Institute of Aeronautical Engineering

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ENGINEERING CHEMISTRY

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UNIT 1

ELECTROCHEMISTRY AND BATTERIES

Introduction

- Electrochemistry is the branch of chemistry which deals with the transformation of electrical energy into chemical energy and vice versa. It is the study of phenomena at electrode solution interfaces.
- Electrochemistry deals with the relationship between electrical, chemical phenomena and the laws of interaction of these phenomena. The branch of electrochemistry is of major technical importance.
- The laws of electrochemistry form the basis of electrolysis and electrosynthesis. The knowledge of electrochemistry is of immense importance to study about the causes of destruction of materials due to corrosion. In electro-chemistry, there are two processes: electrolysis and electromotive process. Both these processes are interrelated.

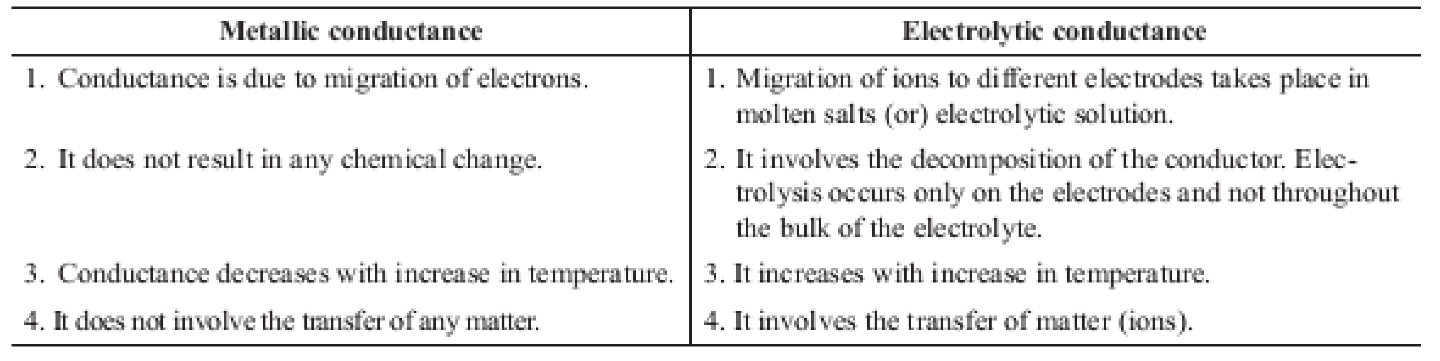
- The two processes above can be summarized as follows:

1. Electrical energy causing chemical reactions → Electrolysis (Electrolytic cell)
2. Chemical reactions producing electrical energy → Electromotive (Galvanic cell)
3. Electromotive → Electron + Motion

❖ Conductance:

- The substances which allow the passage of electric current are called conductors. Metals such as copper and silver are good conductors of electricity. Substances which allow the electricity to pass through them in their molten states or in the form of their aqueous solutions are called electrolytic conductors or electrolytes and this property is known as electrolytic conductance. Electrolytic conductors conduct electricity due to the migration of ions. The examples of electrolytic conductors are sodium chloride, potassium chloride, etc.
- Electrical conductors are of two types:

  1. Metallic conductors and 2. Electrolytic conductors.



Metallic conductance	Electrolytic conductance
1. Conductance is due to migration of electrons.	1. Migration of ions to different electrodes takes place in molten salts (or) electrolytic solution.
2. It does not result in any chemical change.	2. It involves the decomposition of the conductor. Electrolysis occurs only on the electrodes and not throughout the bulk of the electrolyte.
3. Conductance decreases with increase in temperature.	3. It increases with increase in temperature.
4. It does not involve the transfer of any matter.	4. It involves the transfer of matter (ions).

Electrolytic Conductance:

- Electrolysis is the process of decomposition of electrolyte when electric current is passed through the solution.
- Electrolysis is carried out in an apparatus called electrolytic cell. It contains a +ve electrode called anode and a –ve electrode called cathode. The current enters at anode and leaves at cathode.
- Ohm's law states that the current (I) flowing through a conductor is directly proportional to the potential difference (E) applied across the conductor and is inversely proportional to the resistance of the conductor.

Thus,

$$E \propto I$$

where I is the current in amperes and Vis the potential difference applied across the conductor in volts.

Thus

$$E = IR$$

$$R = \frac{E}{I}$$

where R is the proportionality constant and is known as the resistance of conductor in ohms. Thus, the re-sistance of a conductor is directly proportional to the potential difference applied across the conductor and inversely proportional to the current carried by the conductor.

- **Specific conductance:**

- Specific resistance (*r*) *is defined as the resistance of an electrolyte solution of 1 cm in length and 1* cm^2 cross-section, i.e. resistance of 1 cm3 of the electrolytic solution. The unit of specific resistance is ohm centimetre.
- The reciprocal of specific resistance (*r*) *is called specific conductance. This may be defined as the conductance* of 1 cm3 of a material and is denoted by *K*

❖ Equivalent Conductance:

- Equivalent conductance is of greater importance in case of electrolytic solution. It is defined as the conductance of an electrolyte solution containing 1 g equivalent of the electrolyte. It is usually denoted by L. the relation between equivalent conductance (Λ) and specific conductance is given as-

  $$\Lambda = V \text{ x } K$$

  where *V is the volume of the electrolyte solution in millilitres containing 1 g equivalent of the electrolyte. If* the concentration of the electrolyte solution is *C gL–1, then volume containing 1 g equivalent of the electrolyte* will be 1/C litres or 1000 C ml .
- Thus, by using the above equation,

  $$\Lambda = V \times K$$
  $$= \frac{1000}{C} \times K$$

- The unit of equivalent conductance is ohm–1 cm2eq–1.

- **Molar Conductance:**
- Molar conductance is defined as the conductance of an electrolytic solution containing 1 mol of electrolyte. It is denoted by λ_m. *If Vm ml is the volume of the solution containing 1 g-mol of the electrolyte, then*

$$\lambda_m = V_m \, X \, K$$

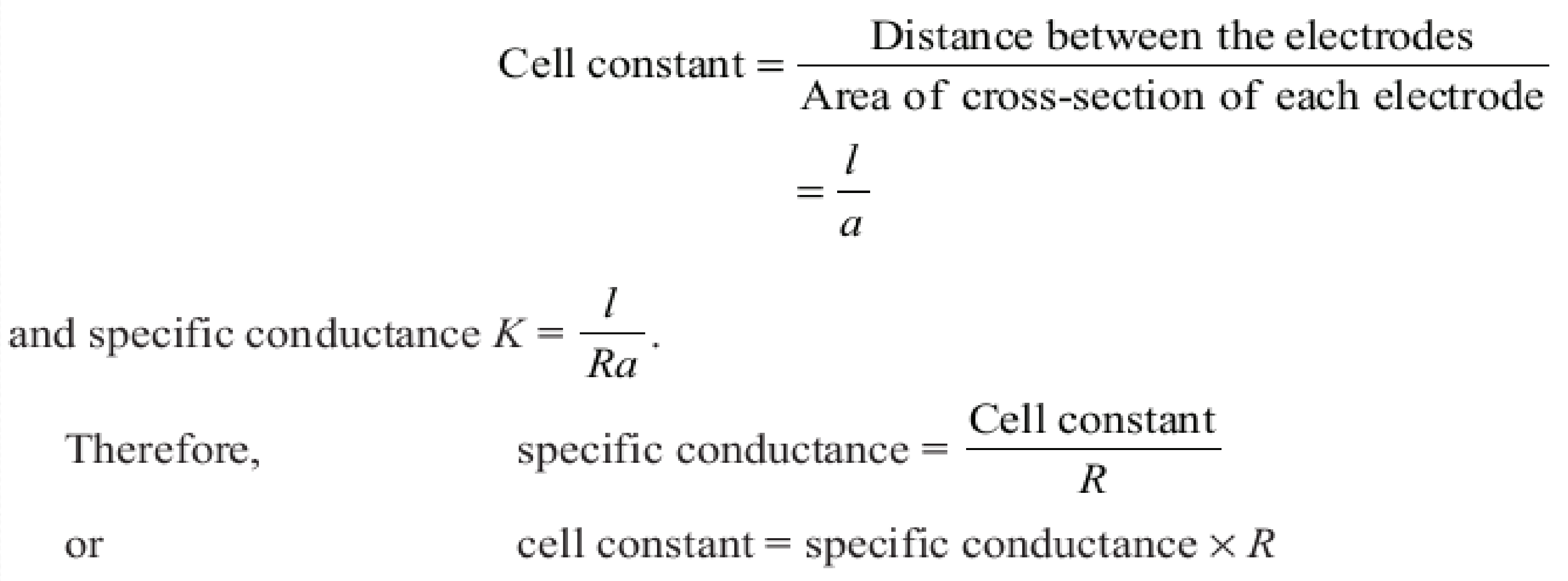
- If *m is the concentration of the solution in moles per litre, then*

