula of a cell may be represented as follows:



$$\mathrm{(-)\ \underset{Anode}{Zn}\ |\ ZnSO_4\,(aq)(1M)\ ||\ CuSO_4(aq)\,(1M)\ |\ \underset{(Cathode)}{Cu\ (+)}}$$

2.4 REVERSIBLE AND IRREVERSIBLE CELLS

When a cell works in a thermodynamically reversible manner, it is called a ***reversible cell***. A cell is said to work reversibly when it is sending out an infinitesimally small current, so that the reaction of the in cell remains in the state of equilibrium.

(a) Reversible Cells They have to satisfy the following conditions:

1. If the cell emf is exactly equal to the emf is supplied from an external source, the cell reaction will stop and no current will be given out by the cell.

External emf = Cell emf
(No current flow)

2. If the external emf is infinitesimally less than the cell emf, the current will flow from the cell which is proportional to the chemical reaction taking place in the cell, e.g. *discharging of the cells*

External emf < Cell emf
(Current flow from cell to external source)

3. If the emf applied externally is greater than the cell emf, the cell reaction is reversed and the current will flow in the opposite direction, e.g. charging in the secondary cells.

External emf > Cell emf
(Current flow from external source to cell)

A familiar example of a reversible cell is that of the Daniel cell. It is represented as

$$Zn/ZnSO_4(1M)\,||\,CuSO_4(1M)/Cu$$

(i) Condition 1

The emf of a Daniel cell is 1.1 volts. If an emf of 1.1 volts is externally applied, the cell reaction stops.

(ii) Condition 2

When the external emf is just smaller than that of the cell, the reaction taking place in the cell is

At anode

$$Zn \longrightarrow Zn^{2+} + 2e^-$$

At cathode

$$Cu^{2+} + 2\,e^- \longrightarrow Cu$$

Overall reaction

$$Zn + Cu^{2+} \longrightarrow Zn^{2+} + Cu \qquad ...(2.1)$$

(iii) Condition 3

When the external emf is just greater than the cell emf, the above cell reaction is reversed.

At anode

$$\mathrm{Cu} \longrightarrow \mathrm{Cu}^{2+} + 2\,e^-$$

At cathode

$$\mathrm{Zn}^{2+} + 2\,e^- \longrightarrow \mathrm{Zn}$$

Overall reaction

$$\mathrm{Cu} + \mathrm{Zn}^{2+} \longrightarrow \mathrm{Cu}^{2+} + \mathrm{Zn} \qquad \text{...(2.2)}$$

Equation (2.2) is an exact reverse of Eq. (2.1). Therefore, the Daniel cell is a reversible cell.

(b) Irreversible Cell A cell is called irreversible when it does not satisfy the three conditions of reversibility. Zinc–acid cell is an example of irreversible cell. It is represented as

$$\mathrm{Zn}/\mathrm{H_2SO_4}/\mathrm{Cu}$$

(i) Condition 1

When the external emf is just smaller than the cell emf, the following reactions take place.

At anode

$$\mathrm{Zn} \longrightarrow \mathrm{Zn}^{2+} + 2e^-$$

At cathode

$$2\mathrm{H}^+ + 2\,e^- \longrightarrow \mathrm{H_2}\uparrow$$

Overall reaction

$$\mathrm{Zn} + 2\mathrm{H}^+ \longrightarrow \mathrm{Zn}^{2+} + \mathrm{H_2}\uparrow \qquad \text{...(2.3)}$$

(ii) Condition 2

When the external emf is just greater than the cell emf, the following reactions take place.

At anode

$$\mathrm{Cu} \longrightarrow \mathrm{Cu}^{2+} + 2e^-$$

At cathode

$$2\mathrm{H}^+ + 2\,e^- \longrightarrow \mathrm{H_2}\uparrow$$

Overall reaction

$$\mathrm{Cu} + 2\mathrm{H}^+ \longrightarrow \mathrm{Cu}^{2+} + \mathrm{H_2}\uparrow \qquad \text{...(2.4)}$$

The reaction (2.4) is not exactly the reverse of the previous one, i.e. the reaction when H_2 is liberated at copper electrode. Since this does not satisfy the conditions of reversibility, it is called an irreversible cell.

2.5 EMF OF AN ELECTROCHEMICAL CELL

> ***'The difference of potential which causes the flow of current from one electrode of higher potential to another electrode of lower potential is called the electromotive force'.***

Thus the emf of a galvanic cell can be calculated using the following relationship.

$$\text{emf} = \left\{\begin{matrix}\text{Standard reduction}\\ \text{potential of right-hand}\\ \text{side electrode}\end{matrix}\right\} - \left\{\begin{matrix}\text{Standard reduction}\\ \text{potential of left-hand}\\ \text{side electrode}\end{matrix}\right\}$$

$$E^\circ_{\text{cell}} = E^\circ_{\text{right}} - E^\circ_{\text{left}}$$

$$\text{emf} = \left\{\begin{matrix}\text{Standard reduction}\\ \text{potential of right-hand}\\ \text{side electrode}\end{matrix}\right\} + \left\{\begin{matrix}\text{Standard oxidation}\\ \text{potential of left-hand}\\ \text{side electrode}\end{matrix}\right\}$$

$$E^\circ_{\text{cell}} = E^\circ_{\text{red}} + E^\circ_{\text{oxi}}$$

Example

The emf of Daniel cell is calculated as follows

$$E^\circ_{\text{cell}} = E^\circ_{\text{Cu}} - E^\circ_{\text{Zn}}$$

The standard reduction potential of copper electrode is 0.34 volt and the standard reduction potential of zinc electrode is – 0.76 volt.

$$E^\circ_{\text{cell}} = 0.34 - (-0.76) = +1.1 \text{ volts}$$

Note: The positive value indicates that the cell reaction is feasible. But if it is negative, the cell reaction is not feasible.

2.5.1 Determination of emf of a Cell

The cell emf cannot be directly determined with a help of a voltmeter, because a part of the cell current is drawn by the cell reaction and causes a change in the actual emf. Potentiometers are used for accurate measurement of such a cell by the application of ***Poggendroff's*** **compensation method**.

The emf of a test cell is determined by applying an equal and opposite external potential from an external source. Consequently, there is no current flow in the circuit. So, the applied potential is therefore equal to the magnitude of the emf of the test cell.

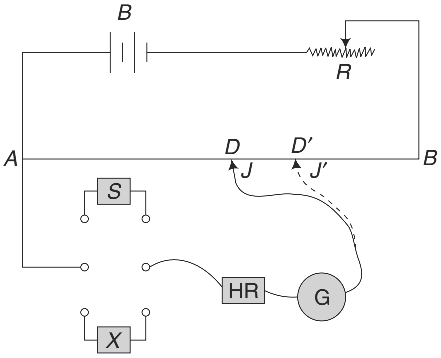


Fig. 2.5 *Measurement of emf of a cell*

The potentiometer consists of a uniform wire *AB* of high resistance. The ends *A* and *B* are connected to a storage battery through a rheostat *R*. The cell of unknown emf (*X*) is connected to the circuit in such a way that its positive end is connected to *A* and its negative end is connected to a sliding contact, through a galvanometer *G*. The sliding contact is moved along the wire *AB*, till there is null deflection in the galvanometer. The position of the sliding contact *D* is noted and the distance *AD* is measured.

$$E_X \propto AD$$

Then the unknown cell is replaced by a standard cell in the circuit. The sliding contact is moved along *AB* till there is no deflection. The position of the sliding contact *D′* is noted and the distance *AD′* is measured.

$$E_S \propto AD'$$

The emf of the unknown cell can be calculated using the following equation

$$\frac{E_x}{E_S} = \frac{AD}{AD'}$$

Knowing the emf of the standard cell (E_S), the emf of the unknown cell (E_X) can be calculated.

$$E_x = \frac{AD}{AD'} \times E_s$$

2.5.2 Applications of emf Measurements

(a) Determination of Solubility of a Sparingly Soluble Salt

The ionic concentration of a solution is calculated from the emf of a concentration cell. In case of a sparingly soluble salt, the salt can be supposed to be completely ionized even in saturated solution. Hence, the ionic concentration is proportional to the solubility of the salt.

For example, the solubility of the sparingly soluble salt silver chloride can be calculated by measuring the emf of the following cell.

This can be done by the construction of a cell by placing the silver electrode in contact with 0.01 N solution of silver nitrate as a cathodic compartment and at the anodic compartment, we have a silver electrode in contact with 0.01 N potassium chloride solutions. The two solutions are connected by a salt bridge.

The cell can be represented as

$$\text{Ag / AgCl, 0.01 N KCl // 0.01 N AgNO}_3\text{ / Ag}$$

A drop of silver nitrate solution is added from the burette to the potassium chloride solution, and a small amount of silver chloride formed is sufficient to develop the emf of the cell.

The emf of the above cell is given by the relation

$$E = \frac{0.0591}{n} \log \frac{C_2}{C_1}$$

Here, the valence of the silver ion, $n = 1$, and concentration of the silver in cathodic compartment, $C_2 = 0.01$ N

$$E = \frac{0.0591}{1} \log \frac{0.01}{C_1}$$

where C_1 is the concentration of Ag^+ ions furnished by AgCl in KCl solution.

By measuring the emf of the cell, the concentration of AgCl is calculated. Multiplying this by 143.5, the equivalent weight of AgCl, we can get the solubility of AgCl in grams/litre.

(b) Determination of the Valency of an Ion

Consider the following concentration cell, which can be represented as

$$\text{M / M}^{n+}\text{ (C}_1\text{) // M}^{n+}\text{ (C}_2\text{) / M}$$

For the above cell, the Nernst equation can be represented as

$$E_{\text{cell}} = \frac{0.0591}{n} \log \frac{C_2}{C_1}$$

By substituting the measured value of emf of a concentration cell and the values of C_1 and C_2 in the equation, the value of n, the number of electrons involved in the cell reaction (called the valency of ions), can be calculated.

(c) Determination of Standard Free Energy Change and Equilibrium Constant

(i) The standard free energy change of a reaction can be calculated as follows

Free energy change $-\Delta G$ joule		Free energy change n mol electrons	Potential in volts E joule/coulomb	Faraday constant F coulomb/ mol electrons
	=			

...(2.5)

(ii) The equilibrium constant of a reaction can be calculated as follows:

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

$$\Delta G^\circ = -2.303\,RT \log K_{eq}$$

$$\log K_{eq} = \frac{-\Delta G^\circ}{2.303\,RT} \qquad \text{...(2.6)}$$

Comparing equations (2.5) and (2.6),

$$\log K_{eq} = \frac{nFE^\circ}{2.303}$$

$$K_{eq} = \text{antilog}\,\frac{nFE^\circ}{2.303\,RT}$$

E° = Standard emf of the cell

K_{eq} = Equilibrium constant

(d) Determination of pH by using a Standard Hydrogen Electrode

A hydrogen electrode is introduced into the solution, the pH of which is to be determined. It is coupled with a standard hydrogen electrode through a salt bridge and the emf of the cell is determined. If E is the emf of the cell,

$$E = -\frac{2.303\,RT}{nF}\log[\mathrm{H^+}] = -0.0591\log[\mathrm{H^+}]$$

$$\mathrm{pH} = \frac{E}{0.0591}$$

Example 1 *The emf of the cell,*

$$Zn/Zn^{2+}\ (1M)\ ||\ Cu^{2+}\ (1M)\ /\ Cu$$

is 1.1 volts. Calculate the standard free energy and predict whether the cell is feasible or not.

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

$$-\Delta G^\circ = 2 \times 96500 \times 1.1$$

$$\Delta G^\circ = -\,2{,}12{,}300$$

The negative value of ΔG° shows that the cell is feasible.

Example 2 *Emf of the cell,*

$$Zn \mid ZnSO_4 \mid\mid AgNO_3 \mid Ag \text{ at } 25°C$$

is 1.5621V.

Calculate the equilibrium constant of the cell.

Solution

$$E^\circ = \frac{RT}{nF} \ln K_{eq}$$

$$1.5621 = \frac{8.314 \times 298}{2 \times 96500} \times 2.303 \times \log K_{eq}$$

$$= \frac{0.0591}{2} \log K_{eq}$$

$$1.5621 = 0.02956 \log K_{eq}$$

$$\log K_{eq} = \frac{1.5621}{0.02956}$$

$$= 52.845$$

$$K_{eq} = 6.999 \times 10^{52}$$

2.6 WESTON STANDARD CADMIUM CELL

A **standard cell** is one which is capable of giving constant and reproducible emf and has negligible temperature coefficient of the emf.

2.6.1 Construction of the Cell

It consists of an 'H' shaped glass vessel, with the lower ends of both arms closed, having a platinum wire sealed into the bottom of each arm.

- **Positive electrode** contains mercury over which a paste of mercurous sulphate (Hg_2SO_4) and mercury is placed.
- **Negative electrode** consists of an amalgam of Cd and Hg, containing about 12 – 15% of Cd by weight.
- **Both electrodes** are sprinkled with some crystals of solid $CdSO_4.8/3H_2O$ as shown in Fig. 2.6.
- **Electrolyte**—The remaining part of the cell is filled with a saturated solution of cadmium sulphate. The upper ends of tube are closed with corks and sealing wax.

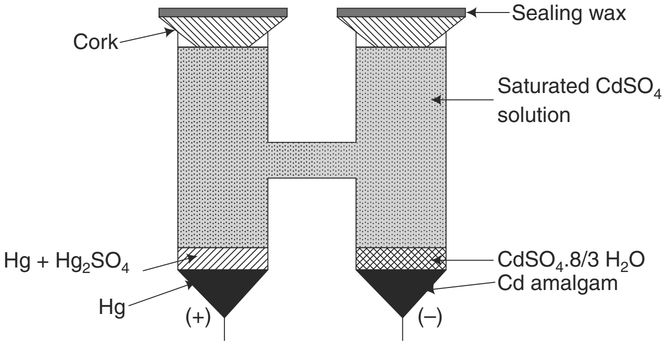


Fig. 2.6 *Weston standard cadmium cell*

2.6.2 Working Mechanism of the Cell

When the cell operates, the following reactions occur at the two electrodes:

At negative electrode

$$Cd(s) \longrightarrow Cd^{2+}\ (aq) + 2\ e^-$$

At positive electrode

$$Hg_2SO_4\ (s) + 2\ e^- \longrightarrow 2\ Hg(l) + SO_4^{2-}\ (aq)$$

Cell representation

12.5% Cd in Hg | 3 $CdSO_4.8H_2O$ (s) || $CdSO_4$ (satd. solution) Hg_2SO_4 | Hg

Advantages

- The cell works for many years at a stretch, without any voltage changes.
- Potential of this cell varies slightly about – 0.09046 volt per degree centigrade.

Note: The purpose of solid crystals of $CdSO_4.8/3H_2O$ is to keep the electrolyte saturated at all temperatures.

2.7 ELECTRODE POTENTIAL

When a metal (M) is dipped in its own salt solution, any one of the following reactions will occur.

(i) Positive metal ions may pass into the solution.

$$M \longrightarrow M^{n+} + ne^-\ \text{(oxidation)}$$

(ii) Positive metals ions from the solution may deposit over the metal.

$$M^{n+} + ne^- \longrightarrow M \text{ (reduction)}$$

Example 1 *When a Zn electrode is dipped in $ZnSO_4$ solution*

Solution When a Zn electrode is in contact with its salt solution of $ZnSO_4$, atoms of Zn from the lattice of the electrode dissolve and move into the solution of $ZnSO_4$ leaving behind its electrons on the metal lattice of the electrode itself (Fig. 2.7). This makes the electrode acquire a negative charge. These negatively charged electrons attract the positively charged Zn^{2+} ions from the solution.

This produces an electrical double layer all around the metal and its known as Helmholtz electrical double layer (Fig. 2.7). This leads to a difference of electrical potential between the metal and the solution.

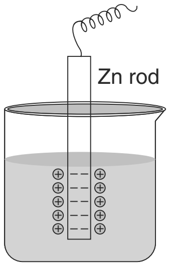


Fig. 2.7 *Helmholtz electrical double layer*

Since there is loss of electrons at this electrode, oxidation is said to have taken place and hence the potential developed at this electrode is called **oxidation potential.**

$$Zn \longrightarrow Zn^{2+} + 2e^- \text{ (oxidation)}$$

Example 2 *When a Cu electrode is dipped in CuSO4 solution*

Solution A Cu electrode is dipped into a solution of $CuSO_4$. The Cu^{2+} ions of the solution adhere on the electrode and hence the electrode attains a positive charge (Fig. 2.8).

To counterbalance the number of positive charges on the electrode, the negatively charged SO_4^{2-} ions from the solution surround the electrode. This develops an electrical double layer which is known as Helmholtz electrical double layer. This causes a difference of electrical potential between the metal and the solution (Fig. 2.8).

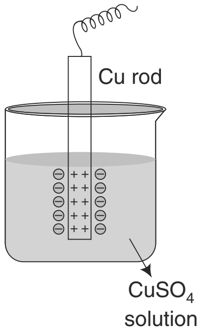


Fig. 2.8 *Helmholtz electrical double layer*

Since there is a gain of electrons at this electrode, reduction is said to have taken place and hence the potential developed at this electrode is called the **reduction potential**.

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

Definitions

(i) **Oxidation Potential:** It is the tendency of an electrode to lose electrons.

(ii) **Reduction Potential:** It is the tendency of an electrode to gain electrons.

(iii) **Electrode Potential:** It is the tendency of an electrode to lose or gain electrons.

(iv) **Single Electrode Potential (E):** It is the tendency of an electrode to lose or gain electrons when it is dipped in its own salt solution.

(v) **Standard Electrode Potential (E°):** It is the tendency of an electrode to lose or gain electrons when it is dipped in its own salt of 1M concentration at 25°C.

Note: If the oxidation potential of an electrode is + X volts, then its reduction potential will have a value of – X volts.

2.7.1 Determination of Electrode Potential

The potential of a single electrode alone cannot be measured. But potential difference between two electrodes can be measured potentiometrically, i.e. we can determine the electrode potential by combining the electrode with another electrode for which the electrode potential is known (reference electrode). For this purpose, the potential of hydrogen electrode has been arbitrarily fixed at zero. Electrode potentials for other metallic electrodes can be measured in comparision with this values.

(a) Determination of Electrode Potential of Zinc Electrode

The zinc electrode half-cell and the reference electrode (SHE) half-cell are electrically connected by a voltmeter between the two electrodes and electrolytically by a salt bridge as shown in Fig. 2.9.

To obtain the cell reaction, the zinc electrode is assigned a –ve charge and the SHE is assigned a + ve charge, and these electrodes are connected to the – ve and + ve terminals of the voltmeter respectively.

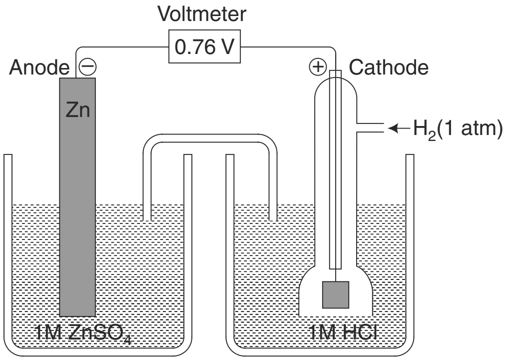


Fig. 2.9 *Reduction potential of zinc*

At anode

$$\mathrm{Zn} \longrightarrow \mathrm{Zn}^{2+} + 2\,\mathrm{e}^-$$

At cathode

$$2\,\mathrm{H}^+ + 2\,\mathrm{e}^- \longrightarrow \mathrm{H}_2\uparrow$$

Cell reaction

$$\mathrm{Zn} + 2\,\mathrm{H}^+ \longrightarrow \mathrm{Zn}^{2+} + \mathrm{H}_2\uparrow$$

Now the voltmeter shows the cell potential as 0.76 volts.

$$E^\circ_{\mathrm{cell}} = E^\circ_{\mathrm{right}} - E^\circ_{\mathrm{left}}$$

where,

$$E^\circ_{\mathrm{cell}} = +\,0.76 \text{ volts}$$

$$E^\circ_{\mathrm{left}} = \text{electrode potential of zinc electrode} = ?$$

$$E^\circ_{\mathrm{right}} = \text{electrode potential of SHE} = 0 \text{ volts}$$

$$0.76 \text{ V} = 0.0 \text{ V} - E^\circ_{\mathrm{Zn}^{2+}}$$

$$E^\circ_{\mathrm{Zn}^{2+}} = -\,0.76 \text{ volts}$$

i.e. the reduction potential of Zn electrode = – 0.76 volts

(b) Determination of Electrode Potential of Copper Electrode

The Cu electrode half-cell is coupled with the SHE half-cell to form a cell. It is seen that the SHE carries a –ve charge and the Cu electrode carries +ve charge. The following reactions take place.

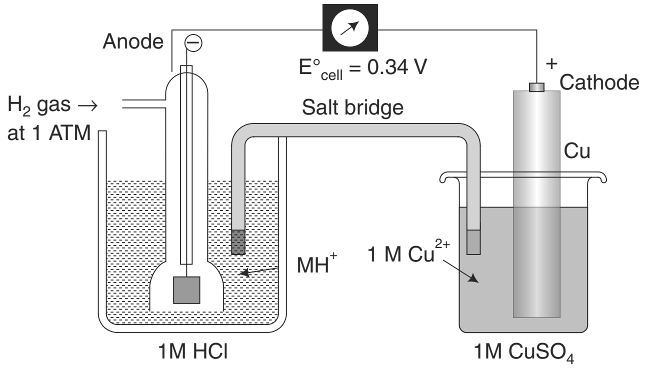


Fig. 2.10 *Reduction potential of copper*

At anode

$$\mathrm{H}_2\,(\mathrm{g}) \longrightarrow 2\,\mathrm{H}^+\,(\mathrm{aq}) + 2\,\mathrm{e}^-$$

At cathode

$$Cu^{2+} (aq) + 2\ e^- \longrightarrow Cu$$

Cell reaction

$$H_2 + Cu^{2+} \longrightarrow Cu + 2H^+$$

The voltmeter shows a cell potential of 0.34 volts.

$$E^\circ_{cell} = E^\circ_{right} - E^\circ_{left}$$

where,

E°_{cell} = + 0.34 volts

E°_{left} = electrode potential of SHE = 0 volts

E°_{right} = electrode potential of Cu electrode = ?

$0.34\ V = E^\circ_{Cu^{2+}} + 0.0\ V$

$E^\circ_{Cu^{2+}} = +\ 0.34$ volt

i.e. the reduction potential of Cu electrode = 0.34 volt

2.8 DETERMINATION OF ELECTRODE POTENTIAL—NERNST EQUATION

Consider the following redox reaction.

$$M^{n+} + ne^- \rightleftharpoons M \qquad ...(2.7)$$

According to Van't Hoff's reaction isotherm,

$$\Delta G = -\ RT \ln K + RT \ln ([\text{Product}]/[\text{Reactant}]) \qquad ...(2.8)$$

We know that

$$\Delta G^o = -\ RT \ln K \qquad ...(2.9)$$

From the above equation

$$\Delta G = \Delta G^o + RT \ln ([\text{Product}]/[\text{Reactant}]) \qquad ...(2.10)$$

Free energy relates with electrode potential by the following equation

$$\Delta G = -\ nFE \quad \text{and} \quad \Delta G^o = -\ nFE^o$$

which on substitution in the above equation, becomes

$$-\ nFE = -\ nEF^\circ + RT \ln \left(\frac{[\text{Product}]}{[\text{Reactant}]}\right) \qquad ...(2.11)$$

Dividing the above equation by – nF,

$$E = E^\circ - \frac{RT}{nF} \ln \left(\frac{[\text{Product}]}{[\text{Reactant}]} \right) \qquad \text{...(2.12)}$$

Nernst Equation for Oxidation Potential

Consider the following oxidation reaction:

$$\text{M} \longrightarrow \text{M}^{n+} + \text{ne}^- \qquad \text{...(2.13)}$$

From the above oxidation reaction, the Nernst equation is modified as,

$$E = E^\circ - \frac{RT}{nF} \ln \left(\frac{[\text{M}^{n+}]}{[\text{M}]} \right) \qquad \text{...(2.14)}$$

$$E = E^\circ - \frac{RT}{nF} \ln \left(\frac{[\text{M}^{n+}]}{a_\text{M}} \right) \qquad \text{...(2.15)}$$

(Since [M] = a_M = activity of the metal ion)

Also $a_\text{M} = 1$ for the all the metals.

And hence the above equation is modified as

$$E_\text{oxi} = E^\circ{}_\text{oxi} - \frac{RT}{nF} \ln [\text{M}^{n+}]$$

or

$$E_\text{oxi} = E^\circ{}_\text{oxi} - 2.303 \frac{RT}{nF} \log [\text{M}^{n+}]$$

or

$$E_\text{oxi} = E^\circ{}_\text{oxi} - \frac{0.0591}{n} \log [\text{M}^{n+}] \qquad \text{...(2.16)}$$

where F = 1 Faraday = 96500 coulombs; and R = 8.314 J/K/mole; T = 298 K

Nernst Equation for Reduction Potential

Consider the following reduction reaction:

$$\text{M}^{n+} + \text{ne}^- \longrightarrow \text{M} \qquad \text{...(2.17)}$$

From the above reduction reaction, the Nernst equation is modified as,

$$E_\text{red} = E^\circ{}_\text{red} - \frac{RT}{nF} \ln \left(\frac{[\text{M}]}{[\text{M}^{n+}]} \right)$$

$$E_\text{red} = E^\circ{}_\text{red} - \frac{RT}{nF} \ln \left(\frac{a_\text{M}}{[\text{M}^{n+}]} \right) \qquad \text{...(2.18)}$$

(Since [M] = a_{M} = activity of the metal ion). Also $a_{\mathrm{M}} = 1$ for the all the metals.

Hence, the above equation is modified as

$$E_{\mathrm{red}} = E^\circ_{\mathrm{red}} - \frac{RT}{nF} \ln \left(\frac{1}{[\mathrm{M}^{n+}]}\right)$$

$$E_{\mathrm{red}} = E^\circ_{\mathrm{red}} + \frac{RT}{nF} \ln [\mathrm{M}^{n+}]$$

$$E_{\mathrm{red}} = E^\circ_{\mathrm{red}} + \frac{0.0591}{n} \log [\mathrm{M}^{n+}] \qquad \ldots(2.19)$$

Nernst Equation for emf of the Cell

$$\text{Emf of the cell} = E_{\mathrm{oxi}} + E_{\mathrm{red}} \qquad \ldots(2.20)$$

From the above equations,

$$E = E^\circ_{\mathrm{Oxi}} - \frac{0.0591}{n} \log [\mathrm{M}^{n+}]_{\mathrm{oxi}} + E^\circ_{\mathrm{red}} + \frac{0.0591}{n} \log [\mathrm{M}^{n+}]_{\mathrm{red}}$$

$$E = E^\circ_{\mathrm{Oxi}} + E^\circ_{\mathrm{red}} + \frac{0.0591}{n} \log [\mathrm{M}^{n+}]_{\mathrm{red}} - \frac{0.0591}{n} \log [\mathrm{M}^{n+}]_{\mathrm{oxi}}$$

$$E = E^\circ + \frac{0.0591}{n} \log \left(\frac{[\mathrm{M}^{n+}]_{\mathrm{red}}}{[\mathrm{M}^{n+}]_{\mathrm{oxi}}}\right) \qquad \ldots(2.21)$$

Equations (2.12), (2.16) and (2.19) are called the Nernst equation for single electrode potential.

From the above equations, the following is clear:

1. If concentration of solution (M^{n+}) is increased, the electrode potential increases and vice versa.
2. If the temperature is increased, the electrode potential increases and vice versa.

Example 3 *Calculate the oxidation potential of Cd/CdSO$_4$, 0.5 M at 298 K.* $E^\circ_{Cd^{2+}/Cd} = -0.403$ *V. Also calculate its reduction potential.*

$$Cd \rightleftharpoons Cd^{2+} + 2e^- \quad (\textit{oxidation})$$

Solution Oxidation potential

$$E_{\mathrm{oxi}} = E^\circ_{\mathrm{oxi}} - \frac{RT}{nF} 2.303 \log \frac{[\mathrm{Cd}^{2+}]}{[\mathrm{Cd}]}$$

$$= 0.403 - \frac{0.0591}{2} \log \frac{0.5}{1}$$

$$= 0.403 - 0.0295 \times (-0.3010)$$

$$E_{\text{oxi}} = 0.411898 \text{ V}$$

$$E_{\text{red}} = -0.411898 \text{ V}$$

Example 4 *Calculate the reduction potential of Cu/CuSO$_4$ (0.8 M) at 298 K. $E°_{red}$ = 0.337 V. If this electrode is connected to the standard calomel electrode, what will be the emf produced? $E°_{red}$ of standard calomel electrode = 0.2422V.*

Solution $\text{Cu}^{2+} + 2\,e^- \rightleftharpoons \text{Cu}$ (reduction)

$$E_{\text{red}} = E°_{\text{red}} - \frac{0.0591}{n} \log \frac{[\text{Cu}]}{[\text{Cu}^{2+}]}$$

$$= 0.337 - \frac{0.0591}{2} \log \frac{1}{0.8}$$

$$= 0.337 - 0.002864$$

The reduction potential of Cu/CuSO$_4$ = 0.3341 V

Given, $E°_{\text{red}}$ of standard calomel electrode = 0.2422 V (so that the standard calomel electrode will work as anode)

The emf of the cell constituted by the experimental electrode and standard Calomel electrode = $E°_{\text{red}} + E°_{\text{oxi}}$

$$= 0.3341 - 0.2422$$

$$= 0.0919 \text{ V}$$

Example 5 *Calculate the emf of a Daniel cell at 25°C, when the concentrations of ZnSO$_4$ and CuSO$_4$ are 0.001 M and 0.1 M respectively. The standard potential of the cell is 1.1 volts.*

Solution The cell is

$$\text{Zn(s)} \,/\, \text{Zn}^{2+}\,(0.001\text{M}) \,//\, \text{Cu}^{2+}\,(0.1\text{M}) \,/\, \text{Cu(s)}$$

$$E_{\text{cell}} = E°_{\text{cell}} + \frac{0.0591}{2} \log \frac{\text{Cu}^{2+}}{\text{Zn}^{2+}}$$

$$= 1.1 + 0.0296 \log \frac{0.1}{0.001}$$

$$= 1.1 + 0.0296\,(2)$$

$$= 1.1592 \text{ V}$$

Example 6 *Find the cell potential of a cell in which the following reactions take place at 25°C.*

$$Zn(s) + Cu^{2+}\ (0.02M)\ Cu(s) + Zn^{2+}\ (0.4M).$$

Solution Given

$$E^\circ_{Zn^{2+}/Zn} = -\,0.76\text{V};\ E^\circ_{Cu^{2+}/Cu} = 0.34\text{ V}.$$

$$\begin{aligned} E_{\text{cell}} &= E^\circ_{Cu^{2+}/Cu} - E^\circ_{Zn^{2+}/Zn} + \frac{0.0591}{2}\log\frac{Cu^{2+}}{Zn^{2+}} \\ &= [0.34 - (-\,0.76)] + 0.0296 \log \frac{0.02}{04} \\ &= 1.1 + 0.0296 \log (0.05) \\ &= 1.1 - 0.0385 \\ &= 1.0615\text{ V} \end{aligned}$$

Example 7 *Calculate E° of the cell:*

$$Zn \mid ZnSO_4 \mid\mid AgNO_3 \mid Ag \text{ at } 25°C$$

$$E^\circ_{Zn/Zn^{2+}} = -\,0.763\text{ V and } E^\circ_{Ag/Ag^{+}} = 0.7991\text{ V}$$

Also, calculate standard free energy and equilibrium constant.

Solution Cell reaction is $Zn + 2Ag^+ \rightleftharpoons Zn^{2+} + 2\,Ag$

Standard emf (E°) of the cell

$$\begin{aligned} E^\circ &= E^\circ_{\text{red}} + E^\circ_{\text{oxi}} \\ &= 0.7991 + 0.763 \\ E^\circ &= 1.5621\text{ V} \end{aligned}$$

Standard free energy

$$\Delta G^\circ = -\,nFE^\circ \qquad ...(1)$$

$$\begin{aligned} &= -\,2 \times 96500 \times 1.5621 \\ &= -\,301485.3\text{ joules mol}^{-1} \\ \Delta G^\circ &= -\,301.485\text{ kJ mol}^{-1} \end{aligned}$$

Equilibrium constant

$$\Delta G^\circ = -\,RT \ln K_{\text{eq}} \qquad ...(2)$$

Comparing equations (1) and (2),

$$-nFE° = -RT \ln K_{eq}$$

$$E° = RT/nF \ln K_{eq}$$

$$1.5621 = \frac{8.314 \times 298}{2 \times 96500} \times 2.303 \times \log K_{eq}$$

$$= \frac{0.0591}{2} \log K_{eq}$$

$$1.5621 = 0.02956 \log K_{eq}$$

$$\log K_{eq} = \frac{1.5621}{0.02956}$$

$$= 52.845$$

$$K_{eq} = 6.999 \times 10^{52}$$

Example 8 *A cell is constituted by cadmium and nickel electrodes as*

$$Cd/Cd^{2+}\ (x\ M)\ ||\ Ni^{2+}\ (2M)\ /\ Ni.$$

The emf of the cell is found to be 0.20 V. Calculate the concentration of Cd^{2+} *ions in the solution.* $E°_{Cd^{2+}/Cd} = -0.40v$; $E°_{Ni^{2+}/Ni} = -0.25$ *V.*

Solution $E°_{Cd^{2+}/Cd} = -0.40$ V;

$$E°_{Ni^{2+}/Ni} = -0.25 \text{ V.}$$

$$E_{cell} = 0.20 \text{ V}$$

$$E_{cell} = E°_{Ni^{2+}/Ni} - E°_{Cd^{2+}/Cd} + \frac{0.0591}{2} \log \frac{[Ni^{2+}]}{[Cd^{2+}]}$$

$$0.20 = -0.25 - (-0.40) + \frac{0.0591}{2} \log \frac{[2]}{[x]}$$

$$0.20 = 0.15 + 0.0295 [\log [2] - \log [x]]$$

$$0.05 = 0.0295 [\log [2] - \log [x]]$$

$$1.6949 = \log [2] - \log [x]$$

$$1.6949 - \log 2 = -\log [x]$$

$$1.6949 - 0.3010 = -\log [x]$$

$$-1.3939 = \log [x]$$

$$[x] = \text{antilog } [-1.3939]$$

Concentration of Cd^{2+} ions in the solution is = 0.04M

2.9 REFERENCE ELECTRODES

The electrode of standard potential with which we can compare the potentials of other electrode is called a reference electrode.

Important reference electrodes are the following:

2.9.1 Hydrogen Electrode

This is a gas electrode. It consists of a thin rectangular platinum foil (1 cm x 1 cm) which is coated with fresh platinum black to increase the adsorption capacity of the metal. This is welded and the end of it is fused into the inner tube through the base. In the inner tube, a little mercury is taken and a Pt wire is introduced to make the external electrical contact. The inner tube is enclosed in an outer jacket having an inlet tube for sending in H_2 gas and has a perforated wider base for the escape of excess of H_2. This unit is dipped in HCl taken in a beaker such that the metal foil remains in the solution.

Working

When pure and dry H_2 gas is passed through the inlet tube, a part of the gas gets adsorbed and the excess bubbles come out through the perforations. Between the H_2 gas adsorbed on the surface of the metal and H^+ of the solution, equilibrium is established and an electrical double layer of opposite charges is formed. The potential developed is called H_2 electrode potential.

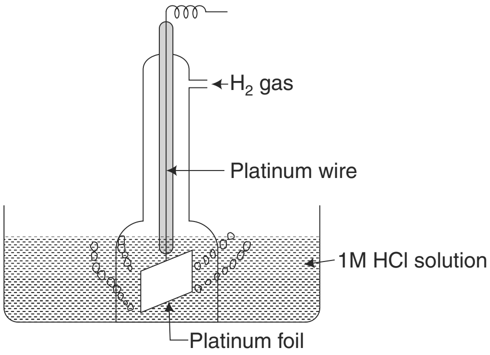


Fig. 2.11 *Standard Hydrogen Electrode*

In the above system, when the H_2 gas at a pressure of 1 atm is bubbled through 1M HCl, the electrode (constructed) or formed is called **Standard Hydrogen Electrode** (SHE) or Normal Hydrogen Electrode (NHE).

This is represented as Pt, H_2 (760 mm of Hg)/H^+ (IM)

Definition The standard hydrogen electrode potential is defined as the potential that is developed between the H_2 gas adsorbed on the Pt metal and H^+ of the solution when the H_2 gas at a pressure of 760 mm of Hg is in equilibrium with H^+ of unit concentration.

Cell reaction

$$H^+ (aq) + e^- \longrightarrow ½\, H_2(g)$$

Electrode Potential of the Hydrogen Electrode

The electrode potential of the hydrogen electrode has been arbitrarily fixed as zero.

It is used

1. For the determination of electrode potential of a metal electrode system
2. For the determination of pH of a solution

Determination of pH using Hydrogen Electrode

A hydrogen electrode may be employed to find the pH value of an unknown solution. For this, the solution whose pH is to be determined is taken in a vessel and a platinum electrode is half dipped in it. A slow current of hydrogen gas at 1 atmosphere is bubbled through the solution.

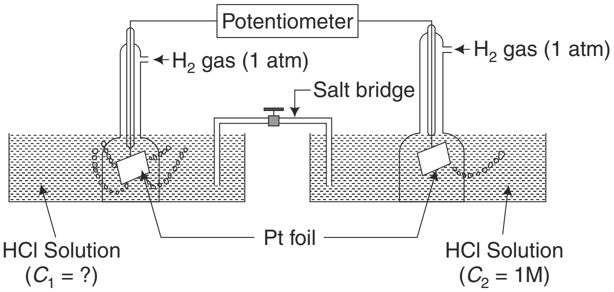


Fig. 2.12 *Measurement of pH by hydrogen electrode*

The platinum catalyses the following electrochemical reaction at the electrode.

$$H^+ (aq) + e^- \longrightarrow ½\, H_2(g)$$

This causes the electrode to develop a definite potential, depending on the H^+ ion concentration on the solution under test.

$$E = E° - \frac{0.0591}{n} \log \frac{[H_2]^{1/2}}{[H^+_{(aq)}]} \text{ at } 25°C$$

$$= 0 - \frac{0.0591}{1} \log \frac{1}{[H^+_{(aq)}]} \text{ at } 25°C,$$

where $H_2 = 1$ atm

$$= -\ 0.0591\ \text{pH}$$

The above half-cell so formed is connected to a standard or normal hydrogen electrode (i.e. having a solution of 1N HCl and an electrode potential of 0 volt). The two solutions are separated by a salt bridge to eliminate liquid junction potential. The emf of the full cell is then determined by means of a potentiometer. Since emf of the reference electrode is zero, therefore the observed emf gives directly the emf of the half-cell containing the solution under test.

$$E_{\text{cell}} = E_{\text{right}} - E_{\text{left}}$$

$$E_{\text{cell}} = 0 - (-\ 0.0591\ \text{pH}) = 0.0591\ \text{pH}$$

$$\text{pH} = \frac{E_{\text{cell}}}{0.0591}$$

Limitations

1. It is rather difficult to regulate the pressure of the H_2 gas to be at exactly 1 atm throughout the experiment.
2. Excess of H_2 bubbling out carries little HCl with it and hence the H^+ concentration decreases. In such a system, it is difficult to maintain the concentration of HCl at 1M.
3. Platinum foil gets easily poisoned by the impurities present in the gas and HCl. In fact, the attainment of equilibrium is ensured by trial and error.
4. If the solution contains any oxidizing agent, the H_2 electrode cannot be used.

Example 9 *The emf of the following cell*

Pt, H_2 (1atm)/ H^+ (unknown) | | H^+(1 M)/H_2 (1atm), Pt, is 0.1773 V. Calculate pH of the given solution.

Solution

$$\text{pH} = \frac{E_{\text{cell}}}{0.0591}$$

$$= \frac{0.1773}{0.0591}$$

$$\text{pH} = 3$$

Example 10 *Calculate the emf of the cell*

Pt, H_2 (1 atm)/ H^+ (pH = 4.0) | | H^+(1 M)/H_2 (1atm), Pt.

Solution

$$\text{pH} = \frac{E_{\text{cell}}}{0.0591}$$

$$E_{\text{cell}} = \text{pH} \times 0.0591$$

$$= 4.0 \times 0.0591$$

$$= 0.2364 \text{ V}$$

2.9.2 Some Other Reference Electrodes

Since a standard hydrogen electrode is difficult to prepare and maintain, it is usually replaced by other reference electrodes, which are known as secondary reference electrodes. These are convenient to handle and are prepared easily.

Calomel Electrode

The calomel electrode is commonly known as the mercury–mercurous chloride electrode. It is otherwise known as secondary reference electrode.

(i) Construction

The calomel electrode consists of a glass tube. At the bottom of the tube, a layer of mercury is placed, over which there is a paste of mercury and mercurous chloride.

The KCl solution is filled with the remaining portion of the cell. The cell is filled with 0.1N, 1.0N and a saturated solution of potassium chloride. Then the electrode may be called decinormal, normal and saturated calomel electrode respectively.

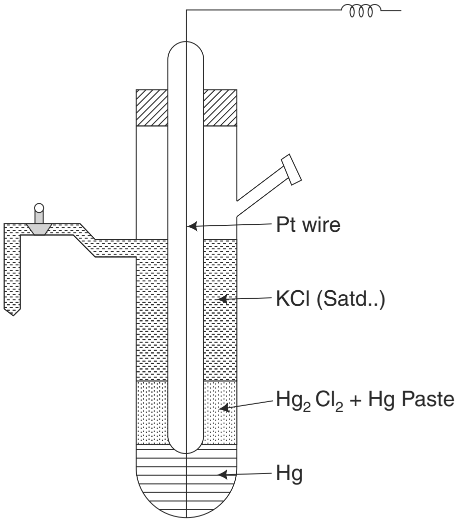


Fig. 2.13 *Standard calomel electrode*

The electrical contact may be made through a platinum wire sealed with a glass tube.

The side arm is provided for making electrical contact through a salt bridge.

Cell representation

$$\text{Hg, Hg}_2\text{Cl}_2\text{ (s)// KCl (satd. solution)}$$

Cell reaction

$$Hg_2Cl_2\ (s) + 2\ e^- \longrightarrow 2\ Hg\ (l) + 2\ Cl^-\ (aq)$$

(ii) Electrode Potential of Calomel Electrode

The potential of the calomel electrode, on the hydrogen scale, has been found to vary with the concentration of the potassium chloride solution used. The reduction potentials for the various KCl concentrations at 25°C are given here.

Concentration of KCl	*Electrode Potential in Volts at 25°C*
Saturated	0.2422 V
1.0N	0.2800 V
0.1N	0.3338 V

(iii) Measurement of pH using Calomel Electrode

The electrode can be coupled with hydrogen electrode containing a solution of unknown pH.

$$\text{Pt, } H_2\ (1\text{atm})/\ H^+\ (C=?)//\ \underset{(\text{satd})}{KCl}/Hg_2Cl_2(s),\ Hg$$

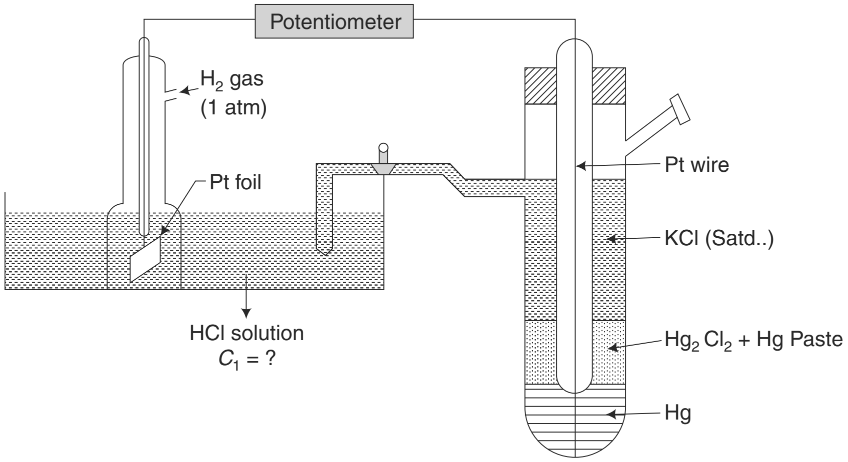


Fig. 2.14 *Measurement of pH using calomel electrode*

The emf of the cell

$$E_{\text{cell}} = E_{\text{right}} - E_{\text{left}} = 0.2422\ \text{V} + 0.0591\ \text{V pH}$$

$$\text{pH} = \frac{E_{\text{cell}} - 0.2422}{0.0591}$$

Example 11 *The emf of the following cell is*

Pt, H_2 *(1atm),* H^+ *(C = ?) | | KCl,* $Hg_2Cl_2(s)$*, Hg 0.4494 V. Calculate pH of the given solution.*

Solution

$$\text{pH} = \frac{E_{\text{cell}} - 0.2422}{0.0591}$$

$$= \frac{0.4494 - 0.2422}{0.0591}$$

$$\text{pH} = 3.5$$

Example 12 *Calculate the emf of the cell*

Pt, H_2 *(1atm),* H^+ *(pH = 4.2) | | KCl,* $Hg_2Cl_2(s)$*, Hg.*

Solution

$$\text{pH} = \frac{E_{\text{cell}} - 0.2422}{0.0591}$$

$$E_{\text{cell}} = 0.0591 \times \text{pH} + 0.2422$$

$$= 0.0591 \times 4.2 + 0.2422$$

$$= 0.49042 \text{ V}$$

2.10 TYPES OF ELECTRODES

An electrochemical cell consists of two electrodes, positive and negative. Each electrode constitutes a half-cell or a single electrode. The commonly used electrodes in different electrochemical cells are

1. Metal–metal ion electrodes
2. Metal–insoluble metal salt electrodes
3. Gas electrodes
4. Glass electrode

2.10.1 Metal–Metal Ion Electrodes

This type of electrode consists of a metal rod (M) dipping into a solution of its metal ions (M^{n+}).

Cell representation

$$M / M^{n+}$$

Electrode reaction

$$M \rightleftharpoons M^{n+} + n\,e^-$$

If the metal rod behaves as a negative electrode (i.e. the reaction involves oxidation), the above equilibrium will shift towards right. Therefore, the concentration of the M^{n+} ions in solution will increase.

Table 2.3 *Types of electrodes*

Types of Electrodes	***Cell Representation***	***Electrode Reaction***	***Electrode Potential***	***Examples***
Metal–metal ion electrodes	M / M^{n+}	$M \rightleftharpoons M^{n+} + ne^-$	$E_M = E^\circ{}_M - \frac{RT}{nF} \ln a_M{}^{n+}$	• Zinc rod dipping in $ZnSO_4$ solution (Zn/Zn^{2+}) • Copper rod dipping in $CuSO_4$ solution (Cu/Cu^{2+}) • Silver rod dipping in $AgSO_4$ solution (Ag/Ag^{2+})
Metal–insoluble metal salt electrodes	$M / MX / X^-$ (a)	$M(s) + X^- \rightleftharpoons MX + e^-$	$E_{M/X^-} = E^\circ{}_{M/X} - \frac{RT}{nF} \ln \frac{1}{aX}$	• Calomel electrode: mercury–mercurous chloride in contact with a solution of KCl • Mercury–Mercuric sulphate in contact with a solution K_2SO_4. • Silver wire coated with AgCl immersed in KCl solution.
Gas electrode	$Pt,X_2 /X^+$	$X^+{}_{(aq)} + e^- \rightleftharpoons \frac{1}{2} X_{2(g)}$	$E_M = E^\circ{}_M - \frac{RT}{nF} \ln a_{X+}$	• Hydrogen electrode • Chlorine electrode
Glass electrode	Ag/AgCl (s), HCl (0.1 M)/ Glass	$H^+{}_{(aq)} + e^- \rightleftharpoons \frac{1}{2} H_{2(g)}$	$E_G = E^\circ{}_G + 0.0591$ pH	• Glass electrode

On the other hand, if the metal rod behaves as a positive electrode (i.e. the reaction involves reduction), the equilibrium will shift towards the left. Therefore, the concentration of the M^{n+} ions in solution will decrease.

Electrode potential

$$E_M = E^\circ{}_M - \frac{RT}{nF} \ln a_M^{n+}$$

Examples

- Zinc rod dipping in $ZnSO_4$ solution. (Zn/Zn^{2+})
- Copper rod dipping in $CuSO_4$ solution (Cu/Cu^{2+})
- Silver rod dipping in $AgSO_4$ solution (Ag/Ag^{2+})

2.10.2 Metal–Insoluble Metal Salt Electrodes

This type of electrode consists of a metal (M) covered by a layer of sparingly soluble salt (MX) dipping into a solution containing a common anion (X^-).

Cell representation

$$M/MX/X^-(a)$$

Electrode reaction

$$M(s) + X^- \rightleftharpoons MX + e^-$$

Electrode potential

$$E_{M/X^-} = E^\circ_{M/X} - \frac{RT}{nF}\ln\frac{1}{aX^-}$$

Examples

- Calomel electrode: mercury–mercurous chloride in contact with a solution of KCl
- Mercury–Mercuric sulphate in contact with a solution K_2SO_4
- Silver wire coated with AgCl immersed in KCl solution

2.10.3 Gas Electrode

Gases like hydrogen, chlorine, etc., bubble in an acid solution and can be used to form gas electrodes. The acid employed contains the ions of the gas used. Since these gases are nonconductors of electricity, metals like platinum are used for making electrical contact in the circuit. These metals are not attacked by the acids.

(a) Hydrogen Electrode

Hydrogen gas is bubbled into HCl solution.

The equilibrium is represented as

$$H^+_{(aq)} + e^- \rightleftharpoons \tfrac{1}{2} H_{2(g)}$$

The electrode is represented as

$$Pt, H_2\ (1\ atm)/\ H^+\ (1M)$$

The reaction from left to right is reduction, where hydrogen ions change to hydrogen gas by absorbing electrons. The electrode is reversible with respect to hydrogen gas.

(b) Chlorine Electrode

In this electrode, chlorine gas at a given pressure is bubbled into a solution of hydrochloric acid.

The reaction is

$$\tfrac{1}{2} Cl_2\ (g) + e^- \rightleftharpoons Cl^-$$

The reaction from left to right is reduction. Chlorine gas changes into chloride ion by gaining an electron.

The electrode is represented as

$$\text{Pt, Cl}_2\text{ (g)/Cl}^-$$

The electrode is reversible with respect to chloride ion.

2.10.4 Glass Electrodes (Internal Reference Electrode)

A glass electrode is the universally employed electrode for pH measurement.

(a) Construction

The glass electrode is made of a special glass of relatively low melting point and high electrical conductivity. It is a special type of glass bulb containing Na_2O (22%), CaO (6%) and SiO_2 (72%). This glass bulb is filled with 0.1 N hydrochloric acid and a silver wire coated with silver chloride is immersed in it. Here Ag/ AgCl acts as an internal reference electrode.

The glass electrode is represented as

$$\text{Ag/ AgCl (s), HCl (0.1 M)/Glass}$$

HCl in the bulb furnishes a constant H^+ ion concentration. Thus, it is a silver–silver chloride electrode reversible with respect to Cl^- ions.

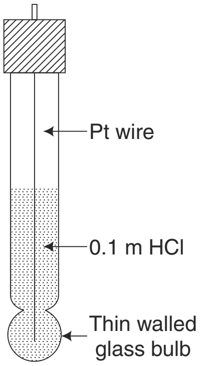


Fig. 2.15 *Glass electrode*

A glass electrode is used as the 'internal reference electrode'. The pH of the solutions, especially coloured solutions containing oxidizing or reducing agents, can be determined.

(b) Working Mechanism of Glass Electrode

The response of a glass electrode to H^+ ion activity is a result of complex processes at the interface between the glass membrane (50 μm) and the solutions on either side of it. The membrane itself is permeable to Na^+ and Li^+ ions but not to H^+ ions. The glass membrane is coated with hydrated silica. H^+ ions in the test solution modify this layer to an extent that depends on their activity in the solution and the charge modification of the outside layer is transmitted to the inner layer by the Na^+ and Li^+ ions in the glass. H^+ ion activity gives rise to a membrane potential by this indirect mechanism.

(c) Determination of pH of a Solution using Glass Electrode

The glass electrode is placed in the solution under test and coupled with a saturated calomel electrode.