$$\lambda_m = \frac{1000 \times K}{m}$$

- The unit of λ_m *is* $S\ m^2\ mol^{-1}$ *or* $ohm^{-1} cm^2 mol^{-1}$

❖Cell Constant:

- It is a constant characteristic of the cell in which the electrolyte is taken and its value depends on the distance between the electrodes and the area of cross-section of the electrodes.



$$\text{Cell constant} = \frac{\text{Distance between the electrodes}}{\text{Area of cross-section of each electrode}}$$

$$= \frac{l}{a}$$

and specific conductance $K = \frac{l}{Ra}$.

Therefore, $\text{specific conductance} = \frac{\text{Cell constant}}{R}$

or $\text{cell constant} = \text{specific conductance} \times R$

- If the area of cross-section is in cm^2 and distance between the electrodes is in cm, the unit of cell constant is cm^{-1}.

Variation of Conductance with Dilution:

- On dilution, the volume of an electrolyte solution increases. Thus, the number of ions furnished by the electrolyte per unit volume is decreased. Hence, the specific conductance decreases on progressive dilution.
- Electrolytes are of two types: (i) strong electrolytes (ii) weak electrolytes.

Strong Electrolytes:

- These electrolytes are completely ionized at ordinary concentration. They show an increase in conductance at lesser dilutions. For example, salts such as KCl, NaCl, $BaCl_2$, $CaCl_2$, etc.; acids such as HCl, H_2SO_4, etc.;and strong bases such as NaOH, KOH, $Ca(OH)_2$, $Mg(OH)_2$, etc.; have very high equivalent conductance at ordinary concentration. Since the conductance of a solution of a given electrolyte depends on the number and speed of ions, these two factors will be considered in the determination of conductance.

1. Strong electrolytes are completely ionized at ordinary concentration; hence, with increase in dilution,the number of ions will remain the same as before.
2. In the case of concentrated electrolyte, the speed of ions is very low; but on dilution, the speed of ions will be more. This is because the interionic forces of attraction of the oppositely charged ions decrease on dilution. Thus, the equivalent conductance at infinite dilution reaches its maximum value due to increase in the speed or mobility of ions but not due to the number of ions in case of strong electrolytes.

Weak Electrolytes:

- These electrolytes dissociate into a very small extent at ordinary concentration.

1. In dilute solution, the interionic attraction forces between the ions are not significant since the ions move freely. Thus, on dilution, there is a little or no effect on the speed of ions in the electrolytic solution.
2. On dilution, the degree of dissociation increases so that the number of ions increases. Thus, the equivalent conductance increases on dilution because of the increase in the number of ions in the electrolytic solution.

❖Effect of Concentration on Equivalent Conductance

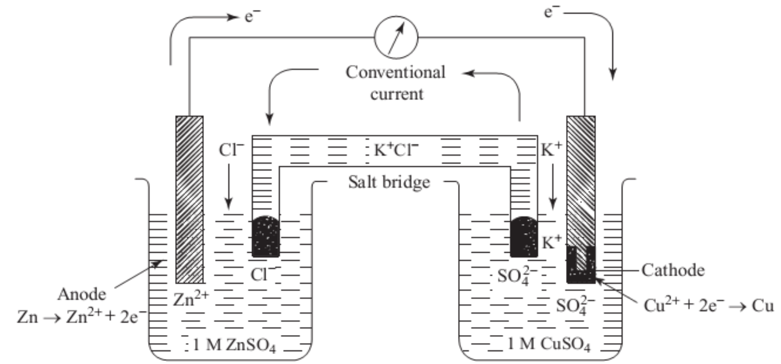
- Let us consider a weak electrolyte *AB, which is ionised as*

$$AB \rightleftharpoons A^{\oplus} + B^{\ominus}$$

- When the electrolyte solution is diluted, more electrolyte molecules break up and more ions are formed,i.e., the degree of dissociation is increased. As a result of which the solution exhibits enhanced conductivity. If the process of dilution is continued, more and more electrolyte molecules undergo dissociation. But at some stage of dilution all the electrolyte molecules are ionised, i.e. ionisation is completed and at that point on further dilution, no more ions are produced and equivalent conductance does not increase. This limiting value is known as equivalent conductance at infinite dilution (Λ_o or Λ_∞).
- Strong electrolytes are completely ionised in solution at all concentrations and hence one would not expect any variation of equivalent conductance with concentration (dilution). But it is found that for strong electrolytes, equivalent conductance (Λ) increases with dilution, and the cause of this variation isfundamentally different from weak electrolytes. The conductivity of an electrolyte depends on the speed and concentration of ion. The motion of an ionic species in an electric field is retarded by the oppositely charged ions due to inter-ionic attraction. On dilution, the concentration of electrolyte decreases and the retarding influence of oppositely charged ions decreases. Consequently, the speed of ions increases, and the equivalent conductance of electrolyte is increased

❖ Galvanic Cell

- A galvanic cell is made of two half cells. One is oxidation or anodic half cell and the other one is reduction or cathodic half cell.
- Daniel cell is an example of galvanic cell having zinc and copper electrodes. The first half cell consists of zinc electrode dipped in ZnSO4 solution and the second half cell is made of copper electrode dipped in copper sulphate solution. Both half cells are connected externally by metallic conductor (connecting wire) and internally by a bent glass tube having saturated solution of a strong electrolyte (KCl) called salt bridge. It acts as a bridge between the two half cells.



- A zinc or a copper galvanic cell can be represented as

  Zn/ZnSO4 || CuSO4/Cu
- The double bar shows a salt bridge, i.e. electrolyte–electrolyte junction. The chemical reactions taking place at both electrodes may be written as follows:

  At anode: Oxidation takes place with the liberation of two electrons.

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

  At cathode : Reduction occurs and cuprous ion is reduced to metallic copper.

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

  The overall reaction is

  $Zn + Cu^{+2}\ Zn^{+2} + Cu$
- The electrode showing oxidation reaction is anode and the other electrode where reduction occurs is cathode. As per IUPAC convention, the anode is always represented on the left and the cathode always represented on the right side of the cell.
- As the connection is complete, the flow of electrons will be externally from anode to cathode and internally from cathode to anode through the salt bridge. The flow of current is due to the difference in electrode potentials of both the electrodes. The potential difference in the cell is called the EMF and is measured in volts. It can be measured by the potentiometer. The flow of current becomes slow after using the electrodes for a long time because of the polarization of the electrodes.

- **Salt bridge: Salt bridge is a U-shaped tube containing concentrated solution of an inert electrolyte such as**
- KCl, KNO_3, and K_2SO_4 or a paste of inert electrolyte (whose ions do not take part in redox reaction and do not react with the electrolyte) in agar–agar medium or gelatin.

Functions of salt bridge:

- Salt bridge helps to complete the circuit by allowing the ions to flow from one solution to the other without mixing the two solutions.
- It helps to maintain electrical neutrality of the solution in the two half cells.

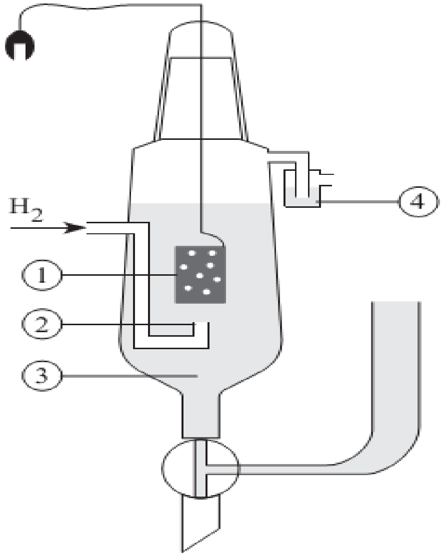
Reference Electrodes

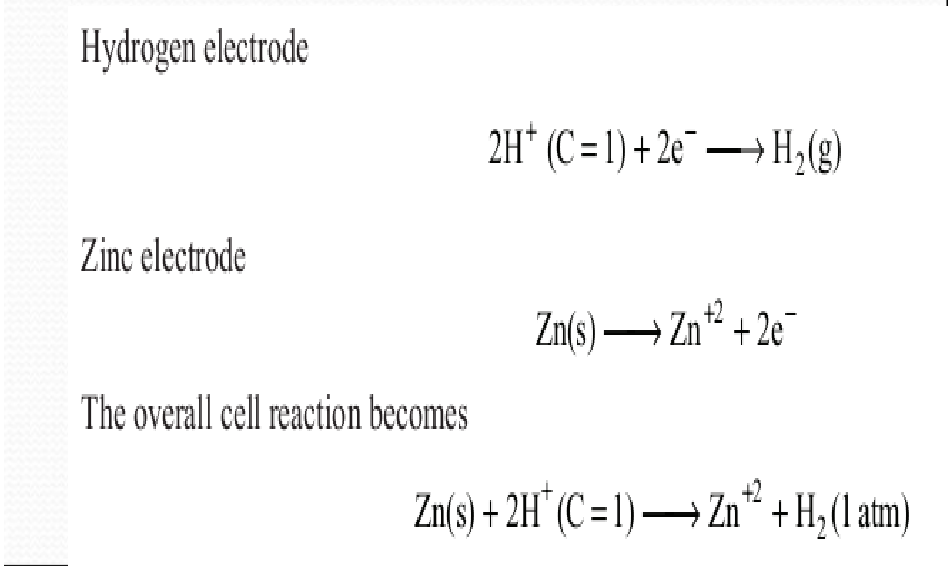
- The potential of half cell or single electrode potential is the potential difference between the metal and its salt solution in which it is dipped.
- The determination of the potential of a single electrode is not possible. Since any circuit necessarily contains two electrodes, a reference electrode is an electrode which has a stable and well known potential. It is used as half cell to build an electrochemical cell and to determine the potential of other electrode.
- A fixed potential difference is applied between the working electrode and the reference electrode; this potential drives the electrochemical reaction at the working electrode surface. The current produced from the electrochemical reaction at the working electrode is balanced by a current flowing in the opposite direction at the counter electrode. The examples of reference electrodes are standard hydrogen electrode, calomel electrode, silversilver chloride electrode, etc.

Standard Hydrogen Electrode (Normal Hydrogen Electrode:

- It is a redox electrode which is widely used as reference electrode. It can be used as either anode or cathode depending upon the nature of the half cell for which it is used. The SHE consists of a platinum electrode immersed in a solution with a hydrogen ion concentration of 1.0 M. The platinum electrode is made of a small square of platinum foil which is platinised and known as platinum black. [Platinum black provides a surface on which the hydrogen gas can be in contact with the hydrogen ions (aq.).]

1. Platinised platinum electrode
2. Hydrogen blow
3. Solution containing hydrogen ion concentration of unit molarity
4. Seal for prevention of the oxygen interference





Hydrogen electrode

$$2H^{+}(C=1)+2e^{-}\longrightarrow H_2(g)$$

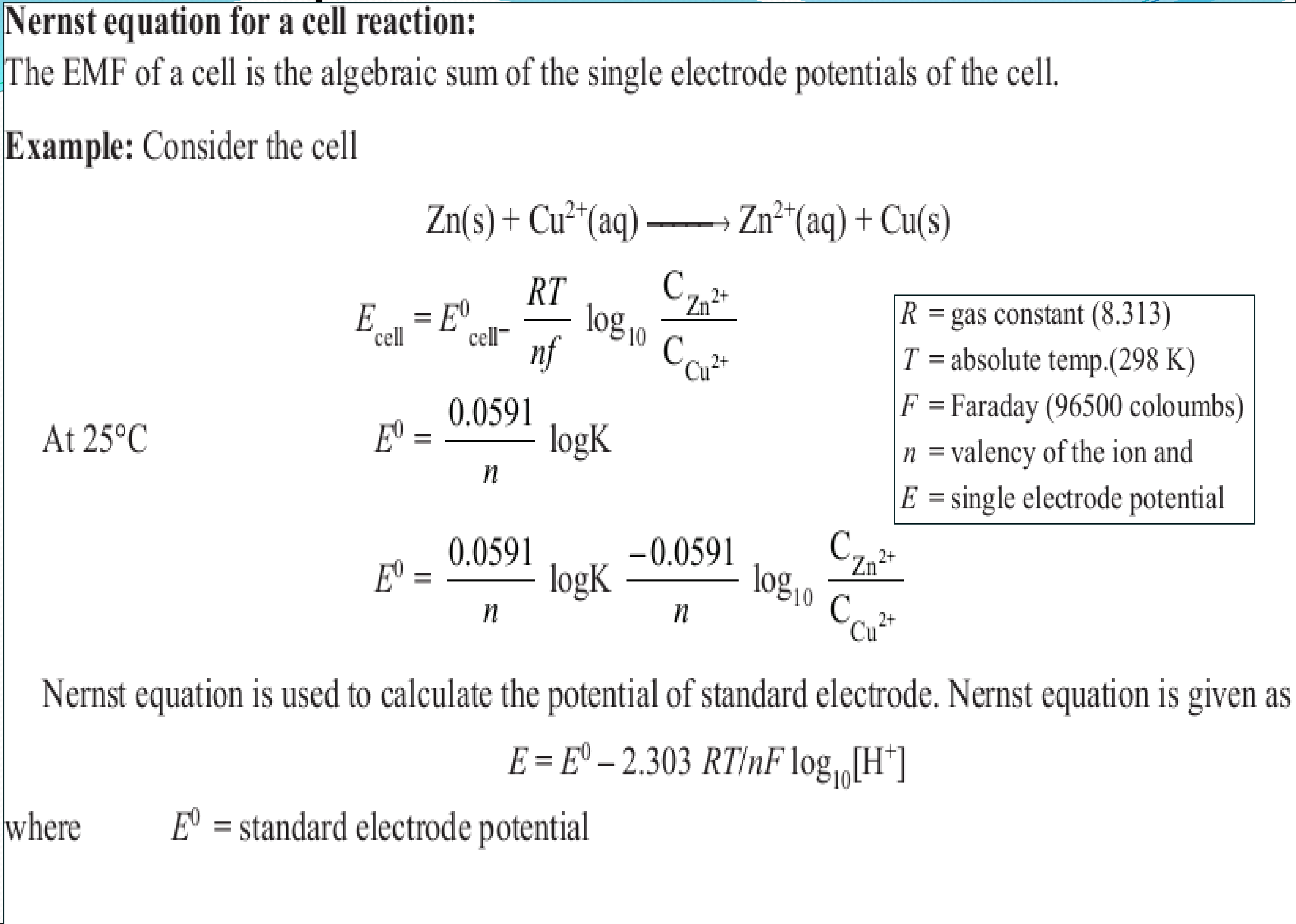
Zinc electrode

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

The overall cell reaction becomes

$$Zn(s)+2H^{+}(C=1)\longrightarrow Zn^{+2}+H_2(1\,atm)$$

❖Nernst equation for a cell reaction:



Nernst equation for a cell reaction:

The EMF of a cell is the algebraic sum of the single electrode potentials of the cell.