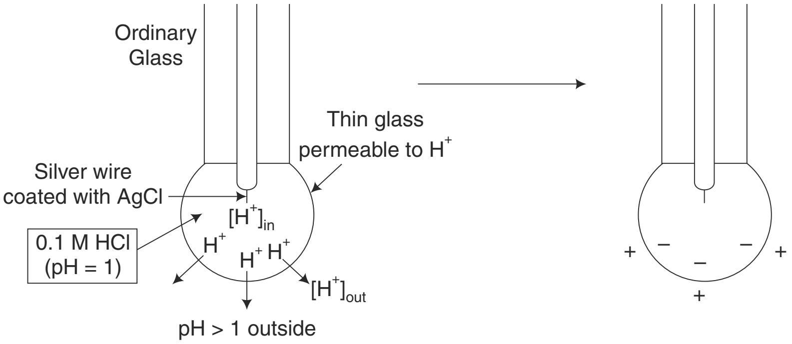


Fig. 2.16 *Mechanism of glass electrode* $E_G = E^\circ_G + 0.0591$ *pH*

The cell assembly is represented as

Ag/AgCl (s), HCl (0.1 M)/Glass/Solution of
Unknown pH//Satd. Calomel Electrode

The emf of the cell is measured. From the emf, pH of the solution is calculated as follows.

$$E_{\text{cell}} = E_{\text{right}} - E_{\text{left}}$$
$$= 0.2422 - [E^\circ_G + 0.0591 \text{ pH}]$$

Therefore,

$$\text{pH} = \frac{0.2422 - E_{\text{cell}} - E^\circ_G}{0.0591}$$

(d) Advantages of Glass Electrode

(i) It can be easily constructed and readily used.

(ii) The results are accurate.

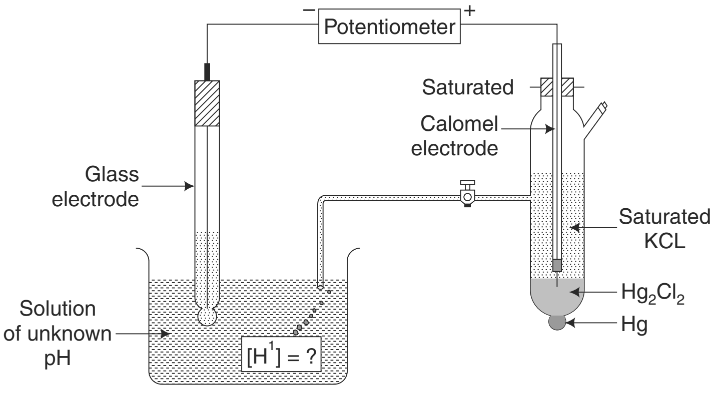


Fig. 2.17 *Determination of pH by glass electrode*

(iii) It is not easily poisoned.
(iv) It can be used in turbid coloured and colloidal solutions.

(e) Limitations

(i) Since the resistance is quite high, special electronic potentiometers are employed for measurement.
(ii) The glass electrode can only be used in solutions with a the pH range of 0 to 10.

2.11 ELECTROCHEMICAL SERIES OR EMF SERIES—IMPORTANCE OF ELECTRODE POTENTIAL

By measuring the potentials of various electrodes versus a standard hydrogen electrode (SHE), a series of standard electrode potentials has been established. When the electrodes (metals and nonmetals) in contact with their ions are arranged on the basis of the increasing values of their standard reduction potentials, the resulting series is called the **electrochemical** or **electromotive** or **activity series** of the elements.

By international convention, the standard potentials of electrodes are tabulated for reduction half-reactions, indicating the tendencies of the electrodes to behave as cathodes towards SHE. Those with positive $E°$ values for reduction half-reactions do in fact act as cathodes versus SHE, while those with negative $E°$ values of reduction half-reactions behave instead as anodes versus SHE. The electrochemical series is shown in Table 2.4.

Table 2.4 *Standard electrode potential (half-cell potentials of some metals with respect to SHE at 25°C)*

Element	***Electrode Reaction (Reduction)***	***Standard Electrode Reduction Potential E°, Volt***	
Li	$Li^+ + e^- = Li$	−3.05	Anodic
K	$K^+ + e^- = K$	−2.925	↑
Ca	$Ca^{2+} + 2e^- = Ca$	−2.87	
Na	$Na^+ + e^- = Na$	−2.714	
Mg	$Mg^{2+} + 2e^- = Mg$	−2.37	
Al	$Al^{3+} + 3e^- = Al$	−1.66	
Zn	$Zn^{2+} + 2e^- = Zn$	−0.7628	
Cr	$Cr^{3+} + 3e^- = Cr$	−0.74	
Fe	$Fe^{2+} + 2e^- = Fe$	−0.44	Pt-Reference
Cd	$Cd^{2+} + 2e^- = Cd$	−0.403	
Ni	$Ni^{2+} + 2e^- = Ni$	−0.25	

Table Contd...

Table Contd...

Sn	$Sn^{2+} + 2e^- = Sn$	–0.14	
H_2	$2H^+ + 2e^- = H_2$	0.00	Pt-Reference
Cu	$Cu^{2+} + 2e^- = Cu$	+0.337	↓
I_2	$I_2 + 2e^- = 2I^-$	+0.535	
Ag	$Ag^+ + e^- = Ag$	+0.799	
Hg	$Hg^{2+} + 2e^- = Hg$	+0.885	
Br_2	$Br_2 + 2e^- = 2Br^-$	+1.08	
Cl_2	$Cl_2 + 2e^- = 2Cl^-$	+1.36	
Au	$Au^{3+} + 3e^- = Au$	+1.50	
F_2	$F_2 + 2e^- = 2F^-$	+2.87	Cathodic

2.11.1 Characteristics of Electrochemical Series

(i) The negative sign of standard reduction potential indicates that an electrode when joined with SHE acts as anode, and oxidation occurs on this electrode. For example, the standard reduction potential of zinc is – 0.76 volt. When a zinc electrode is joined with SHE, it acts as anode (–ve electrode), i.e. oxidation occurs on this electrode. Similarly, the +ve sign of standard reduction potential indicates that the electrode when joined with SHE acts as cathode and reduction occurs on this electrode.

(ii) The metals on the top (having high negative values of standard reduction potentials) have the tendency to lose electrons readily. These are active metals. The activity of metals decreases from top to bottom. The nonmetals on the bottom (having high positive values of standard reduction potentials) have the tendency to accept electrons readily. These are active nonmetals. The activity of nonmetals increases from top to bottom.

(iii) The substances which are stronger reducing agents than hydrogen are placed above hydrogen in the series. The substances which are stronger oxidizing agents than H^+ ions are placed below hydrogen in the series.

2.11.2 Importance or Significance of Electrochemical or emf Series or Applications of Electrochemical Series

(a) Reactivity of Metals

The activity of the metal depends on its tendency to lose an electron or electrons, i.e. tendency to form cations (M^{n+}). This tendency depends on the magnitude of standard reduction potential. The metal which has a high negative value (or smaller positive value) of standard reduction potential readily loses the electron or electrons and is converted into a cation. Such a metal is said to be chemically active.

The chemical reactivity of metals decreases from top to bottom in the series. The metal higher in the series is more active than the metal lower in the series. Some examples are illustrated below.

(i) Alkali metals and alkaline earth metals having high negative values of standard reduction potentials are chemically active. These react with cold water and evolve hydrogen. These readily dissolve in acids forming corresponding salts and combine with those substances which accept electrons.

(ii) Metals like Fe, Pb, Sn, Ni, Co, etc., which lie a little down in the series, do not react with cold water but react with steam to evolve hydrogen.

(iii) Metals like Cu, Ag and Au which lie below hydrogen are less reactive and do not evolve hydrogen from water.

(b) Relative Ease of Oxidation or Reduction

The higher the value of standard reduction potential, the greater is the tendency to get reduced form.

(i) The positive sign of reduction potential indicates that the electrode reaction occurs in the forward direction, i.e. reduction direction. Fluorine has higher positive value of standard reduction potential (+2.65 V) and shows higher tendency towards reduction.

(ii) The negative sign of reduction potential indicates that the electrode reaction occurs in opposite direction, i.e. backward direction. It means the reduced form has a greater tendency to lose electrons and get oxidized. Thus, lithium (–3.01V) has the highest negative reduction potential and shows higher tendency to lose electrons.

(c) Displacement of One Species by the Other

We now try to predict whether a given metal will displace another from its salt solution. A metal higher in the series will displace the metal from its solution which is lower in the series, i.e. the metal having low standard reduction potential will displace that metal from its salt solution which has a higher value of standard reduction potential. A metal higher in the series has greater tendency to provide electrons to the cations of the metal to be precipitated.

For example, we can know whether copper will displace zinc from its solution or vice versa. We know that $E^\circ_{Cu/Cu^{2+}} = +\ 0.34$ V and $E^\circ_{Zn^{2+}/Zn} = -\ 0.76$ V. Cu^{2+} has much greater tendency to get Cu form than Zn^{2+} has in acquiring Zn form. In other words, zinc will displace copper from its solution.

$$Zn + Cu^{2+} \longrightarrow Zn^{2+} + Cu$$

(d) Reducing Power of Metals

Reducing nature depends on the tendency of losing electron or electrons. The more the negative reduction potential, more is the tendency to lose electron or electrons. Thus, reducing nature decreases from top to bottom in the electrochemical series. The power of the reducing agent increases as the standard reduction potential becomes more and more negative.

Sodium is a stronger reducing agent than zinc and zinc is a stronger reducing agent than iron.

Elements	***Reduction Potential***	***Reducing Nature***
Na	– 2.71	Decreases
Zn	– 0.76	↓
Fe	– 0.44	

Alkali and alkaline earth metals are strong reducing agents.

(e) Oxidizing Nature of Nonmetals

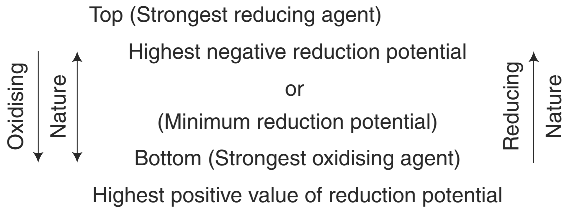
Oxidizing nature depends on the tendency to accept an electron or electrons. More the value of reduction potential, higher is the tendency to accept an electron or electrons. Thus, oxidizing nature increases from top to bottom in the electrochemical series. The strength of an oxidizing agent increases as the value of reduction potential becomes more and more positive.

F_2 (fluorine) is a stronger oxidant than Cl_2, Br_2 and I_2.

Cl_2 (chlorine) is a stronger oxidant than Br_2 and I_2.

Elements	***Reduction Potential***	***Oxidizing Nature***
I_2	+ 0.53	Increases
Br_2	+ 1.06	↓
Cl_2	+ 1.36	
F_2	+ 2.85	

Thus, in the electrochemical series,



Top (Strongest reducing agent)

Highest negative reduction potential

or

(Minimum reduction potential)

Bottom (Strongest oxidising agent)

Highest positive value of reduction potential

(f) Hydrogen Displacement Behaviour

(i) Displacement of Hydrogen from Dilute Acids by Metals

The metals which can provide electrons to H^+ ions present in dilute acids for reduction evolve hydrogen from dilute acids.

$$M \longrightarrow M^{n+} + ne^- \text{ (oxidation)}$$

$$2H^+ + 2e^- \longrightarrow H_2 \text{ (reduction)}$$

The metal having negative values of reduction potential possesses the property of losing an electron or electrons.

Thus, the metals occupying top positions in the electrochemical series readily liberate hydrogen from dilute acids and on descending in the series, the tendency to liberate hydrogen gas from dilute acids decreases.

The metals which are below hydrogen in the electrochemical series like Cu, Hg, Au, Pt, etc., do not evolve hydrogen from dilute acids.

Example 1 *Zinc reacts with dil. H_2SO_4 to give H_2 but Ag does not. Why?*

Solution $Zn + H_2SO_4 \longrightarrow ZnSO_4 + H_2\uparrow$

$$E^\circ_{Zn} = -0.76 \text{ volts}$$

The metal with a positive reduction potential (i.e. the metal placed below H_2 in the emf series) will not displace hydrogen from an acid solution.

$$Ag + H_2SO_4 \longrightarrow \text{No reaction}$$

$$E^\circ_{Ag} = +0.80 \text{ volt}$$

(ii) Displacement of Hydrogen from Water

Iron and the metals above iron are capable of liberating hydrogen from water. The tendency decreases from top to bottom in the electrochemical series.

Alkali and alkaline earth metals liberate hydrogen from cold water but Mg, Zn and Fe liberate hydrogen from hot water or steam.

(g) Calculation of Standard emf of the Cell

Using E° of anode half-cell and cathode half-cell, the standard emf can be calculated.

$$E^\circ_{cell} \text{ or standard emf of a cell} = \boldsymbol{E^\circ_{cathode} - E^\circ_{anode}}$$

(h) Predicting Feasibility or Spontaneity of the Cell Reaction

In a reversible cell, when the cell yields electrical energy, there is a fall in free energy (or) $-\Delta G = nFE$.

Gibbs	Cell Potentials	Spontaneous Direction
$\Delta G < 0$	$E_{\text{cell}} > 0$	Spontaneous
$\Delta G = 0$	$E_{\text{cell}} = 0$	Equilibrium
$\Delta G > 0$	$E_{\text{cell}} < 0$	Nonspontaneous

(i) Determination of Equilibrium Constant for a Reaction

Standard electrode potential can be used to determine the equilibrium constant for a reaction.

We know that

$$-\Delta_G^0 = RT \ln K = 2.303RT \log K$$

$$\log K = \frac{-\Delta_G^0}{2.303RT}$$

$$\log K = \frac{nFE^\circ}{2.303RT} \quad \left[-\Delta_G^0 = nFE^\circ\right]$$

So, from the value of E° for a cell reaction, its equilibrium constant can be calculated.

2.12 POTENTIOMETRIC TITRATION

Potentiometric titration is a very important application of emf measurement. In this method, a cell is constructed in which at least one of the electrodes is reversible with respect to one of the ions taking part in the titration reaction.

2.12.1 Theory

We know that the potential of an electrode dipping in a solution of an electrolyte depends upon the concentration of active ions (i.e. which changes the electrode potential).

$$E = E^\circ + \frac{RT}{nF} \log C$$

A small change in the active-ion concentration in the solution changes the electrode potential correspondingly. During the course of titration, the concentration of the active ion decreases, thereby the electrode potential of the indicator electrode decreases. Thus, the measurement of the indicator electrode potential can serve as a good indication of end point or equivalence point of the titration reaction. The potential of the indicator electrode is usually measured potentiometrically by connecting it with a reference electrode like saturated calomel electrode.

2.12.2 Detection of End Point

The emf of a cell changes by the addition of a small amount of titrant. So the concentration of reversible ion in contact with indicator electrode changes. We thus record the change in emf with every small addition. The change of potential will be slow at first; but at equivalence, the point charge will be sharp or quite sudden. The values are then plotted against corresponding volume changes. A curve like the one shown in Fig. 2.18a is obtained. The end point corresponds to the point of inflexion, i.e., the point where the slope of the curve is maximum as shown. Alternatively, change in emf with every small addition of titrant (i.e. $\Delta E/\Delta V$) is plotted against volume V. The maximum of the curve gives the end point (Fig. 2.18 b).

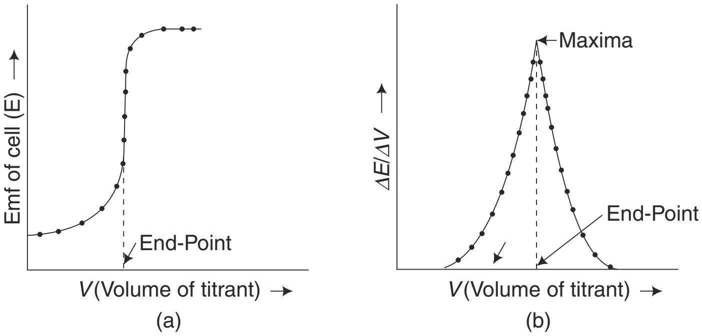


Fig. 2.18 *(a) In potentiometric titration, the point of inflection is the end point. (b) Plot of $\Delta E/\Delta V$ against volume (maxima gives the more accurate end point)*

Potentiometric titrations, are classified into three types:

(a) Acid–base titrations
(b) Oxidation–reduction (redox) titrations
(c) Precipitation titrations

(a) Acid–base Titration

In acid–base titration, quinhydrone electrode is employed as indicator electrode. The reference electrode is, generally, the saturated calomel electrode. A definite volume of the given acid solution is taken in a large beaker. To it, a pinch of quinhydrone is added and a stirrer and a platinum electrode are dipped in it. This electrode is then connected to a saturated calomel electrode through a potentiometer. On adding a standard alkali solution from the burette, the emf of the cell increases at first gradually, but at the end point, the rate of change of potential will be suddenly quite large.

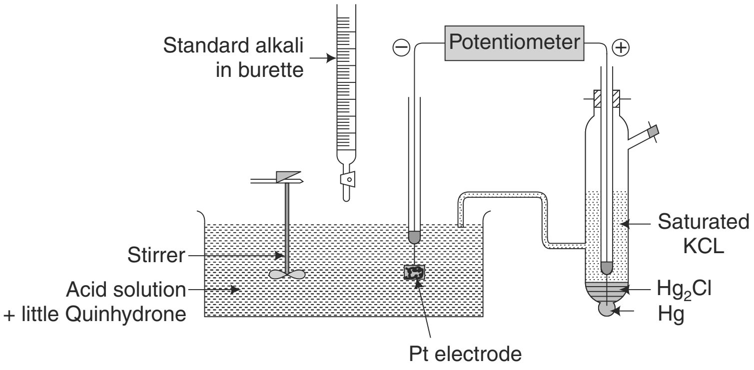


Fig. 2.19 *Acid–base potentiometric titration*

The end point of the titration is then located by plotting $\Delta E/\Delta V$ versus V as shown in Fig. 2.18 and the maximum point on the curve gives the end point.

(b) Redox Titrations

Titrations involving oxidizing agents ($K_2Cr_2O_7$ or $KMnO_4$) and reducing agents (like ferrous salt) can be followed potentiometrically by using a platinum indicator electrode.

$$K_2Cr_2O_7 + 6FeSO_4 + 7H_2SO_4 \longrightarrow K_2SO_4 + Cr_2(SO_4)_3 + 3Fe_2(SO_4)_3 + 7H_2O$$

The apparatus for titration of a ferrous salt with acidified $K_2Cr_2O_7$ is illustrated in Fig. 2.20.

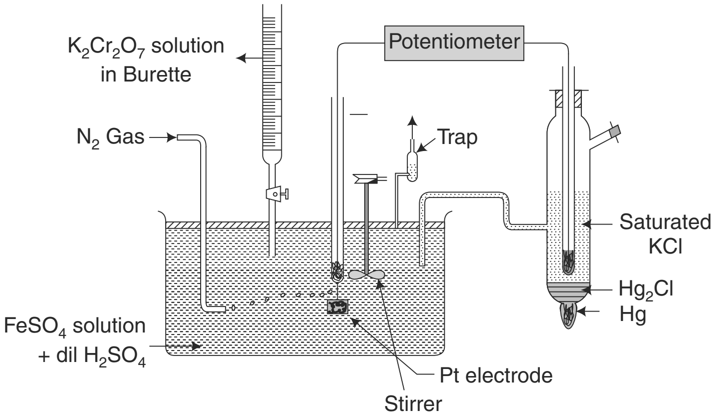


Fig. 2.20 *Potentiometric redox titration*

The initial concentration of an ion such as Fe^{2+} can be found by titrating with a strong oxidizing agent such as Cr^{6+}. The titration is carried out in one side of a cell whose other half is a reference electrode:

$$Pt(s) \mid Fe^{2+}, Fe^{3+} \mid\mid \text{reference electrode (calomel electrode)}$$

Initially, the left cell contains only Fe^{2+}. As the titrant is added, the ferrous ion is oxidized to Fe^{3+} in a reaction that is virtually complete:

$$3Fe^{2+} + Cr^{6+} \longrightarrow 3Fe^{3+} + Cr^{3+}$$

The cell potential is followed as the Fe^{2+} is added in small increments. Once the first drop of titrant has been added, the potential of the left cell is controlled by the ratio of oxidized and reduced iron according to the Nernst equation

$$E = 0.68 - 0.0591 \log \frac{[Fe^{3+}]}{[Fe^{2+}]}$$

On adding $K_2Cr_2O_7$ from the burette, emf of the cell will increase first slowly, but at the equivalence point, Fe^{2+} will have been totally consumed (the large equilibrium constant ensures that this will be so), and the potential will then be controlled by the concentration ratio of Cr^{6+}/Cr^{3+}.

The idea is that both species of a redox couple must be present in reasonable concentrations for a concentration to control the potential of an electrode of this kind. If one works out the actual cell potentials for various concentrations of all these species, the resulting titration curve looks much like the familiar acid–base titration curve. The end point is found not by measuring a particular cell voltage, but by finding what volume of titrant gives the steepest part of the curve.

(c) Precipitation Titrations

In this titration, a silver electrode dipping in silver nitrate solution is used as the working or indicator electrode. This electrode is connected with a saturated calomel electrode through a salt bridge of ammonium nitrate.

We may illustrate the method by the titration of $AgNO_3$ with a standard KCl solution run from the burette. An Ag electrode dipping in $AgNO_3$ solution is used as the indicator electrode. The potential of the Ag^+/Ag half-cell is measured by connecting it with saturated calomel electrode through a salt bridge of NH_4NO_3. As the titration proceeds, by the addition of standard potassium chloride solution from the burette into the silver nitrate solution, the concentration of Ag^+ ions decreases, due to the precipitation of Ag^+ ions as AgCl.

$$Ag^+NO_3^- + K^+Cl^- \longrightarrow AgCl + K^+NO_3^-$$

The reduction potential of the indicator electrode (Ag) goes on decreasing progressively on the addition of KCl. At the end point, the concentration change of Ag^+ is quite rapid. At the end point, the Ag^+ concentration becomes very small on account of slight solubility of AgCl. If addition of KCl is continued, the Ag^+ion concentration is not affected, except for a very small decrease, due to decrease in solubility of AgCl on account of common ion (Cl^-) effect.

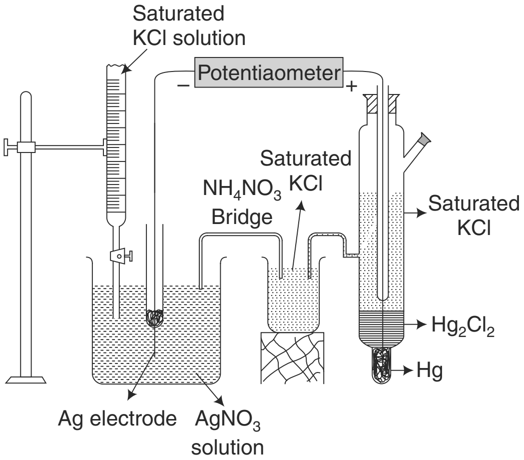


Fig. 2.21 *Potentiometric precipitation titration*

Therefore, addition of KCl beyond end point causes only a very small decrease in electrode potential or emf of the cell. On plotting $\Delta E/\Delta V$ versus V, the point of maxima gives the end point.

Advantages of Potentiometric Titrations

- Potentiometric titrations can be carried out in coloured solutions, where indicators cannot be used.
- There is no need of prior information about the relative strength of titrant before the titration.

2.13 CONDUCTOMETRIC TITRATIONS

Conductometric titration is a volumetric method based on the measurement of conductance of the solution during the titration.

The conductance of a solution should be based on

- The number and charge on the free ions,
- The mobility of the ions

2.13.1 Process

Titrations are usually carried out by taking a solution to be titrated in a beaker kept in a water bath at constant temperature in which a conductivity cell is dipped and connected to a conductivity bridge. The titrant is added from the burette. The whole arrangement may be represented as in Fig. 2.22. The solution is stirred and conductance is measured after each addition. If the conductance of a solution is recorded during the course of titration and plotted against the volume of the titrant added, we get straight lines. The end point can be obtained by finding out the point of their intersection.

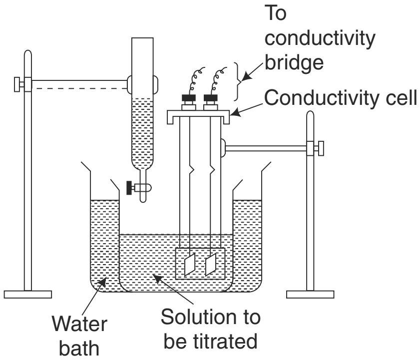


Fig. 2.22 *Conductometric titration*

2.13.2 Types of Conductometric Titrations

- Acid–base titration
- Precipitation titration
- Replacement titration
- Redox (oxidation–reduction) titration
- Complexometric titration

(a) Strong Acid vs Strong Base (HCl vs NaOH)

A known amount of acid (HCl) is taken in the conductivity cell and the alkali (NaOH) in the burette. Initially, the conductivity of the HCl is high—this is due to the presence of fast moving H^+ions (Point *A* in the graph). As the NaOH is added gradually, conductance will go on decreasing until the acid has been completely neutralized (indicated by the line *AB*) in this method.

This is due to the replacement of rapid-moving H^+ ions by slow-moving Na^+ ions. The point '*B*' indicates complete neutralization of all H^+ ions.

$$\underset{\text{Acid}}{HCl} + \underset{\text{Base}}{NaOH} \longrightarrow \underset{\text{Salt}}{NaCl} + \underset{\substack{\text{Water}\\\text{(unionised)}}}{H_2O}$$

Further addition of NaOH will introduce the fast-moving OH^- ions. Therefore, the conductance, after reaching a certain minimum value, will start to increase (indicated by the line *BC*).

On plotting the conductance adjacent to the volume of alkali added, the two lines cross at a point '*B*' to provide the end point. This method corresponds to the volume of NaOH necessary for neutralization. Additional adding up of alkali hoists the conductance piercingly as there is a surplus of hydroxide ions. A graph is drawn among the volume of supplementary NaOH and the conductance of the solution.

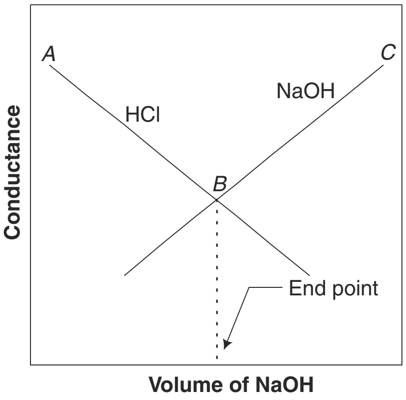


Fig. 2.23 *Plot of titration of strong acid vs strong base*

(b) Weak Acid vs Strong Base (CH_3COOH vs NaOH)

The solution containing acetic acid in the beaker has a very low conductance. During the titration of acetic acid with sodium hydroxide, a highly ionized salt, CH_3COONa, is formed.

The reaction may be represented as

$$CH_3COOH + Na^+ + OH^- \longrightarrow CH_3COO^- + Na^+ + H_2O$$

For every addition of sodium hydroxide to the acetic acid, the conductance value slightly increases up to the equivalence point. At the equivalence point, further addition of alkali introduces excess of fast-moving OH^- ions. The conductance therefore increases more rapidly after the end point is reached.

On plotting the conductance against volume of alkali added, the two straight lines are obtained and where they intersect give the end point.

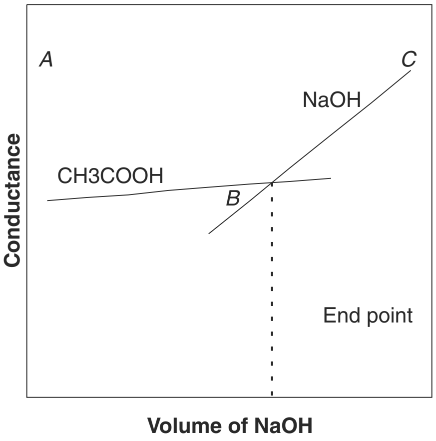


Fig. 2.24 *Titration plot for weak acid vs strong base*

(c) Mixture of Weak and Strong acid with Strong Base (HCl and CH_3COOH vs NaOH)

When a mixture of a weak and a strong acid like CH_3COOH and HCl is titrated against a strong base, a curve *ABCD* is obtained. Due to common-ion effect, the ionization of a weak acid is suppressed in the presence of a strong acid. So the neutralization of a strong acid occurs first and then the neutralization of a weak acid starts.

Therefore, the first point of intersection refers to equivalence point of complete neutralization of strong acid and the second point of intersection C is the equivalence point for the complete neutralization of the mixture.

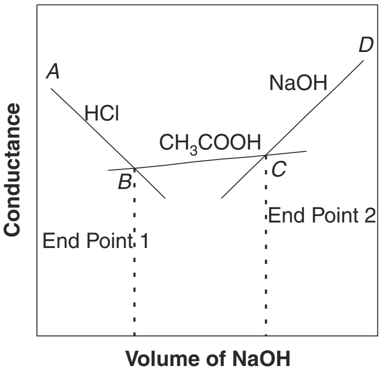


Fig. 2.25 *Titration of plot of a mixture of weak and strong acid with strong base*

2.13.3 Advantanges of Conductometric Titrations

1. This method can be used with very diluted solutions.
2. This method can be used with coloured or turbid solutions in which the end point cannot be seen clearly.
3. This method can be used in which there is no suitable indicator.
4. It has many applications, i.e. it can be used for acid–base, redox, precipitation, or complex titrations.

2.14 BATTERIES

A battery is an arrangement of several electrochemical cells connected in series that can be used as a source of direct electric current.

A cell is one that contains only one anode and cathode, but a battery contains several anodes and cathodes.

Types of Batteries

(a) Primary Battery or Primary Cells

In the case of a primary battery, the electrode and the electrode reactions cannot be reversed by passing an external electrical energy. The reactions occur only once and after use, they become dead. Therefore, they are not rechargeable.

Example: Dry cell, mercury cell

(b) Secondary Battery or Secondary Cells

In case of a secondary battery, the electrode reactions can be reversed by passing an external electrical energy. Therefore, they can be recharged by passing an electrical current and used again and again. These are also called storage cells or accumulators.

Example: Lead–acid storage cell, nickel–cadmium cell

2.15 LEAD ACCUMULATOR OR ACID STORAGE CELL

A typical lead–acid battery comprises of the following components:

(a) **Anode:** Pb grid with spongy lead
(b) **Cathode:** Pb–Sb with lead dioxide
(c) **Electrolyte:** 28–30% of H_2SO_4 acid.

The anode of the cell is a lead grid filled with spongy lead, while the cathode of the cell is a lead–antimony grid containing PbO_2. The anode and cathode of the battery is separated by inserting an inert porous material in between them. The electrolyte is about 28–30 % H_2SO_4 (sp. gr. 1.2 at 25%C). The whole set up of a number of such cells is enclosed inside an ebonite case.

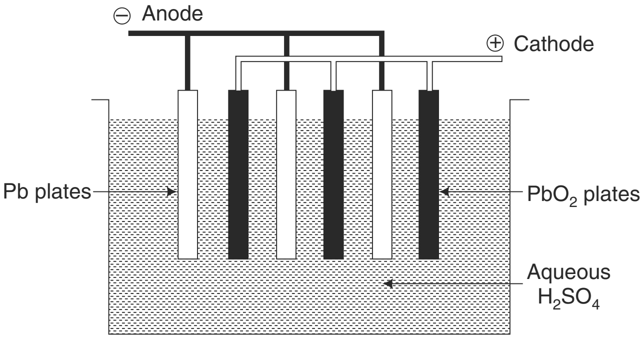


Fig. 2.26 *Lead accumulator or acid storage cell*

The cell may be represented as

$$Pb/PbSO_4\ //\ H_2SO_4\ (aq)/PbO_2/Pb$$

Discharge Reactions of a Battery

During the discharge process, the electrode reaction a cell can be as follows:

Discharge Reaction

At anode

$$Pb \longrightarrow Pb^{2+} + 2\ e^-$$
$$Pb^{2+} + SO_4^{2-} \longrightarrow PbSO_4$$
$$Pb + SO_4^{2-} \longrightarrow PbSO_4 + 2\ e^- \qquad ...(2.22)$$

At cathode

$$PbO_2 + 4\ H^+ + 2\ e^- \longrightarrow Pb^{2+} + 2\ H_2O$$
$$Pb^2 + SO_4^{2-} \longrightarrow PbSO_4$$
$$PbO_2 + 4\ H^+ + SO_4^{2-} + 2\ e^- \longrightarrow PbSO_4 + 2\ H_2O \qquad ...(2.23)$$

Overall cell reaction during use (discharging)

$$Pb + PbO_2 + 4\,H^+ + 2\,SO_4^{2-} \longrightarrow 2PbSO_4 + 2\,H_2O + \text{Energy} \quad ...(2.24)$$

The voltage produced during the discharge process is 2.0 V. The $PbSO_4$ formed during the discharge process gets adhered to the electrodes. The $PbSO_4$, thus deposited on the electrode interface is utilized again during the charging process of the cell. As a result, the concentration of H_2SO_4 decreases and hence the density of H_2SO_4 falls below 1.2 g/ml. So the battery needs recharging.

Charging Reaction of a Battery

The cells of a battery can be charged by reversing the electrode reactions. This can be achieved by applying a higher emf of an external source. During the charging process, each cell of a battery acts as an electrolytic cell. Lead and lead dioxides are deposited on their respective electrodes.

The electrode reactions taking place during charging are, the following:

At anode

$$PbSO_4 + 2\,H_2O \longrightarrow PbO_2 + 4\,H^+ + SO_4^{2-} + 2\,e^- \quad ...(2.25)$$

At cathode

$$PbSO_4 + 2\,e^- \longrightarrow Pb + SO_4^{2-} \quad ...(2.26)$$

The net reaction during charging is

$$2\,PbSO_4(s) + 2H_2O + \text{Energy} \longrightarrow Pb + PbO_2\,(s) + 4H^+ + SO_4^{2-} \quad ...(2.27)$$

In general, if the lead–acid battery is reversible with a better cycle life then the net battery cell reaction during discharging–charging processes for a cycle can be represented as,

$$Pb + PbO_2 + 4\,H^+ + 2\,SO_4^{2-} \underset{\text{Charging}}{\overset{\text{Discharging}}{\rightleftharpoons}} 2PbSO_4 + 2\,H_2O + \text{Energy}$$

Applications

1. Lead–acid batteries are widely used for SLI system (Starting-Lighting-Ignition) of road automobiles.
2. They are also used in telephone exchanges, railway tracks, broadcasting, power stations, etc.

Note:

(i) Overcharging or excessive charging may continue the electrolysis of water. This results in the liberation of H_2 and O_2 gases at the electrodes and may build up high pressure. Further, it may reduce the acid level and may damage the exposed electrode. Therefore, a catalyst like Sb is incorporated into the Pb plate, which enables the combination by H_2 and O_2 to form H_2O.

(ii) During discharge, the battery functions as an electrochemical cell (voltaic cell); while during charging the battery functions as an electrolytic cell.

(a) Electrochemical Cell

- Negative plate—Anode; Pb undergoes oxidation to form $PbSO_4$.
- Positive plate—Cathode; PbO_2 undergoes reduction to form $PbSO_4$.

(b) Electrolytic Cell

- Negative plate—Cathode; $PbSO_4$ undergoes reduction to form Pb.
- Positive plate—Anode; $PbSO_4$ undergoes oxidation to form PbO_2.

2.16 NICKEL–CADMIUM BATTERIES (NICAD)

Nickel–cadmium batteries are examples of rechargeable alkaline batteries. During charging and discharging, there is no loss of products (the products stick to the electrodes) and no gas evolution occurs at the active electrodes (anode and cathode). They have low internal resistance, long shelf life (> 20 years) without any significant maintenance and good cycle life (> 1000 cycles). Their capacity varies with the size of anode and cathode materials. They have the cell voltage of 1.35 – 1.40 V irrespective of the size of electrodes.

The active materials used in the battery system are the following:

Anode: Cadmium as a mixture of metal oxide and/or hydroxide.

Cathode: Nickel oxyhydroxide

Electrolyte: Aqueous KOH

The nickel–cadmium battery is represented as

$$\text{Cd, CdO/KOH/NiO (OH)}$$

The OCV of a fully charged cell is about 1.35 volts.

Chemistry During Discharging

At anode

Oxidation of cadmium takes place. Cd^{2+} ions, so formed, combine with OH^- ions to form Cd $(OH)_2$.

$$Cd \longrightarrow Cd^{2+} + 2e^-$$

$$Cd^{2+} + 2OH^- \longrightarrow Cd\ (OH)_2$$

Net anode

$$Cd + 2OH^- \longrightarrow Cd\ (OH)_2 + 2e^-$$

At cathode

Reduction of nickel oxyhydroxide takes place.

$$2NiO\ (OH) + 2H_2O + 2e^- \longrightarrow 2Ni(OH)_2 + 2OH^-$$

Net cell reaction

$$Cd + 2NiO\ (OH) + 2H_2O \longrightarrow Cd(OH)_2 + 2\ Ni(OH)_2$$

Chemistry During Charging

The charging process is similar to that of a lead storage battery. When the current is passed in the opposite direction, the electrode reaction gets reversed. As a result, Cd gets deposited on the anode and NiO(OH) on the cathode.

The net reaction during charging is

$$Cd(OH)_2 + 2Ni(OH)_2 \longrightarrow Cd + 2NiO(OH) + 2H_2O$$

Applications

It is used in calculators, electronic flash units, transistors and cardless appliances.

Advantage

1. It is smaller and lighter.
2. It has longer life than lead storage cell.
3. Like a dry cell, it can be packed in a sealed container.

Disadvantage

It is more expensive than a lead storage battery.

2.17 LITHIUM BATTERY—THE BATTERY OF THE FUTURE

It is a solid-state battery as it uses a solid electrolyte and not a solution or a paste. In this battery, the anode is lithium and the cathode is made of TiS_2. The solid electrolyte used in this is a polymer which permits the passage of ions but not that of electrons. The cell reactions are

At Anode

$$Li\ (S) \longrightarrow Li^+ + e^-$$

At Cathode

$$TiS_2\ (S) + e^- \longrightarrow TiS_2^-$$

Overall reaction

$$Li(S) + TiS_2(S) \longrightarrow Li^+ + TiS_2^-$$
$$Li^+ + TiS_2^- \longrightarrow LiTiS_2$$

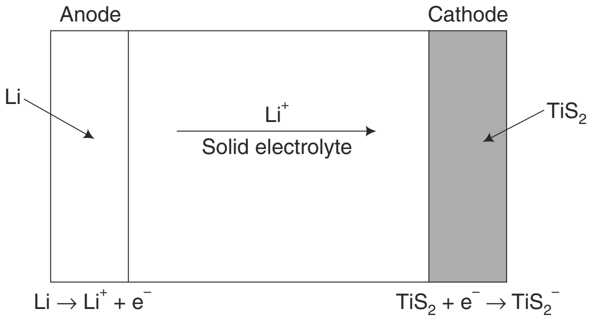


Fig. 2.27 *Solid state lithium battery*

It produces a cell voltage of 3 V. It is rechargeable. Several other types of secondary lithium batteries are also known; the Li/MnO_2, Li/V_2O_5, Li/MoO_2 and Li/Cr_3O_8 are some among these.

The lithium battery is considered to be the cell of the future because

- Its cell voltage is high, 3 V
- Lithium being a light-weight metal, only 7 g (1 mole) of material is required to produce 1 mole of electrons
- Li has the most negative $E°$ value and therefore generates a higher voltage than other types of cells
- All the constituents of the battery are solids and, therefore, there is no risk of leakage from the battery
- This battery can be made in a variety of sizes and shapes

Lithium–Sulphur Battery

This is a rechargeable battery. Its anode is made of lithium. Sulphur is the electron acceptor; the electron from lithium is conducted to sulphur by a graphite cathode. β-alumina ($NaAl_{11}O_{17}$) is used as the solid electrolyte.

It allows the Li ions to migrate through its lattice easily, to equalize the charge, but not the big polysulphide product ions.

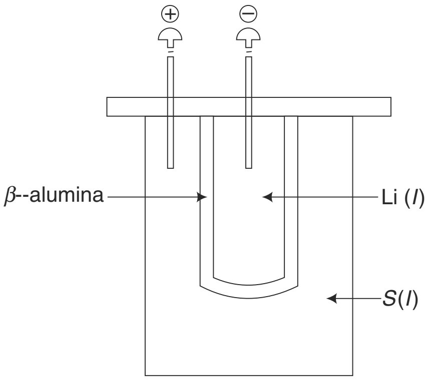


Fig. 2.28 *Lithium–Sulphur battery*

This battery is operated at high temperatures as S and Li must be in their molten states for the operation of the cell reactions:

Anode

$$2\text{Li (S)} \longrightarrow 2\text{Li}^+ + 2e^-$$

Cathode

$$\text{S} + 2e^- \longrightarrow \text{S}^{2-}$$

Overall

$$2\text{Li(S)} + \text{S} \longrightarrow 2\text{Li}^+ + \text{S}^{2-}$$

The S^{2-} formed reacts with elemental sulphur to form the polysulphide ion:

$$\text{S}^{2-} + n\ S \longrightarrow [\text{S}_{n+1}]^{2-}$$

The direct reaction between Li and S, detrimental to current production, is prevented by the intervening alumina in the cell.

Advantages

- The alkali metal–sulphur battery is light in weight unlike the lead–acid battery.
- It has a high energy density.
- Its use in electric cars is being slated commercially.

2.18 FUEL CELLS

Fuel cells are electrochemical cells having a separate fuel–oxidant system that produces the electrochemical reaction in which the fuel is oxidized at the anode. Like other electrochemical cells, fuel cells also consist of an electrolyte and two electrodes.

The basic principle of fuel cells are the same as that of electrochemical cells, but the main difference in function of the cell is that the electrochemical energy is provided by a fuel and an oxidant stored outside the cell in which the electrochemical reaction takes place. Hence, electrical power can be produced from these fuel cells as long as the cells are supplied with fuels and oxidants.

Theory

In fuels, the chemical energy is converted to heat which is transformed to mechanical energy that finally produces the electrical energy. But in fuel cells, the chemical energy is directly converted to electrical energy. This direct conversion of chemical energy to electrical energy has

100% efficiency. The cell representation of any fuel cell can be given as follows.

Fuel/Electrode//Electrolyte//Electrode/Oxidant

At the anode, the fuel gets oxidized liberating electrons and the oxidation products of the fuel. The electrons liberated from the anode reduce the oxidant at the cathode. Thus, the electron circuit or current density is established.

$$\text{Fuel} + \text{Oxygen} \longrightarrow \text{Oxidation Product} + \text{Electricity}$$

Alkaline Fuel cell (AFC) or Hydrogen–Oxygen Fuel Cells

In alkaline fuel cells, the electrolyte is an alkali such as potassium hydroxide (30–40% aqueous solution). Alkaline fuel cells make use of high-purity hydrogen as fuel and oxygen as oxidant. This kind of fuel cell is otherwise known as hydrogen–oxygen fuel cell. The electrodes are generally embedded with catalysts. Wide choices of catalysts are available for these cells such as platinum, silver, gold, metal oxides, etc. An alkaline fuel cell with a circulating electrolyte is free from impurity formation and it also acts as a cooling liquid.

Fuel cells combine hydrogen and oxygen to produce electricity and water. Hydrogen is fed into the anode of the fuel cell. Air provides the oxygen (oxidant) and enters the fuel cell at the cathode. As shown in Fig. 2.29, the actual chemistry depends on the fuel cell type. Using the Proton Exchange Membrane Fuel Cell (PEMFC), as an example, the hydrogen is split into two streams at the anode: positive hydrogen protons and negative electrons. The hydrogen proton (H^+) stream passes through the electrolyte to the cathode but the electrolyte precludes the passage of the electron stream. The electron stream is instead driven through an external circuit, forming an electric current. This electric current is then available for powering a load with the electrons returning to the cathode to bring closure to the fuel-cell electrochemical process. In particular, the electrons combine with the hydrogen protons and the oxygen at the cathode to create water. As noted in Fig. 2.29, while the basic principles of all fuel cells are the same, the electrolytes, conducting ions and operating temperatures differ between fuel-cell types.

At anode

$$H_2 \longrightarrow 2H^+$$
$$2H^+ + 2OH^- \longrightarrow 2H_2O + 2e^-$$

At cathode

$$O_2 + 2H_2O + 4\,e^- \longrightarrow 4OH^-$$

Net reaction

$$H_2 + 2\,OH^- \longrightarrow 2H_2O + 2\,e^-$$

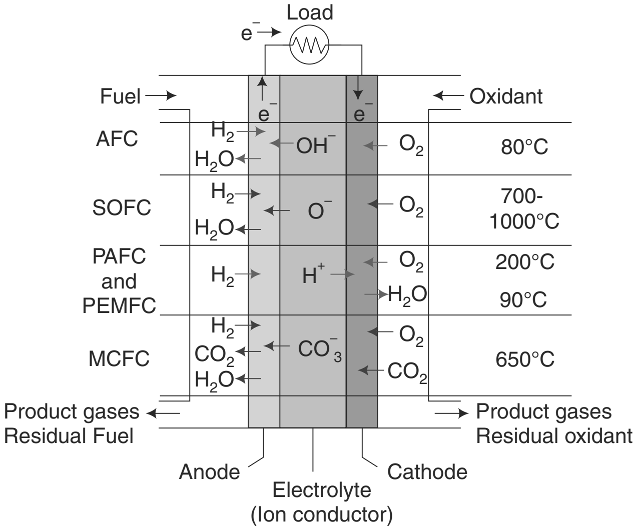


Fig. 2.29 *Fuel-cell operation*

Five major types of fuel cells have been (or are being) developed and are generally identified according to the type of electrolyte used.

The five major types of fuel cells are

1. Alkaline Fuel Cell ('AFC,' ~80°C)
2. Proton Exchange Membrane Fuel cell ('PEM fuel cell,' ~90°C)
3. Phosphoric Acid Fuel Cell ('PAFC,' ~200°C)
4. Molten Carbonate Fuel Cell ('MCFC,' ~650°C)
5. Solid Oxide Fuel Cell ('SOFC,' 700–1000°C)

Advantages of Fuel Cells

1. Fuel cells have a high efficiency of energy conversion (75% to 83%), i.e. chemical energy to electrical energy.
2. Fuel cells make use of hydrocarbon gas from fossil fuel and the resultant emissions of pollutants are within the permissible limits.
3. Fuel cells have low maintenance cost
4. Fuel cells have a quick start system.

5. The regenerative hydrogen–oxygen fuel cell systems have great applications in space research. They also produce potable water as an end product.
6. In fuel cells, low-cost fuels can be used, provided they are operated at higher temperatures.

2.19 SOLAR ENERGY

The sun is the ultimate source of energy, directly or indirectly for all other forms of energy. The nuclear fusion reactions occuring inside the sun release enormous quantities of energy in the form of heat and light. The solar energy received by the near earth space is approximately 1.4 kilojoules/second/m^2, known as **solar constant**.

At present, due to modern scientific development, we are using solar energy for various purposes. In general, we can use solar energy in two types of systems.

1. Solar photovoltaic power system
2. Solar thermal energy system

2.19.1 Solar Photovoltaic Power System

- In this method, the solar radiation is transformed into electricity through the solar cells, called photovoltaic cells or PV cells.
- Solar cells are made of thin wafers of semiconductor materials like silicon and gallium. When solar radiation falls on them, a potential difference is produced which causes flow of electrons and produces electricity.
- A group of solar cells joined together in a definite pattern forms a solar panel which can harness a large amount of solar energy and can produce electricity enough to run street light, irrigation water pumps, etc.
- Household lights, radio, television, pump sets and other electrical appliances can be operated with the electricity produced from solar radiation.
- Electricity needed to operate railway signals are generated by this method.
- Electricity required for satellites in space is produced from the solar panels attached to them.
- Electricity produced from solar energy helps very much for operating communication systems, lighthouses and offshore platforms located in regions where electricity cannot be easily supplied.

2.19.2 Solar Thermal System

By using solar thermal collectors, the heat received from the sun can be converted into thermal energy.

By concentrating solar radiation, various solar thermal devices like solar cookers, water heaters, desalination systems, solar refrigerators, solar dryers and solar microorganism removers, etc., can be operated.

(a) Solar Cooker

A solar cooker makes use of solar heat by reflecting the solar radiation using a mirror directly on to a glass sheet, which covers the black insulated box within which the raw food is kept. A new design of solar cooker is now available which involves a spherical reflector (concave or parabolic reflector) instead of a plane mirror that has more heating effect and hence greater efficiency.

The food cooked in solar cookers is more nutritious due to slow heating. However, it has the limitation that it cannot be used at night or on cloudy days. Moreover, the direction of the cooker has to be adjusted according to the direction of sun rays.

(b) Solar Water Heater

It consists of an insulated box painted black from inside and having a glass lid to receive and store solar heat. The inside of the box has a black painted copper coil through which cold water is made to flow in, which gets heated and flows out into a storage tank. The hot water from the storage tank fitted on the rooftop is then supplied through pipes into buildings like hotels and hospitals.

(c) Solar Furnace

Here, thousands of small plane mirrors are arranged in concave reflectors, all of which collect the solar heat and produce as high a temperature as 3000°C.

QUESTIONS

Two-Mark Questions with Answers

1. **Differentiate between metallic and electrolytic conductors.**
   (i) Metallic conduction involves the flow of electrons in a conductor, whereas electrolytic conduction involves the movement of ions in a solution.

(ii) In case of a metallic conductor, conduction decreases with increase of temperature. But in an electrolytic conductor, conduction increases with increase of temperature due to increase in number of ions with respect to temperature.

2. Write the cell representation and cell reaction of a calomel electrode.

Cell representation

$$\text{Hg}, \text{Hg}_2\text{Cl}_2\ (\text{s}), \text{KCl}\ (\text{satd. solution})$$

Cell reaction

$$\text{Hg}_2\text{Cl}_2\ (\text{s}) + 2\ \text{e}^- \longrightarrow 2\ \text{Hg}\ (\text{l}) + 2\ \text{Cl}^-\ (\text{aq})$$

3. What is an electrolytic cell? Give examples.

Electrolytic cells are cells in which electrical energy is used to bring about chemical reaction. The redox reaction in an electrolytic cell is nonspontaneous. Electrical energy is required to induce the electrolysis reaction, e.g. electrolysis of water, electroplating, etc.

4. Explain galvanic cell with examples.

Galvanic cell is a device in which a redox reaction is utilized to get electrical energy. Galvanic cell is also commonly referred to as *voltaic* or *electrochemical cell*, e.g. ***Daniel cell***. It consists of zinc electrode, dipping in $ZnSO_4$ solution (where oxidation takes place) and a copper electrode, dipping in $CuSO_4$ solution (where reduction takes place).

5. Draw the diagram and cell representation of a Daniel cell.

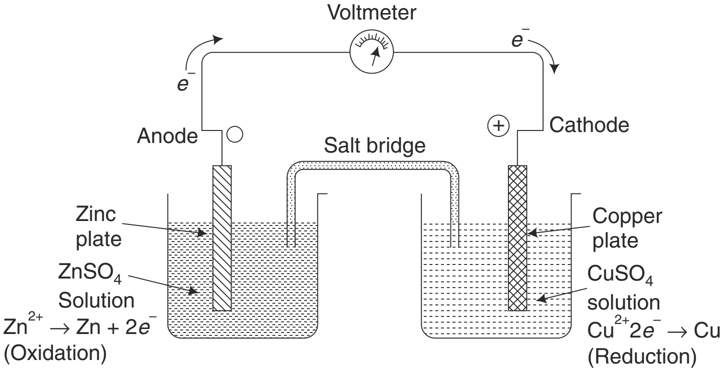


Fig. 1 *Diagram of a Daniel cell*

Cell representation

$(-)\ \text{Zn} \mid \text{ZnSO}_4(\text{aq})(1\text{M}) \mid\mid \text{CuSO}_4(\text{aq})\ (1\text{M}) \mid \text{Cu}\ (+)$

Anode (Cathode)

6. **Define standard electrode potential.**

Standard electrode potential is defined as the tendency of an electrode to lose or gain electrons when it is dipped in its own salt of 1M concentration at 25°C.

7. **Write the Nernst equation for single-electrode potential and explain the terms involved.**

$$E = E^\circ - \frac{RT}{nF} \ln \left(\frac{[\text{Product}]}{[\text{Reactant}]} \right)$$

E = electrode potential of the electrode
E° = standard electrode potential of the electrode
R = gas constant
T = temperature (25°C)
N = number of valency electrons involved
F = faraday
[Product] = concentration of the product
[Reactant] = concentration of the reactant

8. **What is reference electrode? Give examples.**

The electrode of standard potential with which we can compare the potentials of other electrode is called a reference electrode, e.g. Standard Hydrogen Electrode (SHE) and calomel electrode.