Example: Consider the cell

$$\mathrm{Zn(s)} + \mathrm{Cu^{2+}(aq)} \longrightarrow \mathrm{Zn^{2+}(aq)} + \mathrm{Cu(s)}$$

$$E_{\text{cell}} = E^0{}_{\text{cell}} - \frac{RT}{nf} \log_{10} \frac{\mathrm{C}_{\mathrm{Zn}^{2+}}}{\mathrm{C}_{\mathrm{Cu}^{2+}}}$$

R = gas constant (8.313)
T = absolute temp.(298 K)
F = Faraday (96500 coloumbs)
n = valency of the ion and
E = single electrode potential

At 25°C $$E^0 = \frac{0.0591}{n} \log \mathrm{K}$$

$$E^0 = \frac{0.0591}{n} \log \mathrm{K} \frac{-0.0591}{n} \log_{10} \frac{\mathrm{C}_{\mathrm{Zn}^{2+}}}{\mathrm{C}_{\mathrm{Cu}^{2+}}}$$

Nernst equation is used to calculate the potential of standard electrode. Nernst equation is given as

$$E = E^0 - 2.303\ RT/nF \log_{10}[\mathrm{H}^+]$$

where E^0 = standard electrode potential

Substituting the values, we get

$$E = E^0 - 0.0591 \log H^+$$

$$E = E^0 - 0.0591 \text{ pH}$$

Using the Nernst equation, the EMF of the complete cell (E) may be expressed as

$$E = E^0 - \frac{2.303\,\text{RT}}{2\text{F}} \log \frac{C_{\text{Zn}^{+2}} \times C_{\text{H}_2}}{C_{\text{Zn}} \times C^2_{\text{H}^+}} \tag{1.10}$$

Concentration of hydrogen gas by convention is taken to be unity when passed at one atmosphere pressure. The concentration of solid is also taken to be unity and $C_{\text{H}^+} = 1$.

Eq. (1.10) becomes

$$E = E^0 - \frac{2.303\,\text{RT}}{2\text{F}} \log C_{\text{Zn}^{+2}} \tag{1.11}$$

The EMF of the cell, E is a measure of potential of the zinc electrode because the electrode potential of SHE is assigned zero.

- **Electrochemical series:-**

  The electrode potentials of different electrodes can be finding using standard hydrogen electrode. The potential of hydrogen electrode is assumed as zero volts. So the measured Emf. Itself is the standard electrode potential of that electrode.

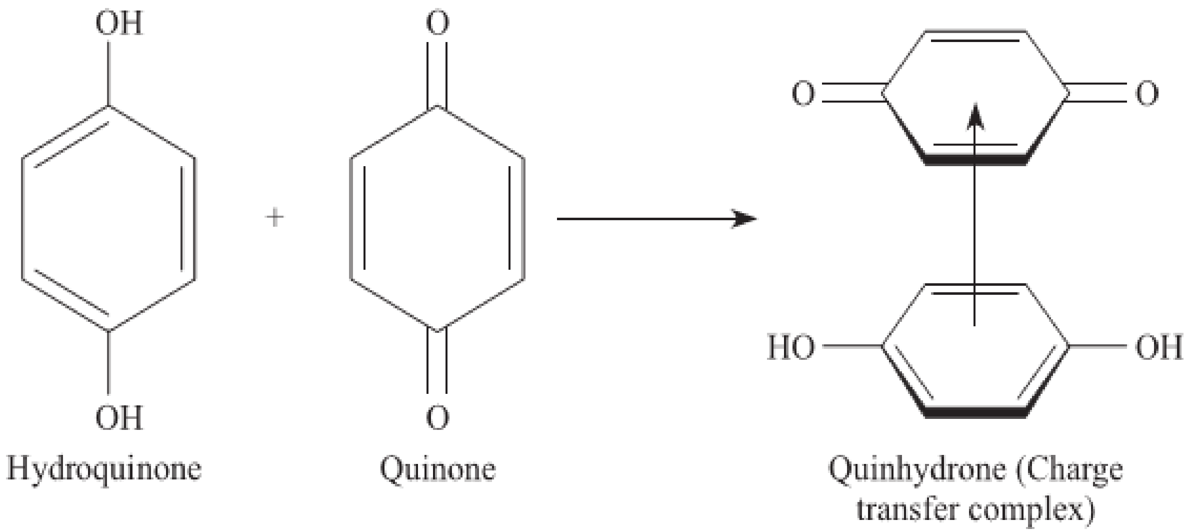
The arrangement of different electrode potential s of different electrodes from highest

- -ve to highest +ve are called electrochemical series.

Electrode	**Half cell reaction**	**E^{0}volts (standard reduction potential**
L_i^+/Li	Li^++e^- Li	-3.04
K^+/K	K^+ +e^- K	-2.9
Ca^{+2}/Ca	Ca^{+2} +2e^- Ca	-2.8
Na^+/Na	Na^++e- Na	-2.7
Mg^{+2}/Mg	Mg^{+2} +2e^- Mg Zn^{+2} +2e^- Zn	-2.3
Zn^{+2}/Zn		-0.76
Fe^{+2}/Fe	Fe^{+2} +2e^- Fe	-0.4
H^+/H_2,pf	H^+ + e^- H_2 Cu^{+2} + 2e^- Cu	+ 0
Cu^{+2}/Cu		+0.15
Ag^+/Ag	Ag^+ + e^- Ag	+ 0.7
Pt,Cl_2/Cl^-	Cl_2+ 2e^- 2Cl^-	+ 1.3
Pt,F_2/F^-	F_2 + 2e^- 2F^{--}	+ 2.8

Quinhydrone Electrode:

- It is a type of redox electrode which can be used to measure the H^+ion concentration of a solution. The electrode consists of an inert metal electrode (a platinum wire) in contact with quinhydrone crystals and a water-based solution. Quinhydrone is slightly soluble in water, formed by equi–molar mixture of hydroqui-none and quinone.

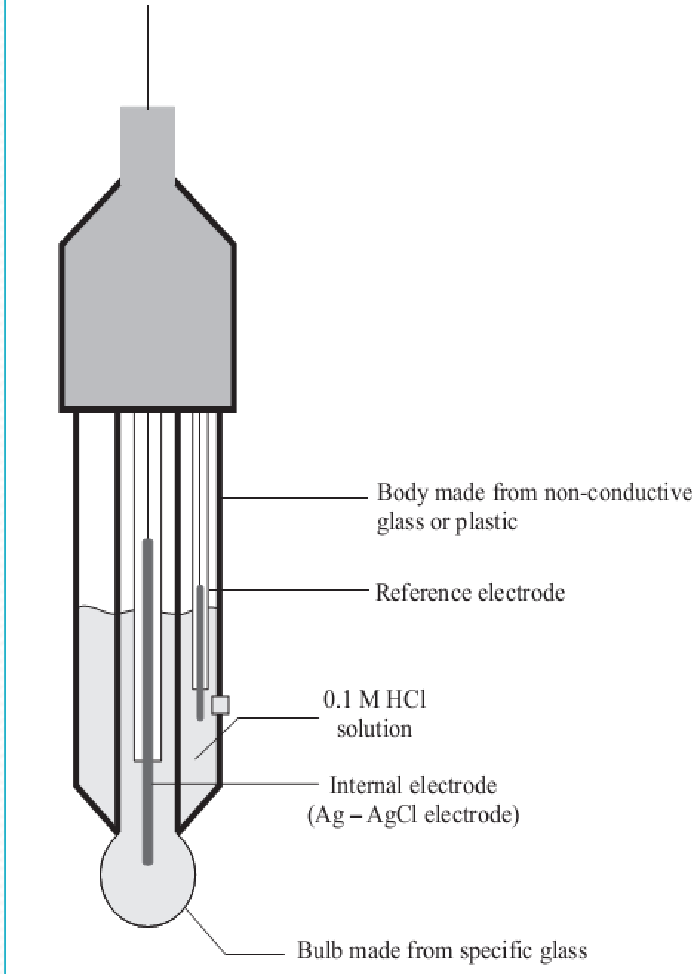


Ion Selective Electrode:

- ✓ An ion selective electrode is a sensor which converts the activity of a specific ion dissolved in a solution into an electrical potential which can be measured by a voltameter or pH-meter, e.g. glass electrode.

- **Glass Electrode:** A glass electrode is a type of ion-selective electrode and consists of a thin-walled glass bulb attached to a glass tube. A very low melting point and high electrical conductivity glass are used for the construction of this bulb. The glass tube contains a dilute solution of constant pH of HCl (0.1 N) solution. A silver–silver chloride electrode or platinum wire is immersed as reference electrode in the HCl solution.

A Glass Electrode



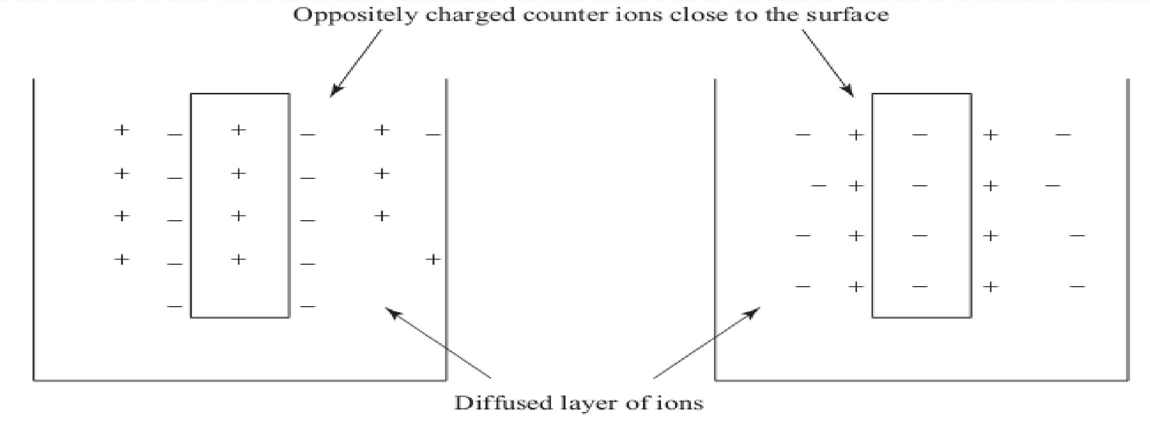
ELECTRODE POTENTIAL

- When a metal rod is dipped in its salt solution (electrolyte), the metal atom tends either to lose electrons (oxidation) or to accept electrons (reduction). The process of oxidation or reduction depends on the nature of metal. In this process, there develops a potential between the metal atom and its corresponding ion called the electrode potential.

  Oxidation: $\mathrm{M} \rightarrow \mathrm{M}n^{+} + ne^{-}$

  Reduction: $\mathrm{M}n^{+} + ne^{-} \rightarrow M$

- The tendency of oxidation results in the dissolution of metal and in the release of electron density on the surface of metal with respect to electrolyte solution. Similarly in reduction, the positive charge density is more on the surface of metal with respect to the solution. Consequently, they attract oppositely charged particles and form a double layer of charge called the Helmholtz electrical double layer
- There is a dynamic equilibrium between metal and metal ion, and the potential difference between the two is called the electrode potential or the equilibrium potential. It is measured in volts. The potential difference for oxidation reaction is called the oxidation potential and that of reduction is called the reduction potential.



❖Batteries or Commercial Cells

- *Definition-*

a) A battery is a storage device used for the storage of chemical energy and for the transformation of chemical energy into electrical energy.

b) Battery consists of group of two or more electrical cells connected together electrically in series.

c) Battery acts as a portable source of electrical energy.

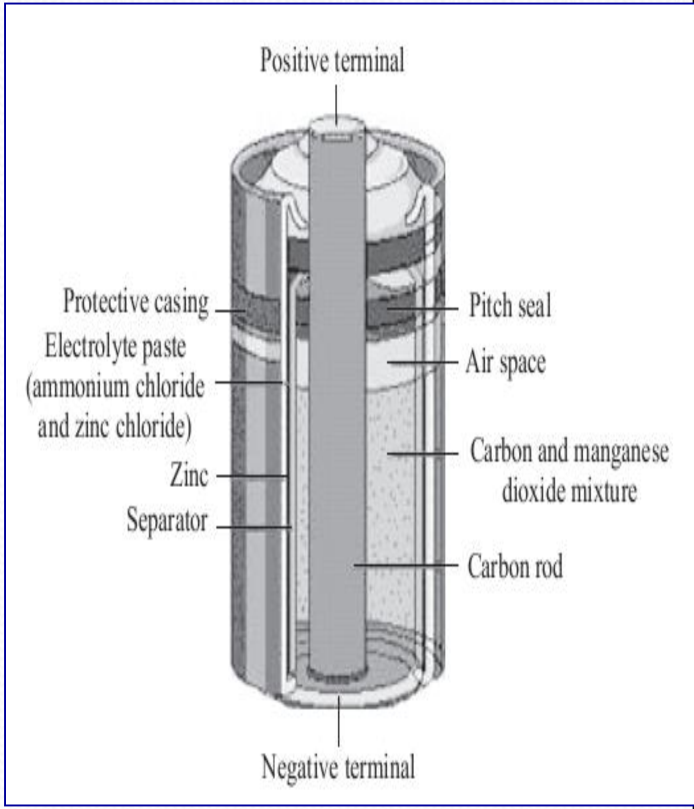
- **Batteries are of three types, namely,**

1. Primary batteries (or) primary cells
2. Secondary batteries (or) secondary cells

- **Primary Cell:**
- In a primary cell, a chemical reaction proceeds spontaneously and its free energy is converted into electrical energy. The production of electrical energy at the expense of the free energy of the cell is called discharging of the cell. But in a secondary cell, electrical energy is passed into the cell when a chemical reaction is induced, and the products remain on the electrodes. These products react in the backward direction at our choice and liberate free energy in the form of electrical energy. These cells accumulate electrical energy in the form of chemical reaction and later on the reaction is reversed to release electrical energy. This process is called charging of the cell.
- **Examples of primary cells:**

  Voltaic cells, Daniel cell, Leclanche cell, Weston cadmium cell, and lithium cell.