9. **Differentiate between primary and secondary batteries.**

S.No	***Primary Batteries***	***Secondary Batteries***
1.	In these cells, the electrode and the electrode reactions cannot be reversed by passing an external electrical energy.	In these cells, the electrode reactions can be reversed by passing an external electrical energy.
2.	The reaction occurs only once and after use they become dead. Therefore, they are not rechargeable.	They can be recharged by passing electrical current and used again and again. These are also called storage cells or accumulators.

10. **Define electromotive force.**

It is defined as the difference of potential which causes the flow of current from one electrode of higher potential to an other electrode of lower potential.

11. **Differentiate between electrolytic and electrochemical cells.**

S.No	***Electrolytic Cells***	***Electrochemical Cells***
1.	Electrolytic cells are cells in which electrical energy is converted to chemical energy, e.g. electrolysis.	Electrochemical cells are cells in which chemical energy is converted to electrical energy, e.g. Daniel cell.
2.	The cathode carries negative charge. The anode carries positive charge.	The cathode carries positive charge. The anode carries negative charge.

3.	Here the electrons are supplied to the cell from the external battery, i.e., electrons move in through the cathode and comes out from the anode.	But electrons are drawn from the cell, i.e., electrons move from anode to cathode through the external circuit.
4.	The extent of chemical reaction occurring at the electrodes is governed by Faraday's law of electrolysis.	The emf of the cell depends on the concentration of the electrolytes and the chemical nature of the electrode.

12. What is the cell reaction of a Weston standard cadmium cell?

At negative electrode

$$\text{Cd(s)} \longrightarrow \text{Cd}^{2+}\text{(aq)} + 2\,\text{e}^-$$

At positive electrode

$$\text{Hg}_2\text{SO}_4\text{(s)} + 2\,\text{e}^- \longrightarrow 2\,\text{Hg(l)} + \text{SO}_4^{2-}\text{(aq)}$$

13. How can we determine the change in free energy value using emf of the cell?

Change in free energy can be calculated by using the following equation:

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

where ΔG° = change in free energy
n = number of valency electrons
F = faraday
E° = standard electrode potential

14. A voltmeter cannot be used in the precise measurement of emf of a galvanic cell. Why?

The emf of the cell cannot be determined accurately by connecting a voltmeter directly between the two electrodes of the cell, because during such a measurement, a part of the cell current is drawn, thereby causing a change in the actual emf.

15. Define emf series.

The various electrodes are arranged in the order of their increasing values of standard electrode reduction potential on the hydrogen scale. This arrangement is called *electrochemical series* or *emf series*.

16. What are the advantages of potentiometric titrations?

- Potentiometric titrations can be carried out in coloured solutions where indicators cannot be used.
- There is no need of prior information about the relative strength of titrant before the titration.

17. **Write the charging and discharging reaction of an Ni–Cad battery.**

$$\mathrm{Cd + 2\,NiO\,(OH) + 2H_2O \underset{Charging}{\overset{Discharging}{\rightleftharpoons}} Cd(OH)_2 + 2Ni(OH)_2}$$

18. **What are batteries? How do they differ from cells?**

    A battery is an arrangement of several electrochemical cells connected in series that can be used as a source of direct electric current.

    A cell is one that contains only one anode and cathode, but a battery contains several anodes and cathodes.

Ten-Mark Questions

1. Describe the construction and working of a galvanic cell.
2. What is the emf series? Discuss the importance of emf series.
3. Derive Nernst equation for single-electrode potential.
4. Describe the various types of electrodes.
5. Write short notes on the following.
    1. Calomel electrode
    2. Glass Electrode
6. What is emf? How is the emf of the unknown cell is measured?
7. Derive the Nernst equation for emf of a cell.
8. What is a reversible and irreversible cell? Explain with examples.
9. Explain in detail about potentiometric titrations.
10. Calculate the emf of the cell

    Zn/Zn^{2+} (0.1 M) ?? Ag+ (10.0 M)/Ag, given that $E°_{Zn^{2+}/Zn} = -0.76$ V and $E°_{Ag^+/Ag} = +0.80$ V. Write down the cell reaction.
11. Explain the acid–base titration carried out in potentiometric titration.
12. Describe Weston standard cadmium cell.
13. Discuss in detail about lead–acid battery.
14. Write the cell construction, cell reaction of Ni–Cad during charging and discharging.

15. Describe the cell representation and cell reaction of
    1. Calomel electrode
    2. Chlorine electrode
16. Using emf measurements, show how the following is determined:
    1. Solubility of sparingly soluble salt
    2. Valency of the ion
    3. Determination of the standard free energy

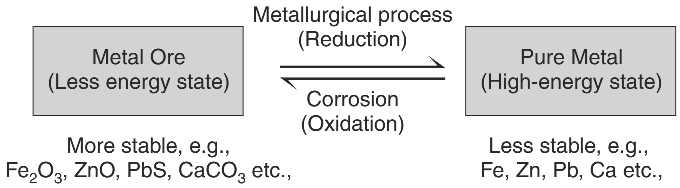
UNIT
3

Corrosion and Its Control Methods

3.1 INTRODUCTION

Corrosion is a general term that refers to the deterioration and ultimate destruction of a metal due to its reaction with the surrounding (or) environment such as gaseous, moisture, liquid, etc.

In nature, metals except noble metals such Au, Pt, etc., are not found in free state due to their reactivity. The metals are thermodynamically unstable in their free state. They are stable in the form of certain compounds like oxides, carbonates, hydroxyl carbonates, sulphides, chlorides and silicates, etc. It is the ore (as their oxides, carbonates, hydroxyl carbonates, sulphides, chlorides and silicates) from which the metals are extracted by metallurgical processes. A metallurgical process requires a large amount of heat energy.



For example, when iron is exposed to the atmosphere containing oxygen and water vapour, it reverts to its metallic oxide Fe_2O_3. n H_2O which is an ore of iron.

Definition

Corrosion can be defined as any process of destructive disintegration or alteration of a metal or alloy caused by direct chemical attack or by electrochemical reaction with its environment. In the case of iron and steel, corrosion is often referred to as rusting.

In other words, corrosion is a process in which the gradual dissolution or oxidation of a metal takes place.

Industrial development and domestic applications involve the use of metals and alloys. Corrosion causes a heavy loss to industries in particular and imparts the economic status of a society in general. The annual loss for corrosion in India is around ₹600 crores. The loss due to corrosion includes the cost of repair or replacement of the corroded component or equipment. By making proper use of existing corroded materials and techniques for corrosion prevention, about 25% of the estimated amount (₹150 crores in India) can be saved.

Since it is impossible to eliminate corrosion, extensive research work has been undertaken to minimize corrosion rather than to prevent corrosion.

3.2 CLASSIFICATION OF CORROSION

The corrosion process is classified on the basis of mechanisms.

1. Dry corrosion, or chemical corrosion
2. Wet corrosion, or electrochemical corrosion

3.2.1 Dry Corrosion, or Chemical Corrosion

This type of corrosion occurs through direct chemical action of the environment or atmospheric gases such as oxygen, halogen, H_2S, SO_2, N_2 or anhydrous inorganic liquids in close contact with the metal.

This can be classified as follows,

(a) Corrosion by oxygen (oxidation corrosion)
(b) Corrosion by other gases (Cl_2, H_2S and H_2)
(c) Liquid–metal corrosion

(a) Corrosion by Oxygen (Oxidation Corrosion)

Direct attack of metals by oxygen at low or high temperatures, in the absence of moisture, leads to **oxidation corrosion**. The resultant **metal oxide** is known as a **corrosion product**.

The rates of oxidation of metals at ambient temperatures are low but at higher temperatures, oxidation is also kinetically favoured. Alkali metals

(Li, Na, K, Rb, etc.) and alkaline earth metals (Ba, Ca, Sr, etc.) are even rapidly oxidized at low temperatures whereas at higher temperatures, almost all metals except Ag, Au and Pt are oxidized.

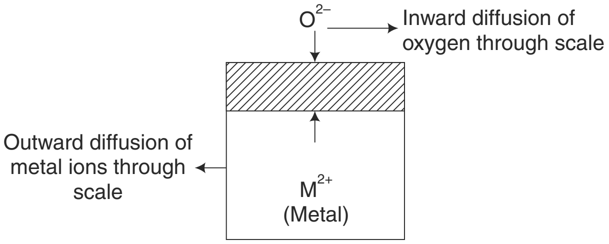


Fig. 3.1 *Oxidation corrosion*

Mechanism The following type of reactions may take place during the oxidation corrosion.

(i) At Anode

Oxidation first occurs at the surface of the metal resulting in the formation of metal ions (M^{2+}) with the liberation of free electrons.

$$M \longrightarrow M^{2+} + 2\,e^- \quad \text{(Oxidation)}$$

(ii) At Cathode

The liberated electron will be taken up by the oxygen and is converted into oxide ion (O^{2-})

$$\tfrac{1}{2}O_2 + 2e^- \longrightarrow \underset{\text{(Oxide ion)}}{O^{2-}} \quad \text{(Reduction)}$$

(iii) Net Reaction

Metal ion combines with oxide ions forming the metal oxide film.

$$M + \tfrac{1}{2}O_2 \longrightarrow M^{2+} + O^{2-} \longrightarrow \underset{\text{Metal oxide}}{MO}$$

Types of Metal Oxide Film

It is essential to know the nature of the metal oxide films formed, because it decides the further action on the metal surface. There are generally four types of metal oxide films.

(i) Stable film

A stable oxide layer is a fine grained in structure and forms a compact surface adhered tightly to the metal surface. The oxide films formed on the surface of the metals are impervious in nature and stop further oxygen attack. Thus, the stable film acts as a protective coating.

Examples: Al, Sn, Pb, Cu, etc.

(ii) Unstable film

Unstable oxide layers are mainly produced on the surface of noble metals which decompose reversibly to the metal and the oxide which is liberated in the form of oxygen. In this case, the corrosion is a continuous process.

$$\text{Metal Oxide} \rightleftharpoons \text{Metal} + \text{Oxygen}$$

Examples: Au, Pt, Ag, etc.

(iii) Porous film

The oxide layers formed in some cases have pores or cracks. In such a case, the atmospheric oxygen can easily move into the metal surface through pores or cracks of the layer. So corrosion is a continuous process.

Examples: Li, Na, K, Fe, etc.

(iv) Volatile film

The oxide layer formed in some cases is volatile. So the oxide film volatilizes as soon as it is formed. The fresh metal surface is kept exposed all the time for further attack. Thus it acts as a nonprotective coating.

Example: Molybdenum oxide film (MoO_3)

Pilling–Bedworth Rule

The protective or nonprotective oxide layer formation in metals is governed by a rule known as ***"Pilling–Bedworth rule".*** *According to this rule,*

$$\text{Specific volume ratio} = \frac{\text{Volume of metal oxide film formed}}{\text{Volume of metal ion consumed}}$$

If the volume of the oxide formed is equal to or greater than the volume of the metal from which it is formed, the oxide layer is nonporous and therefore protective in nature.

Examples: Oxides of Al, Sn, Pb, Cu, etc.

Whereas, if the volume of the oxide formed is less than the volume of the metal from which it is formed, the oxide layer is porous and therefore nonprotective in nature.

Examples: Oxides of Li, Na, K, Mg, Ca, Sr, etc.

(b) Corrosion by Other Gases

Other gases such as Cl_2, SO_2, H_2S, CO_2, F_2 and NO_x can also cause corrosion. In dry atmosphere, these gases react with metal and form corrosion products which may form a protective or nonprotective film on the metal surface.

For example,

(i) Chlorine attacks on silver forms AgCl film, which is protective and nonporous, so it prevents further corrosion.

$$Cl_2 + 2Ag \longrightarrow \underset{\text{(Nonporous film)}}{2AgCl}$$

(ii) Sn reacts with dry Cl_2 gas present in the atmosphere and forms volatile $SnCl_4$ which volatilizes immediately. So the corrosion is a continuous process.

$$2Cl_2 + Sn \longrightarrow \underset{\text{(Volatile film)}}{SnCl_4}$$

(iii) Hydrogen Embrittlement or Hydrogen Corrosion

At high temperature, H_2S reacts with steel containing Fe and forms FeS scale. It is porous and corrosion is a continuous process.

Metals combine with H_2S gas to liberate atomic hydrogen.

$$H_2S + Fe \longrightarrow FeS \quad + \underset{\text{(Atomic hydrogen)}}{2[H]}$$

The atomic hydrogen is very reactive, penetrates the metal and occupies the voids of the metal.

$$[H] + [H] \longrightarrow H_2$$

The atomic hydrogen recombines inside the metal and develops pressure which leads to cracking of the metal. This is known as '**hydrogen embrittlement**' or **'hydrogen corrosion'.**

(iv) Decarburisation

Atomic hydrogen is formed by dissociation of H_2 gas at high temperature.

$$H_2 \longrightarrow [H] + [H]$$

$$C + H \longrightarrow CH_4$$

The atomic hydrogen is highly reactive and combines with carbon present in the metal forming CH_4 gas which leads to cracking of the metal surface. The process of decrease in carbon content in steel is known as **'decarburisation of steel**'.

(c) Liquid–Metal Corrosion

This type of corrosion is due to the chemical action of flowing liquid metals on solid metal/alloys at high temperatures.

As a result of this corrosion, the solid metal becomes weak because it involves either

1. Dissolution of a solid metal by a liquid metal, or
2. Due to the penetration of the liquid metal into the solid metal.

Such types of corrosion are found in nuclear power plants.

3.2.2 Wet (or) Electrochemical Corrosion

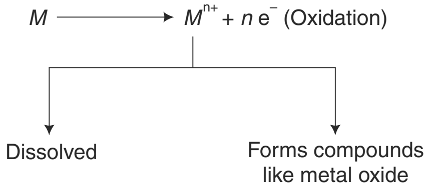
The prime conditions for this type of corrosion are

1. The conducting electrolytic liquid is in contact with metal
2. Two dissimilar metals are partially dipped in the electrolyte

In the above condition, one part of the metal becomes the anode and the remaining part becomes cathode.

(a) At Anodic Area

Oxidation takes place with the liberation of free electrons. Hence, the anodic metal is destroyed either by dissolution, or forms compounds such as oxides.



(b) At Cathodic Area

In this area, reduction reaction takes place (i.e. gain of electrons). Dissolved metal ions in the medium accept the electrons to form some ions like OH^-, O^{2-}. The metallic ions and nonmetallic ions formed (at cathode) diffuse towards each other through a conducting medium and form a corrosive product somewhere between the anode and cathode.

(c) Mechanism

(i) At Anodic Area

$$\mathrm{M} \longrightarrow \mathrm{M}^{n+} + n\,\mathrm{e}^- \text{ (Oxidation)}$$

The anodic reaction involves dissolution of metal as corresponding metal ions with the liberation of free electrons.

(ii) At Cathodic Area

Depending upon the nature of electrolytic solution, the cathodic reaction consumes electrons either by

1. Hydrogen evolution mechanism or
2. Oxygen Absorption mechanism

This can be explained as follows.

1. Hydrogen Evolution Mechanism

This type of corrosion mechanism takes place when base metals are in contact with acidic solutions or the solutions are completely free from dissolved oxygen.

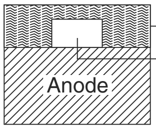


Fig. 3.2 *Hydrogen evolution*

'All metals above hydrogen in the electrochemical series have a tendency to get dissolved (undergo corrosion) in acidic solution with simultaneous evolution of hydrogen gas'.

Example When iron metal is in contact with an acidic environment, hydrogen evolution mechanism takes place.

In this type of corrosion, the **anodes** usually possess **very large area** whereas the **cathodes** have **small areas**.

At anodic area

Iron undergoes dissolution to give Fe^{2+} ions with the liberation of free electrons.

$$Fe \longrightarrow Fe^{2+} + 2\ e^- \text{ (Oxidation)}$$

At cathodic area

The liberated electrons flow from the anodic area to the cathodic area, where hydrogen ions (H^+) get reduced to hydrogen gas ($H_2\uparrow$).

$$2H^+ + 2e^- \longrightarrow H_2 \uparrow \text{ (Reduction)}$$

The overall reaction is

$$Fe + 2H^+ \longrightarrow Fe^{2+} + H_2 \uparrow$$

2. Oxygen Absorption Mechanism

This type of corrosion mechanism takes place when base metals are in contact with neutral, aqueous or slightly alkaline solution with some amount of dissolved atmospheric oxygen.

Example Rusting of paint-coated iron in neutral, aqueous or slightly alkaline solution with some amount of dissolved atmospheric oxygen.

The surface of the iron is usually coated with a thin film of iron oxide. However, the oxide film/paint coated iron develops some cracks on the surface. When a water droplet falls on the crack, the **crack area** acts as **anode** (small area) and the **remaining part of the iron** acts as **cathode** (large area).

At anodic area

Iron metal dissolves as Fe^{2+} with the liberation of electrons.

$$Fe \longrightarrow Fe^{2+} + 2\ e^- \text{ (Oxidation)}$$

At cathodic area

The liberated electrons flow from the anodic area to the cathodic part through the metal where the electrons are taken up by the dissolved oxygen to form OH^- ions.

$$1/2\ O_2 + 2\ e^- + H_2O \longrightarrow 2OH^- \text{ (Reduction)}$$

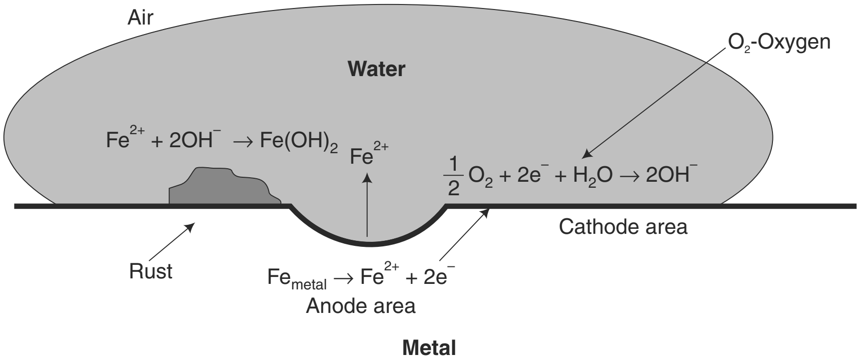


Fig. 3.3 *Oxygen absorption mechanism*

The overall reaction

The Fe^{2+} ions (at anode) and OH^- ions (at cathode) react to produce ferrous hydroxide precipitate $Fe(OH)_2$.

$$Fe + ½\, O_2 + H_2O \longrightarrow Fe^{2+} + 2OH^- \longrightarrow Fe(OH)_2$$

If enough oxygen is present, ferrous hydroxide is converted into ferric hydroxide.

$$4Fe(OH)_2 + O_2 + 2H_2O \longrightarrow 4Fe(OH)_3 \text{ (or) } \underset{\text{Yellow Rust}}{Fe_2O_3 . 3H_2O}$$

Table 3.1 *Differences between chemical and electrochemical corrosion*

Sl. No	***Dry or Chemical Corrosion***	***Wet or Electrochemical Corrosion***
1.	It occurs in dry state.	It occurs in presence of moisture or electrolyte.
2.	It involves direct chemical attack by the environment.	It involves the setting up of a huge number of galvanic cells.
3.	It follows adsorption mechanism.	It follows the mechanism of electrochemical reaction.
4.	Corrosion product accumulates on the same spot, where corrosion occurs.	Corrosion occurs at anode while products gather at cathode.
5.	Uniform corrosion behaviour is seen, i.e. either the whole surface of the metal in contact with the medium corrodes, or it does not.	Localized corrosion occurs, i.e. one metal surface alone is corroding even though both metal surfaces are in contact with the medium.
6.	Even a homogeneous metal surface gets corroded by this process.	Heterogeneous or bimetallic contact condition produces corrosion.
7.	Only heat evolution can be observed.	Due to electron flow from the site of oxidation to site of reduction, current flow can be observed.
8.	It is a slow and self-controlled process.	It is a fast and continuous process.
9.	Example: Tarnishing of silver	Example: Rusting of iron

3.3 TYPES OF ELECTROCHEMICAL CORROSION

Electrochemical corrosion is of two types.

1. Galvanic (bimetallic) cell corrosion
2. Differential aeration corrosion or concentration cell corrosion

3.3.1 Galvanic (Bimetallic) Corrosion

Galvanic (also called 'dissimilar metal corrosion' or wrongly 'electrolysis') refers to corrosion damage induced when two dissimilar materials are coupled in a corrosive electrolyte.

When a galvanic couple forms, one of the metals in the couple becomes the anode and corrodes faster than it would all by itself, while the other becomes the cathode and corrodes slower than it would alone. For galvanic corrosion to occur, three conditions must be present:

1. Electrochemically dissimilar metals must be present.
2. These metals must be in electrical contact.
3. The metals must be exposed to an electrolyte.

This is the most common type of corrosion and is also known as bimetallic corrosion. When two dissimilar metals (e.g. Zn and Cu) are electrically connected and are exposed to an electrolyte (aqueous electrolyte solution or moisture), the **metal higher in the electrochemical series** acts as the **anode** and dissolves into the solution (i.e. corrodes) and the **metal lower in the electrochemical series,** or more noble, acts as the **cathode**.

The cathodic reaction mechanism depends on the electrolyte, i.e. in the **acidic medium** (electrolyte), the corrosion takes place with the **evolution of hydrogen** gas whereas in **neutral or alkaline medium** (electrolyte), **absorption of oxygen** takes place.

Example 1 *In a Zn/Fe couple, the alloy is exposed to neutral/alkaline electrolyte,* ***zinc*** *will acts as* ***anode*** *(higher in electrochemical series) and* ***undergoes corrosion*** *whereas* ***Fe*** *(lower in electrochemical series) acts as* ***cathode*** *and is* ***not affected.***

The following reactions are taking place at anode and cathode.

At anode

$$\mathrm{Zn} \longrightarrow \mathrm{Zn}^{2+} + 2e^- \text{ (oxidation)}$$

At cathode

$$\frac{1}{2} O_2 + H_2O + 2e^- \longrightarrow 2OH^- \text{ (Reduction)}$$

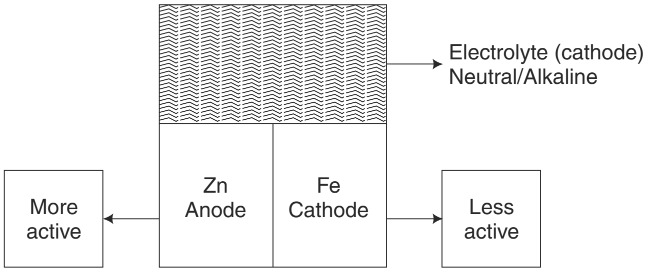


Fig. 3.4 *Galvanic corrosion (Zn/Fe)*

Overall reaction

$$Zn + \frac{1}{2} O_2 + H_2O \longrightarrow Zn^{2+} + 2OH^- \longrightarrow Zn(OH)_2$$

Example 2 *In an Fe/Cu couple, the alloy is exposed to neutral/alkaline electrolyte,* ***Fe*** *acts as* ***anode*** *(higher in electrochemical series) and* ***undergoes corrosion,*** *whereas* ***Cu*** *(lower in electrochemical series) acts as* ***cathode*** *and is* ***not affected.***

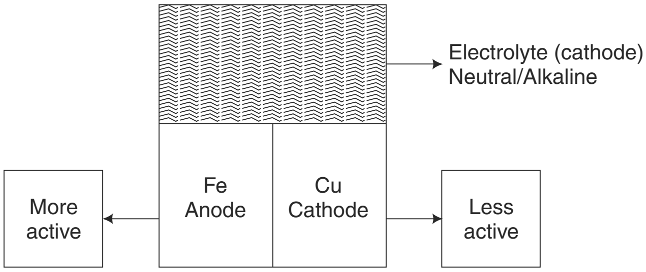


Fig. 3.5 *Galvanic corrosion (Fe/Cu)*

The following reactions take place at anode and cathode.

At anode

$$Fe \longrightarrow Fe^{2+} + 2\,e^- \text{ (Oxidation)}$$

At cathode

$$\frac{1}{2} O_2 + H_2O + 2e^- \longrightarrow 2OH^- \text{ (Reduction)}$$

Overall reaction

$$Fe + \frac{1}{2} O_2 + H_2O \longrightarrow Fe^{2+} + 2OH^- \longrightarrow Fe(OH)_2$$

Examples:

1. Steel screws in a brass marine hardware
2. Steel pipe connected to copper plumbing

Avoidance of Galvanic Corrosion

The following methods may be followed for the avoidance of galvanic corrosion.

(i) Avoid Mixing of Metals If only one material is used in a construction, the problem is avoided. But in case of alloys, selection of metals should be very close in the emf series.

(ii) Prevent Electrical Contact It is often practical to prevent electrical contact between the dissimilar metals. This may be achieved either by the use of nonconducting (e.g. rubber or plastic) spacers, spool pieces or gaskets, perhaps in conjunction with sleeves around bolts (or) providing insulating material. For the same reason, a gap may be left between galvanized roofing and a stainless steel down-pipe.

(iii) Prevent the Wetted Junction The third condition can be removed by ensuring that no electrolyte remains at the intermetallic junction—this may require extra attention to drainage or to protection from the weather. A good covering of paint or sealant over the junction can be effective to avoid galvanic corrosion.

(iv) Use the Area Effect to Avoid Galvanic Corrosion The area effect should also be considered in avoiding corrosion damage, i.e. the area of the cathode is always smaller than anodic area.

3.3.2 Concentration Cell Corrosion, or Differential Aeration Corrosion

Concentration cell corrosion occurs when two or more areas of a metal surface are in contact with different concentrations of the same solution or different concentrations of dissolved oxygen in the electrolyte.

(a) Causes

1. It is due to the local difference in metal ion concentration.
2. It is caused by the local temperature difference.
3. It is due to inadequate agitation or slow diffusion of metal ions.

Differential aeration corrosion occurs when a metal is partially immersed in a solution; the metal inside the solution has very poor aeration when compared with the metal that is outside the solution. This causes difference in potential between differently aerated areas.

The area where there is **less oxygen exposure** will acts as **anode** and the **exposed to more oxygen** area will behaves as **cathode**. (This is acting like a concentration cell and concentration-cell corrosion current is produced.) Concentration-cell corrosion is otherwise known as **differential aeration corrosion**.

(b) Mechanism

At anode

$$M \longrightarrow M^{n+} + ne^{-} \text{ (oxidation)}$$

The electron will move to the cathodic site.

At cathode

Depending upon the electrolyte, the cathodic reaction will follow either hydrogen evolution or oxygen absorption mechanism.

In acidic electrolyte,

$$2H^{+} + 2e^{-} \longrightarrow H_2\uparrow \text{(Reduction)}$$

In alkaline/neutral electrolyte,

$$\tfrac{1}{2}\,O_2 + H_2O + 2e^{-} \longrightarrow 2OH^{-} \text{ (Reduction)}$$

OH $^{-}$ ion will move faster and reach the anodic area and corrosion will be seen in the pit. This is called **'pitting corrosion'.**

Example 3 *When iron metal is partially immersed in a solution, the metal inside the solution has very poor aeration when compared with the metal that is outside the solution. The* ***less aerated part*** *acts as* ***anode*** *and the* ***more aerated part*** *acts as* ***cathode.***

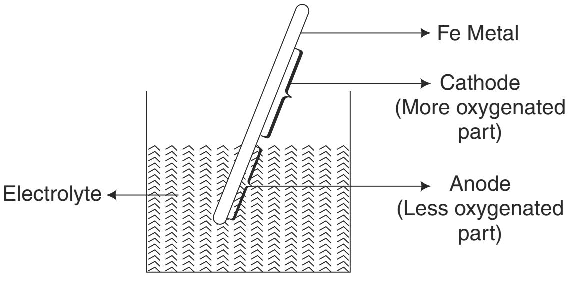


Fig. 3.6 *Concentration-cell corrosion (metal/electrolyte)*

The following reactions are taking place at anode and cathode.

At anode

$$\text{Fe} \longrightarrow \text{Fe}^{2+} + 2\ e^- \text{ (Oxidation)}$$

At cathode

$$\tfrac{1}{2}\ O_2 + H_2O + 2e^- \longrightarrow 2OH^- \text{ (Reduction)}$$

Overall reaction

$$\text{Fe} + \tfrac{1}{2}\ O_2 + H_2O \longrightarrow \text{Fe}^{2+} + 2OH^- \longrightarrow \text{Fe(OH)}_2$$

Thus, differential aeration corrosion occurs on the following occasions.

1. Micropores on a metallic surface (pitting corrosion)
2. Oil, impurity (or) corrosion product on a metallic surface
3. Water in a particular spot on a metal (for a long time)
4. Crossed fencing
5. Joint of iron metals by iron washer
6. A metal surface partially immersed in water
7. A metal surface partly covered with dust, sand, etc.

Other examples for this type of corrosion are

(a) Pitting corrosion
(b) Pipeline corrosion
(c) Crevice corrosion
(d) Corrosion on wire fence

(a) Pitting Corrosion

Pitting corrosion is an electrochemical oxidation–reduction (redox) process. It occurs within localized holes (cells) on the surface of metals covered with a thin oxide film, which inhibits anodic dissolution. When corrosion does occur, it sometimes hollows out a narrow hole, pits and cavities in the metal. The bottoms of these pits tend to be deprived of oxygen, thus promoting further growth of the pit into the metal.

Pitting corrosion starts with the small crevices (pits). Once pit formation is established, **the metallic part below the pit** becomes the **anode** and further corrosion takes place at the anodic area. The **other parts of the metal** become the **cathode** and absorb the liberated electron from the anode.

Example 4 *The metal parts partially covered with dust, sand, water drops, etc. is an example for* ***pitting corrosion****.*

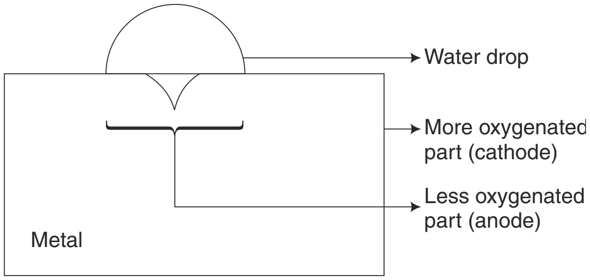


Fig. 3.7 *Pitting corrosion*

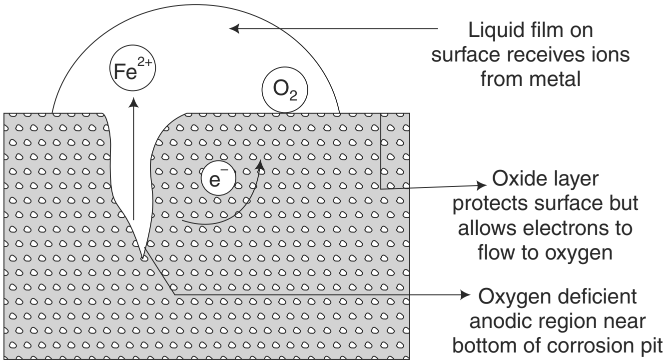


Fig. 3.8 *Pitting corrosion*

The **area covered by the drop of water** acts as an **anode** due to less oxygen concentration and suffers corrosion. The **uncovered area** (freely exposed to air) act as a **cathode** due to high oxygen concentration.

The rate of corrosion will be more when the area of cathode is larger and the area of anode is smaller.

The following reactions are taking place at anode and cathode.

At anode

$$\text{Fe} \longrightarrow \text{Fe}^{2+} + 2\,e^- \text{ (Oxidation)}$$

At cathode

$$\tfrac{1}{2}\, O_2 + H_2O + 2e^- \longrightarrow 2OH^- \text{ (Reduction)}$$

Overall reaction

$$\begin{array}{c} \text{Fe} + 1/2\ O_2 + H_2O \longrightarrow \text{Fe}^{2+} + 2OH^- \longrightarrow \text{Fe(OH)}_2 \\ \hfill \downarrow \\ \hfill [O] \\ \hfill \downarrow \\ \hfill \text{Fe(OH)}_3 \end{array}$$

This type of intense corrosion is called **pitting corrsion**.

(b) Pipeline Corrosion

Differential aeration corrosion may also occur in different parts of the pipeline. The buried pipelines or cables passing from one type of soil to another, say, from clay (less aerated) to sand (more aerated) may get corroded due to differential aeration.

(c) Crevice Corrosion

When a crevice between different metallic objects is in contact with liquids, the crevice becomes the anodic region due to less oxygen in the crevice area and corrosion takes place. But the exposed area acts as the cathode.

(d) Corrosion on Wire Fence

This type of corrosion also takes place in the wire fence. In this case, the areas where the wires cross are less aerated than the other parts of the fence. The corrosion takes place at the wire crossings because the less aerated part act as anode.

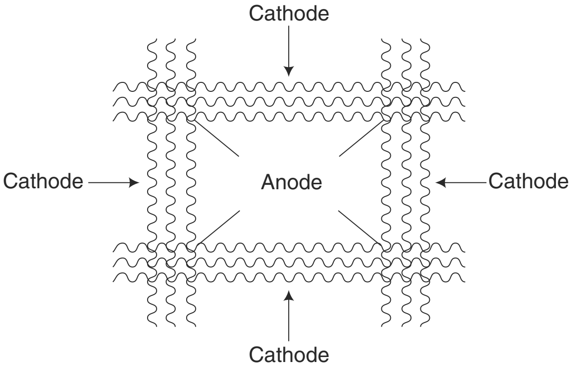


Fig. 3.9 *Corrosion on a wire fence*

3.4 GALVANIC SERIES

In the emf series, a metal higher in the series is more anodic and undergoes corrosion faster than the metal below it.

For example, Li corrodes faster than Mg; Zn corrodes faster than Fe; Fe corrodes faster than Sn; Cu corrodes faster than Ag, and so on. But in some cases, this generalization is not so.

For example, in a Zn-Al couple, Zn (below Al in the emf series) is corroded, while Al acts cathodic and is protected. This kind of opposite reactions are due to the fact that metals like Al develop strongly adhering Al_2O_3 on the surface. This makes their electrode potential more (+) ve or less (–) ve.

From the above observation, it is clear that emf series doesn't account for the corrosion of all metals and alloys.

Table 3.2 *Galvanic Series (Metals in sea water at 25˚C)*

Corroded end or Anodic	1. Mg
or Least noble	2. Mg alloy
↑	3. Zn
	4. Al
	5. Cd
	6. Al alloy
	7. Low-carbon steel
	8. Cast iron
	9. High nickel cast iron
	10. Stainless steel (active)
	11. 50-50 Lead–Tin
	12. Pb
	13. Sn
	14. Ni-Mo-Fe alloy
	15. Silver
	16. Ti
↓	17. Graphite
Protected end or cathodic	18. Gold
or Most noble	19. Platinum

In order to give useful information about corrosion of metals and alloys, a more practical series have been formulated on the basis of studying corrosion behaviour (oxidation potential) of metals and alloys in a given environment like sea water.

Definition

Different testing metals and alloys are coupled with a calomel electrode and dipped in sea water. The oxidation potential of the different metals and alloys are determined at 25°C and tabulated in the descending order. **Metals occupying higher positions in the series undergo corrosion in a vigorous manner.** The above series is called **galvanic series** and it gives more information about the corrosive tendencies of the different metals.

Table 3.3 *Differences between electrochemical series (emf) and galvanic series*

Sl. No	*Electrochemical Series (emf)*	*Galvanic Series*
1.	In this series, metals are arranged in the order of their increasing values of standard reduction potential on the hydrogen scale, i.e. electrode potential is measured for a metal without any oxide film on them.	This series was developed by studying corrosion behaviour of metals and alloys in unpolluted sea water without their oxide films.
2.	The position of a given metal in the emf series is permanently fixed.	The positions of a given metal depend on the other metal used for making the alloy, (i.e position is not fixed).
3.	It gives no information regarding the position of alloys.	It includes alloys in galvanic series and accounts their corrosion behaviour.
4.	It comprises of metals and nonmetals.	It comprises metals and alloys.
5.	It predicts the relative displacement tendencies.	It predicts the relative corrosion tendencies.

3.5 FACTORS INFLUENCING RATE OF CORROSION

Corrosion is a kind of reaction that takes place in the metal by the influence of its environment. Hence both (i) the nature of the metal, and (ii) the nature of the environment play an equal part in the corrosion of the metal. The following are the factors responsible for the corrosion.

3.5.1 Nature of the Metal

(a) Position of Metal in the Galvanic Series

The extent of corrosion depends upon the position of the metal in the galvanic series. When two metals are in electrical contact, **the metal higher up in the galvanic series** becomes **anodic** and suffers corrosion. Further, the rate and severity of corrosion depend upon the difference in their positions in the galvanic series. The greater the difference, the faster the corrosion of anodic metal.

(b) Relative Areas of Anode and Cathode

Corrosion will be severe if the anodic area is small and the cathodic area is large. Larger cathodic area of the cathode will create a demand for more electrons, which can be met by the smaller area of the anode, only by undergoing more corrosion.

(c) Overpotential

Corrosion rate is **inversely proportional** to the overvoltage of a metal in the corrosive environment. For example, when Zn metal is placed in 1 N H_2SO_4, it undergoes corrosion with evolution of H_2 gas. Initially, the rate of corrosion is quite slow, because of high overvoltage of 0.7 V. But after the addition of a few drops of $CuSO_4$, the corrosion of zinc is accelerated due to decrease in H_2 overvoltage to 0.33 V. Thus reductions in overvoltage of the corroding metal/alloy accelerate the corrosion rate.

(d) Nature of the Surface Film

The rate of corrosion is influenced by the nature of the metal oxide film formed on the metal surface. According to **Pilling–Bedworth rule**,

$$\text{Specific volume ratio} = \frac{\text{Volume of metal oxide film formed}}{\text{Volume of metal ion consumed}}$$

- **Specific volume ratio > 1**; the oxide film formed will be nonporous and it protects the metal from further corrosion.

  Example: Oxides of Al, Sn, Pb, Cu, etc.
- **Specific volume ratio < 1**; the oxide film formed is porous, through which oxygen can easily diffuse and is therefore nonprotective in nature.

  Example: Oxides of Li, Na, K, Mg, Ca, Sr, etc.

(e) Purity of the Metal

Impurity present in a pure metal creates heterogeneity and leads to galvanic corrosion. If the percentage of purity increases, the corrosion rate decreases.

For example, iron impurity present in Zn metal forms an electrochemical cell and undergoes corrosion.

Metal	*% of purity*	*Corrosion Rate*
Zinc	99.999	1
	99.99	2650
	99.95	5000

(f) Stress

The metal part under stress can become the anode and undergo corrosion. This type of corrosion is called stress corrosion.

3.5.2 Nature of the Environment

(a) Temperature The rate of chemical reactions and diffusion of ions increases with temperature. Hence, corrosion increases with temperature. A passive metal may become active at higher temperature.

(b) Humidity Concentration of water vapour present in the atmosphere is known as humidity. If the humidity increases, the corrosion rate also increases. But at a particular point, a sudden increase in the corrosion rate is observed, called **critical humidity**.

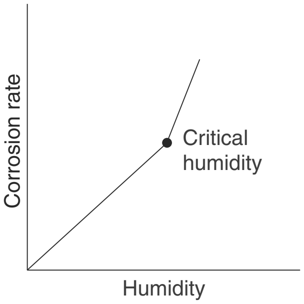


Fig. 3.10 *Critical humidity*

(c) Presence of Corrosive gases Corrosive gases like SO_2, H_2S, fumes of HNO_3, H_2SO_4, acetic acid, etc., enhance the corrosion rate.

(d) Presence of suspended solids Suspended particles like chemically active, chemically inactive and chemically neutral dust particles enhance the corrosion rate.

(e) pH The corrosion rate is maximum when the environment is more acidic (pH = 5) and minimum when the environment is more alkaline (pH = 11). In general, an acidic medium is more corrosive than alkaline or neutral medium.

3.6 CORROSION-CONTROL METHODS

Corrosion is very harmful for metals or alloys. Since metals and alloys disintegrate or waste every year, corrosion costs a huge amount of money, effort and time and it is necessary to protect the metals or alloys against corrosion by some methods.

Some of the corrosion control methods are given below.

(a) Corrosion Control by Modifying the Metal

- By selection of the metal
- By using pure metals
- By proper alloying
- By proper design

(b) Cathodic Protection Method

- Sacrificial anodic protection
- Impressed current cathodic protection

(c) By using Inhibitors

- Anodic inhibitors
- Cathodic inhibitors
- Vapour-phase inhibitor

(d) Changing the environment

- De-aeration
- De-activation

- Dehumidification
- Alkaline neutralization

(e) By using Protective Coating

3.6.1 Cathodic Protection Method

The anode is the electrode at which a net oxidation reaction occurs, whereas cathodes are electrodes at which net reduction reactions occur. All cathodic protection systems require an anode, a cathode, an electric circuit between the anode and cathode, and an electrolyte. Thus, cathodic protection will not work on structures exposed to air environments. The air is a poor electrolyte, and it prevents current flowing from the anode to the cathode. **The principle involved in cathodic protection is to force the metal to behave like a cathode.**

Cathodic protection can be accomplished by two widely used methods:

(a) Sacrificial Anodic Protection

Coupling a given structure (say Fe) with a more active metal such as zinc or magnesium, produces a galvanic cell in which the active metal works as an anode and provides a flux of electrons to the structure, which then becomes the cathode. The cathode is protected and the anode progressively gets destroyed, and is hence, called a **sacrificial anode.**

(b) Impressed-current Cathodic Protection

The second method involves impressing a direct current between an inert anode and the structure to be protected. Since electrons flow to the structure, it is protected from becoming the source of electrons (anode). In impressed current systems, the anode is buried and a low-voltage dc current is impressed between the anode and the cathode.

(a) Sacrificial Anodic Protection Method

A sacrificial anode, or sacrificial rod, is a metallic anode used in cathodic protection where it is intended to be dissolved to protect other metallic components. The more active metal is more easily oxidized than the protected metal and corrodes first (hence the term 'sacrificial'); it generally must oxidize nearly completely before the less active metal will corrode, thus acting as a barrier against corrosion for the protected metal. In this method, the metallic structure to be protected is made the cathode by connecting it with the more active metal (anode metal). Because of this, all the corrosion will concentrate only on the active metal. The artificially made anode thus gradually corrodes protecting the original metallic structure. Hence, this process is otherwise known as **sacrificial anodic protection**.

Typical materials for sacrificial anodes are magnesium (**for soil**) and aluminium/zinc/galvalum/indium alloys (**for sea water or seabed**).

Example 1 *This method is used for the protection of ships and boats. Sheets of Mg or Zn are hung around the hull of the ship (Fig. 3.11).*

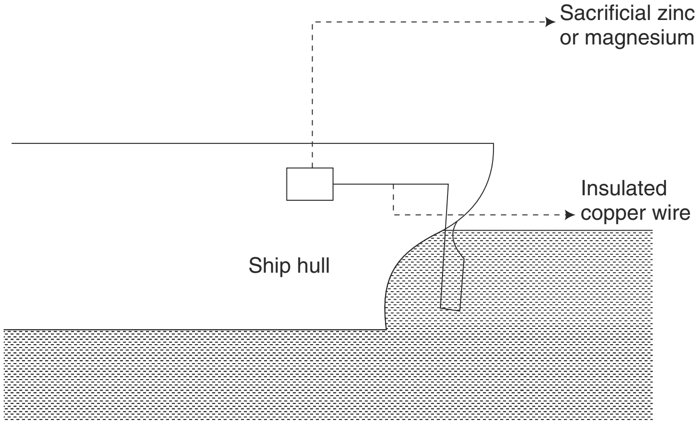


Fig. 3.11 *Sacrificial anodic protection of ship*

Zn or Mg act as anodes compared to iron (ship or boat is made of iron), so corrosion concentrates on Zn or Mg. Since they are sacrificed in the process of saving iron, they are called **sacrificial anodes**.

Sacrificial anodes are used on water-based vessels, such as yachts and powerboats, to minimize the corrosion of vital metal parts such as hulls and propellers. Conventionally made of zinc, aluminum and magnesium, boat anodes are designed for use in particular water types and with specific boat models. The number and size of anodes is determined by the type of material and the surface area being protected.

Choosing the Correct Anode

Generally, boat owners should choose the anode most suitable for the type of water they berth in. Naturally, some boats will move between salt and freshwater, or be berthed in areas where water will change between brackish water or freshwater. In these cases boat owners must choose a cathodic protection system to minimize corrosion in all environments.

Not all anodes are suitable for use in every type of water. For example, if zinc or aluminum anodes are left in freshwater they will develop a layer of oxide which will stop the anode from working. On the other hand, aluminum anodes will operate effectively in brackish water whilst zinc anodes will become unreactive. If the wrong type of metal is chosen for the water type, the anode will become useless.

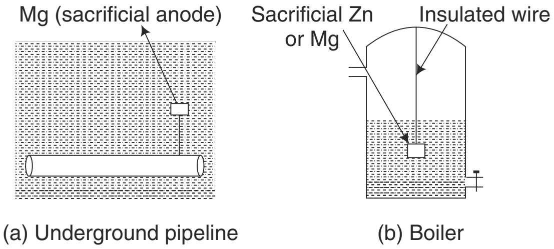
Water	**Metal Anode**
Salt water	Zinc or aluminum anodes
Brackish water	Aluminum anodes
Freshwater	Magnesium anodes

Other applications of sacrificial anodic protection are

(a) Protection of underground pipelines, cables from soil corrosion [Fig. 3.12 (a)]

(b) Insertion of Mg sheets into domestic water boilers to prevent the formation of rust [Fig. 3.12 (b)]

(c) Calcium metal employed to minimize engine corrosion.



(a) Underground pipeline (b) Boiler

Fig. 3.12 *Sacrificial anodic protection*

(b) Impressed-Current Cathodic Protection Method

For larger structures, Impressed-Current Cathodic Protection (ICCP) systems are more common because sacrificial anodes generally will not economically deliver enough CP current to protect pipelines longer than several dozen kilometres.

Impressed-current cathodic protection systems are thus often used for very long-distance pipelines or large plants having many large tanks or large buried metallic structures to protect.

In this method, an impressed current is applied in the opposite direction of the corrosion current to nullify it, and the corroding metal is converted from anode to cathode.

This can be done by connecting the negative terminal of the battery to the metallic structure to be protected, and the positive

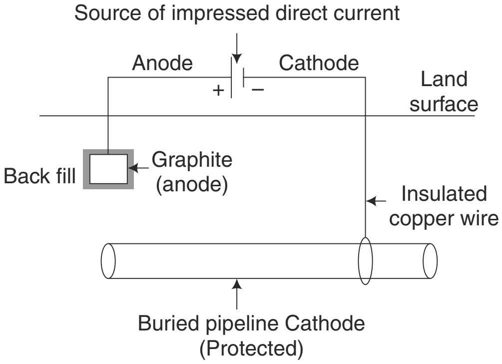


Fig. 3.13 *Impressed-current cathodic protection*

terminal of the battery is connected to an inert anode. Inert anodes used for this purpose are graphite and platinized titanium. The anode is buried in a 'backfill' (containing a mixture of gypsum, coke, breeze, sodium sulphate). The 'backfill' provides good electrical contact to the anode (Fig. 3.13).

CP is used to protect steel pipelines, storage tanks, steel piles, ships, offshore oil platforms and onshore oil-well casings, marine piers and laid-up strips, etc.

Table 3.4 *Comparison of sacrificial anode (galvanic method) and impressed-current cathodic method*

Sl. No	*Sacrificial Anode Method*	*Impressed Current Method*
1.	It is a simple system.	It is a more complex system than sacrificial anode systems.
2.	No external power supply is necessary.	External power supply must be present.
3.	This method requires periodical replacement of sacrificial anode.	Here, anodes are stable and do not disintegrate.
4.	Investment is low.	Investment is more.
5.	Soil and microbiological corrosion effects are not taken into account.	Soil and microbiological corrosion, corrosion effects are taken into account.
6.	This is a most economical method especially when short-term protection is required.	This method is well suited for large structure and long-term operations.
7.	This method is suitable when the current requirement and the resistivity of the electrolytes are relatively low.	This method can be practiced even if the current requirement and the resistivity of the electrolyte are high.
8.	The voltage differences between anode and cathode are limited in sacrificial anode systems to approximately 1 V or even less than 1V.	Impressed-current systems can use larger voltage differences.
9.	Fixed driving voltage.	Adjustable voltage.
10.	Low maintenance.	Higher maintenance.
11.	Does not cause stray current corrosion.	Stray dc currents can be generated.

3.6.2 Corrosion Inhibitors

This is a process of modifying the environment by adding certain chemicals to the corroding medium. These chemicals are known as corrosion inhibitors, as they arrest the anodic or cathodic reactions, i.e. a corrosion inhibitor is a substance which reduces the corrosion of a metal, when it is added in small quantities to the corrosive environment.

Types of Inhibitors

(i) Anodic Inhibitors

Anodic inhibitors retard the corrosion reaction, occurring at the anode, by forming an insoluble compound with a newly produced metal ions of anode. This precipitate will then be adsorbed on the metal (anode) surface, forming a protective film or barrier and thereby reducing the corrosion rate.

Anodic inhibitors should be used in enough amounts to cover the metal surface completely with the protective film, as otherwise corrosion will be concentrated on the remaining areas resulting in pitting corrosion.

Examples: Chromates, molybdates, nitrates, phosphates, tungstates or other ions of transition elements with high oxygen content.

(ii) Cathodic Inhibitors

In an electrochemical corrosion, the cathodic reactions are of two types depending upon the environment.

1. In an Acidic Solution

In an acidic solution, the cathodic reaction is evolution of hydrogen

$$2H^+ + 2e^- \longrightarrow H_2\uparrow \text{ (Reduction)}$$

The functions of cathodic inhibitors in acidic environment are the following:

1. *To decrease the formation of hydrogen at the cathode:* This can be done by adding organic inhibitors like amines, pyridines, etc., which are adsorbed at the metal surfaces.
2. *To increase the overvoltage of hydrogen:* This can be done by adding antimony and arsenic oxides which deposit adherent film of metallic arsenic and antimony at the cathodic areas.

Examples: Organic inhibitors like anilines and its derivatives, mercaptans, heterocyclic nitrogen compounds, thioureas etc.

2. In a Neutral Solution

In a neutral solution, the cathodic reaction is absorption of oxygen or formation of hydroxyl ions.

$$\tfrac{1}{2} O_2 + H_2O + 2e^- \longrightarrow 2OH^- \text{ (Reduction)}$$

Here, the formation of OH^- ion is only due to the presence of oxygen. So the corrosion can be controlled in two ways.

(a) *By eliminating the oxygen from the corroding medium* (neutral solution), thereby formation of OH^- ions are inhibited. This can be done by either adding reducing agents like **Na_2SO_3, N_2H_4** or by deaeration.

(b) *By retarding the diffusion of O_2 to the cathodic areas* eliminates the formation of OH^- ions from the neutral solution. This can be done by adding **Mg, Zn or Ni salts**. These react with OH^- ions form insoluble hydroxides, which are deposited on the cathode forming less impermeable self-barriers. Hence they retard the diffusion of O_2 to cathode.

Examples: Sodium sulphite (Na_2SO_3), hydrazine (N_2H_4).

(iii) Vapour-phase Inhibitors (VPI) or Volatile Corrosion Inhibitors (VCI)

This type of inhibitors are organic inhibitors, which readily vaporize (sublimes) and form a protective layer on the metal surface. VPI are used to avoid corrosion in closed spaces, storage containers, packing materials and sophisticated equipments, etc.

Examples: Dicyclohexylammonium nitrate (DCHAN), benzotriazole, Phenyl thiourea, etc.

3.7 PROTECTIVE COATINGS

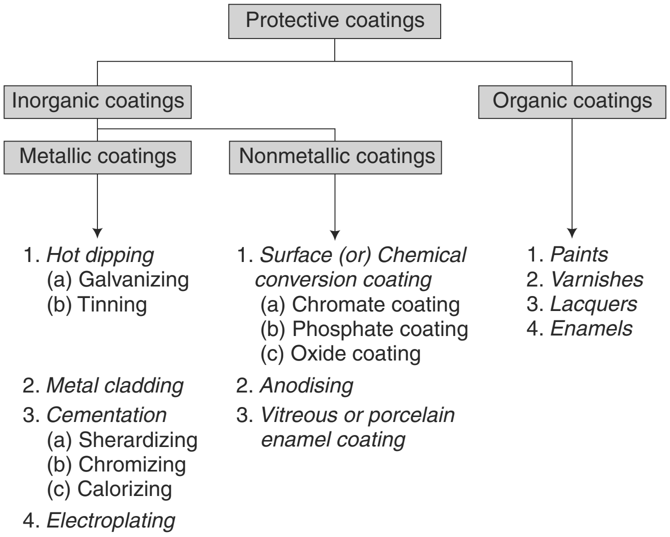
Protective coatings are used to protect the metals from corrosion. Protective coatings act as a physical barrier between the coated metal surface and the environment. However, they are also used for the decorative purpose. In addition to corrosion protection and decoration, they impart some special properties such as hardness, electrical properties, oxidation resistance and thermal insulating properties to the protected surface.

(a) Main Requirements

Protective coatings should be chemically inert to the environment at any temperature and pressure conditions.

(b) Classifications

Protective coatings are broadly of two types, i.e., inorganic and organic. They are further classified as shown below.



Coatings like paints, varnishes, lacquers and enamels are called organic coatings. They are applied on the metallic surfaces for both corrosion resistance and decoration.

3.8 PRE-TREATMENT OF METAL SURFACE OR PREPARATION OF MATERIAL FOR COATING

The base-metal surface is usually contaminated with rust, scale, oil, grease, etc. For proper adhesion of plating or coating, the metal surface (base metal) to be plated should be free from these impurities. If they are present at the time of coating, it will give porous and discontinuous coatings. So these impurities should be removed by proper pre-treatment methods. This is called **pre-treatment of metal surface.** This usually involves three steps.

1. **Degreasing:** It is a process of removal of grease, oil and other surface contaminants.
2. **Descaling:** It removes loose and hard oxide scale from the metal surface.
3. **Etching:** It is a treatment to secure adhesion or a polishing to improve the appearance of applied coating.

The following methods are used to achieve the fresh metal surface for providing protective coating.

(a) Mechanical Method

This method is used for descaling purpose, i.e., to remove loose scale and oxides. The various methods are hammering, scraping, wire brushing sandblasting, etc. Sandblasting is done when a slightly roughened surface is desired. It is the process in which sand or abrasives along with an air steam under pressure of 25–100 atm is concentrated on the metal surface.

(b) Chemical Method

The following methods are used for both degreasing and descaling, i.e., for removing oils, grease and rust from the metal surface.

(i) Solvent Cleaning: Solvents such as alcohols, acetone, xylene, toluene, chlorinated hydrocarbons, etc., are generally used in solvent cleaning. This is followed by cleaning with steam and hot water containing wetting agents.

(ii) Alkali Cleaning: In alkali cleaning, chemicals like sodium hydroxide, trisodium phosphate, sodium silicate, soda ash, etc., are used. This is useful in removing oil paints. The base metal containing paint coating is removed by keeping it in an alkali cleaning agent (NaOH + Na_3PO_4 + Na_2CO_3). This cleaning is always to be followed by a thorough rinsing with water.

(iii) Acid Pickling: Basic natures of rusty scales are removed by pickling. It is a process of dipping the object in hot dilute acids such as H_2SO_4, HCl, HF, H_3PO_4 and HNO_3. Brass and bronze are pickled by a mixture of H_2SO_4, HCl and a small amount of HNO_3. Iron and steel surfaces are pickled in H_3PO_4 or in H_2SO_4 followed by H_3PO_4.

(c) Electrochemical Method

This method is used where the oxide scales cannot be removed by the other methods. The metal whose surface has to be cleaned is made either anode (cathode pickling) or cathode (anode pickling). The electrolyte is usually in acid solution or an alkali solution and on passing a direct current, the dissolution of the oxide scales at anode or cathode takes place.

3.9 ELECTROPLATING OR ELECTRODEPOSITION

3.9.1 Principle

Electroplating is the process in which the coating metal is deposited on the base metal by passing a direct current through an electrolytic solution containing the soluble salt of the coating metal.

Base Metal The metal which is coated upon is known as the base metal.

Coat Metal The metal applied as coating is referred to as coat metal. The coat metal should be chemically inert and resistant to corrosion and should preferably have low melting point.

The base metal to be plated is made the cathode of an electrolytic cell, whereas the anode is either made of the coating metal itself or an inert material of good electrical conductivity.

Example: Graphite.

3.9.2 Objectives

(a) On Metals

1. To increase the resistance to corrosion of the coated metal
2. To improve the hardness and physical appearance of the article
3. To increase the decorative and commercial values of the article

4. To increase resistance to chemical attack
5. To improve the properties of the surface of the article

(b) On Nonmetals

1. To increase strength
2. To preserve and decorate the surfaces of nonmetals like plastics, wood, glass, etc.
3. For making the surface conductivity by utilization of light weight, nonmetallic materials

3.9.3 Process

Electroplating is carried out in an electrolytic cell. Before electroplating, the article to be plated is first treated with dil. HCl (or) dil. H_2SO_4 to clean the surface. The cleaned article is then made the cathode of an electrolytic cell. The anode is either the coating metal itself or an inert material of good electrical conductivity (like graphite).

The electrolyte is a solution of a soluble salt of a metal (to be deposited). The anode and cathode are dipped in an electrolytic solution kept in an electroplating tank. The tank is made of glass, enameled iron, and stoneware.

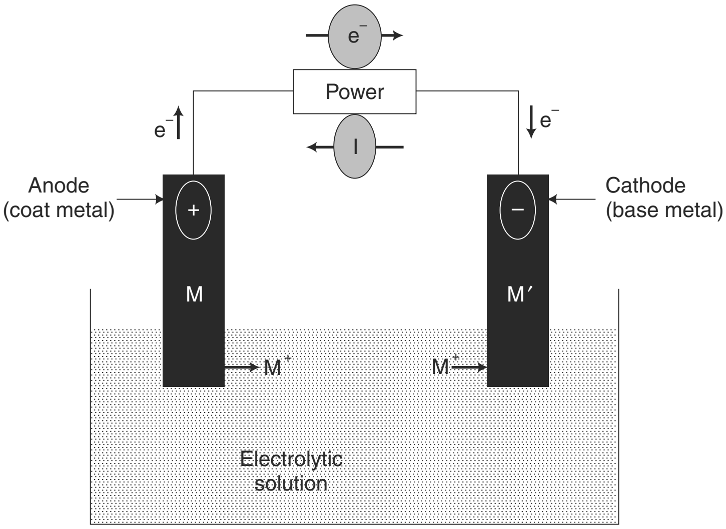


Fig. 3.14 *Electroplating*

The electrodes are dipped in this electrolytic solution and a direct current of electricity is passed. On electrolysis, the anode (coat metal) dissolves into the electrolytic bath and the metal ions from a bath solution are migrated and deposited as metal over the cathode (base-metal article to be plated).

$$M \longrightarrow M^{n+} + ne^- \quad \text{(dissolution at the anode)}$$

$$M^{n+} + ne^- \longrightarrow M \quad \text{(deposition at cathode)}$$

When a direct current is passed from a battery, coating metal ions migrate to the cathode and get deposited there. Thus, a thin layer of coating metal is obtained on the article (at cathode).

In order to get a strong, adherent and smooth deposit, certain additives (glue, gelatin, etc.) are added to the electrolytic bath. In order to improve the brightness of the deposit, brightening agents are added in the electrolytic bath. The favorable conditions for a good electrodeposit are optimum temperature, optimum current density and low metal-ion concentrations.

Advantages of Electroplating

A very thin coating (useful for deposition of costly metals like Au, Ag) can be obtained by adjusting suitably the factors responsible for controlling the thickness of coating.

3.9.4 Factors Affecting Electroplating

1. Surface Treatment: Cleaning of the article is essential for a strong adherent electroplating. Oily substances present in the base metal should be removed by solvent cleaning.

2. Concentration of Coating Metal Ion: Low concentration of the metal ions in the electrolyte will produce a uniform coherent metal deposition.

3. Thickness: Thickness of the deposit should be minimized in order to get a strong adherent coating.

4. Current Density: Current density used for electroplating should be optimum, because high current density produces loose and powdery deposit and low current density decreases the rate of electrodeposition.

5. Additives: Additives like gelatin and glue are added to electrolytic bath in order to get a strong, adherent and mirror-smooth coating.

6. Electrolyte: The electrolyte selected should have a good conductivity of current.

7. pH: The pH of the electrolytic bath must be properly maintained to get the deposition effectively. Usually, acidic pH 5–6 is preferred for high conductivity.

8. Stirring: should not be fast, since it will hinder the good adherence of coating metal atoms on the base metal and so a porous and rough deposit will be formed. Hence, mild stirring is done.

Table 3.5 *Electroplating of some metals and conditions*

Metal Deposited	*Anode*	*Cathode*	*Electrolyte*	*Operating Temperature*	*Current Density*	*Additives*
Copper	Pure copper plates	Metal article	$CuSO_4$	40–50°C	35–40 mA cm^2	–
Nickel	Pure Ni pellets or pieces in Ti mesh basket	Metal article	Solution of $NiSO_4 + NiCl_2$ + Boric acid	40–70°C	20–30 mA cm^2	Saccharin
Gold	Pure gold	Metal article	Gold + KCN	60°C	5–10 mA cm^2	–
Chromium	Pb–Sn (or) Pb-Sb alloy coated with PbO_2 (or) stainless steel	Metal article	Chromic acid + H_2SO_4 in 100: 1 ratio	40–50°C	100–200 mA cm^2	SO_4^{2-}

3.10 ELECTROLESS PLATING

Non-electrical plating of metals and plastics are used to achieve uniform coatings by a process of controlled autocatalytic (self-continuing) reduction. Discovered in 1944 by **A Brenner** and **G E Riddell**, electroless plating involves the deposition of such metals as copper, nickel, silver, gold, palladium on the surface of a variety of materials by means of a reducing chemical bath. It is also used in mirroring, in which a clean surface of glass is dipped into an ammoniacal silver solution mixed with Rochelle salt or with a nitric acid–cane-sugar alcohol solution.

Nonmetallic surfaces, such as plastics, must be chemically treated prior to electroless plating. The major expansion of electroless plating has come in the area of plastics, as in the plating of printed electronic circuits. A large number of consumer goods are coated by this method to create durable and attractive surfaces.

Definition It is a process of deposition of a metal from its salt solution on a catalytically active surface by a suitable reducing agent without using electricity.

Process First, M-ions are formed from its salt solution and then the reduction is accomplished by the presence of a reducing agent. Metallic ions are reduced to the metal with the help of reducing agents. Once a metal is formed, it gets plated over a catalytically activated surface.

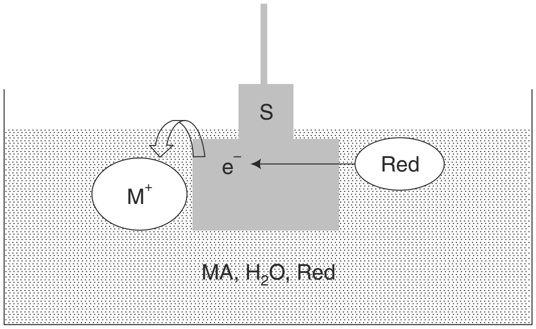


Fig. 3.15 *Electroless plating*

$$M^{2+} + 2e^- \text{ (from reducing agent)} \longrightarrow \underset{\substack{\text{(Deposited over}\\ \text{a catalytically}\\ \text{active surface)}}}{M} + \text{Oxidized product}$$

The common reducing agents are formaldehyde, Hypophosphorous acid, alkali borohydrides and alkali diboranes.

A number of metals like nickel, cobalt, copper and some precious metals can be deposited by electroless plating. The most popular metal deposited electrolessely is nickel.

3.10.1 Various Steps involved in Electroless Plating

The various steps involved are as follows:

(a) Surface Preparation for Electroless Plating

This is achieved by using any one of the following methods:

(i) **Etching:** Impurities are removed from the surface by acid treatment.

(ii) **Electroplating:** A thin layer of the metal or any other suitable metal is electroplated on the surface.

(iii) **Treatment of Surface with Stannous Chloride and Palladium Chloride Alternatively:** Nonconducting surfaces such as plastics or printed circuit boards are treated with Stannous Chloride and Palladium Chloride.

(b) Preparation of Plating Bath

The main constituents of the electroless solution are

(i) Metal salts to provide metal ions for deposition (coat metal)

(ii) Reducing agents like formaldehyde and hypophosphite for the reduction of metal ions to metal atoms

(iii) Complexing agents like EDTA and trisodium citrate to complex metal ions to prevent bulk decomposition

(iv) A stabilizer like thiourea to prevent the decomposition of plating bath solution

(v) Accelerators like succinates and fluorides to accelerate the reduction process

(vi) Brighteners like cadmium ions and lead ions to improve the brightness of the deposit

(vii) PH controlled by the buffer

3.10.2 Advantages of Electroless Plating

1. No electrical contact or electrical power is needed.
2. Plastics, insulators and semiconductors can also be plated by electroless plating.
3. It is readily adoptable for three-dimensional coverage.
4. This method enhances deposit uniformity.
5. Resulting deposits have unique chemical, mechanical and magnetic properties.

Table 3.6 *Differences between electroplating and electroless plating*

Sl. No	***Electroplating***	***Electroless Plating***
1.	It is carried out by passing electrical energy.	Here, there is no need of electrical energy.
2.	Here, a separate anode is used.	Anodic reaction takes place on the surface of the substrate.
3.	Plating on semiconductors and insulators are difficult.	Plating on semiconductors and insulators are easy.

3.11 SURFACE-CONVERSION COATING

Surface conversion is done for passiving the surface. This can be done by chemical or electrochemical reactions brought at the surface of the base metal. The resultant adherent coating on the surface of the base metal gives good protection from corrosion. Such coatings are also used as an excellent base for the application of paints and enamels.

Important surface conversion coatings are

- Phosphate coatings
- Chromate coatings
- Chemical oxide coatings

3.11.1 Phosphate Conversion Coating

Phosphate coatings are used for corrosion resistance or as a foundation for subsequent coatings. The chemicals used in this coating are the dilute solution of phosphoric acid and phosphate salts. It is either applied via spraying or immersion. The applied mixture reacts with the surface of the part being coated to form a layer of insoluble, crystalline phosphates.

Some type of phosphate coatings and their uses are given below.

S. No	***Type of phosphate coating***	***Mode of application***	***Uses***
1.	Manganese phosphate	By immersion	Corrosion resistance and lubricity
2.	Iron phosphate	By immersion or spraying	base for further coatings/paintings
3.	Zinc phosphate	By immersion or spraying	rust proofing and lubricant base layer.

(a) Process

It is the chemical conversion coating in which the base metal is treated with a dilute solution of phosphoric acid (less than 1%) and phosphates. Iron, zinc or manganese phosphate salts are dissolved in a solution of phosphoric acid. When steel or iron parts are placed in the phosphoric acid, a classic acid-and-metal reaction takes place. This causes the dissolved salt to fall out of solution and forms an insoluble complex of metal phosphate compound. This metal phosphate compound forms an adherent deposit over the base metal.

The following is a typical phosphating procedure:

1. Cleaning the surface
2. Rinsing
3. Surface activation (in some cases)
4. Phosphating
5. Rinsing
6. Neutralizing rinse (optional)
7. Drying
8. Application of supplemental coatings: lubricants, sealers, oil, etc.

(b) Uses

1. Phosphate coatings are often used to provide corrosion resistance; however, phosphate coatings on their own do not provide this because the coating is porous. Therefore, oil or other sealers are used to achieve corrosion resistance. This coating is called a phosphate and oil (P and O) coating.

2. Most phosphate coatings are used as a base for further coating and/or painting and also increase the resistance of the films to humidity.
3. Zinc phosphate coatings are frequently used in conjunction with sodium stearate (soap) to form a lubrication layer in cold and hot forging. The zinc phosphate is, in fact, abrasive and it is the soap which performs the actual lubrication.

3.12 ANODIZED COATING

Anodized coatings are made by anodic oxidation process. This leads to the formation of protective, corrosion resistant, electrically insulating oxide film on the surface of nonferrous metals like Al, Zn, Mg and their alloys. **Anodized coating** is an electrochemical process in which the **base metal** is the **anode.** Anodizing involves the electrolytic oxidation of a surface to produce a tightly adherent oxide scale, which is thicker than the naturally occurring film.

It is carried out by passing moderate direct current through a bath in which the metal or alloy is suspended from anode at **35°C to 40°C**. The bath usually contains sulphuric acid, chromic acid, oxalic acid, phosphoric acid or boric acid.

3.12.1 Aluminum Anodizing

Aluminum anodizing is an electrochemical process in which an oxide (anodic) layer is chemically built on the surface of the metal. This oxide layer acts as an insulator and can be dyed in a wide variety of colours. Anodizing provides surface-corrosion protection along with an excellent substrate for decorative finishes.

Anode:	Aluminium (**base metal**)
Cathode:	Any inert material of good electrical conductivity (lead/stainless steel)
Electrolyte:	Sulphuric acid, chromic acid, oxalic acid or phosphoric acid
Temperature:	35ºC to 40ºC
Current density:	Moderate current density

On electrolysis, the oxygen liberated at the anode combines with aluminium to form oxide. An oxide film, initially very thin, grows on the metal surface and increases in thickness. The outer part of the oxide film formed is very porous and easily prone to corrosion. Hence, the anodized surface containing pores can be sealed by treatment with hot water/

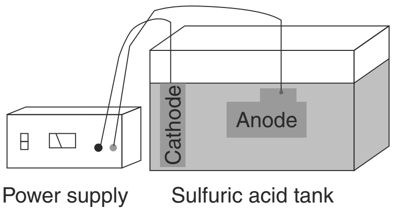


Fig. 3.16 *Aluminium anodizing*

steam for more than a few minutes. This treatment converts aluminium oxide into its monohydrate ($Al_2O_3.H_2O$) which occupies more volume, thereby the pores are sealed. An other solution used for sealing is dilute sodium dichromate. These anodized coatings may be coloured with organic dyes and inorganic pigments to give surface coloration for decorative effects.

Anodized coatings on Zn can be obtained by making Zn as the anode in an electrolytic bath containing chromic acid or chromates.

Applications Aircraft parts, refrigerators, pistons, reflectors, machine parts, etc., are anodized by this method.

Some of the common anodizing processes used in the industries are

- Hard-coat anodizing
- Bulk anodizing
- Sulphuric acid anodizing

3.13 HOT DIPPING

It is a process of producing a coating of low-melting point metal such as Zn, Sn, Pb, Al, etc., over the surface of Fe, steel and copper which have high melting points.

Base metal:	High-melting-point metal	(Fe, steel and copper)
Coat metal:	Low-melting-point metal	(Zn, Sn, Pb, Al etc)

The two most widely used hot-dipping methods are

1. Galvanizing
2. Tinning

3.13.1 Galvanizing

Galvanizing is the process of coating of zinc on iron or stainless-steel sheets.

(a) Process

The iron or stainless-steel article (e.g. sheet, pipe, wire) surface is first cleaned by acid pickling with dilute H_2SO_4 solution for 15–20 minutes at 60–90°C. This treatment removes any scale, rust (oxide layer) and impurities on the metal surface. The article is then washed well with water and dried. It is then dipped in the bath containing molten zinc, maintained at 425–430°C. The surface of the bath is kept covered with a flux, i.e. ammonium chloride, which is used for cleaning the surface of the metal and also to prevent oxide formation. When the article is taken out, it is found to have been coated with a thin layer of zinc. In order to get uniform thickness, it is passed through a pair of hot rollers, which removes any superfluous (excess) of zinc. Then, it is annealed at a temperature of 650°C and finally, cooled slowly.

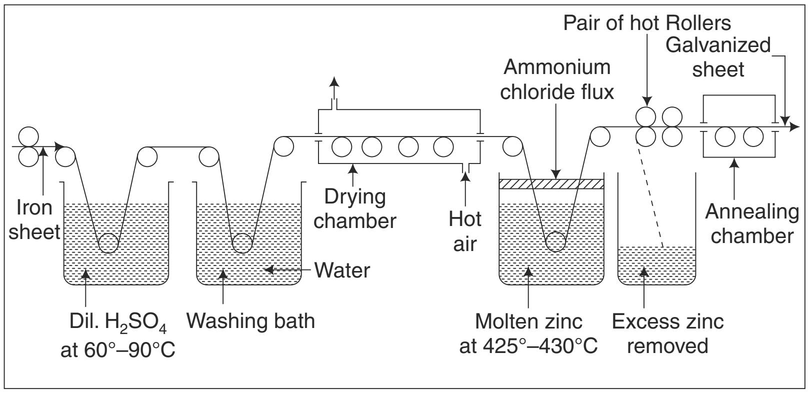


Fig. 3.17 *Galvanizing process*

(b) Uses

It is most widely used for protection of iron from atmospheric corrosion in the form of roofing sheets, wires, pipes, bolts, screws, buckets, tubes, etc. It may be pointed here that zinc gets dissolved in dilute acids to form highly toxic (or poisonous) compounds. Hence, galvanized utensils cannot be used for preparing and storing foodstuffs, especially acidic ones.

3.13.2 Tinning

Tinning is the process of coating of tin on iron or stainless-steel sheets.

(a) Process

In this process, iron or stainless-steel sheets are first treated with dilute sulphuric acid to remove the oxide scale on the surface. After this, it is passed through a bath containing zinc chloride flux. It helps the molten metal to adhere to the metal sheet. And then it is passed through the tank of molten tin which is kept at 230–235°C. In this process, palm oil helps to protect the hot tin-coated surface against oxidation. In order to get uniform thickness, it is passed through a pair of hot rollers, which removes any superfluous (excess) of tin. Then, it is annealed and finally, cooled slowly.

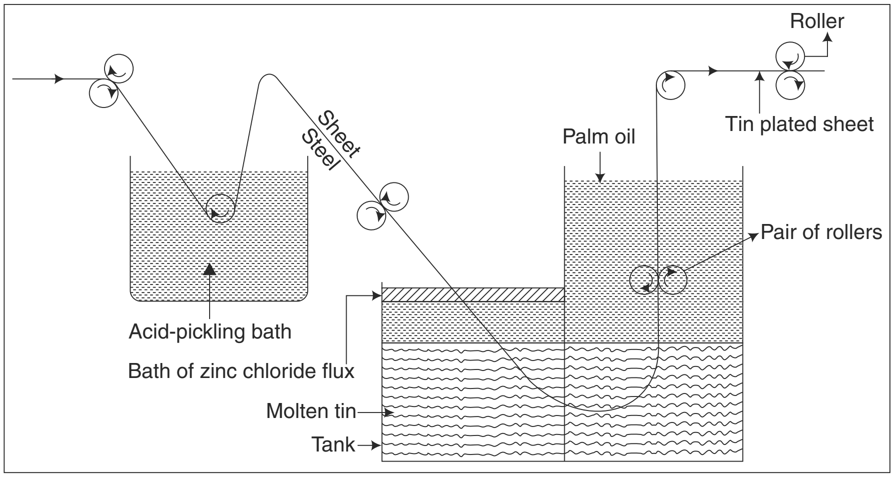


Fig. 3.18 *Tinning process*

(b) Uses

Tin-plated iron is used in food containers because of its nontoxic nature.

Table 3.7 *Differences between galvanizing and tinning*

Sl. No	*Galvanizing*	*Tinning*
1.	It is a process of coating of Zn on iron/steel.	It is a process of coating of Sn on iron/steel.
2.	It cannot be used for making food containers, because Zn reacts with food acids forming highly toxic zinc compounds.	It can be used for making containers for storing and packing food products.

3.14 PAINTS

Paint is a mechanical dispersion of one or more finely divided pigments in a medium (thinner + vehicle). When paint is applied to a metal surface, the thinner evaporates, while the vehicle undergoes slow oxidation forming a pigmented film.

(a) Requisites (or) Characteristics of a Good Paint

A good paint should satisfy the following requirements:

1. It should spread easily on the metal surface.
2. It should have high covering power.
3. It should not crack on drying.
4. It should adhere well to the surface.
5. The colour of the paint should be stable.
6. It should be corrosion-and water resistant.
7. It should give a smooth and pleasing appearance.
8. It should dry quickly.
9. The colour should be stable to the effect of atmosphere and other agencies.

(b) Pigment Volume Concentration (PVC)

It is an important criterion or a guide for the paint manufacturer to prepare paints with desired properties.

Generally, the characteristics of paints depend on the nature and quantities of pigments, extenders and vehicles present in the paint. The following equation is used to calculate the PVC.

$$\text{PVC} = \frac{\text{Volume of the pigment in the paint}}{\text{Volume of the pigment in the paint + Volume of nonvolatile vehicle in the paint}}$$

If the volume of PVC increases, the durability, adhesion and consistency of the paint decreases. The pigment volume concentration of a paint should be kept within the limit.

3.14.1 Constituents of Paints

The important constituents of paints are as follows:

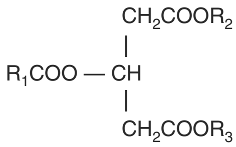
1. Pigments
2. Thinner (or) solvent
3. Vehicle (or) drying oil
4. Drier
5. Antiskinning agent
6. Plasticizers
7. Fillers (or) extenders.

Table 3.8 *Constituents of paints and their functions*

Sl. No	***Constituents***	***Function***	***Example***
1.	Pigments It is a solid substance which imparts colour to the paint.	(i) To give the desired colour (ii) To cover the manufacturing defects (iii) To protect from UV light. (iv) To provide strength to the paint (v) To increase weather resistance of the film	*White:* Pb,TiO_2, ZnO *Blue:* Indigo, Prussian Blue *Red:* Red lead, chrome red *Green:* Chromium oxide, Cr-green *Yellow:* Cr-yellow, Cd-yellow *Black:* Graphite, carbon black
2.	*Thinner or solvent* This is a volatile portion of the medium. It easily evaporates after application of the paint.	(i) Used to dilute the paints in order to make it easy to apply on the surface (ii) Reduces the viscosity of the paint (iii) It dissolves vehicles, oil, pigment, etc., and produces a homogeneous mixture. (iv) It increases the penetrating power of the vehicle.	Turpentine oil, kerosene, alcohol
3.	*Vehicle or drying oil* It is a nonvolatile portion of a medium and film-forming material.	(i) It is used to dissolve the pigment and holds the pigment on the metal surface. (ii) It imparts water repellency, durability, and toughness to the film.	Coconut oil, linseed oil, castor oil, soyabeen oil.
4.	*Driers* Substances used to accelerate the process of drying	They act as catalysts or oxygen carriers and increase the rate of drying process.	Litharge, borates, resinates and tungstates of heavy metals of Pb,Zn,Mn and Co.
5.	*Antiskinning agent*	To prevent skinning of the paint	Polyhydroxy phenol
6.	Plasticizers	They increase the elasticity of the film and to minimize its cracking.	Triphenyl phosphate, tributyl phosphate, trycresyl phosphate, tertiary amyl alcohol.
7.	Fillers or extenders Inert materials which improve the properties of the paint	(i) They increase the volume of the paint and reduce the cost. (ii) They fill the voids in the film. (iii) It increases the durability of the paint. (iv) It prevents shrinkage and cracking.	Gypsum, asbestos, China clay, talc, $BaSO_4$

3.14.2 Mechanism of Drying of (Paints) Drying Oils

1. Drying oils are fatty oils which are extracted from seeds.
2. The fatty oils are triesters of glycerol.
3. Formula of fatty oil (drying oil) is



$$\begin{array}{rl} & CH_2COOR_2 \\ & | \\ R_1COO - & CH \\ & | \\ & CH_2COOR_3 \end{array}$$

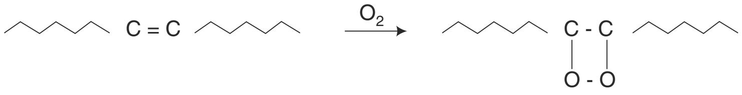
   where, R_1, R_2, R_3, are radicals derived from aliphatic unsaturated acids (palmitic acid, oleic acid)

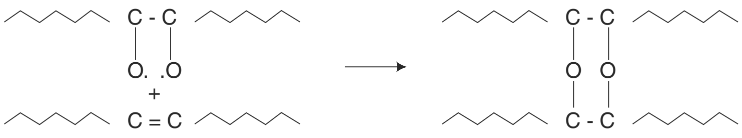
4. The paint containing these types of drying oils, when exposed to air, becomes a cross-linked polymer by reaction with oxygen in the atmosphere.
5. In general, oils containing fatty acids having conjugated double bonds dry faster than those that have nonconjugated double bonds.

The mechanism of drying oils has not been completely understood. However, according to acceptable mechanism, the oil containing double bond absorbs oxygen to form peroxides, diperoxides and hydroperoxides. The film takes of oxygen continuously and decomposes. The peroxy radicals formed are polymerized and condensed to give cross-linked polyperoxides which are tough, elastic, coherent, hard, insoluble, infusible and stable. These polyperoxides are decomposed by light and heat to form ether linkages.

Mechanism

1. The oil after application to the surface becomes solidified. It is called drying and hence the oil is called '**drying oil**'.
2. The double bonds (unsaturation centers) present in the oil absorb oxygen from the air and form peroxides (with 0–0) linkages. These linkages react with adjacent chain unsaturation centres and form cross links.





These cross links when continued sufficiently, solidification of the liquid oil takes place.. This is only one of the mechanisms that is possible.

If the unsaturation centres (carbon–carbon double bonds) increase, the capacity for O_2 absorption is also increases. Then the drying process takes place quickly.

3.14.3 Special Paints

These paints are not only used as a coating material for metal and material parts, but also used in some special areas like fire retarding, as water repellents and in advertising. So these paints are called special paints.

Some of the important special paints are as follows:

(a) Fire-retardant Paints

They contain fire-retardant chemicals like calcium ammonium phosphate, magnesium ammonium phosphate, calcium carbonate, urea formaldehyde, chlorinated rubber, etc., which decompose at elevated temperature producing non-inflammable gases like CO_2, NH_3 and HCl respectively. At elevated temperature, they form a barrier between air and inflammable substrates of the paint and cover the flame quickly and extinguish the fire.

Uses They are mainly used in wooden houses.

(b) Temperature Indicating Paints

They contain thermochromes. Thermochromes are the substances which undergo colour changes at different temperatures.

The main ingredients are amine salts of copper, iron, manganese, cobalt and nickel, etc. They are used in outer walls of the reactors and furnaces to indicate the temperature of the reaction, so that it can be stopped at a particular stage.

Uses Used in the outer walls of the reactors and furnaces to indicate the temperature by its colour change.

(c) Water-repellant Paints

The active ingredients present in the paints are silicone resins and silicone oils. They are prepared from organo ethoxy silane and organo chlorosilanes by hydrolysis and condensation. This is dissolved in a suitable solvent with required amount of pigments. These are sprayed on the surface to effectively avoid the wetting of the surface by water.

Paints containing asphalt or bitumen are also used for waterproofing.

Uses

- Used mainly for masonary surface
- Used in ships, boats and marine equipments.

(d) Luminous Paints

Luminous paints contain luminophore pigments which fluoresce under the influence of light. There are two types of luminous paints:

1. Fluorescent paint
2. Phosphorescent paint

(i) Fluorescent Paint

The absorption of light and emission of radiation takes place simultaneously. Such a paint emits radiation only when exposed to light. As soon as the exciting radiation is cut off, emission of radiation ceases. The main ingredients are ZnS mixed with cadmium sulphide, copper sulphide or silver sulphide.

Uses They are used in TV screens, advertising signs, instrument dials, etc.

(ii) Phosphorescent Paint

Delayed fluorescence is called **phosphorescence.** In this paint, the emission of radiation continues for some time even after the light has stopped falling. The active ingredients are a mixture of cadmium sulphide and strontium sulphide.

Uses They are used to illuminate maps and aircraft instruments at night.

QUESTIONS

Two-Mark Questions with Answers

1. **Define corrosion.**

   Corrosion can be defined as any process of destructive disintegration or alteration of a metal or alloy caused by direct chemical attack or by electrochemical reaction with its environment.

   (OR)

   In other words, corrosion is a process in which the gradual solution or oxidation of a metal takes place, e.g. rusting of iron.

2. **What is oxidation corrosion?**

   Oxidation Corrosion is nothing but the direct attack of metals by oxygen at low or high temperatures in the absence of moisture.

3. **State the Pilling–Bedworth rule.**

   The protective or nonprotective oxide layer formation in metals is governed by a rule known as *Pilling–Bedworth rule*. According to this rule,

$$\text{Specific volume ratio} = \frac{\text{Volume of metal oxide film formed}}{\text{Volume of metal ion consumed}}$$

   If the volume of the metal oxide ≥ volume of the parent metal then the oxide film will be nonporous or the volume of the metal oxide < volume of the parent metal, the oxide layer will be porous and tend to undergo further corrosion.

4. **What is decarburization?**

   The atomic hydrogen is highly reactive and combines with carbon present in the metal and forms CH_4 gas which leads to cracking of the metal surface. The process of decrease in carbon content in steel is known as decarburization of steel.

$$H_2 \longrightarrow [H] + [H]$$
$$C + H \longrightarrow CH_4$$

5. **What is hydrogen embrittlement?**

   Metals combine with H_2S gas to liberate atomic hydrogen.

$$H_2S + Fe \longrightarrow FeS + \underset{\text{(Atomic hydrogen)}}{2[H]}$$

   The atomic hydrogen recombines inside the metal and develops pressure which leads to cracking of the metal. This is known as *hydrogen embrittlement* or *Hydrogen Corrosion*.

6. **What is concentration-cell corrosion?**

   Concentration-cell corrosion occurs when a metal or two metals are in contact with different concentrations of the same solution or different concentration of dissolved oxygen in the electrolyte. It is also known as differential aeration corrosion.

7. **Write any four differences between dry and wet corrosion.**

Sl. No	***Dry or Chemical Corrosion***	***Wet or Electrochemical Corrosion***
1.	It occurs in dry state, e.g. tarnishing of silver.	It occurs in presence of moisture or electrolyte, e.g. rusting of iron.
2.	It involves direct chemical attack by the environment.	It involves the setting up of a huge number of galvanic cells.

3.	It follows adsorption mechanism.	It follows the mechanism of electrochemical reaction.
4.	Uniform corrosion behaviour is seen.	Localized corrosion occurs.
5.	It is a slow and self-controlled process.	It is a fast and continuous process.

8. **What is critical humidity?**

Concentration of water vapour present in the atmosphere is known as humidity. If the humidity increases, the corrosion rate also increases. But at a particular point, a sudden increase in the corrosion rate is observed, called **Critical humidity**.

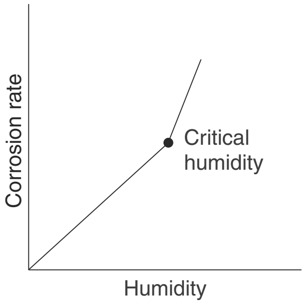


Fig. 2 *Plot of humidity against corrosion rate*

9. **What is the galvanic Series?**

The oxidation potential of the different metals and alloys are determined at 25°C and tabulated in the descending order. *metals occupying higher positions in the series undergo corrosion in vigorous manner*. The above-said series is called *galvanic series* and it gives more information about the corrosive tendencies of the different metals.

10. **Write any four applications of sacrificial anodic protection method.**

    1. On water-based vessels such as yachts and powerboats, to minimize the corrosion of vital metal parts such as hulls and propellers
    2. Protection of underground pipelines, cables from soil corrosion
    3. Insertion of Mg sheets into the domestic water boilers to prevent the formation of rust
    4. Calcium metal is employed to minimize engine corrosion

11. What are anodic inhibitors?

Anodic inhibitors are the substances which retard the corrosion reaction occurring at the anode, by forming an insoluble compound with a newly produced metal ion of anode.

Examples Chromates, molybdates, nitrates, phosphates, tungstates or other ions of transition elements with high oxygen content

12. Write any two differences between sacrificial anodic protection and impressed current cathodic protection method.

Sl. No.	*Sacrificial Anode Method*	*Impressed Current Method*
1.	No external power supply is necessary.	External power supply must be present.
2.	This method requires periodical replacement of sacrificial anode.	Here, anodes are stable and do not disintegrate.
3.	It is a simple system and investment is low.	It is a more complex system than sacrificial anode systems, and investment is more.

13. Why do we need pretreatment for metal surface?

The base metal surface is usually contaminated with rust, scale, oil, grease, etc. For proper adhesion of plating or coating, the metal surface (base metal) to be plated should be free from these impurities. If they are present at the time of coating, it will give porous and discontinuous coatings.

14. Define electroplating.

Electroplating is the process in which the coating metal is deposited on the base metal by passing a direct current through an electrolytic solution containing the soluble salt of the coating metal, e.g. electroplating of copper.

15. Define electroless plating.

Electroless plating is a process of deposition of a metal from its salt solution on a catalytically active surface by a suitable reducing agent without using electricity.

16. Write any three differences between electroplating and electroless plating.

Sl.No	*Electroplating*	*Electroless Plating*
1.	It is carried out by passing electrical energy.	Here, there is no need of electrical energy.
2.	Here, a separate anode is used.	Anodic reaction takes place on the surface of the substrate.
3.	Plating on semiconductors and insulators are difficult.	Plating on semiconductors and insulators are easy.

17. **What is anodized coating?**

    Anodized coating is an electrochemical process in which the *base metal* is the *anode*. Anodizing involves the electrolytic oxidation of a surface to produce a tightly adherent oxide scale which is thicker than the naturally occurring film.

18. **Write any two differences between hot dipping (galvanizing) and tinning.**

Sl.No	*Galvanizing*	*Tinning*
1.	It is a process of coating of Zn on iron/steel.	It is a process of coating of Sn on iron/steel.
2.	It cannot be used for making food containers, because Zn reacts with food acids and forms highly toxic zinc compounds.	It can be used for making containers for storing and packing of food products.

19. **What is the purpose of adding thinners to paints? Give examples.**

    (i) A thinner is added to dilute the paint in order to make it easy to apply on the surface.

    (ii) It reduces the viscosity of the paint.

    (iii) It dissolves vehicles, oil, pigment, etc., and produces homogeneous mixture.

    Examples Turpentine oil, kerosene, alcohol

Ten-Mark Questions

1. Describe the mechanism of electrochemical corrosion.
2. What are the types of metal oxide films formed? Explain it in detail.
3. Write short notes on concentration-cell corrosion.
4. Explain the important factors which influence the rate of corrosion of a metal.
5. Discuss the mechanism of
   - (i) Chemical corrosion
   - (ii) Pitting corrosion.
6. Write brief notes on
   - (i) Sacrificial anodic protection method
   - (ii) Impressed current cathodic protection method
7. Write a note on application of inhibitors in corrosion control.

8. (i) Define corrosion inhibitors.
   (ii) What are the types of corrosion inhibitors? Explain it briefly.
9. What are the important constituents of paint? Explain its functions in detail.
10. Discuss in detail about pretreatment of metal surface.
11. Describe the mechanisms of drying of oil in paint?
12. What are the main objectives of electroplating? Give an account of the method used in electroplating of nickel on steel.
13. Explain the following:
    (i) Pilling–Bedworth rule
    (ii) Decarburization
    (iii) Hydrogen embrittlement
14. Write short notes on
    (i) Phosphate conversion coating
    (ii) Anodization
15. With a neat diagram explain the process of
    (i) Hot dipping
    (ii) Tinning

UNIT

4

Fuels

"Everything is available in the world for human need but not for human greed".

4.1 INTRODUCTION

In recent years, the human population has grown at a very fast rate. Along with the increase in population, living standards have also improved. This increase of population and living standards has resulted in a tremendous increase in the requirement of energy. Most of the developed and developing countries derive their energy from fossil fuels such as petroleum, coal and natural gas. The fossil fuels are nonrenewable—hence, they are depleting in an alarming rate. It is the basic responsibility of every citizen to conserve the nonrenewable resources. This chapter deals with the details of various kinds of fuels, how they are extracted and purified, their combustion and quantity of energy released, etc.

A **fuel** is any material that can be used to generate energy to produce mechanical work in a controlled manner. In other words, it is a substance that produces energy, mostly usable heat. Most fuels produce energy when they are burnt in air. The processes used to convert fuel into energy include chemical reactions, such as combustion, and nuclear reactions such as nuclear fission or nuclear fusion. Fuels are also used in the cells of organisms in a process known as **metabolism**. Hydrocarbons are, by far, the most common source of fuel in current use, but many other substances can be used as well.

Any matter which on combustion (i.e. burning) produces heat energy is called a fuel.

Example: Wood, charcoal, coal, kerosene, petrol, diesel, producer gas, oil gas, etc.

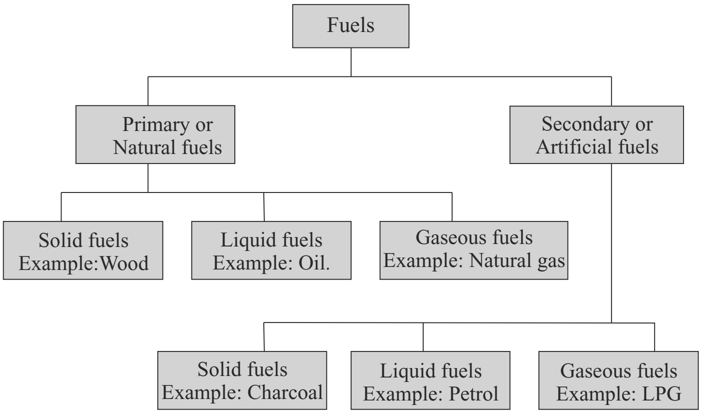
4.2 CLASSIFICATION OF FUELS

The fossil fuels are classified into the following categories:

(i) Primary or natural fuels—These are found in nature.

(ii) Secondary or artificial fuels—These are derived from primary fuels.

Primary and secondary fuels may also be divided into three classes, namely solid, liquid and gaseous fuels.



4.2.1 Fossil Fuels

Fossil fuels are those which have been derived from fossil remains of plant and animal life.

Fossil fuels are hydrocarbons, primarily coal and petroleum (liquid petroleum or natural gas), formed from the fossilized remains of dead plants and animals by exposure to heat and pressure in the earth's crust over hundreds of millions of years. The term 'fossil fuel' also includes hydrocarbon-containing natural resources that are not derived entirely from biological sources, such as tar sands. These are properly known as *mineral fuels*.

4.2.2 Requirements of a Good Fuel

A good-quality and economical fuel should have the following characteristics:

(a) High Calorific Value

A good-quality fuel should have its calorific value as high as possible, since the work derived is directly proportional to the heat energy released.

(b) Moderate Ignition Temperature

Low ignition temperature may result in a fire accident during storage and transportation. On the other hand, very high ignition temperature may result in difficulties during the ignition. Hence, a good-quality fuel should have moderate ignition temperature.

(c) Low Quantity of Noncombustible Matters

The presence of noncombustible matter will result in low calorific value, high quantity of ash generation and additional cost for transportation. Hence, a good fuel should have low level of noncombustible matter.

(d) Lesser Moisture Content

The moisture present in the fuel will consume some amount of heat for its own evaporation and also reduce the calorific value, and increase the transportation and storage cost. The presence of moisture is not desirable in a good-quality fuel.

(e) Free from Objectionable and Harmful Gases like CO, SO_x, H_2S

On combustion, the fuel should not release harmful and objectionable gases like **CO, SO_x, H_2S, NO_x,** etc.

(f) Moderate Velocity of Combustion

Low rate of combustion may lead to unnecessary loss of heat due to radiation. On the other hand, a high rate of combustion leads to out-of-control burning. For a smooth and continuous supply of heat, the fuel must burn with moderate velocity.

(g) Controllable and Stoppable Combustion

For easy start-up and stoppage, the combustion should be controllable.

(h) The fuel should not pose any difficulty in transportation.

(i) The fuel should have more availability at affordable cost.

4.3 COMBUSTION

Combustion, or burning, is the sequence of exothermic chemical reactions between a fuel and an oxidant accompanied by the production of heat and conversion of chemical species.

The release of heat can result in the production of light in the form of either a glow or a flame. Fuels of interest often include organic compounds (especially hydrocarbons) in the gas, liquid or solid phase.

During the process of combustion, carbon, hydrogen, etc., combine with oxygen with liberation of heat.

The combustion reaction can be explained as

$$C + O_2 \longrightarrow CO_2 + 94 \text{ kcal}$$

$$2H_2 + O_2 \longrightarrow 2H_2O + 68.5 \text{ kcal}$$

The calorific value of a fuel depends mainly on the amount of carbon and hydrogen.

4.3.1 Principle of Combustion

***Combustion** refers to the rapid oxidation of fuel accompanied by the production of heat, or heat and light. Complete combustion of a fuel is possible only in the presence of an adequate supply of oxygen.*

Carbon, hydrogen and sulphur in the fuel combine with oxygen in the air to form carbon dioxide, water vapour and sulphur dioxide, releasing 8080 kcal, 34500 kcal and 2240 kcal of heat respectively. Under certain conditions, carbon may also combine with oxygen to form carbon monoxide, which results in the release of a smaller quantity of heat (2430 kcal/kg of carbon). Carbon burned to CO_2 will produce more heat per kg of fuel than when CO or smoke are produced.

$$\begin{aligned}
C + O_2 &\longrightarrow CO_2 + 8080 \text{ kcal/kg of carbon} \\
2C + O_2 &\longrightarrow 2\,CO + 2430 \text{ kcal/kg of carbon} \\
2H_2 + O_2 &\longrightarrow 2H_2O + 34500 \text{ kcal/kg of hydrogen} \\
S + O_2 &\longrightarrow SO_2 + 2240 \text{ kcal/kg of sulphur}
\end{aligned}$$

Not all of the energy in the fuel is converted to heat; some is absorbed by the steam generation equipment. So the main challenge in combustion efficiency is directed toward unburnt carbon (in the ash or incompletely burnt gas), which forms CO instead of CO_2.

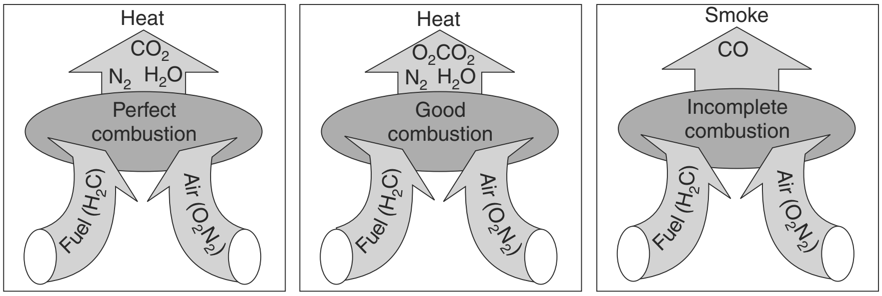


Fig. 4.1 *Types of combustion*

4.3.2 Calorific Value

It is the most important characteristic property of any fuel.

> ***Calorific value may be defined as the amount of heat liberated by the complete combustion of a unit mass of a fuel.***

The quantity of heat can be measured by the following units.

(i) Calorie
(ii) Kilocalorie
(iii) British thermal units
(iv) Centigrade heat units

> ***Calorie is the amount of heat required to raise the temperature of 1 g of water by 1°C (i.e. 15 to 16°C).***

Calorific value is divided into two types:

(a) Higher or gross calorific value
(b) Lower or net calorific value

(a) Gross or High Calorific Value (GCV or HCV)

> ***It is the total heat generated when a unit quantity of fuel is completely burnt and the products of combustion are cooled to room temperature.***

For example, when a fuel containing hydrogen is burnt, it undergoes combustion and will be converted to steam. If the combustion product is cooled to room temperature, the steam gets condensed into water and the latent heat is evolved. Therefore, the latent heat of condensation of 'steam', so liberated, is included in gross calorific value.

Dulong's Formula for the Calculation of Calorific Value

Calorific value of a fuel is the sum of the calorific values of all the combustible constituents present in the fuel.

Dulong's formula for the theoretical calculation of calorific value is

$$\text{GCV or HCV} = \frac{1}{100}\left[8080\,C + 34500\left(H - \frac{O}{8}\right) + 2240\,S\right]\ \text{kcal/kg}$$

where, C, H, O and S represent the percentage of the corresponding elements in the fuel which is determined by the ultimate analysis.

It is based on the assumption that the calorific values of C, H and S are found to be 8080, 34500 and 2240 kcal, when 1 kg of the fuel is burnt completely. However, all the oxygen in the fuel is assumed to be present in combination with hydrogen in the ratio H : O as 1 : 8 by weight. So the surplus hydrogen available for combustion is $H - \frac{O}{8}$.

(b) Net or Lower Calorific Value (NCV or LCV)

It is the net heat produced when a unit quantity of fuel is completely burnt and the products of combustion are allowed to escape.

NCV = GCV – Latent heat of condensation of steam produced

Consider the following combustion reaction:

$$\underset{\substack{2\text{ g}\\1}}{H_2} + 1/2\ \underset{\substack{16\text{ g}\\8}}{O_2} \longrightarrow \underset{\substack{18\text{ g}\\9}}{H_2O}$$

1 part by weight of H_2 produces 9 parts by weight of H_2O.

The latent heat of steam is 587 cal/g.

Therefore, the latent heat of condensation of steam produced by H amount of hydrogen is

$$= \frac{9}{100}H \times 587 = 0.09\,H \times 587$$

where, H = % of H_2 in the fuel.