Dry Cell (leclanche Cell)



Secondary Cells (or) Accumulator Batteries:

- In secondary cells, the cell reaction can be made to proceed in the reverse direction by passing direct current through it from an external source. Therefore, it can operate in both the ways, i.e., it receives electrical energy and also supplies it. When it supplies electrical energy, it operates like an electrochemical cell and gets rundown. The cell needs to be recharged. During recharging, it operates like an electrolytic cell.
- Example:

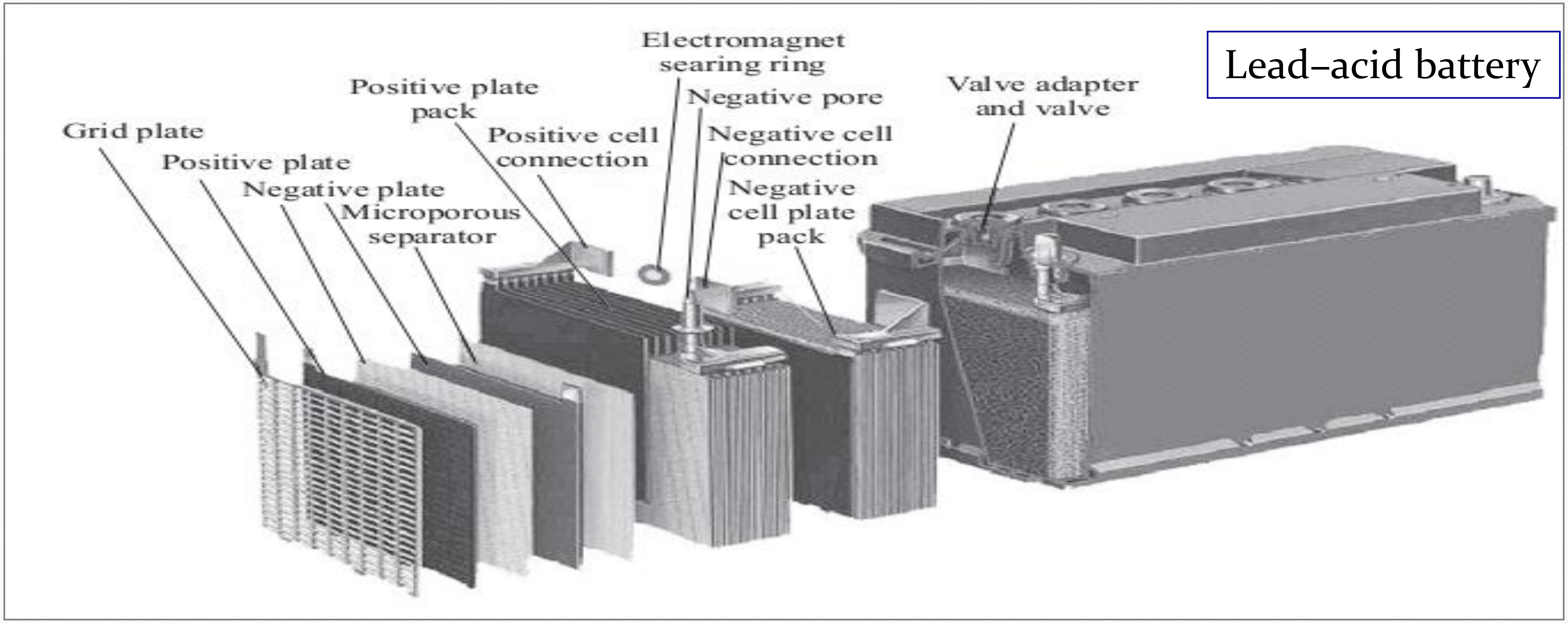
✓ Lead storage battery

✓ Nickel–cadmium battery

✓ Lithium-ion cell battery

❖ Lead–acid battery:

- If a number of cells are connected in series, the arrangement is called a battery. The lead storage battery is one of the most common batteries that are used in the automobiles. A 12 V lead storage battery is generally used, which consists of six cells, each providing 2 V. Each cell consists of a lead anode and a grid of lead packed with lead oxide as the cathode. These electrodes are arranged alternately, separated by a thin wooden piece and suspended in dil. H_2SO_4(38%), which acts as an electrolyte. Hence, it is called lead-acid battery.



Lead–acid battery

- **Lead Storage Cells:**
  - To increase the current output of each cell, the cathode and the anode plates are joined together, keeping them in alternate positions. The cells are connected parallel to each other (anode to anode and cathode to cathode). The cell is represented as Pb|$PbSO_4$(s), H_2SO_4(aq.)|$PbSO_4$(s), Pb

- **Nickel – Cadmium cells: (Ni-Cd Cell)**
- **Anode:** Cd
- **Cathode:** Nickel oxy hydroxide Ni O OH
- **Electrolyte**: Aqueous KOH
- **Emf**: 1.4V
- **Cell reaction:**
- **Anode:** $Cd + 2\ oH^- \quad Cd\ (OH)_2 + 2\ e^-$
- **Cathode:** $NiO\ OH + 2\ H_2O + 2\ e^- \quad Ni\ (OH)_2\ H_2O + OH^-$
- **Applications:**
- Calculators, digital cameras, pagers, laptops, tape recorders, flash lights, medical devices, electrical vehicles, space applications.
- **Advantages**: - Good performance in low temperature long life.

- **Applications of Batteries:**

- Lead Acid battery is used in Automobile and construction equipment, Standby / backup system,for engine batteries.
- Ni-Cd cell is used in Calculators, digital cameras, pagers, laptops, tape recorders, flash lights, medical devices, electrical vehicles, space applications.

THEORETICAL QUESTIONS

- 1. What are concentration cells? Explain an electrolyte concentration cell and its application.
- 2. Describe the construction of a glass electrode. How is it significant in its applications?
- 3. Derive Nernst’s equation. How is it useful?
- 4. Discuss the working principle of the primary batteries.
- 5. What is a galvanic cell? Also describe a Daniel cell.
- 6. Differentiate between an electrochemical cell and an electrolytic cell.
- 7. What is electrochemical series? Discuss its three important applications.
- 8. Describe the construction and working of a calomal electrode.
- 9. Describe the construction of a galvanic cell. Write down the electrode reactions and the formula for its EMF.
- 10. What are fuel cells? Explain the working of the hydrogen–oxygen fuel cell?

- **Problem**
- 1. The resistance of 0.1 N solution of an electrolyte is 40 ohms. If the distance between the electrodes is 1.2cm and the area of cross-section is 2.4cm. Calculate the equivalent conductivity.
- A: Distance between electrodes l = 1.2cm
- Area of cross-section a = $2.4cm^2$
- Cell const. = = 0.5cm-1
- Normality of given solution = 0.1 N.
- Resistance R = 40 ohms.
- Specific conductance K =
- = = 0.0125
- Equivalent Conductivity =
- =
- = $125\ ohm^{-1}cm^2\ eq^{-1}$

UNIT 2

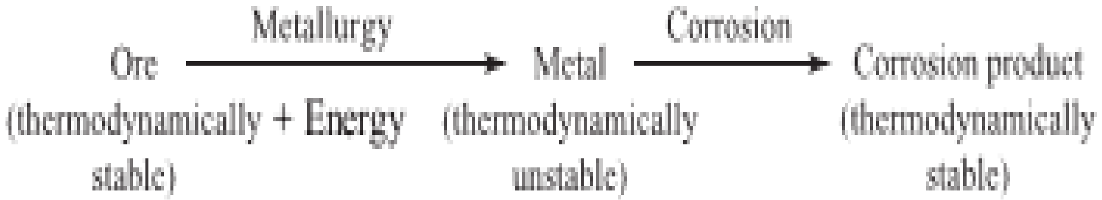
CORROSION AND ITS CONTROL

- **Introduction**
- Corrosion is a process of formation of the compound of pure metal by the chemical reaction between metallic surface and its environment.
- It is an oxidation process.
- It causes loss of metal. Hence, disintegration of a metal by its surrounding chemicals through a chemical reaction on the surface of the metal is called corrosion.
- Thus, corrosion is defined as destruction or deterioration of metals by chemical reaction.
- Example: Formation of rust on the surface of iron, formation of green film on the surface of copper.
- The responsible factors for the corrosion of a metal are the metal itself, the environmental chemicals,temperature and the design

❖ Causes of Corrosion

- In nature, metals are not found in free state due to their reactivity. It is the ore from which the metals are extracted by metallurgical processes. Metallurgy requires a large amount of heat energy.