Thus,

$$\text{NCV} = \text{GCV} - \frac{9}{100}\text{H} \times 587\ \text{kcal/kg}$$

$$\text{NCV} = \text{GCV} - 0.09\ \text{H} \times 587\ \text{kcal/kg}$$

Example 1 *Calculate the gross and net calorific values of a coal sample having the following compositions: C = 80 %, H_2 = 08 %, O_2 = 08 %, S = 2 % and ash = 2. Latent heat of steam is = 587 cal/g.*

Solution

(i) Gross Calorific Value (GCV)

$$\text{GCV} = \frac{1}{100}\left[8080\,C + 34500\left(H - \frac{O}{8}\right) + 2240\,S\right]\ \text{kcal/kg}$$

$$= \frac{1}{100}\left[8080 \times 80 + 34500\left(8 - \frac{8}{8}\right) + 2240 \times 2\right] \text{kcal/kg}$$

$$= \frac{1}{100}\,[646400 + 241500 + 4480]\ \text{kcal/kg}$$

$$= \frac{1}{100}\,[892380]\ \text{kcal/kg}$$

$$= 8923.8\ \text{kcal/kg}$$

(ii) Net Calorific Value (NCV)

$$= \text{GCV} - \frac{9}{100}\,\text{H} \times 587\ \text{kcal/kg}$$

$$= 8923.8 - \frac{9}{100} \times 8 \times 587\ \text{kcal/kg}$$

$$= 8923.8 - 422.64\ \text{kcal/kg}$$

$$= 8501.16\ \text{kcal/kg}$$

Example 2 *Calculate the gross and net calorific values of a coal sample having the following compositions: C = 63 %, H_2 = 19 %, O_2 = 03 %, S = 13 % and ash = 2. Latent heat of steam is = 587 cal/g.*

Solution

(i) Gross Calorific Value (GCV)

$$\text{GCV} = \frac{1}{100}\left[8080\,C + 34500\left(H - \frac{O}{8}\right) + 2240\,S\right] \text{kcal/kg}$$

$$= \frac{1}{100}\left[8080 \times 63 + 34500\left(19 - \frac{3}{8}\right) + 2240 \times 13\right] \text{kcal/kg}$$

$$= \frac{1}{100}\,[509040 + 642562 + 29120]\ \text{kcal/kg}$$

$$= \frac{1}{100}\,[1180722]\ \text{kcal/kg}$$

$$= 11807.22\ \text{kcal/kg}$$

(ii) Net Calorific Value (NCV)

$$= \text{GCV} - \frac{9}{100}\,\text{H} \times 587\ \text{kcal/kg}$$

$$= 11807.22 - \frac{9}{100} \times 19 \times 587\ \text{kcal/kg}$$

$$= 11807.22 - 1003.77\ \text{kcal/kg}$$

$$= 10803.45\ \text{kcal/kg}$$

Example 3 *Calculate the gross and net calorific values of a solid fuel having 80% of carbon and 20% of hydrogen. Latent heat of steam is = 587 cal/g.*

Solution

(i) Gross Calorific Value (GCV)

$$= \frac{1}{100}\left[8080\ C + 34500\left(H - \frac{O}{8}\right) + 2240\ S\right] \text{ kcal/kg}$$

Here, the % of O_2 and S are zero.

$$= \frac{1}{100}\left[8080 \times 80 + 34500\left(20 - \frac{0}{8}\right) + 2240 \times 0\right] \text{ kcal/kg}$$

$$= \frac{1}{100}\,[646400 + 690000] \text{ kcal/kg}$$

$$= \frac{1}{100}\,[1336400] \text{ kcal/kg}$$

$$= 13364 \text{ kcal/kg}$$

(ii) Net Calorific Value (NCV)

$$= \text{GCV} - \frac{9}{100}\,\text{H} \times 587 \text{ kcal/kg}$$

$$= 13364 - \frac{9}{100} \times 20 \times 587 \text{ kcal/kg}$$

$$= 13364 - 1056.6 \text{ kcal/kg}$$

$$= 12307.4 \text{ kcal/kg}$$

Example 4 *A coal sample on analysis gives C = 75 %, H_2 = 6 %, O_2 = 3.5 %, S = 03 % and the rest ash. Calculate the gross and net calorific values of the fuel. Latent heat of steam is = 587 cal/g.*

Solution

(i) Gross Calorific Value (GCV)

$$= \frac{1}{100}\left[8080\ C + 34500\left(H - \frac{O}{8}\right) + 2240\ S\right] \text{ kcal/kg}$$

$$= \frac{1}{100}\left[8080 \times 75 + 34500\left(6 - \frac{3.5}{8}\right) + 2240 \times 3\right] \text{ kcal/kg}$$

$$= \frac{1}{100}\,[606000 + 191906 + 6720] \text{ kcal/kg}$$

$$= \frac{1}{100}\,[804626] \text{ kcal/kg}$$

$$= 80462.6 \text{ kcal/kg}$$

(ii) Net Calorific Value (NCV)

$$= \text{GCV} - \frac{9}{100}\text{H} \times 587 \text{ kcal/kg}$$

$$= 80462.6 - \frac{9}{100} \times 6 \times 587 \text{ kcal/kg}$$

$$= 80462.6 - 316.98 \text{ kcal/kg}$$

$$= 80145.62 \text{ kcal/kg}$$

Example 5 *On analysis, a coal sample has the following composition by weight: C = 75 %, O_2 = 04 %, S = 05 %, and ash = 3%. Net calorific value of the fuel is 9797.71 kcal/kg. Calculate the percentage of hydrogen and gross calorific value of coal.*

Solution

(i) Gross Calorific Value (GCV)

We know that,

$$\text{GCV} = [\text{NCV} + 0.09\text{H} \times 587] \text{ kcal/kg}$$

$$= [9797.71 + 0.09\text{H} + 587] \text{ kcal/kg}$$

$$= [9797.71 + 52.8 \text{ H}] \text{ kcal/kg} \qquad \ldots(1)$$

$$\text{GCV} = \frac{1}{100}\left[8080\,C + 34500\left(H - \frac{O}{8}\right) + 2240\,S\right] \text{kcal/kg}$$

$$= \frac{1}{100}\left[8080 \times 75 + 34500\left(H - \frac{4}{8}\right) + 2240 \times 5\right] \text{kcal/kg}$$

$$= \frac{1}{100}[606000 + 34500\,H - 17250 + 11200] \text{ kcal/kg}$$

$$= [6060 + 345\,H - 172.5 + 112] \text{ kcal/kg}$$

$$= 5999.5 + 345\,H \text{ kcal/kg} \qquad ...(2)$$

Equation (2) is substituted in Equation (1).

$$9797.71 + 52.8\,H = 5999.5 + 345\,H$$

$$9797.71 - 5999.5 = 345\,H - 52.8\,H$$

$$3798.21 = 292.2\,H$$

$$H = \frac{3798.21}{292.2}$$

% of H_2 = 12.99 (i.e. 13 %)

Substituting the value of H_2 in the GCV equation,

$$\text{GCV} = \frac{1}{100}\left[8080 \times 75 + 34500\left(13 - \frac{4}{8}\right) + 2240 \times 5\right] \text{kcal/kg}$$

$$\text{GCV} = \frac{1}{100}[606000 + 431250 + 11200]\ \text{kcal/kg}$$

$$= \frac{1}{100}[1048450]\ \text{kcal/kg}$$

$$= 10484.5\ \text{kcal/kg}$$

4.4 THEORETICAL CALCULATION OF MINIMUM AIR REQUIRED FOR COMBUSTION

Any fuel which is used for combustion should be burnt completely to ensure complete and efficient combustion of fuel. It is essential that the fuel is burnt in sufficient quantity of air to oxidize all the combustible matter under appropriate conditions.

The essential conditions which are maintained are

- Intimate mixing of air with combustible matter, and
- Sufficient time to allow the combustion process to be completed.

Incomplete combustion may occur if any one of these factors is inappropriate.

- **The elements usually present in common fuels which enter into the process of combustion are mainly C, H, S and O.**
- **Nitrogen, ash and CO_2 (if any) present in the fuel are incombustible matters and hence they do not consume any oxygen during combustion.**
- **Air contains 21% of oxygen by volume and 23% of oxygen by weight.**

Hence, from the amount of oxygen required by the fuel, the amount of air can be calculated.

The amount of oxygen required for complete combustion of a fuel can be calculated from the combustion equations. By calculating the weight and volume of oxygen required for complete combustion of a fuel, it is easy to calculate the volume and weight of air required for the complete combustion.

Combustion of Carbon

	C	$+ \; O_2 \longrightarrow$	CO_2
By volume	1 vol	1 vol	1 vol
By weight	12 g	32 g	44 g

1 part by volume of carbon requires 1 part by volume of oxygen for complete combustion.

(or)

12 g of carbon requires 32 g of oxygen for complete combustion (to give 44 g of CO_2).

1 g of carbon requires 32/12 g of oxygen for complete combustion.

$\therefore$ C g of carbon requires $= \dfrac{32C}{12}$ g of oxygen

(or)

C parts by weight of carbon requires $= \dfrac{32C}{12}$ parts by weight of O_2

Combustion of Hydrogen

	H_2	+ $1/2\ O_2$	$\longrightarrow H_2O$
By volume	1 vol	0.5 vol	1 vol
By weight	2 g	16 g	18 g

1 part by volume of hydrogen requires 0.5 part by volume of oxygen for complete combustion.

(or)

4 g of hydrogen requires 32 g of oxygen for complete combustion.

1 g of hydrogen requires 32/4 g of oxygen for complete combustion.

$\therefore$ **H** g of hydrogen requires $= \dfrac{32 \times H}{4}$ g of O_2

(or)

H parts by weight of hydrogen requires $= \dfrac{32 \times H}{4}$ parts by weight of O_2

The oxygen present in the fuel consumes some amount of hydrogen to form water. So, the quantity of hydrogen taken up by oxygen will not take part in the combustion reaction. Therefore, the quantity of hydrogen taken up by the oxygen will be deduced from the total hydrogen in the fuel.

Now, the quantity of hydrogen available for the combustion reaction will be $H - \dfrac{O}{8}$ where H is the total quantity of hydrogen and O is the total quantity of oxygen in the fuel. (in water, the quantity of hydrogen in combination with oxygen is one-eighth of the weight of oxygen).

$\therefore \left(H - \frac{O}{8}\right)$ parts by weight of hydrogen requires $\dfrac{H - \frac{O}{8} \times 32}{4} =$ $8\left(H - \frac{O}{8}\right)$ parts by weight of O_2

Combustion of Sulphur

$$S + O_2 \longrightarrow SO_2$$

	S	O_2	SO_2
By volume	1 vol	1 vol	1 vol
By weight	32 g	32 g	64 g

1 part by volume of sulphur requires 1 part by volume of oxygen for complete combustion.

(or)

32 g of sulphur requires 32 g of oxygen for complete combustion.

S g of sulphur requires $= \frac{32 \times S}{32} =$ S g of O_2

(or)

$\therefore$ **S** parts by weight of sulphur requires $= \frac{32 \times S}{32} = S$ parts by weight of O_2

Combustion of Nitrogen

Since nitrogen do not undergo combustion, the oxygen requirement is nil.

Consequently, the theoretical amount of oxygen required for the complete combustion of 1kg of solid or liquid fuel is

$$\text{Theoretical minimum } O_2 = \left[\frac{32}{12} \times C + 8\left(H - \frac{O}{8}\right) + S\right] \text{kg}$$

Since mass % of O_2 in air is 23, the amount of air required theoretically for combustion of 1 kg of the fuel is,

$$\text{Air (theoretical) (by weitht)} = \frac{100}{23}\left[\frac{32}{12} \times C + 8\left(H - \frac{O}{8}\right) + S\right] \text{kg}$$

$$\text{Air (theoretical) (by volume)} = \frac{100}{21}\left[\frac{32}{12} \times C + 8\left(H - \frac{O}{8}\right) + S\right] \text{litre}$$

Excess Air for Combustion

It is necessary to supply excess air for complete combustion of the fuel. It is found out from the theoretical amount of air as follows.

The amount of air required if excess air is supplied.

$$\boxed{\frac{\text{Theoretical amount of air}}{100} \times [100 + \% \text{ of excess air}]}$$

4.5 FLUE-GAS ANALYSIS [ORSAT'S METHOD]

During combustion, a fuel is burnt in the combustion chamber with the help of air from the atmosphere. The mixture of gases (like CO_2, O_2, CO, etc.) coming out from the combustion chamber is called ***flue gas***. The analysis of a flue gas will give an insight into the complete or incomplete combustion process and also the efficiency of the engine. Orsat's apparatus is used for the analysis of flue gas.

Construction of Orsat's Apparatus

It consists of a water-jacketed burette connected in series to a set of three absorption bulbs, each containing a stopcock at the bottom. The other end is provided with a three-way stopcock, and the free end is further connected with a U-tube packed with fused $CaCl_2$ with a coverage of glass wool at both the ends of the U tube. The lower end of the burette is connected to a water reservoir by means of a long rubber tubing.

The **bulb I** consists of 'potassium hydroxide' solution and it absorbs only CO_2.

The **bulb II** consists of 'alkaline pyrogallol' solution and it absorbs only CO_2 and O_2.

The **bulb III** consists of 'ammoniacal cuprous chloride' solution and it absorbs CO_2, O_2 and CO.

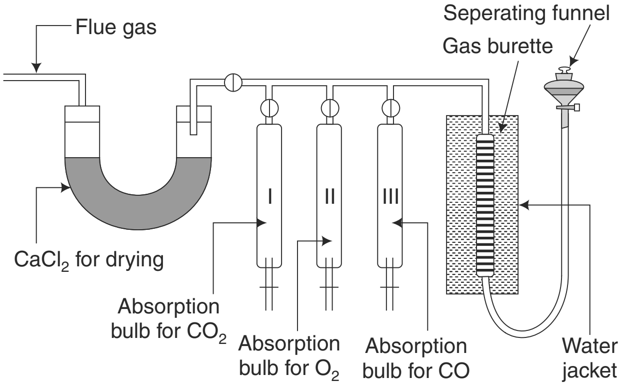


Fig. 4.2 *Orsat's apparatus*

Working of Orsat's Apparatus

At the beginning of the analysis, the absorption bulbs are filled with their respective solutions. The three-way stopcock is opened to the atmosphere and the reservoir is raised, till the burette is completely filled with water and air is excluded from the burette. The three-way stopcock is now connected to the flue-gas supply, the flue gas is sucked into the burette, and the volume of flue gas is adjusted to 100 cc by raising and lowering the reservoir. Then the three-way stop cock is closed.

(a) Absorption of CO_2

The stopper of the absorption bulb I, containing KOH solution, is opened and all the gases is passed into the bulb I by raising the level of water in the burette. The gas enters into the bulb I, where CO_2 present in the flue gas is absorbed by KOH.

The gas is again sent to the burette. This process is repeated several times to ensure complete absorption of CO_2. The decrease in volume of the flue gas in the burette indicates the volume of CO_2 in 100 cc of the flue gas.

(b) Absorption of O_2

The stop-cock of the bulb II is opened after closing the stopcock of the bulb I. The gas is again sent into the absorption bulb-II, where O_2 present in the flue gas is absorbed by alkaline pyrogallol. The decrease in volume of the flue gas in the burette indicates the volume of O_2.

(c) Absorption of CO

Finally, the stopcock of the bulb II is closed and stopcock of the bulb III is opened. The remaining gas is sent into the absorption bulb III, where CO present in the flue gas is absorbed by ammoniacal cuprous chloride. The decrease in volume of the flue gas in the burette indicates the volume of CO. The remaining gas in the burette after the absorption of CO_2, O_2 and CO is taken as nitrogen.

Significance of Flue-gas Analysis

- Based on the composition of the flue gas, it is possible to predict the complete or incomplete combustion process.
- If the flue gas contains any CO, it indicates the incomplete combustion in the combustion chamber and short supply of oxygen.
- If the flue gas contains O_2, it indicates excess supply of air and it is essential to reduce the air supply.

4.6 IMPORTANT TERMS RELATED TO COMBUSTION

4.6.1 Ignition Temperature

It is defined as the lowest temperature to which the fuel must be heated, so that it starts burning smoothly.

Besides sufficient supply of oxygen or air, every fuel requires heating to a definite temperature to start active combustion. This is known as ignition temperature. The ignition temperature of coal is about 300°C. In the case of liquid fuels, the ignition temperature is called the **flash point**, which ranges from 200−400°C. For gaseous fuels, the ignition temperature is in the order of 800°C.

4.6.2 Spontaneous Ignition Temperature (SIT)

It is defined as the minimum temperature at which the fuel catches fire (ignites) spontaneously without external heating.

If a coal, for example, is stored in such a way that heat is slowly dissipated, slow oxidation may produce sufficient heat to raise the temperature to ignite on its own. Fuels which have low ignition temperature can catch fire very quickly. On the other hand, if the ignition temperature is high, it is difficult to ignite the fuel. If the heat evolved in a system is unable to escape, temperature of the system goes on increasing and when SIT is reached, the system burns on its own.

4.6.3 Explosive Range or Limits of Inflammability

Most of the gaseous fuels have two percentage limits, called upper limit and lower limit. Those limits represent the percentage by volume of fuel present in fuel–air mixture. The range covered by these limits is termed the explosive range of the fuel.

For continuous burning, the amount of fuel present in the fuel-air mixture should not go below the lower limit or above the upper limit. For example, the explosive range of petrol–air mixture is 10:1. This means that when the concentration of a petrol–vapour in a petrol–air mixture is between 8 and 12 by volume, the mixture will burn on ignition. When the concentration of petrol vapour in a petrol–air mixture is below 8 (lower limit) or above 12 (upper limit) by volume, the mixture will not burn on ignition.

4.6.4 Calorific Intensity or Flame Temperature

It is the maximum temperature reached when the fuel is completely burnt in the theoretical amount of air.

When the fuel burns with a small flame, the entire heat is concentrated in a small area and the calorific intensity will be high. But while burning solid and liquid fuels as well as some gaseous fuels, much volatile matter is given off resulting in a large flame. Here the heat liberated gets distributed over a wide area and hence the calorific intensity will be low.

4.7 SOLID FUELS

4.7.1 Coal and its Varieties or Ranking of Coal

Coal is classified on the basis of its rank. The rank of coal denotes its degree of maturity. Vegetable matter, under the action of pressure, heat and anaerobic conditions, gets converted into different stages of coal, namely,

Peat → Lignite → Sub-bituminous → Bituminous → Anthracite

Anthracite is the oldest coal from the geological perspective. It is a hard coal composed mainly of carbon with little volatile content and practically no moisture. Lignite is the youngest coal from the geological perspective. It is a soft coal composed mainly of volatile matter and moisture content with low fixed carbon. **Fixed carbon** refers to carbon in its free state, not combined with other elements. **Volatile matter** refers to those combustible constituents of coal that vaporize when coal is heated.

(a) Peat

- Peat, considered to be a precursor of coal, has industrial importance as a fuel in many regions, for example, Ireland and Finland.
- In its dehydrated form, peat is a highly effective absorbent for fuel and oil spills on land and water.

(b) Lignite

- Lignite, also referred to as brown coal, is the lowest rank of coal and used almost exclusively as fuel for electric power generation.
- Jet is a compact form of lignite that is sometimes polished and has been used as an ornamental stone since the Iron Age.

(c) Sub-bituminous Coal

- Sub-bituminous coal, whose properties range from those of lignite to those of bituminous coal, are used primarily as fuel for steam-electric power generation.
- Additionally, it is an important source of light aromatic hydrocarbons for the chemical synthesis industry.

(d) Bituminous Coal

- Bituminous coal, a dense mineral, is black or sometimes dark brown, often with well-defined bands of bright and dull material.
- It is used primarily as fuel in steam-electric power generation, with substantial quantities also used for heat and power applications in manufacturing and to make coke.

(e) Anthracite

- Anthracite, the highest-ranking coal, is a harder, glossy, black coal used primarily for residential and commercial space heating.
- It may be divided further into metamorphically altered bituminous coal and petrified oil, as from the deposits in Pennsylvania.

Here, peat is the most immature coal, hence it is lowest in rank whereas anthracite is the most matured coal, and hence it is highest in rank.

> ***The process of conversion of lignite to anthracite is called coalification (or) metamorphism of coal.***

With the progress of coal-forming reaction, moisture content and oxygen content reduces and percentage of carbon increases. Also, calorific value increases from peat to bituminous.

Fig. 4.3 *Transportation of Coal*

Table 4.1 *Classification of solid fuels and their properties*

Fuel	***Nature***	***Calorific Value kcal–kg***	***Composition %***	***Uses***
Peat	Highly fibrous, light brown in colour	4000– 5400	C = 57 H = 06 O = 35	Domestic fuel, power generation
Lignite	Fibrous, brown-coloured coal	6500–7100	C = 67 H = 05 O = 26	Manufacture of producer gas and steam
Sub-bituminous coal	Black coloured, homogenious smooth mass	7000–7500	C = 77 H = 05 O = 16	Manufacture of gaseous fuels
Bituminous coal	Black, brittle burns with yellow smoky flame	8000–8500	C = 83 H = 05 O = 10	Power generation, coke making, domestic fuel
Anthracite	Hard and most matured coal, burns without smoke	8500–8700	C = 93 H = 03 O = 03	Boiler heating, metallurgical furnace

Table 4.2 *Production of coal by country and year (million tons)*

Country	***2006***	***2007***	***2008***	***Reserve Life (years)***
China	2380	2526	2782	41
USA	1053	1040	1062	224
EU	595	593	587	51
India	447	478	521	114
Australia	385	399	401	190
Russia	309	314	326	481

4.7.2 Analysis of Coal

Ultimate analysis and proximate analysis are used for the determination of the quality of any coal sample. Proximate analysis determines the fixed carbon, volatile matter, moisture and ash percentages. Ultimate analysis is used to determine the percentage of carbon, hydrogen, nitrogen and sulphur present in coal.

(a) Proximate Analysis

- The determination of the amount of moisture, volatile matter, fixed carbon and ash present in coal is called proximate analysis.
- It is useful in deciding its utilization for a particular industrial use.

(i) Estimation of Moisture Content in Coal

Accurately weigh 1 g of powdered dry coal sample in a previously weighed, clean silica crucible. Heat the sample by placing in a hot-air oven at 100 to 105°C for one hour. Then the sample is cooled in a dessicator to room temperature and weighed again. The loss in weight represents moisture.

$$\boxed{\therefore \text{ \% of moisture in coal} = \frac{\text{Loss in weight of coal}}{\text{Weight of coal initially taken}} \times 100}$$

(ii) Estimation of Volatile Matter (VM) in Coal

After the analysis of moisture content, the crucible with the residual coal sample is covered with a lid, and it is heated at 950 ± 20°C for 7.0 minutes in a muffle furnace. Percentage of volatile matter can be calculated from the loss in weight of the coal sample.

$$\boxed{\therefore \text{ \% of volatile matter in coal} = \frac{\begin{array}{c}\text{Loss in weight of}\\ \text{moisture-free coal}\end{array}}{\text{Weight of coal initially taken}} \times 100}$$

(iii) Estimation of Ash in Coal

After the analysis of volatile matter, the crucible with the residual coal sample is heated without lid at 700 ± 50°C for 30 minutes in a muffle furnace.

The percentage of ash content can be calculated from the weight of ash formed.

$$\boxed{\therefore \text{ \% of ash in coal} = \frac{\text{Weight of ash formed}}{\text{Weight of coal taken}} \times 100}$$

(iv) Estimation of Fixed Carbon

It is determined by subtracting the sum of total moisture, volatile matter and ash contents from 100.

$$\boxed{\text{\% of fixed carbon} = 100 - \text{\% of [moisture + VM + ash]}}$$

(v) Significance or Importance of Proximate Analysis

1. Moisture

High moisture content in coal is undesirable because it

- Reduces calorific value of coal
- Increases the consumption of coal for heating purpose
- Lengthens the time of heating

The lesser the moisture content, the better the quality of coal.

2. Volatile Matter

The coal with higher volatile content

- Ignites easily (i.e. it has lower ignition temperature)
- Burns with long yellow smoky flame
- Has lower calorific value
- This gives more quantity of coal gas when it is heated in absence of air.

A good-quality coal should have lesser volatile matter.

3. Ash

- Ash is the combustion product of mineral matters present in the coal. It consists mainly of SiO_2, Al_2O_3 and Fe_2O_3 with varying amounts of other oxides such as Na_2O, CaO, MgO, etc.
- Ash containing oxides of Na, Ca and Mg melts early (low melting ash). During coke manufacture, the low-melting ash forms a fused, lumpy, expanded mass which block the interspaces of the 'grate', thereby obstructing the supply of air leading to irregular burning of coal and loss of fuel.
- High ash content in coal is undesirable because it (a) increases transporting, handling, storage costs, (b) is harder and stronger, and (c) has lower calorific value.

A good-quality coal should contain lesser ash content.

4. Fixed Carbon

It is the pure carbon present in coal.

Higher the fixed carbon content of the coal, higher will be its calorific value.

(b) Ultimate Analysis

The ultimate analysis indicates the various elemental chemical constituents such as carbon, hydrogen, oxygen, sulphur, etc. It is useful in determining the quantity of air required for combustion and the volume and composition of the combustion gases. This information is required for the calculation of flame temperature and the flue duct design etc.

The determination weight percentage of carbon, hydrogen, nitrogen, oxygen and sulphur of the pure coal free from moisture and inorganic constituents is called ultimate analysis.

(i) Determination of Carbon and Hydrogen in Coal

A known amount of coal is burnt in the presence of oxygen, thereby converting carbon and hydrogen of coal into CO_2 ($C + O_2 \rightarrow CO_2$) and H_2O ($H_2 + ½\ O_2 \rightarrow H_2O$) respectively. The products of combustion (CO_2 and H_2O) are made to pass over weighed tubes of anhydrous $CaCl_2$ and KOH, which absorb H_2O and CO_2 respectively.

The increase in the weight of the $CaCl_2$ tube represents the weight of water formed, while increase in the weight of the KOH tube represents the weight of CO_2 formed. The percentage of carbon and hydrogen in coal can be calculated as follows.

Let X—the weight of coal sample taken
Y—the increase in the weight of KOH tube
Z—the increase in the weight of $CaCl_2$ tube

Carbon

$$\underset{12}{C} + \underset{32}{O_2} \longrightarrow \underset{44}{CO_2}$$

44 g of CO_2 contain 12 g of carbon,

i.e, 1 g of CO_2 contains $\frac{12}{44}$ g of carbon.

$\therefore$ Y g of CO_2 contains $\frac{12}{44} \times Y$ g of carbon.

$$\boxed{\%\text{ of C in coal} = \frac{12}{44} \times \frac{Y}{X} \times 100}$$

Hydrogen

$$\underset{2}{H_2} + 1/2\ \underset{16}{O_2} \longrightarrow \underset{18}{H_2O}$$

18 g of water contains 2 g of hydrogen.
1 g of water contains 2/18 g of hydrogen.

$\therefore$ Z g of water contains = $\frac{2}{18} \times Z$ g of hydrogen.

$$\boxed{\%\text{ of hydrogen in coal} = \frac{2}{18} \times \frac{Z}{X} \times 100}$$

(ii) Determination of Nitrogen in Coal

Nitrogen estimation is done by Kjeldahl's method. A known amount of powdered coal is heated with conc. H_2SO_4 and K_2SO_4 in a long-necked flask (called Kjeldahl's flask), thereby converting nitrogen of coal to ammonium sulphate. When the clear solution is obtained (i.e. the whole nitrogen is converted into ammonium sulphate), it is heated with 50% NaOH solution.

$$(NH_4)_2\,SO_4 + 2NaOH \longrightarrow Na_2SO_4 + 2NH_3\uparrow$$

The ammonia, thus formed, is distilled over and is absorbed in a known quantity of standard 0.1N HCl solution. The volume of unused 0.1N HCl is then determined by titrating against a standard NaOH solution.

Thus, the amount of acid neutralized by liberated ammonia from coal is determined.

Let,

Volume of 0.1N HCl initially taken = A ml

Volume of unused HCl = B ml

Acid neutralised by ammonia = $(A - B)$ ml

$$\begin{aligned}\text{We know that 1000 ml of 1N HCl} &= \text{1 mole of HCl}\\ &= \text{1 mole of } NH_3\\ &= \text{14 g of } N_2\end{aligned}$$

$$\therefore\ (A - B) \text{ ml of 0.1N HCl} = \frac{14 \times (A - B) \times 0.1}{1000 \times 1N} \text{ g of } N_2$$

$$X \text{ g of coal sample contains } \frac{14 \times (A - B) \times 0.1}{1000 \times 1N} \text{ g of } N_2$$

$$\boxed{\%\text{ of nitrogen} = \frac{14 \times \text{Volume of acid consumed} \times \text{Normality}}{1000 \times \text{weight of coal sample (X)}} \times 100}$$

(iii) Determination of Sulphur in Coal

A known amount of coal is burnt completely in a bomb calorimeter in the presence of oxygen. Ash, thus obtained, contains sulphur of coal as sulphate, which is extracted with dil HCl. The acid extract is then treated with $BaCl_2$ solution to precipitate sulphate as $BaSO_4$.

The precipitate is filtered, washed, dried and weighed to calculate the sulphur in coal as stated below:

Let,

X = weight of coal sample taken

M = weight of $BaSO_4$ precipitate formed.

$$\underset{32}{S} + 2O_2 \longrightarrow SO_4 \longrightarrow \underset{233}{BaSO_4}$$

233 g of $BaSO_4$ contains 32 g of sulphur.

i.e. 1 g of $BaSO_4$ contains 32/233 g of sulphur.

$\therefore$ M g of $BaSO_4$ contains (32/233) × M g of sulphur

$$\boxed{\% \text{ of sulphur in coal} = \frac{32}{233} \times \frac{M}{X} \times 100}$$

(iv) Significance or Importance of Ultimate Analysis

1. Carbon and Hydrogen

- The amount of carbon and hydrogen is vital for the calculation of air required for complete combustion and design the combustion chamber.
- The percentage of carbon is helpful in the classification of coal.

Good-quality coal should have more percentage of C and H.

2. Nitrogen

- Nitrogen is a noncombustible matter. Hence, it does not have any calorific value, and its presence in coal is undesirable.

Good-quality coal should have very little nitrogen content.

3. Sulphur

- Even though sulphur is a combustible matter, the combustion products of sulphur, i.e. SO_2 and SO_3, are harmful and have corrosion effects on equipment.
- Coal containing sulphur is not suitable for the preparation of metallurgical coke as it affects the properties of the metal.

Presence of sulphur is not desirable in coal.

4. Oxygen

- Presence of oxygen consumes hydrogen, and thereby reduces the calorific value.
- As the oxygen content increases, the moisture content and the moisture will consume some amount of heat for evaporation.

A good-quality coal should contain lesser moisture content.

(c) Carbonisation of Coal

Heating of coal in the absence of air at high temperature to produce a residue coke, tar and coal gas is called carbonisation.

(i) Caking of Coal: When coal is heated strongly, the mass becomes soft and coherent. Then it is called caking of coal.

(ii) Coking of Coal: If the mass produced is hard, porous and strong then it is called coking of coal.

4.8 METALLURGICAL COKE

When bituminous coal is heated strongly in the absence of air, the volatile matter escapes out and a lustrous, dense, strong, porous and coherent mass is left, which is called metallurgical coke.

4.8.1 Properties or Characteristics of Metallurgical Coke

The most important industrial use of coke is in the metallurgical industry, especially in the blast furnace. Good coke for metallurgy should possess the following characteristics.

(i) **Purity** High purity of coke is desirable. The moisture and ash content should be low.

(ii) **Porosity** As the porosity increases, the combustion rate of the coke will increase. This happens because the oxygen comes in contact with coke, which helps for its complete combustion. A good coke should possess high porosity.

(iii) **Strength** The coke should be strong and hard, which helps it to withstand high temperature.

(iv) **Size** The size of the coke should be uniform and medium for uniform heating.

(v) **Calorific Value** The calorific value of good coke should be high.

(vi) **Combustibility** It should burn easily and smoothly.

(vii) **Reactivity** It refers to its ability to react with O_2, CO_2, steam and air. The metallurgical coke must have low reactivity.

(viii) **Cost** It must be cheap and readily available.

4.8.2 Manufacture of Metallurgical Coke

Two types of ovens are mainly used for metallurgical coke production:

(a) Beehive coke-oven process

(b) Otto Hoffman's by-product method

(a) Beehive Coke-oven Process

The beehive oven (due to its shape) is a primitive obsolete process. The oven is a dome-shaped structure and made up of fire bricks. There are two openings, one at the top and the other at the side. Coal is charged through the top circular opening, whereas coke is removed through the side door after carbonization. The side door also acts as an air inlet. Its typical dimensions are, height = 2 m; base diameter = 3.5 m and capacity = 5 tons of coal.

First, some air is supplied into the oven to ignite the coal. The volatile matter present in coal escapes and burns inside. Therefore, heat for carbonization is supplied by burning of volatile matter and partly by coal itself.

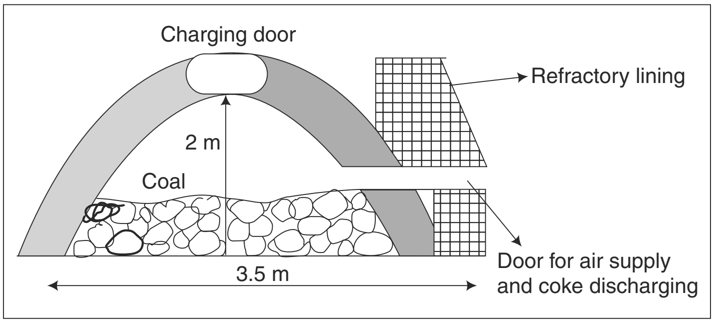


Fig. 4.4 *Beehive coke-oven*

Carbonization proceeds from top to bottom and it takes about 3 to 4 days to complete. The hot coke is then removed through the side door and quenched with water.

Demerits

- It is a batch process.
- Not suitable for large-scale production.
- All the volatile matter present in coal escapes into the atmosphere as waste, we cannot recover any by-product.
- Large coking time and coke yield of only 60% are its other demerits.

(b) Otto Hoffman's By-product Coke Oven

To recover various by-products which are lost in the beehive oven method and also increase the thermal efficiency of the carbonization process, Otto Hoffman developed the modern by-product coke oven. The oven is heated externally by the hot flue gases which come out of the combustion chamber.

The coal is heated in a silica chamber having a size of about 10–12 m long, 3–4 m height and 0.4–0.45 m wide. Each chamber is provided with a charging hole at the top. It is also provided with a gas outlet valve at the top and an iron door at each end for discharging coke.

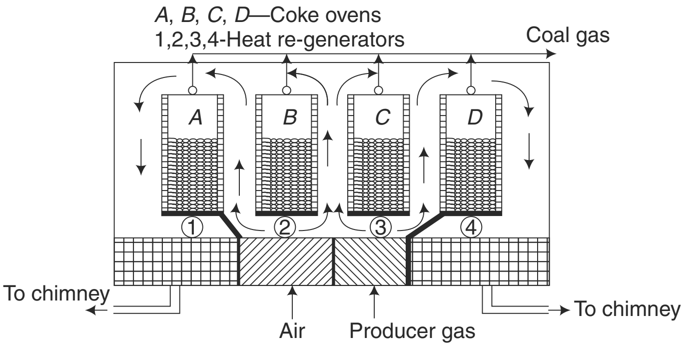


Fig. 4.5 *Otto Hoffman by-product coke oven*

The finely crushed coal is introduced through the charging door at the top of the chambers which are then closed. The chambers are heated up to 1200°C by burning pre-heated air and the producer-gas mixture in the interspaces between the chambers.

The flue gases produced during combustion, before escaping to the chimney, pass on their heat to the walls of chamber first and third hot regenerators. When the first and third hot regenerators attain the temperature for about 1000°C, the flue gas is diverted to second and fourth hot regenerators and the incoming fuel-air mixture is passed through first and fourth regenerators to gain heat and efficient combustion.

For economical heating, the directions of inlet and flue gases are changed frequently. The above system of recycling the flue gases to produce heat energy is known as the ***regenerative system of heat economy.*** When the process is complete, the coke is removed and quenched with water.

In this process, complete carbonization takes about 12–18 hours. The yield of coke is about 70%.

(c) Recovery of By-products

The gas coming out from the oven is known as **coke-oven gas** and is mainly composed of ammonia, H_2S, naphthalene, aromatics, tar, etc.

(i) Removal of Tar

The coke-oven gas is first passed through a tower in which liquor ammonia is sprayed. Tar and dust get collected in a tank below, which is heated by a steam coil to recover back the ammonia sprayed. The ammonia is used again and again.

(ii) Removal of Ammonia

The gas is then passed through the other tower where water is sprayed. Ammonia gets converted to NH_4OH.

(iii) Benzene and Other Aromatic Compounds

The gas is then passed through the next tower in which creosote oil is sprayed. Benzene and other aromatic compounds are dissolved in the oil and recovered.

(iv) Hydrogen Sulphide

The gas then enters into a purifying chamber packed with Fe_2O_3, which removes any sulphur compound present in coal gas.

(d) Advantages

- High thermal efficiency and less carbonization time.
- Valuable gases (like coal gas, ammonia, benzene, etc.) are recovered as by products.
- Heating is done externally by producer gas.

4.9 LIQUID FUELS

> *"Loss of even one drop of oil every second can cost you over 4000 litres a year".*

4.9.1 Petroleum

Petroleum, or crude oil is a naturally occurring oily, bituminous liquid composed of various organic chemicals. It is found in large quantities below the surface of the earth and is used as a fuel and as a raw material in the chemical industry. Modern industrial societies use it primarily to achieve a degree of mobility on land, at sea, and in the air, something that was barely imaginable less than 100 years ago. In addition, petroleum and its derivatives are used in the manufacture of medicines, fertilizers, foodstuffs, plastics, building materials, paints, etc.

The approximate composition of petroleum is

C = 80 – 84%
H = 10 – 14 %
S = 0.1 – 0.5 %
N + O = Negligible

(a) Formation of Petroleum

Petroleum is formed under the earth's surface by the decomposition of marine organisms. The remains of tiny organisms that live in the sea and, to a lesser extent, those of land organisms are carried down to the sea by rivers and of plants that grow on the ocean bottoms are enmeshed with the fine sands and silts that settle to the bottom in quiet sea basins. Such deposits, which are rich in organic material, become the source for the generation of crude oil.

(b) Classification of Petroleum

- Three broad classes of crude petroleum exist: ***the paraffin types, the asphaltic types, and the mixed-base types***.
- The paraffin types are composed of molecules in which the number of hydrogen atoms is always two more than twice the number of carbon atoms. The characteristic molecules in the asphaltic types are naphthenes, composed of twice as many hydrogen atoms as carbon atoms.
- The mixed-base group has both paraffin hydrocarbons and naphthenes.
  - (i) Paraffin-based oil contains mainly *n*-alkanes, e.g. **Pennsylvanian and gulf coast oil**.
  - (ii) Asphalt base oil contains aromatic and alicyclic hydrocarbons. e.g. **Californian oil**.
  - (iii) Mixed-base oil contains higher proportion of aromatics and naphthenes (cyclo alkanes), e.g. **Mexican oil**.

(c) Oil Recovery

The oil industry has developed methods for supplementing the production of crude oil that can be obtained mostly by taking advantage of the natural reservoir energy. These supplementary methods, collectively known as enhanced oil-recovery technology, can increase the recovery of crude oil. Two successful supplementary methods are in use at this time: water injection and steam injection.

(i) Water Injection

In a completely developed oil field, the wells may be drilled upto anywhere from 60 to 600 m (200 to 2,000 ft) from one another, depending on the nature of the reservoir. If water is pumped into alternate wells in such a field, the pressure in the reservoir as a whole can be maintained or even increased. In this way, the rate of production of the crude oil also can be increased; in addition, the water physically displaces the oil, thus increasing the recovery efficiency. In some reservoirs with a high degree of uniformity and little clay content, water flooding may increase the recovery efficiency to as much as 60 per cent or more of the original oil in place. Water flooding was first introduced in the Pennsylvania oil fields, more or less accidentally, in the late 19th century, and it has since spread throughout the world.

(ii) Steam Injection

Steam injection is used in reservoirs that contain very viscous oils, those that are thick and flow slowly. The steam not only provides a source of energy to displace the oil, it also causes a marked reduction in viscosity (by raising the temperature of the reservoir), so that the crude oil flows faster under any given pressure differential.

(iii) Offshore Drilling

Another method to increase oil-field production has been the construction and operation of offshore drilling rigs. The drilling rigs are installed, operated, and serviced on an offshore platform in water up to a depth of several hundred metres; the platform may either float or sit on legs planted on the ocean floor, where it is capable of resisting waves, wind, and in Arctic regions, ice floes. Successful bore holes have been drilled right on target, in this way, to depths of more than 6.4 km (more than 4 miles) from the surface of the ocean.

(d) Refining of Petroleum, or Crude Oil

The process of removing impurities and separating out the oil into various fractions having different boiling points is known as refining of petroleum.

Once oil has been produced from an oil field, it is treated with chemicals and heat to remove water and solids, and the natural gas is separated. The oil is then stored in a tank, or battery of tanks, and later transported to a refinery by truck, railroad tank car, barge, or pipeline. Large oil fields all have direct outlets to major, common-carrier pipelines.

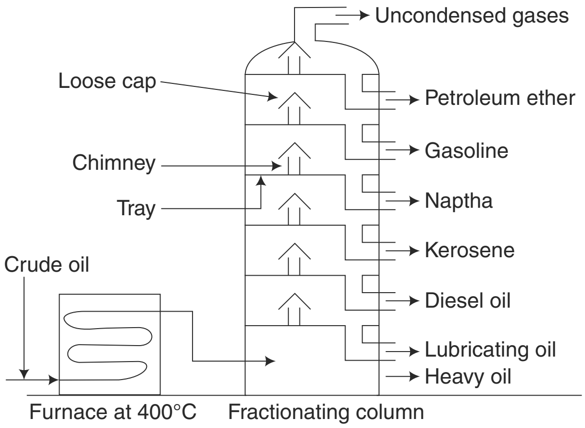


Fig. 4.6 *Distillation of various fractions from petroleum*

(i) Removal of Impurities

The impurities present in the oil are the fine water droplets, NaCl, $MgCl_2$, sulphur, etc. The crude oil is an extremely stable emulsion of oil and salt water. Water is separated from the oil by Cottrell's process using ring electrodes. In this method, the crude oil is allowed to flow between two highly charged electrodes. The colloidal water droplets combine to form large drops, which are then separated from oil.

Modern techniques like electrical desalting are used to remove NaCl and $MgCl_2$ from oil. Sulphur is removed by treating the oil with copper oxide and separated by filtration.

(ii) Fractional Distillation

The purified crude oil is heated in a furnace, called oil heater, where the temperature will be around 400°C. Here the oil gets vapourised. The hot vapours are then sent to the fractionating column.

It is a tall cylindrical tower consisting of a number of horizontal stainless-steel trays at short distances. Each tray is provided with a small chimney, which is covered with a loose cap. The tower will be hot at the lower end and comparatively cooler at the upper end. When the oil vapours go up in the tower, they become cool and condense. The heavier compounds having higher boiling points get cooled first and condensed in the trays whereas the fractions having lower boiling points condense near the top of the tower.

Lower fractions are used after purification while the high-boiling-point fractions are subjected to a cracking operation to get more useful lower fractions.

(e) Important Fractions of Petroleum Distillation

(i) Petrol or Gasoline

- It is a low boiling fraction of petroleum obtained between 40−120° C. It is a mixture of hydrocarbons pentane to octance (in terms of carbon atoms $C_5–C_9$).
- Its calorific value is about 11,250 kcal/kg.
- It is used as fuel in the ICE of automobiles and aeroplanes. Its antiknock value can be improved by the addition of TEL.

(ii) Naphtha

- Naphtha is a light, colourless to straw-coloured liquid which distills off from petroleum between 120–180° C. It is a mixture of hydrocarbons $C_9–C_{10}$ (nonane - decane) carbon atoms.
- The lightest of the distillates are used as solvents for fats and rubber, whereas the heaviest distillates are used for the fuel.
- Naphtha is also called *white spirit* which is used in dry cleaning as varnish thinner, for floor and furniture polishes, etc.

(iii) Kerosene

- It is also a high boiling fraction of petroleum obtained between 180-250° C. It is a mixture of $C_{10} – C_{16}$ hydrocarbons.
- Its calorific value is about 11,100 kcal/kg.
- It is used as domestic fuel and jet engine fuel.

(iv) Diesel

- It is relatively a high boiling point fraction of petroleum obtained between 250-320°C. It is a mixture of hydrocarbons in terms of carbon atoms $C_{15} – C_{18}$.
- Its calorific value is about 11,000 kcal/kg.
- It is used as fuel for compression ignition engines. Its antiknock value can be improved by doping with isoamyl nitrate.

(v) Fuel Oil

- The residue of petroleum after distilling off the lighter fractions is called fuel oil. It is distilled in vacuum into the following fractions.
  (a) Light fuel oil = 350 – 420°C
  (b) Heavy neutral oil = 420 – 500°C
- A typical analysis of fuel oil is C = 86% ; H = 12% ; S = 1% ; H_2O = 0.6%; Sediments = 0.4% .
- Its calorific value is about 9200 kcal/kg.

- It is used as industrial fuel and in the feedstock for thermal cracking plants.

(vi) Asphalt or Tar

- Asphalts are produced by (i) the deep vacuum distillation of fuel oil, and (ii) the oxidation of residual petroleum by air at a higher temperature.
- Asphalts have the highest viscosity of all petroleum-refining products. Petroleum asphalts are marketed in the liquid, semisolid and solid forms.
- They are intended for roadmaking and as roofing material. They are also used for waterproofing of concrete and reservoirs, waterproofing paints and in the prevention of corrosion.

Table 4.3 *Various fractions of petroleum distillation*

S. No	Name of the Fraction	Hydrocarbons in terms of Carbon Atom	Boiling Point in °C	Uses
1.	Uncondensed gases	C_1–C_4	< 30	LPG—domestic fuel
2.	Petroleum ether	C_5–C_7	30–70	Solvents for varnish and rubber
3	Gasoline or petrol	C_5–C_8	40–120	Fuel in ICE of automobiles and aeroplanes
4	Naphtha or Solvent spirit	C_9–C_{10}	120–180	Solvent in dry cleaning
5	Kerosine oil	C_{10}–C_{16}	180–250	Domestic fuel, Jet engine fuel.
6	Diesel oil or gas oil	C_{15}–C_{18}	250–320	Diesel engine fuel
7	Heavy oil	C_{17}–C_{30}	320–400	To produce cracked petrol

4.9.2 Petrol or Gasoline

- It is a low boiling fraction of petroleum obtained between 40–120°C.
- It is a mixture of hydrocarbons pentane to nonane (in terms of carbon atoms C_5–C_9).
- Its calorific value is about 11, 250 kcal/kg.
- It is used as fuel in ICE of automobiles and aeroplanes.
- Its antiknock value can be improved by the addition of **Tetra Ethyl Lead (TEL)**.

The crude oil on fractional distillation yields only about 15–20% gasoline. This is known as straight-run-gasoline.

The quality of straight-run gasoline is not so good. It contains mainly straight chain paraffins, which ignite readily and more rapidly than any other hydrocarbons and hence, it produce knocking (unwanted sound) in IC engines.

In order to overcome these difficulties and also to improve the quality of gasoline, high boiling fractions are cracked into more valuable low boiling fractions suitable for SI engines. The gasoline obtained by cracking is called cracked gasoline.

Cracking

The formation of low boiling hydrocarbons of low molecular weight by the decomposition of high boiling hydrocarbons of high molecular weight is called cracking.

$$\underset{\substack{n\text{-tetradecane} \\ \text{B.pt. 253.7°C}}}{C_{14}H_{30}} \longrightarrow \underset{\substack{n\text{ pentane} \\ \text{B. pt : 36°C}}}{C_5H_{12}} + \underset{\substack{\text{nonene} \\ \text{B.pt. 143°C}}}{C_9H_{18}}$$

4.9.3 Manufacture of Synthetic Petrol

Petrol can be synthesized by any one of the following methods.

I. Polymerization
  (a) Thermal polymerization
  (b) Catalytic polymerization
II. Hydrogenation of coal
  (a) Bergius process or direct process.
  (b) Fisher–Tropsch process or indirect process.
III. Alkylation

I Polymerization

The gases produced in cracking contain C_3 and C_4 olefins (isopropylene, isobutylene, etc.) and alkanes (methane, ethane, propane, butane). These gases undergo polymerization in the presence of a catalyst, (H_3 PO_4) at suitable temperature and pressure to give gasoline (polymer petrol), rich in branched-chain hydrocarbons.

Hence, polymerization is mainly for the production of superior gasoline and is complementary to catalytic cracking.

Polymerization is of two types:

(a) Thermal Polymerization: Polymerisation of cracked gases is carried out at 500–600°C and 70–350 kg/cm^2 pressure. The product is the gasoline and gas oil mixture, from which gasoline is separated by fractionation.

(b) Catalytic Polymerization: This process is carried out in the presence of a catalyst like H_3PO_4. By this method, isobutylene can be polymerized to give higher olefins which is hydrogenated to gasoline hydrocarbons.

II Hydrogenation of Coal

Coal contains 4.5 % of hydrogen, whereas petroleum contains 18 % of hydrogen. So coal is a hydrogen-deficient compound, if coal is heated with hydrogen at high temperature and high pressure, it is converted in to gasoline.

The preparation of liquid fuels from solid coal is called hydrogenation of coal.

Petrol can be synthesized by destructive hydrogenation of coal (Bergius process) and liquification of coal (Fischer–Tropsch process).

(a) Bergius Process, or Direct Process

The raw materials used in this process are coal dust, heavy oil and nickel oleate or tin oleate.

A coal paste is prepared by mixing coal dust with heavy oil and catalyst. It is then pumped into the converter where the paste is heated to 450–500°C under 200–250 atm in presence of hydrogen.

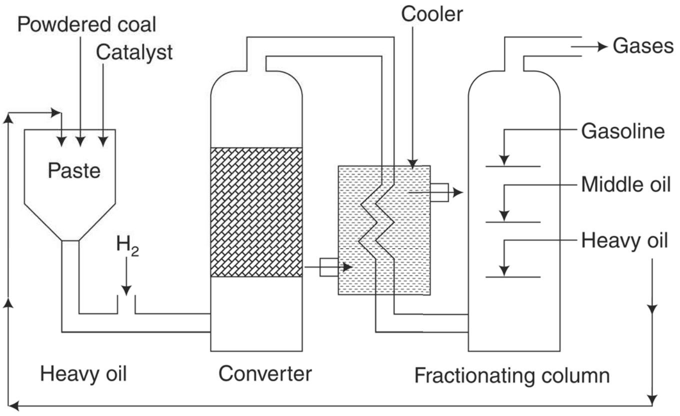
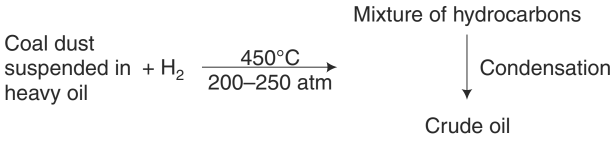


Fig. 4.7 *Bergius process*

The reaction products mainly contain a mixture of hydrocarbons.



$$\begin{array}{l}\text{Coal dust}\\ \text{suspended in}\\ \text{heavy oil}\end{array} + H_2 \xrightarrow[200\text{–}250\ \text{atm}]{450°\text{C}} \text{Mixture of hydrocarbons} \xrightarrow{\text{Condensation}} \text{Crude oil}$$

Since the reaction is exothermic, the vapours leaving the converter are condensed in the condenser to give synthetic petroleum or crude oil.

The oil is then fractionally distilled to give

(i) Petrol

(ii) Middle oil

(iii) Heavy oil

Middle oil is again hydrogenated in presence of solid catalysts to produce more amount of gasoline. Heavy oil is used for making paste with fresh coal dust. The yield is about 60%.

(b) Fischer–Tropsch Process

The raw materials used in this process are hard coke, steam to produce water gas, i.e. water gas is obtained, by passing steam over red-hot coke.

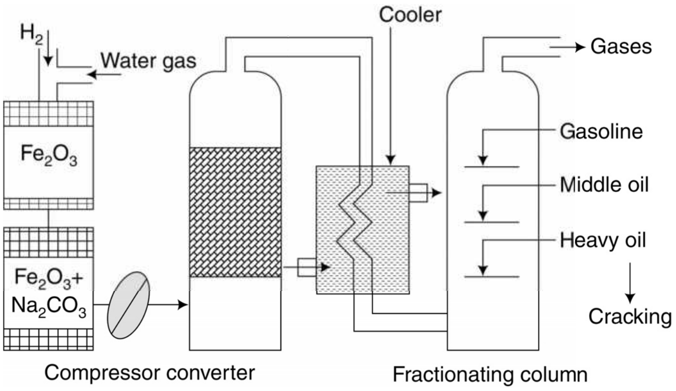


Fig. 4.8 *Fisher–Tropsch process*

$$C + H_2O \xrightarrow{1200°C} \underset{\text{Water gas}}{CO + H_2}$$

The first step in this process is purification of gas. To remove H_2S, the gas is passed through Fe_2O_3 and to remove organic sulphur compounds, the gas is again passed through a mixture of Fe_2O_3 and Na_2CO_3.

The purified gas is compressed to 5–25 atm. and passed over a catalyst bed containing oxides of Th, Co and Mg at 200–300°C. While passing the purified gas through this catalyst bed, it is converted to straight-chain paraffins and olefins.

$$n\,CO + (2n + 1)\,H_2 \longrightarrow \underset{n\text{-paraffins}}{C_nH_{2n+2}} + n\,H_2O$$

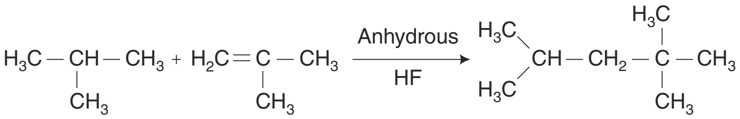
$$n\,CO + 2n\,H_2 \longrightarrow \underset{\text{olefins}}{C_nH_{2n}} + n\,H_2O$$

Since the reactions are exothermic, the vapours leaving the vessel are condensed in the condenser to give petroleum. It is fractionally distilled to yield petrol and heavy oil.

III Alkylation

Replacement of hydrogen atom from a hydrocarbon by an alkyl group is known as alkylation.

Example:



Isobutane Isobutene Iso-octane

The reaction of isobutane and isobutene in the presence of anhydrous HF at room temperature gives iso-octane. This process is highly useful for the production of high-quality petrol.

Table 4.4 *Comparison of straight-run, cracked and polymer gasoline*

S.No	***Straight-run Petrol***	***Cracked Petrol***	***Polymer Petrol***
1.	Obtained from straight distillation of crude oil	Obtained from heavy oil	Obtained from low molecular weight gaseous fraction
2.	Contains only *n*-alkanes.	Contains isoparaffins and aromatics.	Contains more of branched chain hydrocarbons
3.	Composition range C_5–C_9	Narrow range	Very narrow range
4.	Low octane number	Higher octane number	Higher octane number

(c) Purification of Petrol or Gasoline

Gasoline or petrol, obtained either from crude oil or synthetic process, may contain some undesirable impurities. They are mainly unsaturated olefins, colouring matters, sulphur compounds, etc.

The unsaturated olefins get oxidized and polymerized thereby causing gum and sludge formation on storing.

On the other hand, sulphur compounds lead to corrosion of ICE and also affect tetra ethyl lead which is added to gasoline to obtain good petrol. So these undesirable contents must be removed from gasoline. Unsaturated olefins and colouring matter are removed by using adsorbents like Kieselguhr, Fuller's earth, etc.

- Sulphur containing petrol is known as **sour spirit**.
- The process of desulphurization of petrol is called sweetening of petrol.

(d) Desulphurization

It can be done by Doctor's treatment, i.e. petrol is treated with an alkaline solution of sodium plumbite (Doctor's solution).

The resulting disulphide (lead mercaptide) in gasoline are extracted by using suitable solvent. After refining of gasoline, some inhibitors or antioxidants are added in order to retard the oxidation of olefins (olefin peroxide) which cause the formation of gum on storage.