- *Why metals are not found in their free state?* The answer to this question is that the metals are thermodynamically unstable in their free state. Since they are stable in the form of certain compounds, the extracted metal has higher energy. This is given as:



Effect of Corrosion

- Corrosion is a slow process, taking place mainly on the surface of the metals, but the damage caused by it is enormous. The corrosion in metal objects such as equipments, instruments, chemical plants, structures, etc., makes them inefficient. In some types of corrosion it is invisible and seen only when accident occurs. Consequences of corrosion cause a great loss of economy and life. The following harmful effects are specific.

1. Corrosion reduces the thickness of the metal, resulting in the loss of mechanical strength and failure of the structure.
2. Because of the deterioration of appearance, the cost of machine is reduced.
3. Efficiency of a machine is reduced due to corrosion.
4. Because of corrosion, pipes are blocked and pumps are difficult to operate.

5 Boilers are damaged because of corrosion.

6. Buildings and historic monuments are damaged due to corrosion (e.g., Taj Mahal).

Theories of Corrosion:

- There are three theories of corrosion: (i) acid theory, (ii) dry or chemical corrosion and (iii) galvanic or electrochemical or wet corrossion.
- **Acid Theory of Corrosion**

  This theory suggests that corrosion of a metal (iron) is due to the presence of acids surrounding it. According to this theory, iron is corroded by atmospheric carbon dioxide, moisture and oxygen. The corrosion products are the mixture of $Fe(HCO_3)_2$, $Fe(OH)CO_3$ and $Fe(OH)_3$. The chemical reactions suggested are given below:

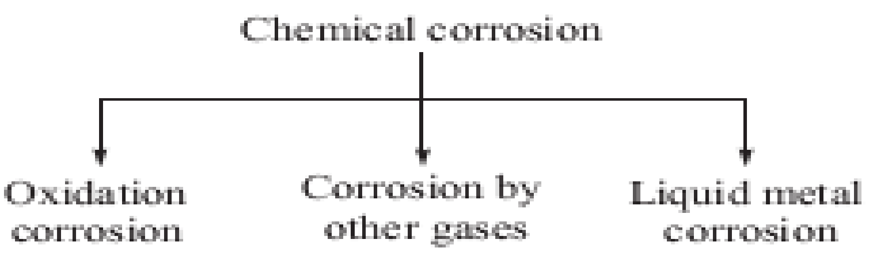
$$Fe + 2CO_2 + H_2O + \frac{1}{2}O_2 \longrightarrow Fe(HCO_3)_2$$

$$2Fe(HCO_3)_2 + H_2O + \frac{1}{2}O_2 \longrightarrow 2Fe(OH)CO_3 + 2CO_2 + 2H_2O$$

$$2Fe(OH)CO_3 + 2H_2O \longrightarrow 2Fe(OH)_3 + 2CO_2$$

- This theory is supported by the analysis of rust that gives the test for CO_3
- 2– ion. Further, the process of rusting is reduced by the presence of lime and caustic soda (these two can absorb CO_2, thus reducing corrosion).

❖ Dry or Chemical Theory of Corrosion:



- According to this theory, corrosion on the surface of a metal is due to direct reaction of atmospheric gases such as oxygen, halogens, oxides of sulphur, oxides of nitrogen, hydrogen sulphide and fumes of chemicals with metal. The extent of corrosion of a particular metal depends on the chemical affinity of the metal towards reactive gas. Oxygen is mainly responsible for the corrosion of most metallic substances when compared to other gases and chemicals.

  Oxidation corrosion (Reaction with oxygen):

  Some of the metals react directly with oxygen in the absence of moisture. Alkali and alkaline earth metals react with oxygen at room temperature and form corresponding oxides, while some metals react with oxygen at higher temperature. Metals such as Ag, Au and Pt are not oxidised as they are noble metals.

❖ Wet or Electrochemical Theory of Corrosion:

- It is a common type of corrosion of metal in aqueous corrosive environment. This type of corrosion occurs when the metal comes in contact with a conducting liquid or when two dissimilar metals are immersed or dipped partly in a solution. According to this theory, there is the formation of a galvanic cell on the surface of metals. Some parts of the metal surface act as anode and rest act as cathode.
- The chemical in the environment and humidity acts as an electrolyte. Oxidation of anodic part takes place and it results in corrosion at anode, while reduction takes place at cathode. The corrosion product is formed on the surface of the metal between anode and cathode.
- To understand the wet theory, let us take the example of corrosion of iron. Oxidation of metal takes place at anode while the reduction process takes place at cathode. By taking rusting of iron as an example, the reaction can be explained as that it may occur in two ways: (i) evolution of hydrogen and (ii) absorption of oxygen

Types of Corrosion

Based on the reactions and physical states, there are different types of corrosions.

- They are
- (a) Crevice corrosion
- (b) Water-line corrosion

- **Waterline corrosion or Concentration cell corrosion**
- This type of corrosion occurs due to electrochemical attack of the metal surface exposed to electrolyte of varying concentrations or varying aeration.
- This type of corrosion is due to
- (i) Difference in concentration of metal ions.
- (ii) Difference in the exposure to air/oxygen (Differential aeration corrosion)
- (iii) Difference in tempDifferential aeration corrosion is the most common type of concentration cell corrosion. When a metal is exposed to different air concentrations, it has been found to be poorly oxygenated of the metal becomes anodic and well oxygenated part becomes cathodic.
- The potential difference is created which causes the flow of electrons from anode (metallic part immersed in NaCl solution) to cathode (exposed to atmosphere).

- **(d) Crevice corrosion:**

  If surface of painted metal is scratched, it will undergo corrosion. The scratched portion acts as small anode and the rest part will act as cathode forming a local cell. Crevice corrosion is formed near joints, rivets and bolts. Changes in the concentration of oxygen/acidic medium causes crevice corrosion.
- **(e) Erosion corrosion:** Due to mechanical wear and tear, corrosion occurs on the surface of a metal and is called erosion corrosion.
- **(f) Soil corrosion:** underground pipes, cables, etc. corrode due to soil corrosion. It is caused due to moisture, pH of soil and micro-organisms.
- **(g) Microbiological corrosion:** Some types of bacteria consume oxygen and cause differential aeration type of system which results in corrosion. The corrosion occurs at the portion poor in oxygen concentration. For example, the bacillus and algae diatoms.

- **Factors Influencing Corrosion:**
- Since corrosion is a process of destruction of metal surface by its environment, the two factors that govern the corrosion process are:

  (i) Metallic and (ii) Environmental

- (i) **Nature of metal:**

  Different properties of a metal are responsible for corrosion. These properties are as follows:

a) Position of metal in galvanic series:
b) Hydrogen over voltage:
c) Purity of metal:
d) Relative areas of anode and cathode:
e) Physical state of the metal:
f) Nature of oxide film:
g) Volatility and solubility of corrosion product:

- (ii) **Nature of environment:**

  The role of environment in the corrosion of a metal is very important. Environmental parameters like temperature, humidity, pH, etc. play important role. The effect is discussed here.

- (a) ***Temperature:*** *The rate of diffusion increases by rise in temperature, hence the rate of corrosion is* also increased. At higher temperature, passive metals also become active and undergo corrosion. But higher temperature reduces the concentration of oxygen and hence corrosion is reduced homogeneous solid solution, hence no local action and no corrosion.
- ***(b) Humidity of air****: In humidity, gases like CO_2, SO_2, NO_x are dissolved which form electrolytes. It* will cause galvanic corrosion. Some oxides are water soluble, humidity washes away the corrosion products and metal surface is further corroded. Other soluble corrosion products can also be washed away by humidity, causing further corrosion.
- ***(c)Impurity of atmosphere****: Pollutants like H_2S, SO_2, CO_2 and acid vapours cause more pollution* where they dissolve. In sea water (salty in nature which acts as an electrolyte) corrosion rate increases. Some suspended particles are dissolved in humidity and form electrolyte which helps in corrosion.
- ***(d) pH value of the medium****: pH value means concentration of H^+ (acidic nature). In acidic medium (pH* less than 7), corrosion is faster. Also, in basic medium pH > 7, some metals such as Pb, Zn, Al, etc. form complexes and hence they corrode.