4.9.4 Engines

Fractions like petrol and diesel oil are used as engine fuels. Piston engines can be divided into Spark Ignition (SI) and Compression Ignition (CI) engines. The former consumes petrol and the latter operates on diesel oil.

SI Engines

Today, internal combustion engines in cars, trucks, motorcycles, aircraft, construction machinery and many others, most commonly use a **four-stroke cycle**. The four strokes refer to intake, compression, combustion (power), and exhaust strokes that occur during two crankshaft rotations per working cycle of the gasoline engine and diesel engine.

1. Intake Stroke On the *intake* or *induction* stroke of the piston, the piston descends from the top of the cylinder to the bottom of the cylinder, reducing the pressure inside the cylinder. A mixture of fuel and air is forced by atmospheric (or greater) pressure into the cylinder through the intake port. The intake valve(s) then close.

2. Compression stroke With both intake and exhaust valves closed, the piston returns to the top of the cylinder compressing the fuel–air mixture. This is known as the *compression* stroke.

3. Power stroke While the piston is close to the top-dead centre, the compressed air–fuel mixture is ignited, usually by a spark plug (for a gasoline or Otto cycle engine) or by the heat and pressure of compression (for a diesel cycle or compression ignition engine). The resulting massive pressure from the combustion of the compressed fuel–air mixture drives the piston back down toward the bottom-dead centre with tremendous force. This is known as the *power* stroke, which is the main source of the engine's torque and power.

4. Exhaust stroke During the *exhaust* stroke, the piston once again returns to the top-dead centre while the exhaust valve is open. This action evacuates the products of combustion from the cylinder by pushing the spent fuel–air mixture through the exhaust valve(s).

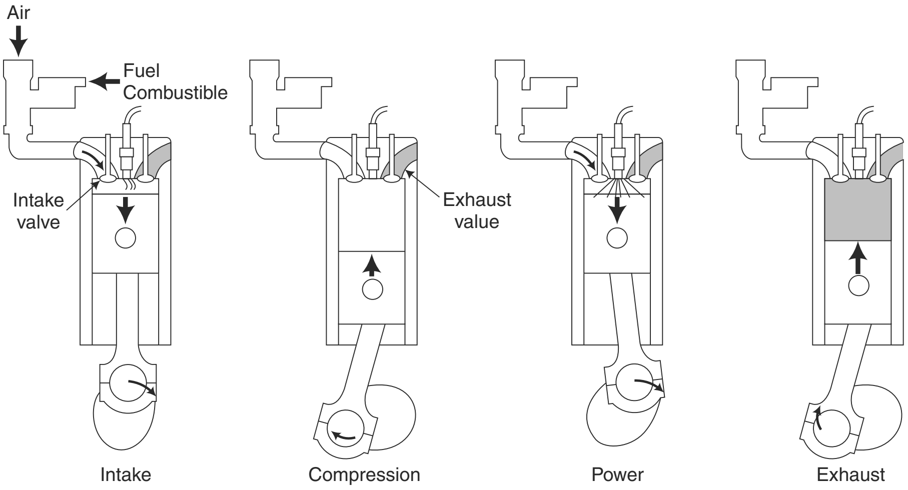


Fig. 4.9 *Various strokes on fuel engines*

(i) Knocking in Internal Combustion Engines

Knocking is a tendency of a fuel (petrol and diesel), which produces a badly and uncontrolled metallic sound in the combustion chamber during the combustion.

(ii) Knocking in SI Engines

A good normal petrol has to burn at the beginning of the power stroke when it is ignited with the help of a spark plug. Instead, a little amount of petrol will start to burn at the end of the second stroke (compression stroke). The rest of the petrol will burn in the third stroke when it is ignited with the spark plug. This produces an unwanted sound in the cylinder, called knocking. Petrol produces premature ignition is called **petrol knock**. This type of knocking creates unwanted sound and also reduces the efficiency of engines.

(iii) Chemical Structure and Knocking

The knocking tendency decreases as follows:

n-alkanes ⟶ Isoparaffins ⟶ Olefins ⟶ Naphthenes ⟶ Aromatics

n-alkanes have the lowest antiknock values. So the presence of maximum quantity of aromatics and minimum quantity of *n*-alkanes is desirable in petrol.

(iv) Measurement of Knocking in SI Engines (Octane Number)

Octane number expresses the knocking characteristics of petrol. The *n*-heptane (a constituent of petrol) knocks very badly, so its antiknock value has been given as zero. On the other hand, iso-octane (also a constituent of petrol) gives very little knocking, so its antiknock value has been given as 100.

Octane number can defined as percentage of iso-octane present in iso-octane and *n*-heptane mixture, which matches the same knocking characteristics of gasoline mixture test sample".

For example, petrol with the same knocking characteristics as a mixture of 90% iso-octane and 10% heptane would have an octane rating of 90. This does not mean that the petrol contains just iso-octane and heptane in these proportions, but that it has the same detonation resistance properties. Because some fuels are more knock-resistant than iso-octane, the definition has been extended to allow for octane numbers higher than 100.

Octane rating does not relate to the energy content of the fuel. It is only a measure of the fuel's tendency to burn in a controlled manner, rather than exploding in an uncontrolled manner. Where octane is raised by blending in ethanol, energy content per volume is reduced.

It is possible for a fuel to have an octane number greater than 100, because iso-octane is not the most knock-resistant substance available. Racing fuels, Liquefied Petroleum Gas (LPG), and alcohol fuels such as methanol or ethanol may have octane ratings of 110 or significantly higher ethanol's octane Number is 129.

(v) Improvement of Antiknock Value (Leaded Petrol)

Typical 'octane booster' gasoline additives include methyl *tert*-butyl ether, ethyl *tert*-butyl ether, isooctane and toluene. Lead, in the form of tetra-ethyl lead, was once a common additive, but since the 1970s, its use in most of the industrialised world has been restricted, and its use is currently limited mostly to aviation gasoline.

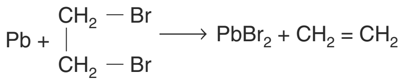
Fig. 4.10 *A US petrol pump offering five different octane ratings*

(vi) Mechanism of Knocking

Knocking follows free-radical mechanism, leading to a chain growth. If the chains are terminated before their growth, knocking will cease. TEL decomposes thermally to form ethyl-free radicals, which combine with the free radicals of knocking process and thus the chain growth is stopped.

Disadvantage of Using TEL

TEL forms lead oxide, which deposits on a spark plug and creates problems. So, to remove it, ethylene dibromide is added. During burning, lead bromide is formed which evaporates away in the heat engines and goes out together with exhaust gases. This creates atmospheric pollution for human beings. Hence, at present aromatic phosphates are used instead of TEL.



$$Pb + \begin{array}{l} CH_2 - Br \\ | \\ CH_2 - Br \end{array} \longrightarrow PbBr_2 + CH_2 = CH_2$$

(vii) Octane Number in India

India's ordinary and premium petrol are of 89–91 octane numbers. The premium petrols are generally ordinary fuels with additives that do not really change the octane value. Two variants, 'Speed 93' and 'Speed 97', were launched, with octane-number values of 93 and 97, but Speed 97 was discontinued. India's vehicles usually have compression ratios under 10:1, thus enabling them to use lower-quality petrol without engine knocking.

4.9.5 Diesel

- It is relatively a high boiling point fraction of petroleum obtained between 250–320°C.
- It is a mixture of hydrocarbons in terms of carbon atoms C_{15}–C_{18}.
- Its calorific value is about 11,000 kcal/kg. It is used as fuel for compression ignition engine.
- Its antiknock value can be improved by doping with isoamyl nitrate.

CI Engines

In a CI engine, air alone is compressed. This raises the cylinder temperature as high as 300°C. Then the oil is injected or sprayed, which must ignite spontaneously. Now combustion products expand and the power stroke begins.

(i) Knocking in CI Engines

Sometimes, even after the compression stroke is over and even after the diesel oil is sprayed, burning may not start. So, more and more fuel is injected automatically and sudden ignition may occur and burn the whole of the oil. Thus delayed ignition results and uncontrolled, excessive combustion produces 'diesel knock'.

So in an SI engine, knocking is due to premature or too early ignition. In CI engines, knocking is due to delayed ignition or ignition lag.

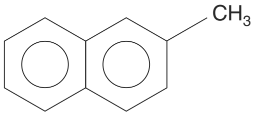
(ii) Measurement of Knocking in CI Engines (Cetane Number)

Cetane Number, or CN, is a measurement of the combustion quality of diesel fuel during compression ignition. It is a significant expression of diesel-fuel quality among a number of other measurements that determine overall diesel-fuel quality.

Cetane ($C_{16}H_{34}$) has a very short ignition delay and hence its cetane number is taken as 100. On the other hand, α-methyl napthalene has a very large ignition delay and hence its cetane number is taken as zero.

Cetane number is defined as the percentage of cetane present in a mixture of α-methyl naphthalene and cetane, which matches the same knocking characteristics of diesel mixture test sample.

$CH_3–(CH_2)_{14}–CH_3$
n-cetane
(cetane number = 100)
n-hexadecane



α-methyl napthalene
(cetane number = 0)

Cetane number is actually a measure of a fuel's ignition delay; the time period between the start of injection and start of combustion (ignition) of the fuel. In a particular diesel engine, higher cetane fuels will have shorter ignition delay periods than lower cetane fuels.

Generally, diesel engines run well with a cetane number from 40 to 55. Fuels with higher cetane numbers, which have shorter ignition delays, provide more time for the fuel combustion process to be completed. Hence, higher-speed diesels operate more effectively with higher cetane-number fuels. There is no performance or emission advantage when the cetane number is raised past approximately 55; after this point, the fuel's performance has no change.

(iii) Chemical Structure and Knocking

The knocking tendency in CI engines increases as follows:

n-alkane → Isoparaffins → Olefins → Naphthenes → Aromatics

Octane numbers decrease in this order. Therefore, an oil of high octane number has a low cetane number and vice versa. Consequently, petroleum crude gives petrol of high octane number and diesel of low cetane number.

(iv) Additives to Improve Cetane Number

- Dimethyl ether may prove advantageous as a future diesel fuel since it has a high cetane rating (55) and can be produced as a biofuel.
- Alkyl nitrates (principally, 2-ethyl hexyl nitrate) and di-*tert*-butyl peroxide are used as additives to raise the cetane number.

(v) Cetane-Number Specifications in Various Countries

- In Europe, diesel cetane numbers were set at a minimum of 38 in 1994 and 40 in 2000. The current standard for diesel sold in the European Union, Iceland, Norway and Switzerland has a minimum cetane index of 46 and a minimum cetane number of 51. Premium diesel fuel can have a cetane number as high as 60.
- Premium diesels may or may not have higher cetane, depending on the supplier. Premium diesel often uses additives to improve cetane number and lubricity, detergents to clean the fuel injectors and minimize carbon deposits, water dispersants, and other additives depending on geographical and seasonal needs.

Table 4.5 *Comparison between petrol and diesel in Internal Combustion Engines (ICE)*

S.No	***Petrol***	***Diesel***
1.	Low boiling petroleum (C_5-C_{10})	High boiling fraction of petroleum contains $C_{15}-C_{18}$ hydrocarbons
2.	Fuel for SI engine	Fuel for CI engine
3.	Knocks due to premature ignition	Knocks due to ignition delay
4.	Knocking tendency measured in octane rating	Knocking tendency measured in cetane rating
5.	Antiknocking is improved through addition of TEL	Antiknocking is improved by doping with isoamyl nitrate
6.	Lower thermal efficiency	Higher thermal efficiency
7.	More consumption	Less consumption

4.9.6 Aviation Petrol

- **Avgas is a high-octane aviation fuel used to power many aircraft and racing cars. Avgas is a abbreviation of aviation gasoline.**
- Avgas is used in aircraft that have pistons or Wankel engines.
- It has an octane number of 100 or even more. Polymerization, alkylation, isomerization and reforming are the processes used to produce or convert ordinary gasoline into aviation gasoline.
- Generally, aviation gasoline is made up of a higher percentage of isoparaffins and a smaller percentage of naphthalenes and aromatics.

- Aviation gasoline possesses higher antiknock value, stability, volatility than ordinary gasoline.

4.10 GASEOUS FUELS

Gaseous fuels in common use are liquefied petroleum gases (LPG), natural gas, producer gas, blast furnace gas, coke-oven gas, etc. The calorific value of gaseous fuel is expressed in kilocalories per cubic metre (kcal/m^3), i.e. at normal temperature (20°C) and pressure (760 mmHg).

4.10.1 Natural Gas

- Methane is the main constituent of natural gas and accounts for about 95% of the total volume.
- Other components are ethane, propane, butane, pentane, nitrogen, carbon dioxide, and traces of other gases.
- Very small amounts of sulphur compounds are also present.
- Since methane is the largest component of natural gas, generally properties of methane are used when comparing the properties of natural gas to other fuels.
- Natural gas is a high-calorific-value fuel requiring no storage facilities.
- It mixes with air readily and does not produce smoke or soot.
- It has no sulphur content.
- It is lighter than air and disperses into air easily in case of leak.

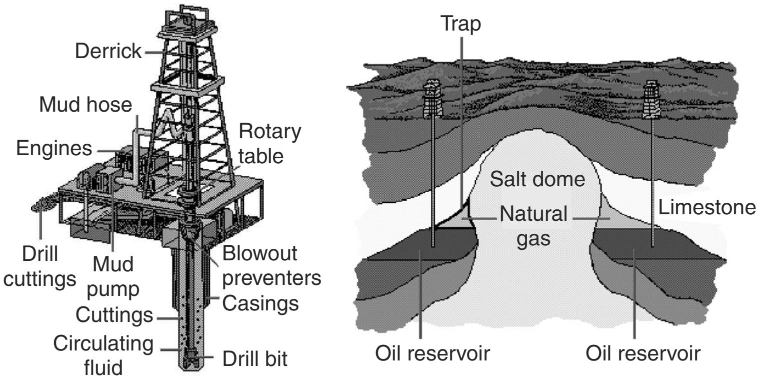


Fig. 4.11 *Natural-gas reservoir*

The composition of natural gas is given below.

Constituent	**Percentage**
Methane	88
Ethane	06
Propane	04
Butane	1–1.5
Pentane	0–0.5

The calorific value is 12,000–14,000 kcal/m^3.

Uses

- It is used as a green fuel for engines, preferably in highly populated cities and areas having dense vehicle population. In India, at New Delhi, all the public transportation vehicles are fitted with engines which use CNG (Compressed Natural Gas) as the fuel.
- It is an excellent domestic and industrial fuel and can be conveyed over very large distances in pipelines.
- It is also used in fuel cells for electricity generation.
- It has recently been used in the manufacture of a number of chemicals by synthetic processes.

4.10.2 Water Gas or Blue Gas

Water gas is essentially a mixture of combustible gases like CO, H_2 with a little non combustible gases like CO_2 and N_2.

(a) Calorific Value Its Calorific value is 2800 kcal/m^3.

(b) Composition The average composition is

$$H_2 = 48\ \%$$
$$CO = 44\ \%$$
$$CO_2,\ N_2 \text{ and } CH_4 = \text{rest}$$

(c) Manufacture A water gas generator is a steel cylindrical vessel. At the top, it is provided with a hopper for adding coke. The water-gas outlet is provided near the top. At the bottom, it is provided with an arrangement of taking out ash formed.

It is obtained by the action of steam on a bed of coke heated to 1000°C.

$$\boxed{C + H_2O + 28\text{ kcal} \longrightarrow CO + H_2}$$

Since the above reaction is endothermic, the coal cools down after a few minutes and the reaction proceeds in a different way to form CO_2 and H_2 instead of water gas ($CO + H_2$).

$$C + 2\,H_2O \longrightarrow CO_2 + 2H_2 - 19\text{ kcal}$$

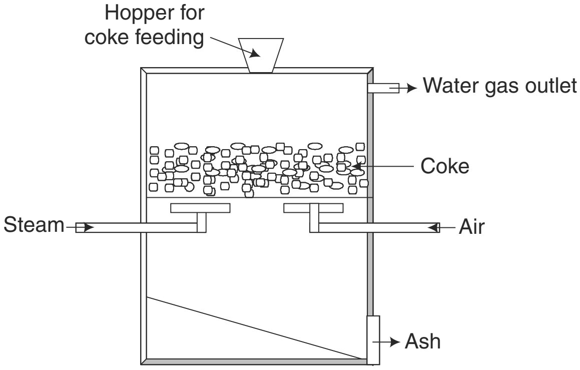


Fig. 4.12 *Water-gas manufacturing unit*

In order to avoid the above undesirable reaction, the blow of air replaces the blow of steam. The following reaction now occurs.

$$C + O_2 \longrightarrow CO_2 + 97\ \text{kcal}$$
$$2C + O_2 \longrightarrow 2CO + 59\ \text{kcal}$$

Due to exothermic reactions, the temperature of the bed rises and when the temperature increases to 1000°C, air entry is stopped and steam is passed again. Thus steam and air are blown alternatively. Therefore, the manufacture of water gas is intermittent.

(d) Properties It has a high calorific value and burns with a nonluminous flame. Its flame is short but very hot.

(e) Uses

- It is used for the manufacture of ammonia by Haber's process.
- Carbureted water gas (water gas + oil gas) is used for lighting and heating purposes.
- Water gas is also used for welding purposes.
- It is used for the manufacture of methyl alcohol.
- It is used for the manufacture of synthetic petrol.

4.10.3 Producer Gas

It is prepared by passing air mixed with a little steam over red-hot coal or a coke bed maintained at above 1100°C in a special reactor called 'Gas Producer'.

(a) Composition

It is a mixture of CO and N_2.

Its average composition is

N_2 = 50 %
CO = 30 %
H_2 = 10 %
CO_2 and CH_4 = rest.

(b) Calorific Value

Its calorific value is 1800 kcal/m^3.

(c) Manufacture

The furnace used for the manufacture of producer gas is known as producer. It consists of a large airtight mild steel cylindrical tower, lined inside with refractory bricks. At the bottom, it is provided with a pipe for blowing air and an arrangement for removing ash. Coal is added through a hopper at the top and producer gas comes out from an exit near the top.

(i) Combustion Zone: When a mixture of air and little steam is passed through a bed of red hot coal, carbon (of the coal) combines with oxygen (of the air) in the lower part of the furnace to form CO_2.

$$C + O_2 \longrightarrow CO_2 + 97 \text{ kcal}$$

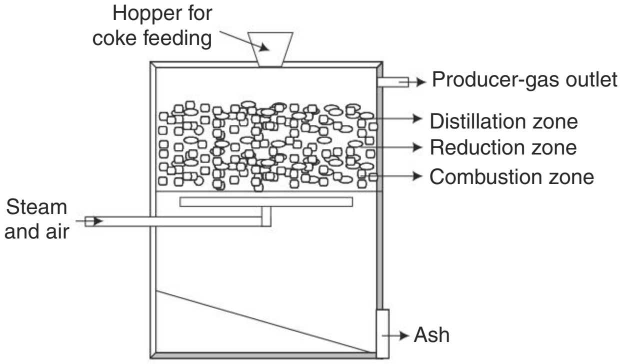


Fig. 4.13 *Producer gas manufacturing unit*

(ii) Reduction Zone: CO_2, so formed, rises up through the red-hot coal and gets reduce to CO during its passage

$$CO_2 + C \longrightarrow 2CO - 39 \text{ kcal}$$

N_2 of air remain unaffected throughout the process. Thus, a mixture of CO and N_2 with traces of CO_2 and hydrocarbons comes out through the exit at the upper end of the producer.

(iii) Distillation Zone This zone is the topmost in the coke bed. The incoming coke is heated by the outgoing hot producer gas which distillates the volatile matter present in the coke.

(d) Properties

It is a poisonous gas.

It is insoluble in water.

It is heavier than air.

(e) Uses

- It is used as fuel for heating open-hearth furnaces (used in steel and glass manufacture), muffle furnaces (used in coal gas and coke manufacture).
- It provides reducing atmosphere in certain metallurgical operations.

4.10.4 Liquefied Petroleum Gas (LPG)

LPG is a predominant mixture of propane and butane with a small percentage of unsaturates (propylene and butylene) and some lighter C_2 as well as heavier C_5 fractions. Included in the LPG range are propane (C_3H_8), propylene (C_3H_6), normal and isobutane (C_4H_{10}) and butylene (C_4H_8). It is obtained as one of the top fractions in the fractional distillation of petroleum.

LPG may be defined as those hydrocarbons, which are gaseous at normal atmospheric pressure, but may be condensed to the liquid state at normal temperature, by the application of moderate pressures.

Although they are normally used as gases, they are stored and transported as liquids under pressure for convenience and ease of handling. Liquid LPG on evaporation produces 250 times more volume of gas.

(a) Composition of LPG

n-butane = 70 %

Isobutane = 17 %

n-propane = 11 %

Butylene and ethane = rest

(b) Calorific Value

Its calorific value is 27,000 kcal/m^3.

(c) Uses

- Used as a fuel for domestic cooking
- Used for heating industrial furnaces
- Used as an alternate for gasoline in automobiles

4.10.5 Coal Gas

- It is a mixture of hydrogen and methane.
- Its calorific value is 5000 kcal/m^3.
- Its approximate composition is 50% H_2 + 30% CH_4 + 7% CO + the rest N_2, CO_2 and alkenes.

(a) Manufacture Coal gas is obtained by destructive distillation of coal at about 1200°C in a vertical coke oven. The coke oven is made up of silica bricks. The oven is charged from the top and closed to restrict the entry of air.

Carbonization is carried out by burning fuel and air. Coal is decomposed into volatile products, which leave at the top of the oven.

$$\text{Coal} \xrightarrow[\text{Absence of air}]{1200^\circ\text{C}} \text{Coke} + \text{Coal gas}$$

The coal gas is mainly composed of impurities such as tar, ammonia, benzol and other aromatic compounds, H_2S, etc.

(b) Purification of Coal Gas The coal gas is passed through a hydraulic main to a water – cooled condenser where much of tar and ammonia are condensed and collected. Then the gas is passed through the other tower where water is sprayed to remove the last portions of tar and ammonia. The gas is passed through the next tower in which creosote oil is sprayed. Benzol and other aromatic compounds are dissolved in the oil and recovered.

Finally, the gas enters into a purifying chamber packed with Fe_2O_3 which removes any sulphur compound present in the coal gas. The purified gas is collected from the exit provided at the top of the purifier.

(c) Uses Coal gas is used as a domestic fuel. It is used for maintaining a reducing atmosphere in metallurgy. It is also used in smelting of metals and alloys.

4.10.6 Biogas

Biogas typically refers to a gas produced by the biological breakdown of organic matter in the absence of oxygen. Biogas originates from biogenic material and is a type of biofuel.

Biogas is made from organic waste matter after it is decomposed. The decomposition breaks down the organic matter, releasing various gases. The main gases released are methane, carbon dioxide, hydrogen and hydrogen sulphide. Bacteria carry out the decomposition or fermentation. The conditions for creating biogas have to be anaerobic, that is without any air and in the presence of water. The organic waste matter is generally animal or cattle dung, plant wastes, etc. These waste products contain carbohydrates, proteins and fat material that are broken down by bacteria. The waste matter is soaked in water to give the bacteria a proper medium to grow. Absence of air or oxygen is important for decomposition because bacteria then take oxygen from the waste material itself and in the process break them down.

The cheapest and easily obtainable biogas is *gobar gas*, which is produced by anaerobic fermentation of cattle dung. The biogas is burnt to raise steam, which can drive turbines to produce electricity.

(a) Gobar Gas

There are two types of biogas plants that are used in India. The first type is the floating gas holder and the next is the fixed concrete-dome gas-holder type. These plants, called *gobar-gas plants* mainly use cattle dung. Generally, a slurry is made from cattle dung and water, which forms the starting material for these plants.

The general composition of biogas is

Compound	%
Methane	50–75
Carbon dioxide	25–50
Nitrogen	0–10
Hydrogen	0–1
Hydrogen sulphide	0–3
Oxygen	0–2

- The main constituent present in gobar gas is methane.
- The calorific value is 5400 kcal/m^3.

A well is made out of concrete. This is called the digester tank. It is divided into two parts. One side has the inlet, from where the slurry is fed to the tank. The tank has a cylindrical dome made of stainless steel that floats on the slurry and collects the gas generated. Hence the name given to this type of plant is floating gas-holder type of biogas plant. The slurry is made to ferment for about 50 days. As more gas is made by the bacterial fermentation, the pressure inside the steel tank increases. The gas can be taken out through an outlet pipe. The decomposed matter expands and overflows into the next chamber in the tank. This is then

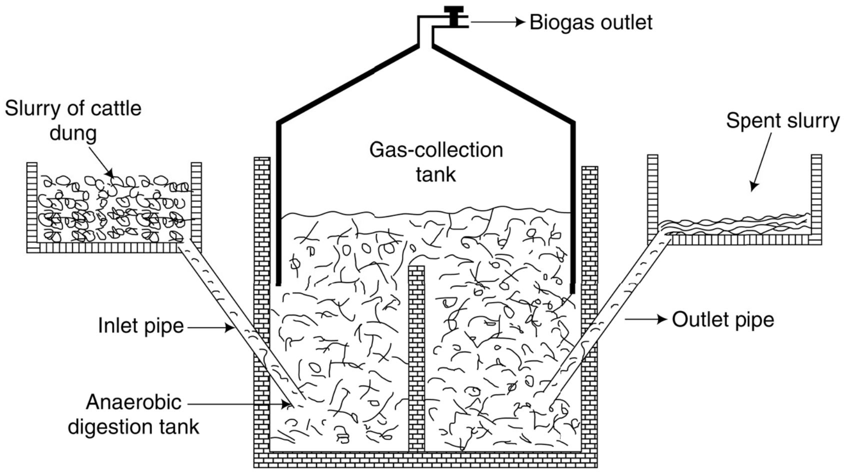


Fig. 4.14 *Diagram of a floating gas-holder type of biogas plant*

removed by the outlet pipe to the overflow tank and is used as manure for cultivation purposes.

(b) Uses of Biogas

- Biogas is used as cooking fuel. This is because biogas burns without smoke, has high calorific value, can be piped into kitchens directly from a plant and is cheaper in cost.
- Biogas can be used to run electric engines such as pumps, as they cause less air pollution.
- Biogas can be used for street lighting as it does not cause any smoke and the illumination obtained can be made to be quite adequate.

4.11 DETERMINATION OF CALORIFIC VALUE BY BOMB CALORIMETER

The bomb calorimeter is used for the estimation of calorific value of a solid or nonvolatile liquid fuel.

(a) Construction It consists of a strong cylindrical stainless-steel container (bomb) which is capable of withstanding high pressure. At the top, a gastight screw cap is provided to which a couple of stainless-steel electrodes and a release valve are fitted. Oxygen is passed through one of these tubular electrodes. A small ring is attached to this electrode which acts as a support for the crucible. The bomb is placed in a copper calorimeter having a known weight of water.

The copper calorimeter is surrounded by an air jacket and a water jacket to prevent loss of heat due to radiation. The calorimeter is provided with an electrical stirrer for stirring water and a Beckmann thermometer.

(b) Working A known weight of the fuel sample is taken in the crucible and the bomb lid is closed tightly. A fine magnesium wire touching the fuel sample is stretched across the electrode. Excess oxygen of 25–30 atm pressure is filled for complete combustion of the fuel. The bomb is kept in a copper calorimeter containing a known weight of water. Initial temperature of water is noted after thorough stirring. When the current is switched on, the fuel in the crucible burns. The heat liberated by the combustion of the fuel raises the temperature of water and the maximum temperature obtained is recorded with continuous stirring. The calorific value of the fuel can now be calculated as follows:

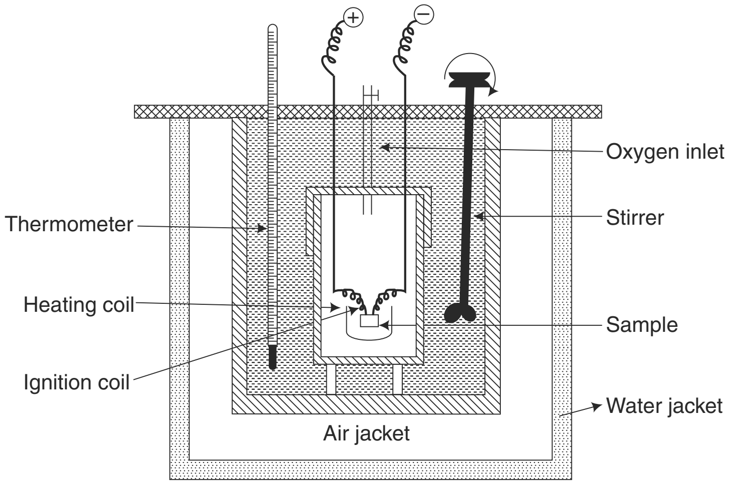


Fig. 4.15 *Bomb calorimeter*

(c) Calculations

Weight of the fuel taken in the crucible = m g

Weight of the water in the calorimeter = a g

Water equivalent of the calorimeter, stirrer bomb and thermometer = b g

Initial temperature of water in the calorimeter = T_1°C

Final temperature of water in the calorimeter = T_2°C

Higher calorific value of the fuel = H

Heat gained by water = $a\,(T_2 - T_1)$ cal

Heat gained by calorimeter = $b\,(T_2 - T_1)$ cal

Total heat gained $= a\,(T_2 - T_1) + b\,(T_2 - T_1)$ cal

$= (a + b)\,(T_2 - T_1)$

Heat liberated by the fuel $= m \times H$

Now, heat liberated by the fuel = Heat gained by water and calorimeter

$$m \times H = (a + b)\,(T_2 - T_1)$$

$$H \text{ (GCV or HCV)} = \frac{(a + b)\,(T_2 - T_1)}{m} \text{ cal/g}$$

NCV can be calculated based on Dulong's formula.

To obtain accurate results, the following corrections are made.

(i) Fuse-wire Correction: The heat released by the magnesium fuse wire is to be subtracted from the total calorific value.

(ii) Acid Correction: During ignition, suphur and nitrogen present in the fuel are oxidized to the corresponding acids.

$$S + 2H + 2O_2 \longrightarrow H_2SO_4 + \text{Heat}$$

$$2N + 2H + 3O_2 \longrightarrow 2HNO_3 + \text{Heat}$$

The heat liberated by the formation of these acids must be subtracted.

(iii) Cooling Correction: During cooling, the calorimeter will lose some amount of heat. To calculate this heat wasted during cooling; the rate of cooling (d t°/min) and actual time for cooling (x minutes) are measured. The cooling correction is added to the temperature difference.

$$\boxed{H = \frac{(a + b)\,(T_2 - T_1 + \text{Cooling correction}) - (\text{Acid + Fuse-wire correction})}{m} \text{ cal/g}}$$

Example 6 *Calculate the volume of air (volume % of O_2 in air = 21) required for complete combustion of 1 litre of CO.*

Solution The combustion equation of CO is written as follows:

$$\underset{1\text{ vol}}{CO} + \underset{0.5\text{ vol}}{1/2\,O_2} \longrightarrow CO_2$$

One volume (litre) of CO requires 0.5 volume (litre) of O_2 for complete combustion.

We know that,

21 litres of O_2 is supplied by 100 litres of air.

$\therefore$ 0.5 litres of O_2 is supplied by $\frac{100 \times 0.5}{21}$ lit of air

= 2.38 litres of air

Result

The volume of air required for the complete combustion of 1 litre of CO = 2.38 litres

---

Example 7 *What is the volume of air required for the complete combustion of 1 m^3 of a mixture containing 75 % of CH_4 and 25 % of C_2H_6?*

Solution

(a) 1 m^3 of the mixture contains

$$\frac{75}{100} = 0.75 \text{ m}^3 \text{ of } CH_4$$

$$\frac{25}{100} = 0.25 \text{ m}^3 \text{ of } C_2H_6$$

(b) The combustion equations of CH_4 and C_2H_6 are written as follows:

(i) $\underset{\text{1 vol}}{CH_4} + \underset{\text{2 vol}}{2O_2} \longrightarrow CO_2 + 2H_2O$

i.e. 1 volume (or m^3) of CH_4 requires 2 volumes (or m^3) of O_2 for complete combustion.

$\therefore$ 0.75 m^3 of CH_4 requires $= \dfrac{2 \times 0.75}{1} = 1.5$ m^3 of O_2

(ii) $\underset{\text{1 vol}}{C_2H_6} + \underset{\text{3.5 vol}}{7/2\ O_2} \longrightarrow 2CO_2 + 3H_2O$

i.e. 1 volume (or m^3) of C_2H_6 requires 3.5 volumes (or m^3) of O_2 for complete combustion.

$\therefore$ 0.25 m^3 of C_2H_6 requires $= \dfrac{3.5 \times 0.25}{1} = 0.875$ m^3 of O_2

(c) Total volume of O_2 required

$$= 1.5 + 0.875 \text{ m}^3$$
$$= 2.375 \text{ m}^3$$

We know that

21 m^3 of O_2 is supplied by 100 m^3 of air.

$\therefore$ 2.735 m^3 of O_2 is supplied by $\dfrac{2.735 \times 100}{21} = 11.31$ m^3 of air

Result

The volume of air required for the complete combustion of 1 m^3 of mixture = 11.31 m^3

Example 8 *Calculate the minimum volume of air required for the complete combustion of 1 m^3 of a gaseous fuel containing the following composition by volume: $CO = 25$ %, $H_2 = 10$ %, $CH_4 = 08$ %, $CO_2 = 5$ %, $N_2 = 50$ % and $O_2 = 2$ %.*

Solution

1 m^3 of fuel contains

(a) $\frac{25}{100} = 0.25$ m^3 of CO

(b) $\frac{10}{100} = 0.10$ m^3 of H_2

(c) $\frac{8}{100} = 0.08$ m^3 of CH_4

(d) $\frac{5}{100} = 0.05$ m^3 of CO_2

(e) $\frac{50}{100} = 0.50$ m^3 of N_2

(f) $\frac{2}{100} = 0.02$ m^3 of O_2

N_2 and CO_2 are noncombustible constituents. They do not burn and do not require any oxygen.

The combustion equations of the remaining constituents are written as follows:

(i) $\underset{1\text{ vol}}{CO} + \underset{0.5\text{ vol}}{1/2\, O_2} \longrightarrow CO_2$

i.e. 1 volume (or m^3) of CO requires 0.5 volume (or m^3) of O_2 for complete combustion.

$$\therefore 0.25 \text{ m}^3 \text{ of CO requires} = \frac{0.5 \times 0.25}{1} \text{ m}^3 \text{ of } O_2$$

$$= 0.125 \text{ m}^3 \text{ of } O_2$$

(ii) $\underset{1\text{ vol}}{H_2} + \underset{0.5\text{ vol}}{1/2\, O_2} \longrightarrow H_2O$

i.e. 1 volume (or m^3) of H_2 requires 0.5 volume (or m^3) of O_2 for complete combustion.

$$\therefore 0.10 \text{ m}^3 \text{ of } H_2 \text{ requires} = \frac{0.5 \times 0.1}{1} \text{ m}^3 \text{ of } O_2$$

$$= 0.05 \text{ m}^3 \text{ of } O_2$$

(iii) $\underset{\text{1 vol}}{CH_4} + \underset{\text{2 vol}}{2O_2} \longrightarrow CO_2 + 2H_2O$

i.e. 1 volume (or m^3) of CH_4 requires 2 volumes (or m^3) of O_2 for complete combustion.

$\therefore$ 0.08 m^3 of CH_4 requires $= \dfrac{0.08 \times 2}{1}$ m^3 of O_2

$= 0.16$ m^3 of O_2

Total volume of O_2 required $= 0.125 + 0.05 + 0.16$ m^3

$= 0.335$ m^3 of O_2

$\therefore$ net volume of O_2 required = Total volume of O_2 required – O_2 already present in the fuel.

$= 0.335 - 0.02$ m^3 of O_2

$= 0.315$ m^3 of O_2

We know that

21 m^3 of O_2 is supplied by 100 m^3 of air.

$\therefore$ 0.315 m^3 of O_2 is supplied by $= \dfrac{0.315 \times 100}{21}$

$= 1.5$ m^3 of air.

Result

The volume of air required for the complete combustion of 1 m^3 of the gaseous fuel = 1.5 m^3

Example 9 *A fuel contains C = 60 %, H_2 = 09 %, O_2 = 08 %, S = 13 %, and the remaining is ash. Calculate the minimum quantity of air required for the complete combustion of 1 kg of the fuel.*

Solution

1 kg of fuel contains

(a) $\dfrac{60}{100} = 0.60$ kg of carbon

(b) $\dfrac{10}{100} = 0.09$ kg of hydrogen

(c) $\dfrac{08}{100} = 0.08$ kg of oxygen

(d) $\dfrac{13}{100} = 0.13$ kg of sulphur

The combustion equations of the various elements present in the fuel are as follows:

(i) $\underset{12\text{ kg}}{C} + \underset{32\text{ kg}}{O_2} \longrightarrow CO_2$

i.e. 12 kg of carbon requires 32 kg of oxygen for complete combustion.

$\therefore$ 0.60 kg of carbon requires $\frac{32 \times 0.6}{12}$ kg of O_2 = 1.6 kg of O_2

(ii) $\underset{2\text{ kg}}{H_2} + \underset{16\text{ kg}}{1/2\, O_2} \longrightarrow H_2O$

i.e. 2 kg of hydrogen requires 16 kg of oxygen for complete combustion.

$\therefore$ 0.09 kg of H_2 requires $\frac{16 \times 0.09}{2}$ kg of O_2 = 0.72 kg of O_2

(iii) $\underset{32\text{ kg}}{S} + \underset{32\text{ kg}}{O_2} \longrightarrow SO_2$

i.e. 32 kg of sulphur requires 32 kg of oxygen for complete combustion.

$\therefore$ 0.13 kg of S requires $\frac{32 \times 0.13}{32}$ kg of O_2 = 0.13 kg of O_2

Total amount of O_2 required = 1.60 + 0.72 + 0.13 kgs
= 2.45 kg of O_2

But the amount of O_2 already present in the fuel = 0.08 kg

$\therefore$ Net amount O_2 required = Total amount of O_2 required – O_2 already present in the fuel
= 2.45 – 0.08 kg of O_2
= 2.37 kg of O_2

We know that

23 kg of O_2 is supplied by 100 kg of air.

$\therefore$ 2.37 kg of O_2 is supplied by $\frac{2.37 \times 100}{23}$ = 10.30 kg of air

Result

The minimum amount of air required for the complete combustion of 1 kg of the fuel = 10.30 kg.

Example 10 *Calculate the minimum amount of air required for the complete combustion of 50 kgs of coal containing C = 75 %, H_2 = 10 %, O_2 = 02 %, S = 05 %, and the rest nitrogen by weight.*

Solution

1 kg of fuel contains

(a) $\frac{75}{100} = 0.75$ kg of carbon

(b) $\frac{10}{100} = 0.10$ kg of hydrogen

(c) $\frac{2}{100} = 0.02$ kg of oxygen

(d) $\frac{5}{100} = 0.05$ kg of sulphur

N_2 is a noncombustible constituent. It does not burn and does not require any oxygen.

The combustion equations of the various elements present in the coal are as follows:

(i) $\underset{12\text{ kg}}{C} + \underset{32\text{ kg}}{O_2} \longrightarrow CO_2$

i.e. 12 kg of carbon requires 32 kg of oxygen for complete combustion.

$\therefore$ 0.75 kg of carbon requires $\frac{32 \times 0.75}{12}$ kg of O_2 = 2.0 kg of O_2

(ii) $\underset{2\text{ kg}}{H_2} + \underset{16\text{ kg}}{1/2\ O_2} \longrightarrow H_2O$

i.e. 2 kg of hydrogen requires 16 kg of oxygen for complete combustion.

$\therefore$ 0.10 kg of H_2 requires $\frac{16 \times 0.10}{2}$ kg of O_2 = 0.80 kg of O_2

(iii) $\underset{32\text{ kg}}{S} + \underset{32\text{ kg}}{O_2} \longrightarrow SO_2$

i.e. 32 kg of sulphur requires 32 kg of oxygen for complete combustion.

$\therefore$ 0.05 kg of S requires $\frac{32 \times 0.05}{32}$ kg of O_2 = 0.05 kg of O_2

Total amount of O_2 required = 2.00 + 0.80 + 0.05 kg
= 2.85 kg

But the amount of O_2 already present in the fuel = 0.02 kg

$\therefore$ net amount O_2 required = Total amount of O_2 required – O_2 already present in the fuel.
= 2.85 – 0.02 kg
= 2.83 kg

We know that

23 kg of O_2 is supplied by 100 kg of air.

∴ 2.83 kg of O_2 is supplied by $\frac{2.83 \times 100}{23}$ = 12.30 kg of air

The amount of air required for 1 kg of coal = 12.30 kg

∴ the amount of air required for 50 kg of coal = 12.30 × 50 kg
= 615 kg

Result

The amount of air required for the complete combustion of 50 kg of the coal = 615 kg

Example 11 *Calculate the minimum amount of air required for the complete combustion of 150 kg of fuel containing 70 % carbon, 15 % hydrogen, 5 % sulphur and the rest nitrogen by weight.*

Solution

1 kg of fuel contains

(a) $\frac{70}{100}$ = 0.70 kg of carbon

(b) $\frac{15}{100}$ = 0.15 kg of hydrogen

(c) $\frac{05}{100}$ = 0.05 kg of sulphur

N_2 is a noncombustible constituent. It does not burn and does not require any oxygen.

The combustion equations of the various elements present in the coal are as follows:

(i) $\underset{12\text{ kg}}{C} + \underset{32\text{ kg}}{O_2} \longrightarrow CO_2$

i.e. 12 kg of carbon requires 32 kg of oxygen for complete combustion.

∴ 0.70 kg of carbon requires $\frac{0.7 \times 32}{12}$ kg of O_2 = 1.87 kg of O_2

(ii) $\underset{2\text{ kg}}{H_2} + \underset{16\text{ kg}}{1/2\, O_2} \longrightarrow H_2O$

i.e. 2 kg of hydrogen requires 16 kg of oxygen for complete combustion.

∴ 0.15 kg of H_2 requires $\frac{0.15 \times 16}{2}$ kg of O_2 = 1.20 kg of O_2

(iii) $\underset{32\text{ kg}}{S} + \underset{32\text{ kg}}{O_2} \longrightarrow SO_2$

i.e. 32 kg of sulphur requires 32 kg of oxygen for complete combustion.

$\therefore$ 0.05 kg of S requires $\dfrac{0.05 \times 32}{32}$ kg of O_2 = 0.05 kg of O_2

Total amount of O_2 required = 1.87 + 1.20 + 0.05 kg
= 3.12 kg

We know that

23 kg of O_2 is supplied by 100 kg of air.

$\therefore$ 3.12 kg of O_2 is supplied by $\dfrac{3.12 \times 100}{23}$ = 13.57 kg of air

The minimum amount of air required for the complete combustion of 1 kg of fuel = 13.57 kg

$\therefore$ the minimum amount of air required for the complete combustion of 50 kg of fuel = 13.57 × 150 kg
= 2035.5 kg

Result

The minimum amount of air required for the complete combustion of 150 kg of the fuel = 2035.5 kg

Example 12 *Calculate the weight and volume of air required for the complete combustion of 1 kg of coke or carbon.*

Solution The combustion equation of carbon is as follows:

$$\underset{12\text{ kg}}{C} + \underset{32\text{ kg}}{O_2} \longrightarrow CO_2$$

12 kg of carbon requires 32 kg of O_2 for complete combustion.

$\therefore$ 1 kg of coke requires $\dfrac{32 \times 1}{12}$ = 2.67 kg of O_2

We know that,

23 kg of O_2 is supplied by 100 kg of air.

$\therefore$ 2.67 kg of O_2 is supplied by $\dfrac{2.67 \times 100}{23}$ = 11.61 kg of air.

We know that,

1 g mole of any substance occupies 22.4 litres

(or)

32 kg of O_2 occupies 22.4 m^3 at NTP [1 m^3 = 1000 litres]

$\therefore$ 11.61 kg of O_2 occupies $\dfrac{22.4 \times 1.61}{32}$ = 8.127 m^3

We know that,

21 m^3 of O_2 is supplied by 100 m^3 of air.

$\therefore$ 8.127 m^3 of O_2 is supplied by $\frac{8.127 \times 100}{21} = 38.70$ m^3 of air

Result

1. The amount of air required for complete combustion of 1 kg of coke = 11.61 kg
2. The volume of air required for complete combustion of 1 kg of coke = 38.70 m^3.

Example 13 *Calculate the minimum theoretical quantity of air needed for the combustion of 10 kg of coal which is 95 % pure.*

Solution The combustion equation of carbon is as follows:

$$\underset{12\text{ kg}}{C} + \underset{32\text{ kg}}{O_2} \longrightarrow CO_2$$

i.e. 12 kg of carbon requires 32 kg of oxygen for complete combustion.

$\therefore$ 10 kg of carbon requires $\frac{32 \times 10}{12}$ kg of O_2 = 26.67 kg of O_2

We know that

23 kg of O_2 is supplied by 100 kg of air.

$\therefore$ 26.67 kg of O_2 is supplied by $\frac{26.67 \times 100}{23}$ kg of air

= 115.96 kg of air.

The amount of air required for the combustion of 10 kg of coal which is 100 % pure = 115.96 kg

The amount of air required for the combustion of 10 kg of coal which is 95 % pure = $\frac{115.96 \times 95}{100} = 110.16$ kg

Result

The amount of air required for the combustion of 10 kg of coal which is 95 % pure = 110.16 kg

Example 14 *A sample of coal was found to have the following percentage composition: C = 75 %, H_2 = 5.2 %, O_2 = 12.8 %, N_2 = 1.2 %, S = 12.8 % and the rest ash. Calculate the amount of air needed for the complete combustion if 1 kg of the coal is burnt with 30 % excess air.*

Solution

1 kg of coal contains

(a) $\frac{75}{100} = 0.75$ kg of carbon

(b) $\frac{5.2}{100} = 0.052$ kg of hydrogen

(c) $\frac{12.8}{100} = 0.128$ kg of sulphur

(d) $\frac{12.8}{100} = 0.128$ kg of oxygen

(e) $\frac{1.2}{100} = 0.012$ kg of nitrogen

N_2 and ash are noncombustible constituents. They do not burn and do not require any oxygen.

The combustion equations of the remaining constituents present in the fuel are as follows:

(i) $\underset{12\text{ kg}}{C} + \underset{\text{kg}}{O_2} \longrightarrow CO_2$

i.e. 12 kg of carbon requires 32 kg of oxygen for complete combustion.

$\therefore$ 0.75 kg of carbon requires $\frac{32 \times 0.75}{12}$ kg of O_2 = 2.0 kg of O_2

(ii) $\underset{2\text{ kg}}{H_2} + \underset{16\text{ kg}}{1/2\, O_2} \longrightarrow H_2O$

i.e. 2 kg of hydrogen requires 16 kg of oxygen for complete combustion.

$\therefore$ 0.052 kg of H_2 requires $\frac{16 \times 0.052}{2}$ kg of O_2 = 0.416 kg of O_2

(iii) $\underset{32\text{ kg}}{S} + \underset{32\text{ kg}}{O_2} \longrightarrow SO_2$

i.e. 32 kg of sulphur requires 32 kg of oxygen for complete combustion.

$\therefore$ 0.128 kg of S requires $\frac{32 \times 0.128}{32}$ kg of O_2 = 0.128 kg of O_2

Total amount of O_2 required = 2.00 + 0.416 + 0.128 kgs
= 2.544 kg of O_2

But the amount of O_2 already present in the fuel = 0.128 kg

∴ Net amount O_2 required = Total amount of O_2 required – O_2 already present in the fuel.

$$= 2.544 - 0.128 \text{ kg of } O_2$$

$$= 2.416 \text{ kg of } O_2$$

We know that

23 kg of O_2 is supplied by 100 kg of air.

∴ 2.416 kg of O_2 is supplied by $\frac{100 \times 2.416}{23}$ = 10.50 kg of air

If 30 % excess air is used = $\frac{\text{Theoretical air} \times [100 + \text{excess air}]}{100}$

$$= \frac{10.5 \times [100 + 30]}{100}$$

$$= 13.65 \text{ kg of air}$$

Result

The volume of air required for the complete combustion of 1 kg of the fuel if 30 % excess air is used = 13.65 kg

QUESTIONS

Two-Mark Questions with Answers

1. **Define fuel.**

   Fuel can be defined as any combustible substance which on proper burning gives large amount of energy in the form of heat, which can be used economically for domestic and industrial purpose.

2. **What is combustion?**

   Combustion or burning is the sequence of exothermic chemical reactions between a fuel and an oxidant accompanied by the production of heat and conversion of chemical species.

3. **What is meant by calorific value?**

   It is the most important characteristic property of any fuel.Calorific value may be defined as 'the amount of heat liberated by the complete combustion of a unit mass of a fuel'.

4. **What is meant by Higher Calorific Value (HCV)?**

   It is the total heat generated when a unit quantity of fuel is completely burnt and the products of combustion are cooled to room temperature.

5. What are the significance of flue-gas analysis?

1. Based on the composition of the flue gas, it is possible to predict the complete or incomplete combustion process.
2. If the flue gas contains any CO, it indicates the incomplete combustion in the combustion chamber and short supply of oxygen.
3. If the flue gas contains O_2, it indicates that excess of air is supplied. It is essential to reduce the air supply.

6. What is ultimate analysis of coal?

The determination weight percentage of carbon, hydrogen, nitrogen, oxygen and sulphur of the pure coal free from moisture and inorganic constituents is called ultimate analysis.

7. Why is coke superior as a metallurgical fuel?

Coke is superior as a metallurgical fuel, because

1. Coke is stronger and more porous than coal
2. Coke contains lesser amount of sulphur than coal
3. Coke does not contain much volatile matter

8. What is metamorphism of coal?

The process of conversion of lignite to anthracite is called coalification or metamorphism of coal.

9. Define refining of petroleum.

The process of removing impurities and separating out the oil into various fractions having different boiling points is known as refining of petroleum.

10. How are coals classified?

Coal is classified on the basis of its rank. The rank of coal denotes its degree of maturity. Vegetable matter, under the action of pressure, heat and anaerobic conditions, gets converted into different stages of coal, namely

Peat → Lignite → Sub-bituminous → Bituminous → Anthracite

11. What is metallurgical coke?

When bituminous coal is heated strongly in absence of air, the volatile matter escapes out and a lustrous, dense, strong, porous and coherent mass is left, which is called metallurgical coke.

12. Define cracking.

Cracking is defined as 'the decomposition of high boiling hydrocarbons of high molecular weight into smaller, low boiling hydrocarbons of low molecular weight'.

13. **What are the advantages of Otto Hoffman's by-product method?**

    Otto Hoffman's by-product method has the following advantages:

    1. High thermal efficiency and less carbonization time
    2. Valuable by-products (like coal gas, ammonia, benzene, etc.) are recovered as by products
    3. Heating done externally by producer gas

14. **Write any four differences between straight-run petrol and cracked petrol.**

S.No	*Straight-run Petrol*	*Cracked Petrol*
1.	Obtained from straight distillation of crude oil.	Obtained from heavy oil
2.	Contains only *n*-alkanes.	Contains iso-paraffins and aromatics
3.	Composition range $C_5 - C_9$	Narrow range
4.	Low octane number	Higher octane number

15. **What is meant by octane number?**

    Octane number can be defined as 'percentage of iso-octane present in iso-octane and *n*-heptane mixture, which matches the same knocking characteristics of a gasoline mixture test sample'.

16. **Write any five differences between petrol and diesel.**

S.No	*Petrol*	*Diesel*
1.	Low boiling petroleum ($C_5 - C_{10}$)	High boiling fraction of petroleum contains $C_{15} - C_{18}$ hydrocarbons
2.	Fuel for SI engine	Fuel for CI engine
3.	Knocks due to premature ignition	Knocks due to ignition delay
4.	Knocking tendency measured in octane rating	Knocking tendency measured in cetane rating.
5.	Anti-knocking is improved through addition of TEL	Anti-knocking is improved by doping with isoamyl nitrate

17. **What is the average composition of water gas?**

    The average composition is

$$H_2 = 48\ \%$$
$$CO = 44\ \%$$
$$CO_2,\ N_2 \text{ and } CH_4 = \text{rest}$$

18. **Mention any two applications of producer gas.**

    1. It is used as fuel for heating open-hearth furnaces (used in steel and glass manufacture), muffle furnaces (used in coal gas and coke manufacture).

2. It provides reducing atmosphere in certain metallurgical operations.

19. What is meant by cetane number?

Cetane number is defined as the percentage of cetane present in a mixture of α-methyl naphthalene and cetane, which matches the same knocking characteristics of a diesel mixture test sample.

20. What is the average composition of liquefied petroleum gas?

Composition of LPG

n-butane = 70 %
Isobutane = 17 %
n-propane = 11 %
Butylene and ethane = rest

21. Classify the hydrocarbons based on their knocking tendency in CI engines.

The knocking tendency in CI engines increases as follows:

n-alkane → Isoparaffins → Olefins → Naphthenes → Aromatics

Ten-Mark Questions

1. Discuss in detail the flue gas analysis using Orsat's apparatus.
2. Explain in detail the classification of solid fuels.
3. Discuss the proximate analysis of coal with its significances.
4. Explain the manufacture of metallurgical coke by beehive coke oven method.
5. Explain the construction and operation of Otto Hoffman's by-product coke oven with a neat diagram.
6. Discuss in detail the Bergius process of petrol manufacturing.
7. Explain the Fischer–Tropsch process of synthetic petrol manufacturing.
8. What is water gas? Discuss the preparation, properties and uses.
9. Explain the manufacture of producer gas with a neat diagram.
10. Discuss the ultimate analysis of coal in detail.
11. What is knocking in Petrol and Diesel? How will you overcome the knocking problem?
12. How is synthetic petrol manufactured by polymerization and alkylation methods?

UNIT

5

High Polymers

5.1 INTRODUCTION

The word polymer is derived from the Greek words ***poly*** meaning 'many' and ***mers*** meaning 'units' or 'parts'. Polymers are generally macromolecules formed by the repeated linking of a large number of small molecules. **The chemistry of these giant molecules is known as 'polymer chemistry' or 'macromolecular chemistry'.** Cellulose, starch, proteins, rubber, resins, etc., are some common examples of naturally occurring polymers. Polymers are widely used in automobiles, defense, electrical goods and computer components. Polymers may be both inorganic and organic in nature. The organic polymers, particularly the synthetic ones, are more important and are the chief products of modern chemical industry. Hermann Staudinger, (1881–1963), a German chemist and one of the pioneers in polymer chemistry was awarded the Nobel Prize in chemistry in 1953 for his outstanding research. In the forthcoming sections, we shall study some important aspects related to organic polymers, particularly the synthetic ones.

5.1.1 Polymers

Polymers are macromolecules built up by linking together a large number of small molecules called monomers.

Example

Polyethylene is a polymer formed by the repeated linking of a large number of ethylene molecules. These units are linked together by covalent bonds.

$$\underset{\text{Ethylene (monomer)}}{n\,CH_2=CH_2} \longrightarrow \underset{\text{Polyethylene (polymer)}}{-(CH_2-CH_2)_n-}$$

5.1.2 Monomer

A monomer is the building block or structural unit of a polymer. It is a small molecule that combines with other molecules to form a polymer.

Example Ethylene

5.2 POLYMERIZATION

Polymerization is a process in which a large number of small molecules combine to form a bigger molecule with or without elimination of the small molecules like water, methanol, etc.

5.2.1 Degree of Polymerization (DP)

The size of a polymer molecule is represented in terms of degree of polymerization. **The number of repeating units or monomers present in a polymer chain is known as degree of polimerization (*n*).** In a polymer molecule, there may be hundreds or thousands or more monomer molecules linked together. It is represented by the following relation.

Degree of Polymerization (DP)

$$= \frac{\text{Molecular weight of the polymeric network}}{\text{Molecular weight of the repeating unit}}$$

Example

$$4\,CH_2=CH_2 \longrightarrow -CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-$$

Here, there are four repeating units present in the polymer chain. So the degree of polymerization is 4.

(i) Oligo Polymers They are polymers with a low degree of polymerization and have a 500–5000 molecular mass range.

(ii) High Polymers They are polymers with high degree of polymerization and have a 10,000–2,00,000 molecular mass range.

5.3 NOMENCLATURE OF POLYMERS

Depending upon the nature of monomeric units, polymers can be categorized into the following categories:

1. Homopolymer
2. Heteropolymer
3. Homochain polymer
4. Heterochain polymer
5. Stereospecific polymer

5.3.1 Homopolymer

If the polymer consists of identical monomers, it is a homopolymer.

$$\text{—M—M—M—M—M}$$

where, M is a monomer.

Example Polyethylene, Polypropylene.

Types Homopolymers are subdivided into three types based on the manner in which monomers are arranged.

(i) Linear Homopolymer

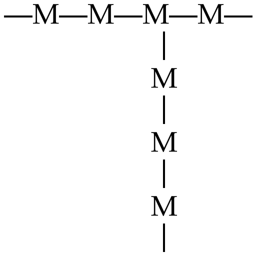
A polymer in which the constituent monomeric units are joined together to form long straight chains is called a linear homopolymers.

$$\text{—M—M—M—M}$$

where M is a monomer.

(ii) Branched Homopolymer

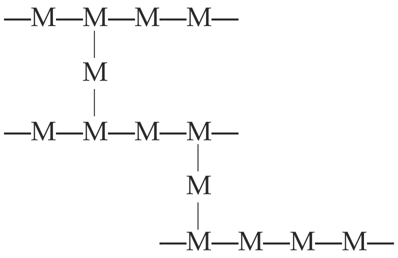
Polymers which consist of side chains attached to the main chain are called branched homopolymers.



$$\begin{array}{c}\text{—M—M—M—M—}\\ \quad\;\;|\\ \quad\;\;\text{M}\\ \quad\;\;|\\ \quad\;\;\text{M}\\ \quad\;\;|\\ \quad\;\;\text{M}\\ \quad\;\;|\end{array}$$

(iii) Cross-linked Homopolymer

Polymers in which the adjacent polymeric chains link together through side chains to form a three-dimensional network structure are called cross-linked homopolymers.



$$\begin{array}{lllllll}
-M- & M & -M- & M- & & & \\
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-M- & M & -M- & M- & & & \\
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 & & & M & & & \\
 & & & | & & & \\
 & & -M & -M & -M & -M- &
\end{array}$$

5.3.2 Copolymer (or) Heteropolymer

A polymer having different types of monomers is known as a copolymer.

Example Nylon, Terylene.

$$— M_1 — M_2 — M_1 — M_2 — M_1 —$$

where M_1 and M_2 are two different monomers.

Types Copolymers are subdivided into four types.

(i) **Regular Copolymer** Monomeric units are arranged regularly.

$$— M_1 — M_2 — M_1 — M_2 — M_1 — M_2 —$$

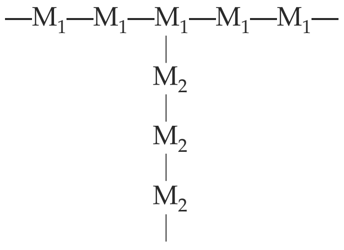
(ii) **Random Copolymer** Here, monomeric units are arranged randomly.

$$— M_1 — M_2 — M_1 — M_1 — M_2 — M_1 —$$

(iii) **Block Copolymer** It is a linear copolymer in which the monomeric units appear as blocks.

$$— M_1 — M_1 — M_1 — M_2 — M_2 — M_2 — M_1 — M_1 — M_1 —$$

(iv) **Graft Copolymer** It is a branched copolymer with one type of monomer (M_1) in the backbone and another kind of monomer (M_2) in the branches.



$$\begin{array}{ccccc}
-M_1- & M_1- & M_1 & -M_1- & M_1- \\
 & & | & & \\
 & & M_2 & & \\
 & & | & & \\
 & & M_2 & & \\
 & & | & & \\
 & & M_2 & & \\
 & & | & &
\end{array}$$

5.3.3 Homochain Polymer

If the main chain is made up of the same species of atoms, the polymer is called a homochain polymer.

Example Polyethylene, Polyvinyl chloride, Polystyrene, etc.

$$—C—C—C—C—C—C—$$

5.3.4 Heterochain Polymer

If the main chain is made up of different atoms, the polymer is called a heterochain polymer.

Example Terylene, Nylon 6:6, Nylon 6, etc.

$$—C—C—N—C—C—N—C—C—$$

5.3.5 Stereospecific Polymer or Tacticity

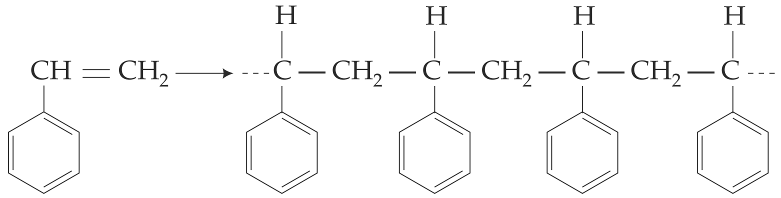
In a polymeric molecule, the arrangement of functional groups, either by an orderly or disorderly manner, with respect to the main chain is called tacticity. Tacticity affects the physical properties of the polymer.

Tacticity originated from the Greek word '*taktikos*' that means **relating to arrangement or order.** This orientation results in three types of stereoregular polymers as follows.

(a) Isotactic Polymer

Polymers in which the functional groups are all located on the same side of the main chain are called isotactic polymers.

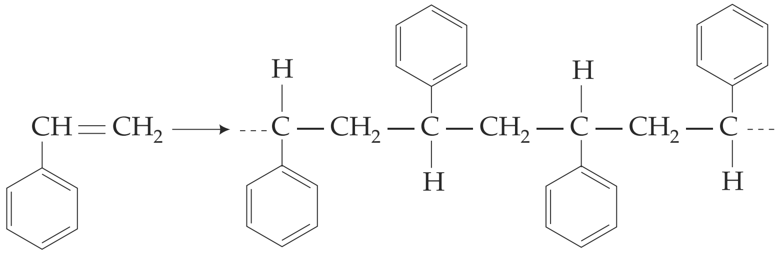
Example Polystyrene



Styrene Isotactic polystyrene

(b) Syndiotactic Polymer

If there is arrangement of functional groups in an alternating fashion around the main chain, the polymer is called a syndiotactic polymer.

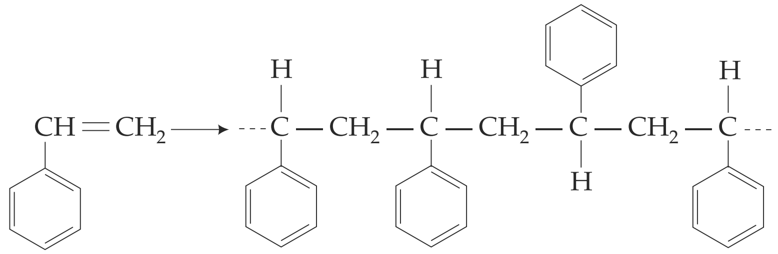


Styrene Syndiotactic polystyrene

(c) Atactic Polymer

If the arrangement of functional groups is located at a random manner around the main chain, the polymer is called an atactic polymer.

Example



Styrene Atactic polystyrene

5.4 FUNCTIONALITY

All types of organic molecules cannot act as monomers. An organic molecule acts as a monomer only when it possesses at least two reactive sites or bonding sites. Functionality is the number of bonding sites or reaction sites present in the monomer.

Example $n\,CH_2 = CH_2 \longrightarrow (-\dot{C}H_2-\dot{C}H_2-)_n$

where • ⟶ bonding site (or) reaction site

(a) Monofunctional

There is only one bonding site in the monomer and thus they are used as **terminators** or **chain stoppers** in polymerization reactions.

Example $\dot{C}H_3COOH, \dot{C}H_3OH$

(b) Bifunctional

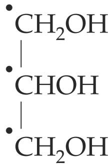
There are two bonding sites in the monomer and thus a linear polymer is formed.

Example $\dot{C}H_2 = \dot{C}H_2, \dot{C}H_2 = \dot{C}H\,Cl$

(c) Trifunctional

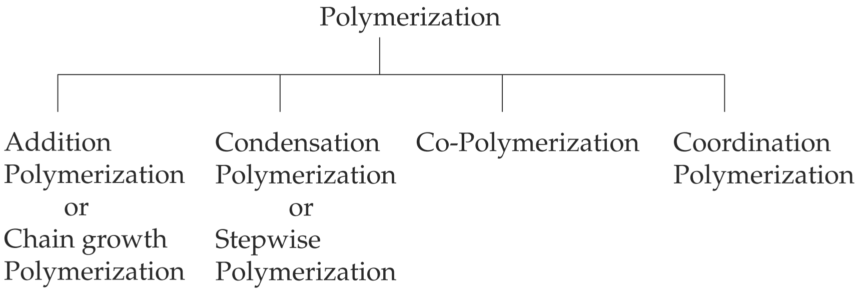
There are three bonding sites in the monomer and hence a cross-linked three-dimensional network polymer is formed.

Example



$$\begin{array}{l} {}^{\bullet}CH_2OH \\ \ | \\ {}^{\bullet}CHOH \\ \ | \\ {}^{\bullet}CH_2OH \end{array}$$

5.5 TYPES OF POLYMERIZATION



5.5.1 Addition or Chain-growth Polymerization

It is a reaction that yields a polymer which is an exact multiple of the original monomeric molecule.

Examples

(i) Polyethylene is produced from ethylene.

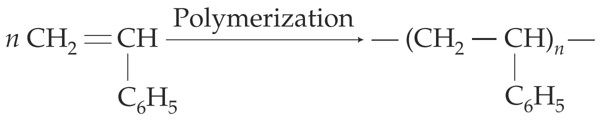
$$\underset{\text{Ethylene}}{n\,CH_2{=}CH_2} \xrightarrow[\text{Catalyst}]{\text{Heat/Pressure}} \underset{\text{Polyethylene (PE)}}{-(CH_2-CH_2)_n-}$$

(ii) Polyvinyl chloride is produced from vinyl chloride.

$$n\,CH_2{=}\underset{\underset{Cl}{|}}{CH} \xrightarrow{\text{Polymerization}} -(CH_2-\underset{\underset{Cl}{|}}{CH})_n-$$

Vinyl chloride PVC

(iii) Polystyrene is produced from styrene.



$$n\,CH_2{=}\underset{\underset{C_6H_5}{|}}{CH} \xrightarrow{\text{Polymerization}} -(CH_2-\underset{\underset{C_6H_5}{|}}{CH})_n-$$

Styrene Polystyrene

- The molecular weight of the polymer is an exact multiple of the monomer.
- Addition polymerization occurs in monomers that contain at least one double bond or triple bond.
- This type of polymerization takes place under suitable conditions, i.e. in the presence of a suitable catalyst and by applying appropriate pressure and temperature.
- An addition polymer is produced by adding a second monomer to the first, and then the third monomer, and so on, until the long chain is produced.

5.5.2 Mechanism of Addition Polymerization

The mechanism of addition polymerization can be explained by any one of the following three types.

1. Free-radical mechanism
2. Ionic mechanism
3. Coordination mechanism or Zeigler–Natta mechanism

All the above mechanisms occur in three consecutive steps, namely,

(i) Initiation,
(ii) Propagation, and
(iii) Termination.

Free-radical Mechanism

Free-radical polymerization is initiated by organic peroxides which decompose to give free radicals. Free radicals are highly reactive species due to the presence of unpaired electrons.

(i) Initiation It involves two reactions.

1. Formation of Free Radical as well as Reactive Species

It involves formation of free radicals by homolytic dissociation of an initiator to yield a pair of free radicals (R·)

$$\underset{\text{(Initiator)}}{I} \longrightarrow \underset{\text{(Free radicals)}}{2R^{\bullet}}$$

Examples

A thermal initiator is a substance used to produce free radicals by homolytic dissociation at high temperature.

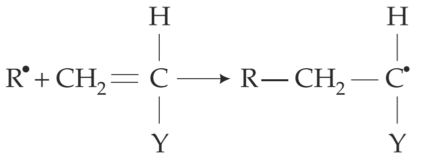
(i) $\underset{\text{Acetyl peroxide}}{CH_3COO\text{-}OOCCH_3} \longrightarrow \underset{\text{Free radicals}}{2\,(CH_3COO)^{\bullet}}$ (or) $2R^{\bullet}$

(ii) $\underset{\text{Benzoyl peroxide}}{C_6H_5COO\text{-}OOC\,C_6H_5} \longrightarrow \underset{\text{Free radicals}}{2\,(C_6H_5COO)^{\bullet}}$ (or) $2R^{\bullet}$

2. The free-radical, thus produced, attaches to a first monomer to produce a chain-initiating species.

$$\underset{\text{Free radical}}{R^{\bullet}} + \underset{\text{monomer}}{M} \longrightarrow \underset{\text{Chain initiating species}}{M_1^{\bullet}}$$

Thus, polymerization of the monomer $CH_2 = CHY$ takes the form



$$R^{\bullet} + CH_2{=}\overset{\displaystyle H}{\underset{\displaystyle Y}{C}} \longrightarrow R{-}CH_2{-}\overset{\displaystyle H}{\underset{\displaystyle Y}{C^{\bullet}}}$$

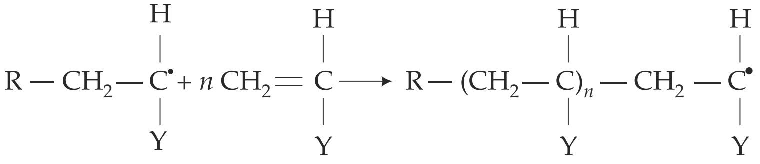
(Chain-initiating species)

The radical $R^{\bullet}$ is referred as *initiator radical* or a *primary radical.*

(ii) Propagation It involves the addition of monomer molecules to a chain-initiating species facilitating the growth of polymer chain.

$$M_1^{\bullet} + M \longrightarrow M_2^{\bullet};\ M_2^{\bullet} + M \longrightarrow M_3^{\bullet}$$

or in general, $M_n^{\bullet} + M \longrightarrow M_{n+1}^{\bullet}$



$$R{-}CH_2{-}\overset{\displaystyle H}{\underset{\displaystyle Y}{C^{\bullet}}} + n\,CH_2{=}\overset{\displaystyle H}{\underset{\displaystyle Y}{C}} \longrightarrow R{-}(CH_2{-}\overset{\displaystyle H}{\underset{\displaystyle Y}{C}})_n{-}CH_2{-}\overset{\displaystyle H}{\underset{\displaystyle Y}{C^{\bullet}}}$$

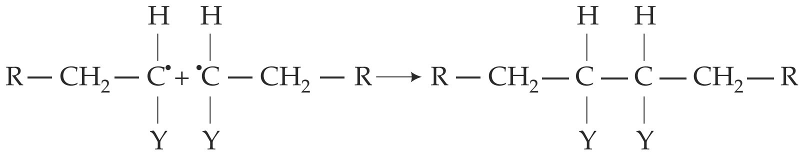
Growing chain
(Living polymer)

The growing chain of the polymer is known as a **living polymer**.

(iii) Termination The growth of polymer chain is terminated either by a coupling reaction or disproportionation.

1. Coupling or Combination

In a coupling reaction, two free-radical polymer chains combine together to form a dead polymer (macromolecule).

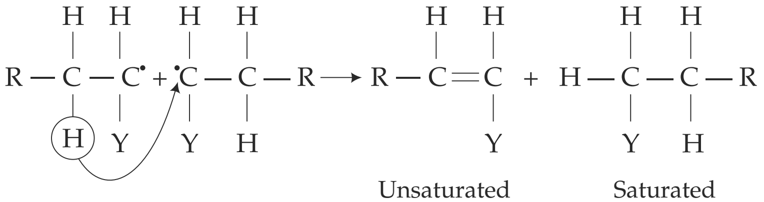


$$R-CH_2-\underset{Y}{\overset{H}{C}}{}^{\bullet}+{}^{\bullet}\underset{Y}{\overset{H}{C}}-CH_2-R \longrightarrow R-CH_2-\underset{Y}{\overset{H}{C}}-\underset{Y}{\overset{H}{C}}-CH_2-R$$

Macromolecule
(Dead polymer)

2. Disproportionation

This reaction involves the transfer of a hydrogen atom from one of the free radical polymer chain to another free radical giving rise to one saturated and one unsaturated polymer molecule.



$$R-\underset{\textcircled{H}}{\overset{H}{C}}-\underset{Y}{\overset{H}{C}}{}^{\bullet}+{}^{\bullet}\underset{Y}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-R \longrightarrow R-\overset{H}{C}=\underset{Y}{\overset{H}{C}} + H-\underset{Y}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-R$$

Unsaturated macromolecule (Dead polymer)

Saturated macromolecule

The product of addition polymerization is known as a **dead polymer**.

5.5.3 Condensation Polymerization or Stepwise Polymerization

This reaction involves the condensation of two functional groups present in the same kind of monomer or different kind of monomers by the elimination of small molecules like H_2O, HCl, NH_3, CH_3OH, etc.,

(a) Condensation Reaction Between two Different Monomers

Example

$$\underset{\text{Hexamethylenediamine}}{n\mathrm{H_2N{-}(CH_2)_6{-}NH_2}} + \underset{\text{Adipic acid}}{n\ \mathrm{HOOC{-}(CH_2)_4{-}COOH}} \xrightarrow{-2n\ \mathrm{H_2O}}$$

$$\underset{\textbf{Nylon 6 : 6 (Polyamide)}}{\mathrm{{-}(NH{-}(CH_2)_6{-}NH{-}CO{-}(CH_2)_4{-}CO)_{\mathit{n}}}}$$

Nylon 6:6 derives its name from the starting materials, adipic acid and hexamethylene diamine, both of which have six carbon atoms. From the above illustration, the following conclusions can be drawn regarding condensation polymerization.

(i) The monomer should have two reactive functional groups.

(ii) The polymerization proceeds by stepwise reaction between reactive functional groups.

(iii) In some cases, both reactive functional groups could be present on the same monomer. In that case, it can lead to a **self-polycondensation reaction.**

(b) Self-condensation of a Monomer Having Different Functional Groups

- Self-condensation of ω-amino caproic acid

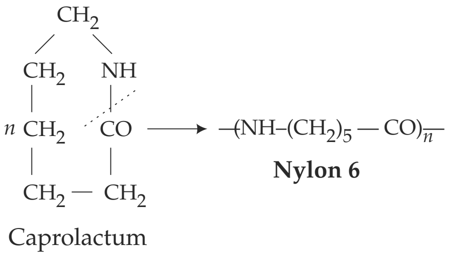
$$\underset{\omega\text{-amino caproic acid}}{n\ \mathrm{H_2N\text{-}(CH_2)_5\text{-}COOH}} \longrightarrow \underset{\text{Nylon-6}}{\mathrm{{-}(HN\text{-}(CH_2)_5\text{-}CO)_{\mathit{n}}{-}}}$$

- Self-condensation of ω-amino decanoic acid

$$n\ \mathrm{H_2N\text{-}(CH_2)_{10}\text{-}COOH} \longrightarrow \underset{\text{Nylon-11}}{\mathrm{{-}(HN\text{-}(CH_2)_{10}\text{-}CO)_{\mathit{n}}{-}}}$$

(c) Ring-opening Polymerization

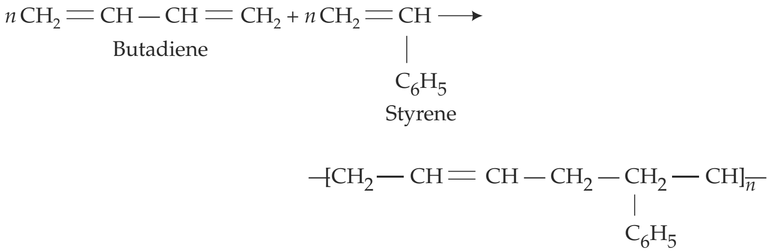
In some cases, condensation polymers are obtained without the elimination of small molecules but it takes place by just opening of cyclic compounds. This type of polymerization is known as **ring-opening polymerization.**



5.5.4 Co-polymerization

Co-polymerization is the joint polymerization of two or more different monomeric species. **High-molecular-weight polymers obtained by co-polymerization are called co-polymers.** In this process, no side products are formed. Co-polymerization can be used to obtain polymeric materials with new properties.

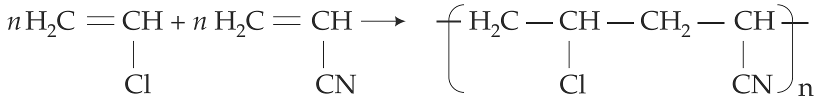
Example (i) Co-polymerization of styrene and butadiene forms Styrene-Butadiene Rubber (SBR) which has superior properties than ordinary synthetic butadiene rubber.



$$\underset{\text{Butadiene}}{n\,CH_2{=}CH{-}CH{=}CH_2} + n\,\underset{\text{Styrene}}{CH_2{=}\underset{\underset{C_6H_5}{|}}{CH}} \longrightarrow -\!\!\left[CH_2{-}CH{=}CH{-}CH_2{-}\underset{\underset{C_6H_5}{|}}{CH_2}{-}CH\right]_n\!\!-$$

Styrene Butadiene Rubber (SBR)

Example (ii) Co-polymerization of acrylonitrile and vinyl chloride is readily soluble in acetone but polyvinyl chloride and polyacrylonitrile are soluble only at higher temperatures.



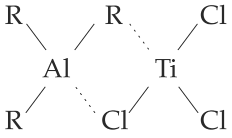
$$n\,H_2C{=}\underset{\underset{Cl}{|}}{CH} + n\,H_2C{=}\underset{\underset{CN}{|}}{CH} \longrightarrow -\!\!\left(H_2C{-}\underset{\underset{Cl}{|}}{CH}{-}CH_2{-}\underset{\underset{CN}{|}}{CH}\right)_n\!\!-$$

Vinyl chloride Acrylonitrile **Poly(vinylchloride-co-acrylonitrile)**

- Chemical and geometrical shapes of polymers can be varied by this reaction and hence it is used to produce unsymmetrical or irregular shape polymers.
- Therefore, **co-polymerization is superior than other** polymerization reactions because it can control various polymeric properties such as hardness, toughness, flexibility, heat resistance, solubility, crystallization tendency, etc.

5.5.5 Coordination or Zeigler–Natta Polymerization

Two scientists, Zeigler and Natta, were awarded the Nobel Prize in 1963 for their outstanding discovery of coordination polymerization. They prepared a coordination complex called Zeigler–Natta catalyst, by reacting a transition metal halide (like $TiCl_4$, $TiCl_3$, $TiCl_2$, $ZrBr_3$, etc.) with organometallic compounds (like triethyl aluminium, trimethyl aluminium). Using the Zeigler–Natta catalyst, **stereospecific polymerization** can be carried out. The structure of a typical Zeigler–Natta catalyst is shown below:



Many other examples exist:

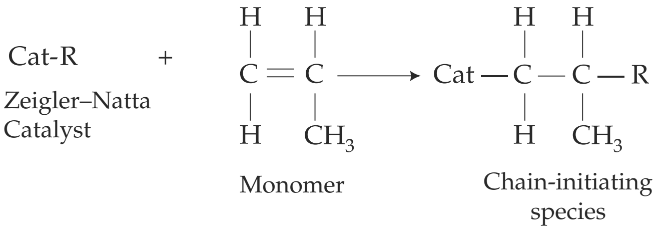
Organometallic Compound	***Transition Metal Salt***
Triethyl aluminium	Titanium tetrachloride
Diethyl $AlCl_3$	Vanadium trichloride
Diethyl $AlCl_2$	Triacetyl acetone vanadium
Butyl lithium	Titanium tetrachloride

It yields polymers of high density and high melting points. In order to explain the mechanism of Zeigler–Natta polymerization, the catalyst is generally represented as Cat-R.

Mechanism

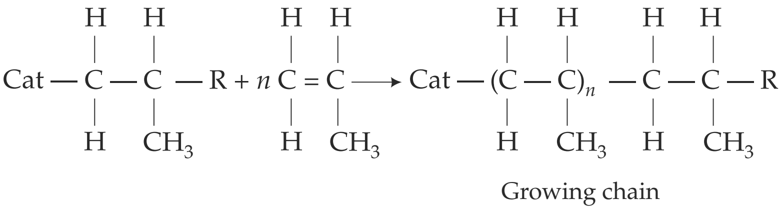
The monomers like propylene, isoprene, etc., follow this mechanism.

(i) Initiation This is the formation of chain-initiating species in which monomer is inserted in between transition metal and alkyl group.



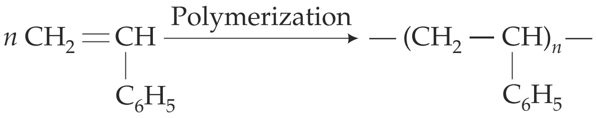
$$\text{Cat-R} + \underset{H}{\overset{H}{C}} = \underset{CH_3}{\overset{H}{C}} \longrightarrow \text{Cat} - \underset{H}{\overset{H}{C}} - \underset{CH_3}{\overset{H}{C}} - R$$

(ii) Propagation Here, the growth of a chain-initiating species is carried out by successive insertion of more number of monomers between the metal and alkyl group.



$$\text{Cat} - \underset{H}{\overset{H}{C}} - \underset{CH_3}{\overset{H}{C}} - R + n\, \underset{H}{\overset{H}{C}} = \underset{CH_3}{\overset{H}{C}} \longrightarrow \text{Cat} - (\underset{H}{\overset{H}{C}} - \underset{CH_3}{\overset{H}{C}})_n - \underset{H}{\overset{H}{C}} - \underset{CH_3}{\overset{H}{C}} - R$$

(iii) Termination The termination process is carried out by addition of an active hydrogen compound (HX).



$$n\,CH_2{=}\underset{\displaystyle C_6H_5}{\underset{|}{CH}} \xrightarrow{\text{Polymerization}} -(CH_2-\underset{\displaystyle C_6H_5}{\underset{|}{CH}})_n-$$

Styrene Polystyrene

5.6 EFFECT OF POLYMER STRUCTURE ON PROPERTIES

The physical, chemical and mechanical properties of a polymer are determined by the nature of monomer units and its structure. The structure acquired by a polymer depends upon the formation and arrangement of its constituent macromolecules. There are several factors involved in deciding the structure and hence the properties of a polymer. They are

1. Strength,
2. Plastic deformation,
3. Crystallinity, and
4. Chemical resistance.

5.6.1 Strength

The strength of a polymer is its resistance to change of shape and mainly depends on the following three factors.

1. Type of attractive forces between molecules. These attractive forces are of two types.
   (i) Strong covalent bond forces
   (ii) Weak van derWaals forces
2. Molecular weight
3. Slipping power

(a) Strength of Linear and Branched-chain Polymers

(i) Types of Attractive Forces: In straight-chain and branched-chain polymers, the individual chains are held by weak van derWaals forces of attraction and they are soft and flexible.

The strength can be increased by increasing the intermolecular van derWaals forces. The intermolecular forces can be greatly increased by the presence of the polar groups like –OH, -COOH, -Cl, -CN, etc., along the chain length, e.g. Nylon, Teflon, etc

(ii) Molecular Weight: Polymers of low molecular weights are quite soft and gummy but brittle to impact at low temperature. But higher-chain polymers are tough and more heat resistant. Thus, by controlling the chain length (or molecular weight), it is possible to vary the physical properties of the polymer from soft and flexible to hard and hornlike substances.

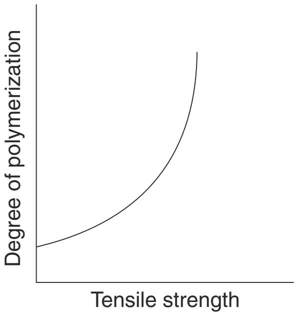
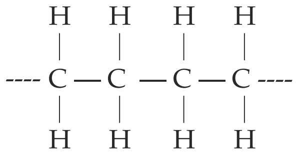


Fig. 5.1

(iii) Slipping Power: It is the movement of one molecule over another. Polymer molecules greatly affect the resistance to slip and consequent deformation of a polymer, and slipping power mainly depends on shape of the molecule.

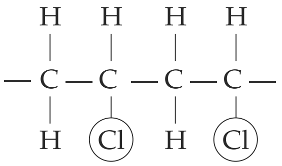
Example: The shape of a polyethylene molecule is simple and uniform, and there is only limited restriction to the movement of one molecule over another, i.e. slipping power is more.



$$\begin{array}{ccccccccc} & \text{H} & & \text{H} & & \text{H} & & \text{H} & \\ & | & & | & & | & & | & \\ \text{----} & \text{C} & — & \text{C} & — & \text{C} & — & \text{C} & \text{----} \\ & | & & | & & | & & | & \\ & \text{H} & & \text{H} & & \text{H} & & \text{H} & \end{array}$$

Polyethylene (PE)

But, PVC molecules have large lumps of chlorine atoms in the chain, and restrict the movement of one molecule over the another. There are strong van derWaals forces, i.e. the slipping power is low. PVC is tough and stronger than polyethylene.



$$\begin{array}{ccccccccc} & \text{H} & & \text{H} & & \text{H} & & \text{H} & \\ & | & & | & & | & & | & \\ — & \text{C} & — & \text{C} & — & \text{C} & — & \text{C} & — \\ & | & & | & & | & & | & \\ & \text{H} & & \text{Cl} & & \text{H} & & \text{Cl} & \end{array}$$

Polyvinyl chloride (PVC)

Due to the presence of a bulky phenyl group, polystyrene possesses greater strength compared to PE and PVC.

(b) Strength of Cross-linked Polymers

In cross-linked polymers, all the structural units are connected by 'strong' covalent forces resulting in a giant solid molecule. Consequently, they are more strong and tough, since the movements of intermolecular chains are totally restricted, e.g. **Bakelite**.

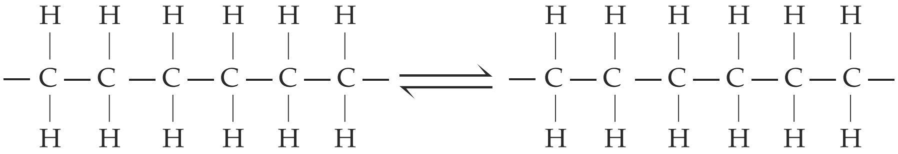
5.6.2 Plastic Deformation

On application of heat and pressure, there is a permanent deformation occurs on a polymer. This property is mainly useful to classify the polymers (thermoplastics or thermosetting plastics).

(a) Plastic Deformation in a Linear Polymer

These are polymeric substances which can be deformed by heat and pressure. This property of thermoplastics is called ***plastic deformation***. Repeated heating and cooling does not affect the chemical nature of the polymer.

Linear polymers show greatest degree of plastic deformation, as the molecules are held by weak van derWaals forces of attraction. Under high temperature and pressure, the forces become weaker. So slippage occurs between the chains. On cooling, they regain their original hardness. Repeated heating and cooling do not affect the nature of the polymer. So plasticity of such polymers is **reversible** and can be remoulded many times. They are called ***thermoplastics,*** e.g. **Polyethylene.**



$$-\underset{\mathrm{H}}{\underset{|}{\overset{\mathrm{H}}{\overset{|}{\mathrm{C}}}}}-\underset{\mathrm{H}}{\underset{|}{\overset{\mathrm{H}}{\overset{|}{\mathrm{C}}}}}-\underset{\mathrm{H}}{\underset{|}{\overset{\mathrm{H}}{\overset{|}{\mathrm{C}}}}}-\underset{\mathrm{H}}{\underset{|}{\overset{\mathrm{H}}{\overset{|}{\mathrm{C}}}}}-\underset{\mathrm{H}}{\underset{|}{\overset{\mathrm{H}}{\overset{|}{\mathrm{C}}}}}-\underset{\mathrm{H}}{\underset{|}{\overset{\mathrm{H}}{\overset{|}{\mathrm{C}}}}}- \rightleftharpoons -\underset{\mathrm{H}}{\underset{|}{\overset{\mathrm{H}}{\overset{|}{\mathrm{C}}}}}-\underset{\mathrm{H}}{\underset{|}{\overset{\mathrm{H}}{\overset{|}{\mathrm{C}}}}}-\underset{\mathrm{H}}{\underset{|}{\overset{\mathrm{H}}{\overset{|}{\mathrm{C}}}}}-\underset{\mathrm{H}}{\underset{|}{\overset{\mathrm{H}}{\overset{|}{\mathrm{C}}}}}-\underset{\mathrm{H}}{\underset{|}{\overset{\mathrm{H}}{\overset{|}{\mathrm{C}}}}}-\underset{\mathrm{H}}{\underset{|}{\overset{\mathrm{H}}{\overset{|}{\mathrm{C}}}}}-$$

(b) Plastic Deformation in Cross-linked Polymer

In giant cross-linked polymers, deformation does not occur on heating because only primary covalent bonds are present throughout the entire structure. Due to the presence of strong covalent bonds, it cannot be easily affected either by heat or pressure. So no slippage occurs in between the chains. Such types of polymers, once moulded, cannot be remoulded and they are called ***thermosetting plastics.*** **Therefore, in thermosetting polymers, plasticity does not increase with increase in temperature.**

5.6.3 Crystallinity

The relative arrangement of the polymer chains with respect to each other results in three types of polymers.

(i) Amorphous polymer
(ii) Crystalline polymer
(iii) Crystallites embedded in an amorphous matrix

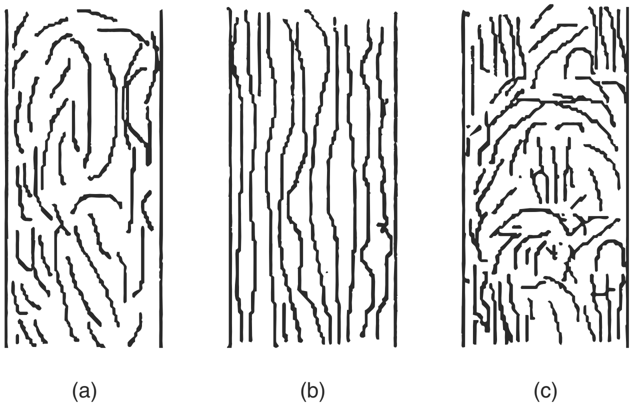


Fig. 5.2 *(a) Amorphous polymer (b) Crystalline polymer (c) Crystalline polymer embedded in an amorphous matrix*

(a) Amorphous Polymer

They have random arrangement of polymer chains and hence the intermolecular forces are weak. Polymers with long chains and bulky side groups of low degree of symmetry, do not crystallise easily and, therefore, form an amorphous state. The amorphous region in a polymer provides flexibility.

Example: Polystyrene, Polyvinyl acetate

(b) Crystalline Polymer

Crystallization imparts denser packing of molecules, thereby increasing the intermolecular forces of attraction. The polymer chains are regularly arranged in a crystalline polymer. So the intermolecular forces are increased, resulting in high density, greater strength and sharper softening point. The tendency of a polymer to be crystalline increases when the polymer chains are linear without any side chain. A completely crystalline polymer tends to acquire brittleness.

Example: Polyethylene, cellulose derivatives

(c) Crystallites Embedded in an Amorphous Matrix

Most of the polymers have crystallites embedded in an amorphous matrix. In such cases, crystallites provide required hardness, rigidity and heat resistance while the amorphous matrix provides flexibility. Co-polymerization decreases crystallinity. In controlling the extent of co-polymerization, the relative extent of crystallites and amorphous region can be adjusted to get the required hardness and flexibility.

5.6.4 Chemical Resistance

The chemical resistance of a polymer is decided by the nature of monomeric units and their molecular arrangement. Chemical attack causes softening, swelling and loss of strength of material.

Examples

(a) Polymers having polar groups like –OH and –COOH are usually soluble in polar solvents like alcohol, water, etc., but they are chemically resistant to nonpolar solvents like benzene, toluene, etc.

(b) Polymers of more aliphatic characters are more soluble in aliphatic solvents.

(c) Polymers of more aromatic characters are more soluble in aromatic solvents.

(d) Polymers having nonpolar groups like $-CH_3$ and $-C_6H_5$ are soluble in nonpolar solvents. But they are resistant to polar solvents like water, ethyl alcohol, etc.

Other factors such as molecular weight, crystallinity and degree of cross linking also determine the chemical resistance.

(i) The tendency to be soluble in a particular solvent decreases with increase of molecular weight of the polymer.

(ii) The chemical resistance of crystalline polymers is more than that of amorphous polymers.

(iii) Greater the degree of cross linking in the polymer, lesser is its solubility.

5.7 PLASTICS

5.7.1 Introduction

(i) Plastics are a new group of ‘engineering materials‘.

(ii) Plastics are ’synthetic organic polymers’.

(iii) Any substance which has the property of ’plasticity‘ is called a plastics.

(iv) Plastics are hard rigid solids at room temperature but they can be moulded in any form with the help of heat and pressure.

5.7.2 Definition

They are organic materials (of high molecular weight). While being processed, can be pushed into almost any desired shape and then retain that shape on application of heat and pressure.

5.7.3 Types of Plastics

Plastics are mainly classified into two types.

(a) Thermoplastics
(b) Thermosetting plastics

(a) Thermoplastics

They soften on heating and harden on cooling. Resoftening and rehardening is also possible.

Examples Polythene, PVC, Polystyrene, Polyester and Polypropylene

(ii) Thermosetting Plastics

They set on heating and cannot be resoftened on cooling.

Examples

- Urea-Formaldehyde
- Phenol-Formaldehyde
- Alkyl resin
- Silicon resin

Table 5.1 *Differences between thermoplastics and thermosetting plastics*

S.No	***Thermoplastics***	***Thermosetting Plastics***
1.	They are prepared by addition polymerization method.	They are prepared by condensation polymerization method.
2.	They are generally linear polymers.	They are generally cross-linked polymers.
3.	They are softer, weaker and less brittle.	They are harder, stronger and more brittle.
4.	They are polymers of smaller molecular weight.	They are polymers of higher molecular weight.
5.	They have low thermal stability.	They have relatively high thermal stability, but prolong heating result in charring.
6.	They can be remoulded.	They cannot be remoulded.
7.	The process is reversible	The process is irreversible.
8.	They soften on heating and regain their original properties on cooling.	They set on heating and cannot be resoftened on cooling.

(Contd.)

Table 5.1 (Contd.)

S.No	Thermoplastics	Thermosetting Plastics
9.	They are easily broken because the molecules are held together by weak van derWaals forces.	They are not easily broken because the molecules are held together by strong covalent bonds.
10.	They expand very much on heating.	They expand in a limited way.
11.	Hardening is not due to chemical reaction.	Hardening is due to chemical reaction.
12.	Scraps can be reused.	Scraps cannot be reused.
13.	They are moulded by injection moulding process.	They are moulded by compression moulding process.
14.	They are soluble in organic solvents.	They are insoluble in organic solvents.
15.	**Example:** Polyethylene, Polypropylene, PVC, etc.	**Example:** Bakelite, Urea-formaldehyde, etc.

5.7.4 Advantages of Plastics

- They are very light but very strong.
- They possess low melting points.
- They can be moulded and have excellent finishing.
- They possess very good strength and toughness.
- They possess good shock-absorption capacity.
- They are corrosion resistant and chemically inert.
- They are good water resistants and possess good adhesiveness.
- They are good electrical insulators.

5.7.5 Disadvantages of Plastics

- They are soft in nature.
- They undergo deformation under load.
- They undergo embrittlement at low temperature.
- They possess low heat resistance and poor ductility.
- They have combustibility.
- Polymer tends to degrade upon exposure to heat and UV radiation.

5.8 INDIVIDUAL POLYMERS

5.8.1 Polyethylene (PE)

Polyethylene is the simplest hydrocarbon polymer and was produced in England during 1933 from the ethylene monomer.

(a) Low-density Polyethylene (LDPE)

(i) Preparation It is prepared by the polymerization of ethylene under high pressure (1000–5000 atm) in presence of oxygen (free-radical initiator).

$$\underset{\text{Ethylene}}{n\,\mathrm{CH_2 = CH_2}} \xrightarrow{\mathrm{O_2}\text{ catalyst}} \underset{\text{LDPE}}{-(\mathrm{CH_2 - CH_2})_n-}$$

(ii) Properties

- This polymer is highly branched and is 40% crystalline.
- Its softening temperature is only 115°C.
- It is soluble in CCl_4, toluene and xylene at high temperature.
- It is ductile in nature.
- It is poor conductor of electricity.

(iii) Uses It is used in making packing films, tablecloths, packing materials, moulded toys, insulation wires, etc.

(b) High-density Polyethylene (HDPE)

(i) Preparation Ethylene can be polymerized at 6–7 atmospheric pressure at 60°–70°C in presence of Zeigler–Natta catalyst.

$$\underset{\text{Ethylene}}{n\,\mathrm{CH_2 = CH_2}} \xrightarrow{\text{Zeigler–Natta cataalyst}} \underset{\text{HDPE}}{-(\mathrm{CH_2 - CH_2})_n-}$$

(ii) Properties

- This polythene is linear and 90% crystalline.
- Its softening temperature is only 135°C and it can be used at higher temperature.
- It is almost insoluble in all the solvents.

(iv) Uses It is used in preparation of toys, containers, pipes, detergent bottles, etc.

Table 5.2 *Differences between low-density polyethylene and high-density polyethylene*

S.No	Low-density Polyethylene	High-density Polyethylene
1.	It is prepared under high pressure using O_2 as a catalyst.	It is prepared under low pressure using Zeigler–Natta catalyst.
2.	It is a branched polymer and has low crystallinity (40%).	It is mostly a linear polymer and highly crystalline (90%).

(Contd.)

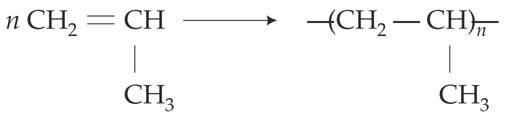
(Table 5.2 Contd.)

S.No	***Low-density Polyethylene***	***High-density Polyethylene***
3.	Density: lower (0.91–0.92 g/ml).	Density: higher (0.965 g/ml).
4.	Melting point is 110–125°C.	Melting point is 144–150°C.
5.	It is soluble in CCl_4, toluene and xylene at high temperature.	It is almost insoluble in all the solvents.
6.	Used for preparing films, tablecloths, packing materials, moulding toys, etc.	Used in preparation of toys, pipes, detergent bottles, containers, etc.
7.	More flexible.	Highly rigid.

5.8.2 Polypropylene (PP)

Polypropylene is prepared from propylene.

(a) Preparation It is obtained by the polymerization of propylene in the presence of Zeigler–Natta catalyst (coordination catalyst)



$$n\,\underset{\displaystyle CH_3}{CH_2 = \underset{|}{CH}} \longrightarrow -\!\!\left(\underset{\displaystyle CH_3}{CH_2 - \underset{|}{CH}}\right)_{\!n}\!\!-$$

Propylene Polypropylene

(b) Properties

- It is a stereoregular, isotactic polymer and highly crystalline in nature.
- It is insoluble in many solvents and soluble in boiling organic solvents.
- It possesses good dielectric property.
- Its melting points is 160°C.
- It is more resistant than polyethylene.

Uses

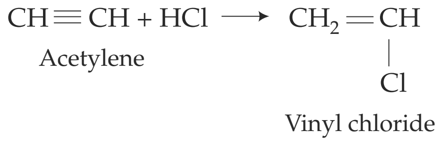
- It is used in the manufacture of squeezing of bottles, textile machinery parts, laboratory articles, sanitary wares and insulation of electrical wires.
- It is used in making moulded parts and fibres.
- Polypropylene fibres are used in handbags, carpets, etc.

5.8.3 Polyvinyl Chloride (PVC)

PVC is the most important of all the polyvinyl plastics and is called **'Koroseal'.**

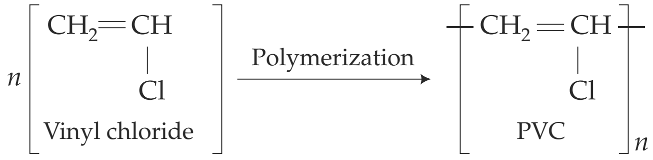
(a) Preparation Vinyl chloride is the monomer used for preparation of PVC. It involves the following two steps.

Step I: Vinyl chloride is prepared by treating acetylene with hydrogen chloride at 60–80°C in the presence of metal chloride as catalyst.



$$\underset{\text{Acetylene}}{CH\equiv CH} + HCl \longrightarrow \underset{\text{Vinyl chloride}}{\underset{\underset{Cl}{|}}{CH_2=CH}}$$

Step II: Polyvinyl chloride is prepared by free-radical polymerization of vinyl chloride. A water emulsion of vinyl chloride having a small amount of benzoyl peroxide is heated under pressure



$$n\left[\underset{\text{Vinyl chloride}}{\underset{\underset{Cl}{|}}{CH_2=CH}}\right] \xrightarrow{\text{Polymerization}} \left[\underset{\text{PVC}}{\underset{\underset{Cl}{|}}{CH_2=CH}}\right]_n$$

(b) Properties

- PVC is a colourless, odourless, chemically inert powder and non-inflammable.
- It is insoluble in inorganic acids and alkalies, but soluble in hot chlorinated hydrocarbons such as ethyl chloride.
- It undergoes degradation in the presence of heat or light.
- Pure resins possess a high softening point (148°C).

(c) Uses

(i) Rigid PVC (or) Unplasticised PVC: Since it has superior chemical resistance and high rigidity, it is used for making sheets, which are employed for tank linings, light fittings, refrigerator components, etc.

(ii) Plasticised PVC: It is used in the production of pipes, cable insulations, table covers and raincoats, etc.

5.8.4 Teflon or Fluon or Poly Tetrafluoro Ethylene (PTFE)

(a) Preparation It is prepared by free-radical addition polymerization of water emulsion of tetrafluoro ethylene at high pressure in the presence of benzoyl peroxide.

$$\underset{\text{Tetrafluoroethylene}}{n\,(CF_2=CF_2)} \xrightarrow{\text{Polymerization}} \underset{\text{PTFE}}{-\!\!(CF_2-CF_2)_n\!\!-}$$

(b) Properties

- Due to high electro negative fluorine atoms, they have strong attractive forces. These forces give the material extreme toughness and high softening point.
- It is a linear and highly crystalline polymer.
- It possesses good electrical and mechanical properties.
- It has a good chemical resistant capacity (except hot alkali metal and hot fluorine).
- It is insoluble in most of the solvents.

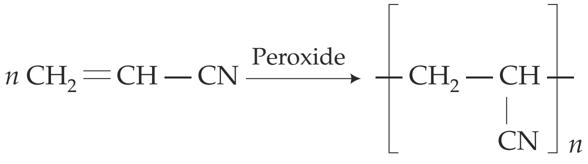
(c) Uses

- It is used as a good electrical insulator in motors, cables, transformers and electrical fittings.
- It is also used as a nonstick coating on frying pans, making gaskets, packings, pump parts, tank linings, etc.
- It is used for preparing non-lubricating bearings, chemical carrying pipes, etc.
- It is used for making stopcocks for burettes and in chemical equipments.

5.8.5 Acrylics or Poly Acrylonitrile or PAN or Orlan or Acrilan

(a) Preparation It is prepared by the polymerization of acrylonitrile in the presence of peroxide. The starting material is prepared by passing a mixture of propene, ammonia, steam and air over a mixture of oxides of molybdenum, cobalt and aluminium.

$$\underset{\text{Propene}}{2CH{=}CH{-}CH_3} + 2NH_3 + 3O_2 \xrightarrow[\text{Mo, Co and Al}]{\text{Oxides of}} \underset{\text{Acrylonitrile}}{2CH_2{=}CH{-}CN} + 6H_2O$$



$$n\,CH_2{=}CH{-}CN \xrightarrow{\text{Peroxide}} \left[CH_2{-}\underset{\displaystyle CN}{\underset{|}{CH}} \right]_n$$

Acrylonitrile **Polyacrylonitrile**

(b) Properties and Uses

- It is a highly crystalline polymer.

- It is the major constituent of acrylic fibres.
- It is used for making fibres, adhesives, nitrile rubber and for impregnating leather and paper.
- It has high resistance to chemicals and has good mechanical properties.
- It is used as a substitute for wool in making fibres.

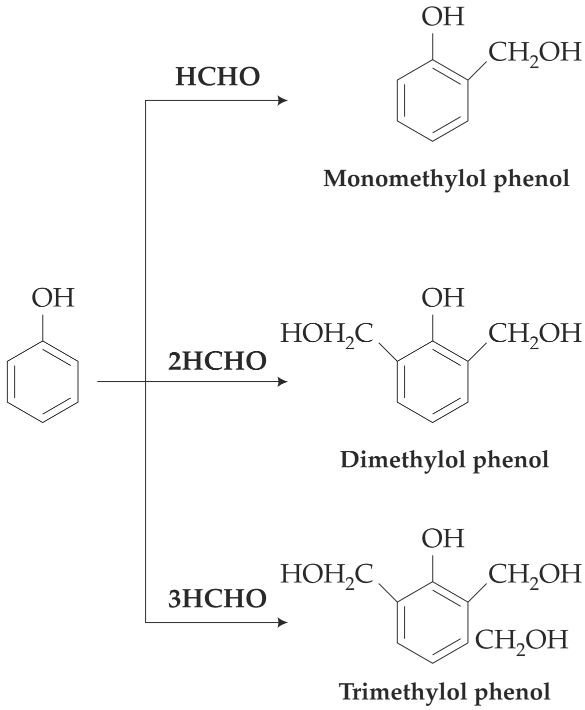
Example: Orlon.

5.8.6 Bakelite or Phenolic Resin or Phenoplast

Phenolic resins are condensation polymers obtained by condensing phenol with formaldehyde in the presence of an acid or alkali catatyst. It is the most important and oldest of synthetic plastics.

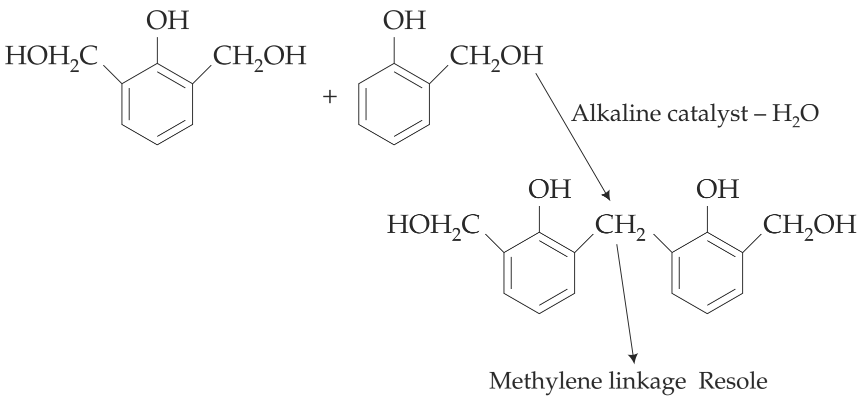
(a) Preparation The reaction proceeds in the following three steps.

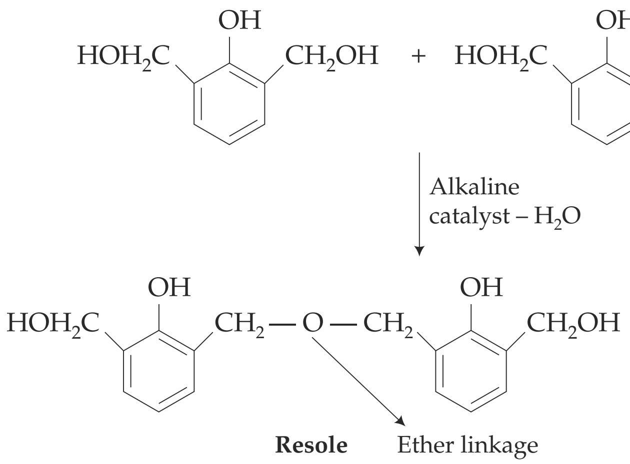
Step I: Methylolation: During the first step, the reaction takes place between phenol and formaldehyde forming mono, di and tri-methylol phenols.



Step II:

(i) Formation of A-stage Resin (Resole)

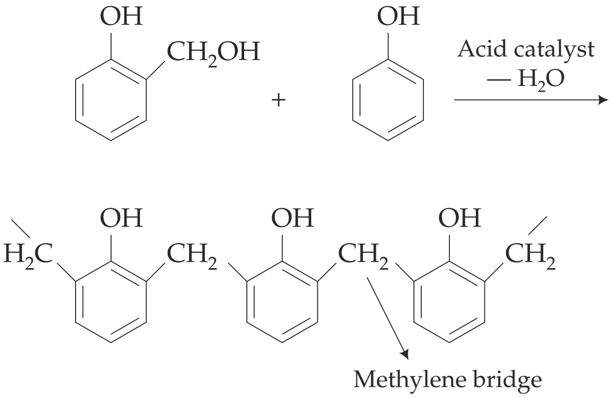




- When excess of formaldehyde is heated with methylol phenols in the presence of an alkaline catalyst, the methylol phenols condense either through methylene linkage or through ether linkages to form resoles.
- Resole is a linear, low-molecular-weight polymer and completely soluble in alkaline solution.

(ii) Formation of B-stage Resin (Novolac or Resitol): When excess of phenol is heated with methylol phenols in the presence of an acidic catalyst, the methylol phenols condense with phenol through methylene linkages to form novolacs.

- Novolac is a linear high-molecular weight polymer and is insoluble in alkaline solutions.

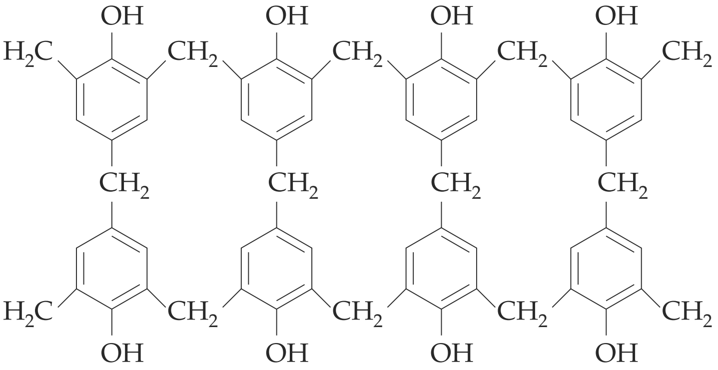


Novolac (or) Resitol

Step III: Production of C-stage Resin (Bakelite)

$$\textbf{A stage Resin + B stage Resin} \xrightarrow{\text{Curing Agent}} \textbf{Bakelite}$$

Heating A-stage Resin or B-stage Resin or both in the presence of a curing agent (hexamethylene tetramine) produces **a hard, rigid, infusible, cross-linked structure** called **Bakelite**.



Bakelite

(i) Properties

- It is a hard, rigid, infusible, water resistant and insoluble solid.
- Bakelite is resistant to acids, salts and most organic solvents, but it is attacked by alkalies because of the presence of –OH groups.
- It acts as an excellent electrical insulators.
- It can withstand high temperature.

(ii) Uses

- It is used for making moulded articles such as radio and TV parts, etc.
- It is used as an adhesive in plywood laminations and in grinding wheels, etc.
- It is commonly used in paints and varnishes.
- It is used for making electrical insulation parts like plugs, switches, heater handles, etc.
- It is also used as ion-exchange resins.

5.8.7 Nylon (Polyamides)—Nylon-6,6

It is a condensation polymer. This is the first synthetic fibre produced from simple molecules. Its chemical name is polyhexamethylene adipamide.

(a) Preparation

Nylon-6,6 is obtained by the polymerization of adipic acid with hexamethylene diamine.

$$\underset{\text{Hexamethylenediamine}}{n\,H_2N\text{—}(CH_2)_6\text{—}NH_2} + \underset{\text{Adipic acid}}{n\,HOOC\text{—}(CH_2)_4\text{—}COOH} \longrightarrow$$

$$\underset{\textbf{Nylon-6,6}}{\text{—}[HN\text{—}(CH_2)_6\text{—}NH\text{—}CO\text{—}(CH_2)_4\text{—}CO]_n} + 2n\,H_2O$$

(b) Properties

- It is tough, strong and crystalline in nature.
- It is easily mouldable and abrasion resistant.
- It has high tensile strength and high elasticity
- It has good chemical resistance.
- It has low coefficient of friction.
- **Kevlar** it is an aromatic polyamide similar to nylon but instead of aliphatic chain, a benzene ring will be present). It is highly temperature resistant.

(c) Uses

- It is used for making nylon thread in textile materials.
- Nylons are used for making filaments for ropes, bristles for toothbrushes and films etc.,
- It is used in automobile industries as self-lubricating bearings, gears, etc.

- It is also used in making shocks, dresses, carpets, etc.

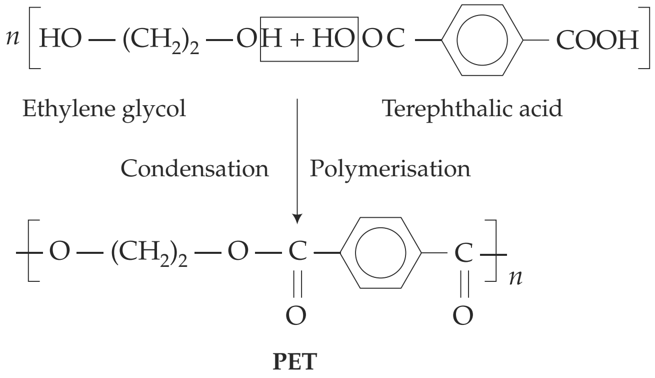
5.8.8 Polyester Resins

Polyesters are the condensation products of dicarboxylic acid with dihydroxy alcohols.

Examples: Polyethylene terephthalate (PET) or Terylene or Dacron.

(a) Polyethylene Terephthalate (PET)

(i) Preparation: It is a saturated polyester, prepared by the condensation of ethylene glycol and terephthalic acid.



(ii) Properties

- It is a good fibre-forming material with high tensile strength and can be converted into commercial fibres.
- It possesses high stretch-resistance, high-crease and wrinkle-resistance.
- It is highly resistant to mineral and organic acids, but is less resistant to alkalies.
- It has low moisture absorption capacity.

(iii) Uses

- It is mostly used for making synthetic fibres like Terylene, Dacron etc.,
- It is used for blending with wool to provide better crease and wrinkle resistance.
- It is used as a glass-reinforcing material in safety helmets, aircrafts, battery boxes, etc.

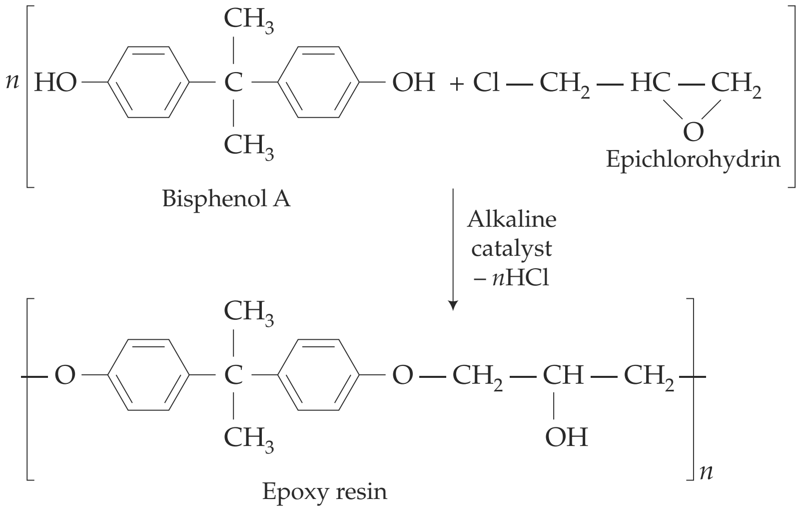
5.8.9 Epoxy Resins or Epoxide Polymers

They are fundamentally polyethers, because the monomeric units have an ether structure (R-O-R). Epoxy Resins are cross-linked thermosetting resins.

(a) Preparation

Epoxy polymers, or epoxy resins, are prepared by condensing epichlorohydrin with Bisphenol-A.

The reactive epoxide and hydroxyl groups give a three-dimensional cross-linked structure. The value of '*n*' ranges from 1 to 20 and the molecular weight ranges between 350 and 8000.



(b) Properties

- Due to the presence of stable ether linkage, they have high chemical resistance to water, acids, alkalies, various solvents and other chemicals.
- They have high flexibility, toughness and possess very good heat resisting property.
- Due to polar nature of the molecules, they produce excellent adhesion property.

(c) Uses

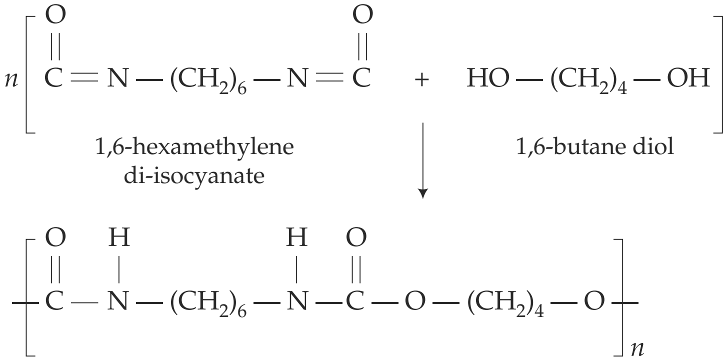
- These are used as surface coatings, adhesives like araldite, glass-fibre reinforced plastics.
- To impart crease resistance and shrinkage control, epoxy resins can be applied over cotton, rayon and bleached fabrics.

- They are used as laminating materials in electrical equipments.
- Moulds made from epoxy resins are used for the production of aircrafts and automobile components.

5.8.10 Poly-Urethane (Perlon-U)

(a) Preparation

Poly-Urethane is commercially obtained from di-isocyanate and diol. Perlon-U (a crystalline polymer) is obtained by the reaction of 1,4-butane diol with 1,6-hexamethylene di-isocyanate.



$$n\left[\overset{\overset{\displaystyle O}{\|}}{C}=N-(CH_2)_6-N=\overset{\overset{\displaystyle O}{\|}}{C} + HO-(CH_2)_4-OH\right] \longrightarrow \left[-\overset{\overset{\displaystyle O}{\|}}{C}-\overset{\overset{\displaystyle H}{|}}{N}-(CH_2)_6-\overset{\overset{\displaystyle H}{|}}{N}-\overset{\overset{\displaystyle O}{\|}}{C}-O-(CH_2)_4-O-\right]_n$$

Poly-Urethane or Perlon-U

(b) Properties

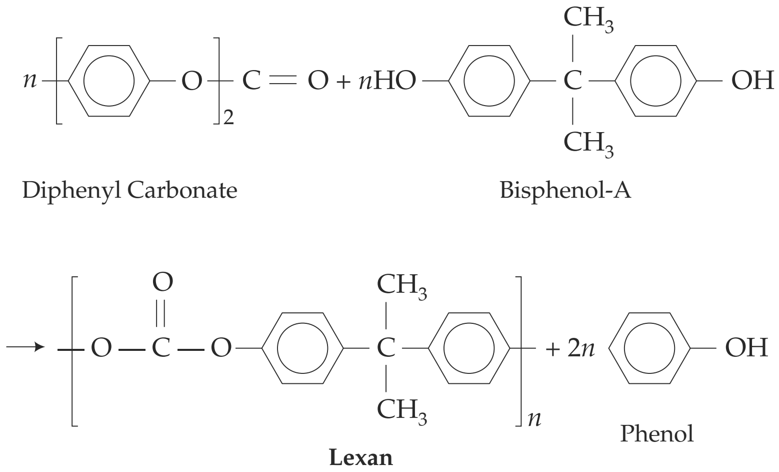
- They are less stable than polyamides.
- They are highly resistant to oxidation.
- They possess excellent flexibility and toughness even at subzero temperatures.
- They are characterized by excellent resistance to abrasion and solvents.
- They are used to produce gaskets, seals and printing rolls.

(c) Uses

- Poly-urethanes are used as coatings, films, foams, adhesives and elastomers.
- They are also used in defence, oceanographic research, mountaineering, etc.
- Poly-urethane fibres are used for formation of garments and swimsuits.
- They are also used as a leather substitute.

5.8.11 Polycarbonate PC (Lexan, Merlon)

Polycarbonates are those polymers which contain a carbonate group as a repeating unit. They are prepared by interaction of diphenyl carbonate with bisphenol-A



(a) Properties

- They are characterized by high tensile strength and impact strength over a wide range of temperature (but have low scratch resistance).
- They are soluble in organic solvents and alkalis.

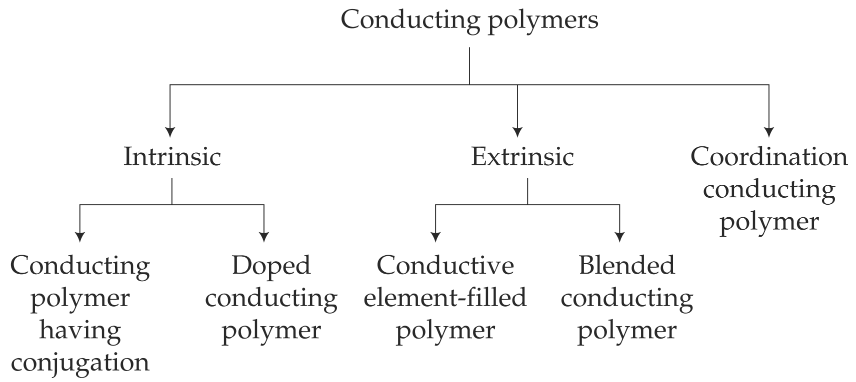
(b) Uses

- They are used for preparing domestic ware, housing for apparatus and electrical insulators in electronic and electrical industries.
- They are used to make ultralight eyeglass lenses, compact discs, DVD’s and food storage containers.
- They are also used in production of sterilizable transparent containers, baby bottles, safety windows in prison and jewellery shops.

5.9 CONDUCTING POLYMERS

Polymers are generally poor conductors of electricity and some polymers such as Teflon are used as insulators. Nowadays, such polymeric materials have been synthesized which possess electrical conductivities, and are called, **conducting polymers**.

5.9.1 Classification



(a) Intrinsic Conducting Polymer (ICP)

These polymers have extensive conjugation in the backbone which is responsible for conductance.

(i) Conducting Polymer having Conjugation

Such a polymer contains a conjugated Π-electron in the backbone which increases its conductivity to a large extent. This is because overlapping of the conjugated Π-electron over the entire backbone results in formation of valence bands as well as conduction bands.

The valence band and conduction band are separated by a band gap. Thus, electrical conduction occurs only after thermal or photolytic activation, to give them sufficient energy to jump the gap and reach lower levels of the conduction band.

Example: Polyacetylene

(ii) Doped Conducting Polymer

It is obtained by exposing a polymer to a charge-transfer agent either in gas phase or in solution. Generally, intrinsic conducting polymers possess low conductivity. But they can be easily oxidized or reduced as they have low ionization potential and high electron affinity. This conductivity can be increased by creating either positive or negative charge on the polymer backbone by oxidation or reduction. This is called doping and is of two types.

- **P-Doping:** It involves treating the intrinsic conducting polymer with a Lewis acid. Oxidation takes place and a positive charge is created on the polymer backbone. Some of P-dopants used are $FeCl_3$, I_2, Br_2, etc.
- **N-Doping:** It involves treating the intrinsic conducting polymer with a Lewis base. Reduction takes place and a negative charge

is created on the polymer backbone. Some of N-dopants used are sodium naphthalide.

(b) Extrinsic Conducting Polymer

In these polymers, conductivity is due to the presence of externally added ingredients in them.

(i) Conductive Element-filled Polymer

In this, the polymer acts as a binder to hold the conducting element (such as carbon black, metallic fibres) together in solid entity. The minimum concentration of the conductive filler which should be added so that polymer starts conducting, is known as **percolation threshold**. These polymers possess good conductivity and are generally low in cost, light in weight, mechanically durable, strong and easily processable in different forms, shapes and sizes.

(ii) Blended Conducting Polymer

These polymers are obtained by blending a conventional polymer with a conducting polymer. Such polymers possess better physical, chemical, electrical and mechanical properties and can be easily processed.

(c) Coordination Conducting Polymers (Inorganic Polymers)

It is a charge transfer complex containing a polymer obtained by combining a metal atom with a polydentate ligand. Degree of polymerization in such polymers is small.

Applications

- It is used in rechargeable light-weight batteries.
- It is used in wiring aircrafts and aerospace components.
- It is also used in solar panels.

5.10 POLYMER BLENDS AND ALLOYS

5.10.1 Polymer Blends

A polymer blend is a simple physical combination of two or more incompatible polymers, e.g. wood is a natural blend of more than one polymer.

5.10.2 Properties

(i) A polymer blend appears as separate phases, when viewed under a microscope.

(ii) Between different polymeric chains, only van derWaals forces, dipole interaction or hydrogen bonding exists.

(iii) The properties of a polymer blend are closely related to the properties of the individual polymer component.

For example, a blend of PMMA (an amorphous polymer) with PVDF (poly vinyldene fluoride, crystalline polymer) is amorphous if the PVDF proportion is below 40%.

(iv) Blending usually improves the properties like processability, impact strength, abrasion resistance, flame retardance, etc.

(v) Sensitive component of a blend may be protected from degradation by blending.

For example, PMMA is degraded by γ-radiation. However, its blend with Styrene-Acrylonitrile (SAN) reduces the rate of degradation.

Examples

(i) ABS plastics are made by blending acrylonitrile-stryrene copolymer with butadiene-stryrene rubber. ABS possesses a high impact strengh, high softening temperature and mouldability. ABS products have a pleasing appearance. They are used in the automobile industry for making panels, door covers, door bands etc. Electroplated ABS is used for reflectors, nameplates and other such jobs, where a bright reflecting surface is required.

(ii) Polycarbonate (PC)-ABS (acrylonitrile-butadiene-styrene) blend is used for making electrical housings and machine parts.

(iii) Nylon 6-PC blend possesses improved thoughness and is employed for making sports equipment and transport containers.

(iv) Polymide polyphenylene sulphide blend possesses properties of both. It has processability and high temperature resistance. It is used as an insulator and electrical connector.

(v) Polydimethylphenylene-polystyrene blend possesses low water absorption, low moulding shrinkage, resistance to hydrolysis and quite good dielectric properties over a wide range of temperature. It finds use in electrical industries, automobile parts, radio and television parts.

5.10.3 Polymer Alloy

Polymer alloy is a compatible mixture of two or more polymers, which interact chemically in the presence of compatibilizers under specific conditions of composition, temperature and pressure. The purpose of a compatibilizer is to provide physical links between semicompatible polymeric materials and to form a polymeric network. Usually, a block of copolymers are used as compatibliers, e.g. chlorosulphonated polythene.

Alloying of two polymers is, usually, done for achieving a specific combination of properties which are not attainable by the use of either of constituent polymers. Alloying of polymers, usually, improves properties like processability, abrasion resistance, impact strength, flame retardance, etc.

Examples

(i) ABS-PC Alloys

ABS-PC alloys possess high softening temperature (110–130°C), good impact strength, good flexural strength, flame retardance and can be electroplated.

Uses: For making typewriters, electronic printers, wheel caps, food mixers, helmets, grills, pump casting and in the medical field as a substitute for stainless steel, since it can be sterilized.

(ii) ABC-PVC Alloy

ABC-PVC alloy possesses good surface gloss, dimensional stability, creep resistance, better flow properties, self-extinguishing property and can be processed at low temperature. Moreover, it can be painted, screenprinted and electroplated.

Uses: In making electronic switch devices, TVs, deflection components, dashboards for passenger cars, connectors to busbars, liners for buses, truck cabs, etc.

5.11 COMPOUNDING OF PLASTICS

Compounding is a process of mixing of raw plastics with other substances to impart special properties to the product. Usually, the high-polymer material is mixed with 4 to 10 ingredients, each of which either discharges a useful function during moulding or imparts some useful property to the finished article. The main types of compounding ingredients and their functions are described below.

5.11.1 Resin or Binders

- Resin is the binder, which holds the different constituents together.
- Thermosetting resins are usually supplied as linearpolymers of comparatively low molecular weight, because at this stage, they are fusible and hence mouldable.

- The conversion of this fusible form into cross-linked infusible form takes place during moulding itself in the presence of catalysts etc.
- They are major portions of plastic, e.g. wood resin, litharge.

5.11.2 Plasticizer

- Plasticizers are materials that are added to resins to increase their plasticity and flexibility.
- Their action is considered to be the result of the neutralization of a part of the intermolecular forces of attraction between macromolecules of resins.
- They impart greater freedom of movement between polymeric macromolecules of resins, thereby increasing the flexibility and plasticity of the compounded material, but at the same time reducing its strength and also decreasing its chemical resistance.
- The most commonly used plasticizers are vegetable oil, camphor, esters of stearic or oleic or phthalic acids and some phosphates like tricresyl phosphate, tributyl phosphate, tetrabutyl phosphate and triphenyl phosphate.

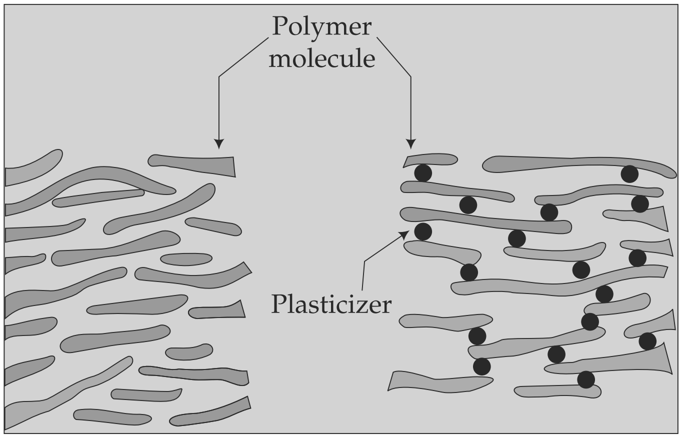


Fig. 5.3 *Action of plasticizer in plastics*

5.11.3 Fillers or Extenders

Addition of fillers leads to hardness, opacity, tensile strength, and workability.

They are added

- To reduce the cost
- Decrease shrinkage during setting

Examples

1. In order to improve the hardness and heat resistance, quartz and mica are added.
2. Addition of barium salts to plastics avoids penetration of *X*-rays.

Besides the above-mentioned fillers, other fillers like china clay, gypsum, paper pulp, carbon black, metallic oxides and talc, are also used.

5.11.4 Lubricants

They help in easy moulding of plastics and avoid plastic material from sticking to fabrication equipment.

Examples: Waxes, oils, stearates and soaps

5.11.5 Catalysts or Accelerators

These are used only in the case of thermosetting resins, to accelerate the condensation polymerization of fusible resin into cross linked infusible products.

Examples: Hydrogen peroxide, benzoyl peroxide, metals like Ag, Cu and Pb, metallic oxides, ammonia and its salts.

5.11.6 Stabilizers

- Stabilizers are added to the moulding components in order to improve the thermal stability of the moulding mix during the processes.
- *Two classifications:* Opaque moulding stabilizers and Transparent moulding stabilizers.

Examples 1. *Opaque moulding stabilizers*—White lead, lead chromate and lead naphthenate.

2. *Transparent moulding stabilizers*—Stearates of lead, barium and calcium.

5.11.7 Pigments and Dyes

In order to impart suitable colours, suitable dyes and pigments are usually added to plastics.

Examples: Chromium trioxide, carbon black, zinc oxide, etc.

- Chromium trioxide provides green colour.
- Carbon black provides black colour.
- Zinc oxide provides white colour.

5.11.8 Anti-oxidants

- The main function of an anti-oxidant is to protect the plastic against UV radiation and oxygen.
- UV radiation weakens and breaks the primary bonds resulting in splitting of long-chain polymer molecules. Because of this, the polymer becomes brittle and stiff.
- Anti-oxidants such as diphenylamine, are used to prevent oxidative degradation in polymer.

5.12 FABRICATION OF PLASTICS

Articles of different shapes can be prepared from polymeric materials by a method called fabrication of plastics. Many methods are employed for fabrication, which depends on the types of plastics. The above-said process of conversion of different-shaped articles is called **moulding process**.

5.12.1 Moulding Process

Some moulding processes are given below:

(a) Compression Moulding

- The compression moulding method is used for both thermo- and thermosetting plastics.
- The raw material used is in the form of loose powder or compacted pills.

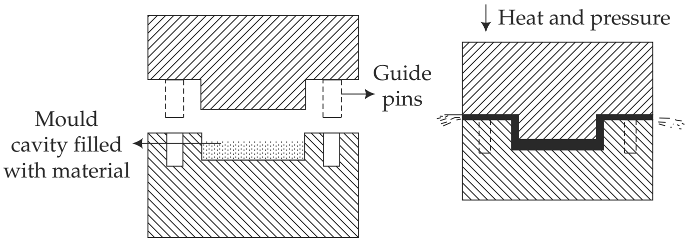


Fig. 5.4 *Compression moulding*

- The correct amount of plastic ingredients must be taken. Then they are filled between the two half pieces of the mould as shown in Fig. 5.4 which are capable of being moved relative to each other.
- High pressure of the order of 100 kg/cm^2 and temperature of the order of 100 to 200°C are applied to complete the curing process.
- The cavities are filled with fluidized plastic.
- The two halves are closed very slowly.
- Finally, curing is done by cooling or heating.
- After curing, the moulded article is taken out by opening the mould parts.

(b) Injection Moulding

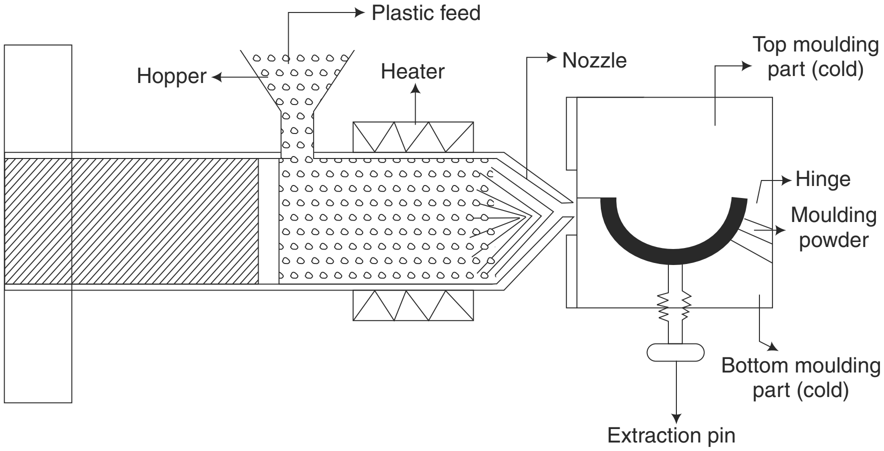


Fig. 5.5 *Injection Moulding*

- This method is commonly used for thermoplastics.
- The moulding powder is fed into a heated cylinder.
- This powder softens under heat and becomes fluid.
- The temperature used in this process is 90–260°C.
- The pressure used is 10,000 to 30,000 psi (pounds/square inch).
- The molten plastic material from the cylinder is then injected through a nozzle under high pressure into the moulding cavity.
- One is a stationary part and another is a movable part.
- After the mould is filled with the molten material under pressure, it is cooled by cold water circulation.

- Afterwards, the mould is opened and the moulded part is pushed out.
- This type of moulding takes shorter time, i.e. the product is obtained within 10 seconds.
- Radio, TV and refrigerator components are manufactured by this type of moulding.

Advantages

This method is the most widely used for moulding of thermoplastics, because of its high-speed production, low mould cost, very less loss of material and low finishing cost.

(c) Extrusion Moulding

This method is mainly used for continuous moulding of thermoplastic materials into articles of uniform cross-section such as pipes, tubes, rods, etc. The moulding material is liquified in a heated chamber. When the material gets softened, it is pushed into a die with the help of a screw conveyer. The die has the required outer shape designed for the finished article. The finished product is cooled by exposure to atmospheric air or by spraying water over it. A long conveyer carries away the cooled product.

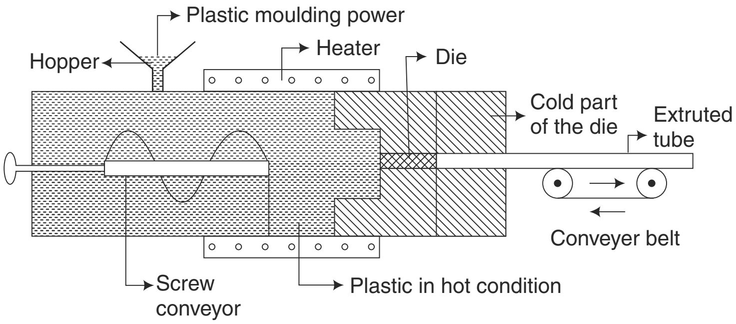


Fig. 5.6 *Extrusion moulding*

(d) Blow Moulding

Most of the hollow plastic materials like PET bottles and toys are manufactured by this technique. Usually, thermoplastic materials like PVC, polystyrene, HDPE, PP can be blow moulded.

A hot softened thermoplastic tube at first as ***parison,*** is placed inside two pieces of the hollow mould. When the two halves of the mould are closed, one end is completely closed and the other end remains in contact with the parison through a blowing pin. Compressed air is now blown to the parison through a blowing pin. The parison is inflated like a balloon and goes on expanding until it comes in intimate contact with the cold interior surface of the hollow mould. The parison ultimately takes the shape of the hollow cavity of the mould under pressure. After cooling, the moulded article is removed from the mould by opening it.

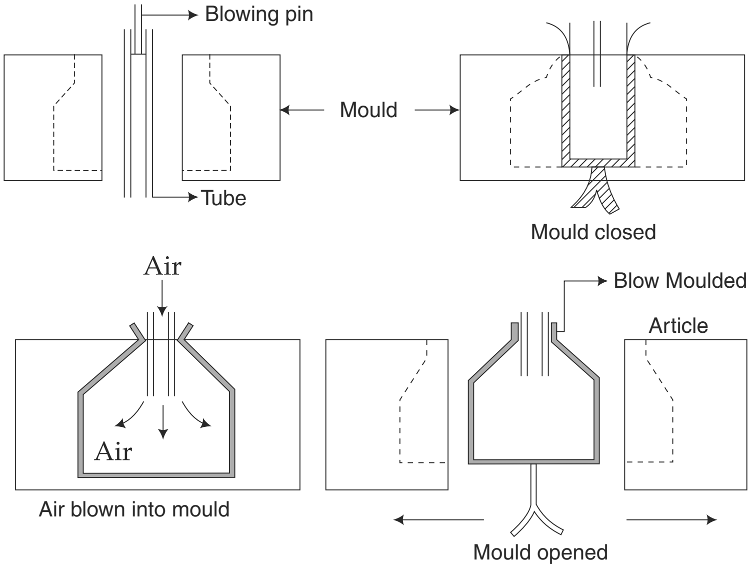


Fig. 5.7 *Blow moulding*

5.13 FOAMED PLASTICS

5.13.1 Introduction

According to American Society for Testing and Materials (ASTM), foamed plastics are biphasic wherein a gas is dispersed in a dispersion medium (like synthetic rubber or plastics). Foamed plastics are made by adding air or gas to a plastic resin to form a spongelike substance. The common resins used for foamed plastics are mainly poly-urethane, polystyrene, polyethylene, polyvinyl chloride, cellulose acetate, epoxy resin, silicones and phenolic resins.

5.13.2 Types

Plastic foams are generally classified as ***open-cell*** and ***closed-cell*** structure foams. An open-cell structure means that the foam has interconnected cells or openings running through the material. A closed-cell structure has closed cells or bubbles. The open-cell structure foam will allow any liquid to pass through like a sponge, whereas the closed-cell structure foam will not allow any liquid to pass through the foam. Closed-structure foams are generally rigid.

5.13.3 Method of Preparation

It is prepared by the following three methods.

(a) Chemical Foaming

In a foamed plastic or rubber, there are two-phase systems in which a gas or air is dispersed into a dispersion medium such as plastic or rubber. In foamed polymers, the fluid polymers such as poly-urethane, PVC, polystyrene, etc., are heated with blowing agents such as calcium carbonate, halocarbons etc., which produce the inert gases that are entrapped inside the polymer matrix.

(b) Mechanical Foaming

The resin in liquid form is vigorously agitated until it becomes a foam of air bubbles. PVC plastisols can be mechanically agitated to produce a foamed polymer.

(c) Physical Foaming

In this process, certain gases like nitrogen, carbon dioxide or air are forced through the molten resin to produce the foamed polymer. Foamed polythene is produced by forcing compressed nitrogen gas into molten polyethylene.

5.13.4 Foamed Plastics

Example: **Thermocole**

(a) Preparation Thermocole is a ***foamed plastic***, obtained by blowing air or gas through molten polystyrene or poly-urethane.

(b) Properties

- It is white in colour and can be made into desired shapes.
- It is light, strong and chemically inert , but attacked by acids.
- Its density is about 20 kg/m^3.
- Its thermal and electrical conductivities are quite low.
- It is also used as a shockproof material.
- Its compressive strength is 117–145 kg/cm^2.
- It can be used up to 55^{o}C.
- It is very soft, so that it can be easily cut by a knife and can be scratched by a nail.

(c) Uses

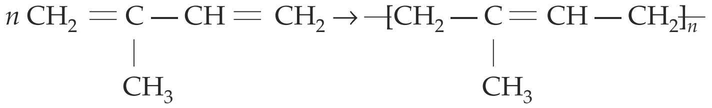
- Thermocole slabs are used for false ceilings in air-conditioned rooms and for good acoustic effect.
- Due to its outstanding thermal insulating property and lower density, it is used as a thermal insulating material (e.g. in refrigeration and air conditioning).
- Since it is a very good shockproof material, it is used as a packing material for electronic equipments.
- It is used for protecting screens in radars.
- It is used for decorative purposes.
- It is also used as an insulating and vapour barrier.

5.14 RUBBER OR ELASTOMERS

Rubbers are noncrystalline in nature and are high polymers that have elastic properties. There are two types of rubber—natural rubber and synthetic rubber.

5.14.1 Natural Rubber

The main source of natural rubber is the tree ***Hevea braziliensis.*** Rubber is obtained from latex collected from cuts made in the bark of the tree. During the treatment of latex, isoprene molecules in latex get polymerized to form poly isoprene.



$$n\,CH_2=\underset{\displaystyle CH_3}{\underset{|}{C}}-CH=CH_2 \rightarrow -\!\!\left[CH_2-\underset{\displaystyle CH_3}{\underset{|}{C}}=CH-CH_2\right]_n\!\!-$$

Isoprene **Poly-isoprene (*cis* form)**

5.14.2 Synthetic Rubber

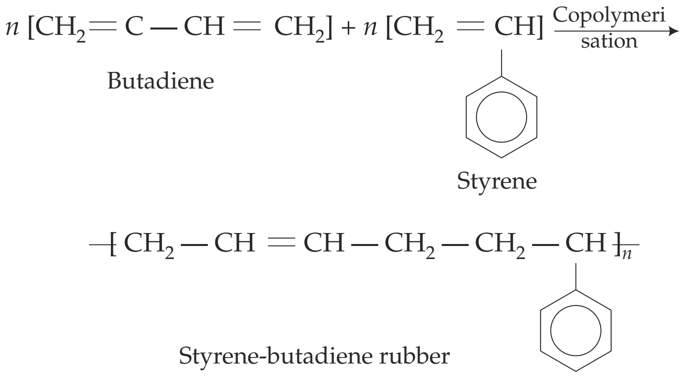
The first synthetic rubber was originally developed in USA during the Second World War as a substitute for natural rubber. They are man-made rubbers which are superior to natural rubber in certain properties.

Examples: Buna-S rubber, butyl neoprene rubber, nitrile rubber, etc.

5.14.3 Buna-S Rubber (SBR) or (GR-S) or Ameripol Rubber

(a) Preparation

It is prepared by co-polymerization of 75% butadiene and 25% styrene at 0°C in the presence of a peroxide catalyst



(b) Properties

SBR on vulcanization gives a cross-linked polymer and posseses high resilience, high load-bearing capacity and high abrasion resistance.

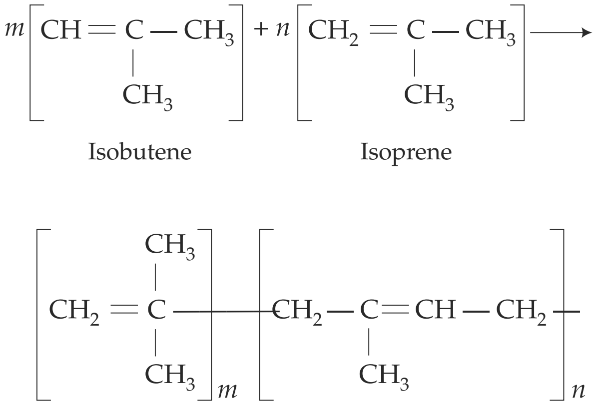
(c) Uses

- It is highly useful in manufacture of motor tyres.
- It is used in manufacture of floor tiles, cable insulations, etc.

5.14.4 Butyl Rubber (GR-I)

(a) Preparation

It is made by co-polymerization of isobutylenes with small amounts of isoprene.



$$m\left[\mathrm{CH}=\underset{\substack{|\\ \mathrm{CH_3}}}{\mathrm{C}}-\mathrm{CH_3}\right]+n\left[\mathrm{CH_2}=\underset{\substack{|\\ \mathrm{CH_3}}}{\mathrm{C}}-\mathrm{CH_3}\right]\longrightarrow$$

Isobutene Isoprene

$$\left[\mathrm{CH_2}=\overset{\substack{\mathrm{CH_3}\\ |}}{\underset{\substack{|\\ \mathrm{CH_3}}}{\mathrm{C}}}-\right]_m\left[-\mathrm{CH_2}-\underset{\substack{|\\ \mathrm{CH_3}}}{\mathrm{C}}=\mathrm{CH}-\mathrm{CH_2}-\right]_n$$

Polyisobutene-co-isoprene **(Butyl rubber)**

(b) Properties

- It is amorphous under normal condition but crystalline on stretching.

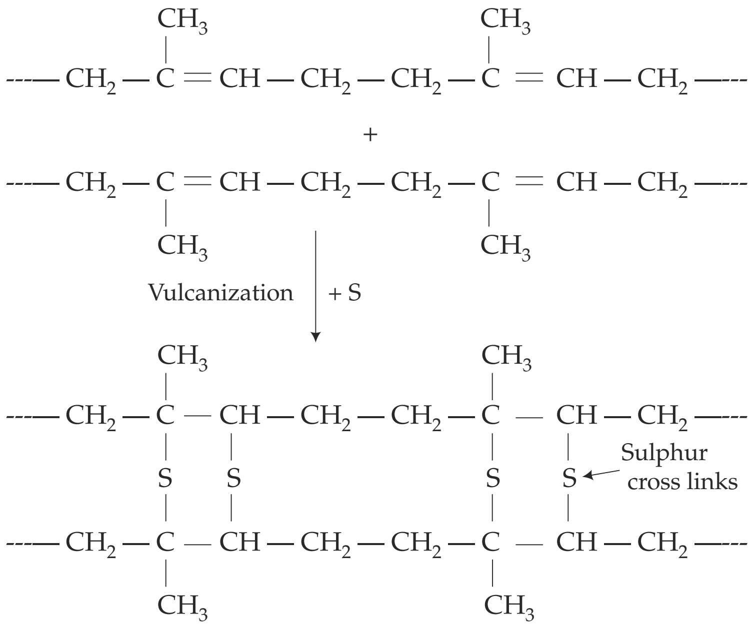
- It is resistant to heat, chemicals, ozone, polar solvents.
- It is soluble in nonpolar solvents such as benzene.

(c) Uses

- Butyl rubber is used in making cycle and automobile tubes.
- It is used for making insulating cables

5.14.5 Vulcanization of Rubber

This process was invented by Charles Goodyear in the year 1839. Natural rubber is a gummy material with poor elasticity. There are no cross links and it permanently undergoes deformation on being stretched. To improve the properties of rubber, it is compounded with sulphur, hydrogen sulphide, etc. Rubber is heated with sulphur at 100–140°C. The tensile strength and chemical resistance are increased. This introduces—S—S—cross links between adjacent hydrocarbon chains and rubber thus obtained is called **vulcanized rubber**.



(a) Example

- 3–5% of sulphur is present in tyre rubber.
- 30% of sulphur is used in battery-case rubber.

(b) Advantages

- It possesses good tensile strength and low tendency to absorb water.
- It is highly resistance to oxidation and organic solvents.
- It is highly resistance to wear and tear.
- It has excellent resilience(articles return to their original shape when applied force is removed).
- It is a better electrical insulator.

Table 5.3 *Comparison between raw rubber and vulcanized rubber*

Raw Rubber	*Vulcanized Rubber*
(i) Resistance to wear and tear is low	(i) Resistance to wear and tear is high
(ii) Low oxidation resistance	(ii) High oxidation resistance
(iii) High water-absorbing capacity	(iii) Low water-absorbing capacity
(iv) Low tensile strength	(iv) High tensile strength
(v) Less durability	(v) High durability
(vi) It has high elongation	(vi) Moderate elongation
(vii) Useful temperature range is 10–60°C	(vii) Useful temperature range is 40–100°C
(viii) Attacked by organic solvents	(viii) Resistant to organic solvents

5.15 COMPOSITES

Engineering materials belonging to different classes have different types of properties. Materials belonging to a particular type have several properties characteristic of their own class but they lack some important properties needed for a particular application. In order to incorporate additional properties in the material, it is mixed with some other materials and a new class of materials called composites are developed.

5.15.1 Definition

A composite material may be defined as, **a material system consisting a mixture of two or more microconstituents, which are mutually insoluble, differing in form or composition and forming distinct phases**. Such a combination of materials possesses properties which are different from those of any of its constituents.

5.15.2 Characteristics of Composites

(i) Higher specific strength
(ii) Lower specific gravity

(iii) Higher specific stiffness
(iv) Low electrical conductivity and thermal expansion
(v) Better creep, fatigue strength, corrosion and oxidation resistance
(vi) Maintain strength even up to high temperature

5.15.3 Constituents of Composites

Important constituents of composites are
(a) Matrix phase
(b) Dispersed phase

(a) Matrix Phase

It is the continuous body constituent, which encloses the composites. Matrix phase may be metals, ceramics and polymers. Composites using this matrix are called
(i) MMC—Metal Matrix Composites
(ii) CMC—Ceramic Matrix Composites
(iii) PMC—Polymer Matrix Composites

Requirement of a Good Matrix Phase

It should be ductile and corrosion resistant and possess high bonding strength between the matrix and dispersed phase.

(b) Dispersed Phase

It is the structural constituent that determines the internal structure of composites.

Example: Fibres, particulates, flakes, whiskers etc.

5.15.4 Types of Composites

Fibre-Reinforced Polymer Composites or Polymer Composites

They are prepared by bonding a reinforcing (fibre) material with a resin matrix and curing them under pressure and heat. Reinforcing agents are alumina, carbon, boron, graphite, glass, etc. The resin matrixes commonly used are polyesters, epoxy, phenolic, silicone and polyamide polymer resins. The choice of fibre used for reinforcing a plastic depends on desired properties of composites thus obtained.

(a) Properties

(i) It possesses high stiffness, strength, fracture strength and fatigue life.
(ii) Since fibre prevents slip and crack propagation, the mechanical properties of FRP gets increased.

(iii) It possesses heat-resistance property and high corrosion resistance.

Properties depend mainly on nature of resin matrix:

- **Polyester resin**—It gives good strength and mechanical properties.
- **Epoxy resin**—Imparts good mechanical properties.
- **Silicone resin**—Provides excellent thermal and electrical properties.
- **Phenolic resin**—To withstand high temperature.
- **Thermoplastics**—Repeatability and repairability capacity.

5.15.5 Types of FRP Composties

There are five **types of FRP composties.**

(i) Glass FRP

(a) Properties

- Excellent corrosion resistance
- High tensile strength
- Low density

(b) Uses

It is used for making automobile parts, storage tanks, plastic pipes, etc.

(ii) Boron FRP

(a) Properties

It possesses excellent stiffness and compressive strength.

(b) Uses

It is used for making horizontal and vertical tails in aeroplanes, stiffening spares, etc.

(iii) Carbon FRP or Advanced Polymer Matrix Composites

(a) Properties

- Low density and excellent corrosion resistance
- Retention of desired properties even at elevated temperatures

(b) Uses

They are used for making sports material, recreational equipment, antenna discs, solar panels and structural components of aircraft and helicopters.

(iv) Aramid FRP (Kevlars)

(a) Properties

- They have high tensile strength but are weak in compression strength.
- They also have special property of ductility and flexibility.

(b) Uses

They are used in structural components in aircraft, helicopter parts, sports goods, pressure vessels, clutch linings, etc.

(v) Alumina FRP

(a) Properties

They possess good abrasion resistance, creep resistance and dimensional stability.

(b) Uses

They are used for making components of engine parts in automobile industry and components of turbine engines.

5.15.6 Metal Matrix Composites

In metal matrix composites, matrix phases used are alloys of aluminium, titanium and nickel. The reinforced materials are Al_2O_3, boron, carbon and SiC.

(a) Properties

They exhibit good thermal stability, high strength, good stiffness and low specific weight. They can withstand elevated temperatures in corrosive environment.

(b) Uses

- MMC's are used in combustion chambers, engine blades, etc.
- MMC's of aluminium and magnesium are used in automotive industry.
- They improve fuel efficiency because of the weight reduction.
- They are also used in biomedical and sports equipment industry.

5.15.7 Ceramic Matrix Composites

The matrix phases used are glass, ceramics, carbides, nitrides, oxides, borides and the reinforcements are Al_2O_3, boron, carbon, SiC and SiO_2.

(a) Properties

They possess good corrosion resistance and high compressive strength.

(b) Uses

They are used in space vehicles, tiles, pump seal, round rings, brake linings, etc.

QUESTIONS

Two-Mark Questions with Answers

1. **What are polymers?**

   Polymers are macromolecules formed by the repeated linking of large number of small molecules called monomers.

2. **Define monomer.**

   A monomer is a micromolecule that combine with each other to form a polymer.

3. **What is meant by polymerization?**

   Polymerization is a process in which a large number of small molecules combine to form a big molecule with or without elimination of small molecules like water.

4. **Define the term degree of polymerisation.**

   The number of repeating units (n) in a polymer reaction is known as the degree of polymerization.

5. **What is meant by oligopolymers?**

   Polymers with low degree of polymerisation are known as oligopolymers and their molecular weight ranges from 500–5000.

6. **What are graft polymers?**

   A branched copolymer with one kind of monomer (M_1) in the main chain and another kind of monomer (M_2) in the side chain is called a graft copolymer.

7. **Define the term 'tacticity'.**

   The orientation of monomeric units or functional groups in a polymer molecule can take place in an orderly or disorderly manner with respect to the main chain, called tacticity.

8. **Define the term 'functionality'.**

   Functionality is the number of bonding sites present in the monomer.

9. **What are living chain polymers and dead polymers?**

   The growing chain of the polymer is known as living polymer. Growth of polymer chain is terminated either by coupling reaction or disproportionation. The product of addition polymerization is known as dead polymer.

10. **Define crystalline polymer.**

    In a crystalline polymer, the polymer chains are regularly arranged. So the intermolecular forces are increased. This results in higher density, greater strength and shorter softening point. The tendency of a polymer to be crystalline increases when the polymer chains are linear without any side chain.

11. **What are thermoplastics?**

    They soften on heating and harden on cooling. Resoftening and rehardening is also possible, e.g. polythene.

12. **How is LDPE is obtained?**

    Low density polyethylene is obtained by the polymerization of ethylene under high pressure using free radical initiator.

13. **How is Teflon prepared?**

    Teflon is prepared by the polymerization of water emulsion of tetrafluoroethylene in the presence of benzoylperoxide under pressure.

14. **What are epoxy resins?**

    These are cross-linked thermosetting resins. They are polyethers because the monomeric units in the polymer have an ether type of structure R-O-R.

15. **What is compounding of plastics?**

    Compounding is mixing of raw plastics with other substances to impart special properties to the product. Usually, the high-polymer material is mixed with 4 to 10 ingredients, each of which either discharges a useful function during moulding or imparts some useful property to the finished article.

16. **What are the uses of lubricants in plastics?**

    Lubricants reduce friction during moulding process between mould and article.

    Lubricants like waxes, oils, stearates, oleates and soaps are employed to make the moulding of plastic easier and to impart a flawless, glossy finish to the products. Lubricants prevent the plastic material from sticking to the fabricating equipment.

17. **What is moulding process?**

    This process involves fabrication of plastic material into desired shape under the influence of heat and pressure in a closed chamber.

18. **Write down the preparation for thermocole.**

    Thermocole is a foamed plastic, obtained by blowing air or gas through molten polystyrene or poly-urethane.

Ten-Mark Questions

1. Explain the term 'Tacticity' with examples.
2. What is Zeigler–Natta polymerization? Explain in detail.
3. Explain the mechanisms involved in addition polymerization in detail.
4. Define the term 'plastics'. What are its types? Mention the advantages of plastics.
5. Write short notes on Bakelite.
6. What are LDPE and HDPE? Give their difference.
7. Write the preparation, properties and uses of (a) acrylics, and (b) polypropylene.
8. Explain the preparation, properties and uses of Nylon and PET.
9. What are epoxy resins? Mention their preparation, properties and uses.
10. Describe the preparation, properties and uses of Perlon-U.
11. What is compounding of plastics? Explain the ingredients and their functions in compounding.
12. What is compression moulding? Explain in detail.
13. Write short notes on (a) extrusion moulding, and (b) blow moulding.
14. What are foamed plastics? Explain the types and method of preparation.
15. Describe the preparation, properties and uses of thermocole.