- **Measurement of Corrosion:**
- The process of corrosion is a slow chemical reaction. During the corrosion process, there is loss of weight of the metal. The loss in mg/dm2 per day or inches per year measures the extent of corrosion.

Rate of corrosion (R) =kw/atd

where w = *loss of weight of metal in milligrams*

a = *area of metal surface in sq. cm*

t = *exposure time for corrosion in 100th part of an hour or a day*

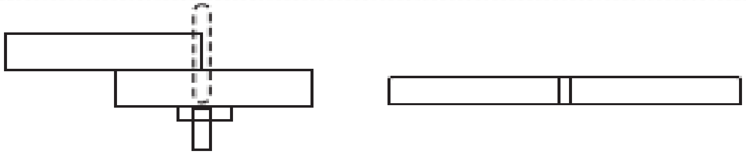
d = *density in g/cm2*

k = *constant of proportionality*

- The condition is that the surface of the metal must be uniform.
- There are several units for the measurement of the rate of corrosion (R), *i.e.* $mg/dm^2/day$, $oz/ft^2/day$, inch/year or millimetre/year.
- A cleaned metal is taken, weighed and exposed for corrosion. Time taken in the process is recorded and then the piece of the metal is taken out; corrosion product is removed and is weighed again. The loss in the weight of the metal is noted which helps to calculate corrosion rate.

- **Protection from Corrosion**
- Metals can be protected from corrosion by various methods. Some of them are as follows:
- . Proper designing
- . Using pure metals
- . Using corrosion inhibitors
- . Modifying the environment
- . Cathodic protection—sacrificial anode, impressed current, cathode
- . Heat treatment
- . Applying surface coatings

- **Sacrificial Anodic Protection:**
- ***Advantages:*** *It is a simple method. It has low maintenance and installation cost. It does not require external* power; cathodic interferences are minimum.
- ***Disadvantages:*** *More than one anode is required. Current output is less. It does not work properly in high* corrosive environment. The sacrificial anode must be replaced periodically as used when it is consumed.
- Due to corrosion, there is a great loss of material and money. Therefore, it is essential to protect metals from corrosion. Since there are two components involved in corrosion—the metal and environment—both are considered in corrosion protection. Following methods have been adopted for the protection of metal from corrosion:
- (i) If it is unavoidable, the anodic area should be very large as compared to the cathodic area.
- (ii) Proper designing of the equipment is the best way of controlling corrosion. The design of the metal should be such that even if corrosion occurs, it is uniform and does not result in intense and localised corrosion.



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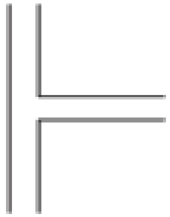
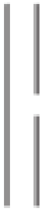


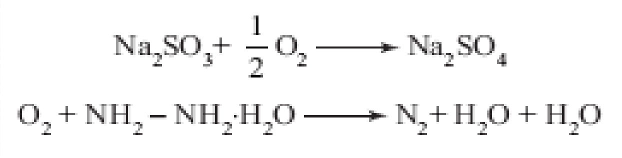


Poor design Best design

- (iii) Two different metals used in the structure should be such that they are occupying near positions in the galvanic series.
- (iv) Putting an insulator between two metals resists corrosion.
- (v) As far as possible, metal used in a structure should be extremely pure. Small amount of impurity causes corrosion.
- (vi) While using an alloy, it should be completely homogeneous.
- (vii) Design or fabricate equipment or metal parts in such a manner that they have minimised sharp edges and corners and also avoid, as far as possible, the crevices in joints, etc.
- (viii) The equipment must be supported on legs to allow the passage of air which prevents differential

Modifying the Environment

- It can be done either by removing the corrosive agents from the environment or by neutralising the corrosive effect by adding certain substances. For example, by deaeration or by deactivation of substance by the addition of chemicals; to deactivate sodium sulphate, oxygen is added to sodium sulphate. To neutralise the acidic character of the corrosive environment due to HCl, $CO2$ and $SO2$, bases like lime, $NH3$ and NaOH are used. The modification of environment also helps in protection from corrosion.
- (i) Deaeration removes oxygen by adjusting temperature and mechanical ageing.
- (ii) Deactivation involves addition of chemicals such as $Na2SO3$, $NH2 – NH2.H2O$ which absorb oxygen.



$$Na_2SO_3 + \frac{1}{2}O_2 \longrightarrow Na_2SO_4$$

$$O_2 + NH_2 - NH_2 \cdot H_2O \longrightarrow N_2 + H_2O + H_2O$$

- (iii) Dehumidification of environment is done by adding alumina or silica gel. These chemicals absorb humidity from metallic surface.

  In humidity, gases such as $CO2$, $H2S$, $SO2$ and HCl give acidic medium responsible for corrosion. They are neutralised by $NH3$ or NaOH or lime.

Cathodic Protection:

- There are some chemicals which reduce the rate of corrosion. These chemicals are called corrosion inhibi-tors. They are of two types, anodicand cathodic. Phosphate, chromate and tungstate protect anode. They form sparingly soluble products which are adsorbed on the surface of metal and hence check corrosion. Cathodic protection is done by organic amines, mercaptans, thiourea and substituted urea. The above chemi-cals retard reduction reaction taking place at cathode. Also, by the use of salts of Mg, Zn or Ni, the insoluble hydroxides of Mg, Zn or Ni are deposited preventing corrosion.

At cathode: $H_2O + \frac{1}{2}O_2 + 2e^- \longrightarrow 2OH^-$

$$Mg^{++} + 2OH^- \longrightarrow \underset{\text{(precipitate)}}{Mg(OH)_2}$$

- For protecting corrosion–electrochemically, there are two methods for the protection from corrosion:

a) Sacrificial anodic protection:

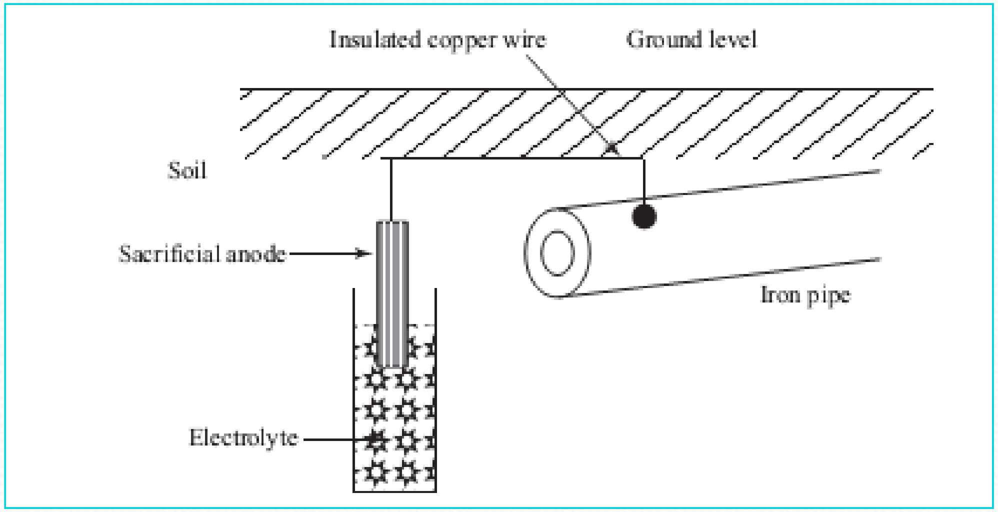
b) Impressed current cathodic protection:

a) Sacrificial anodic protection:

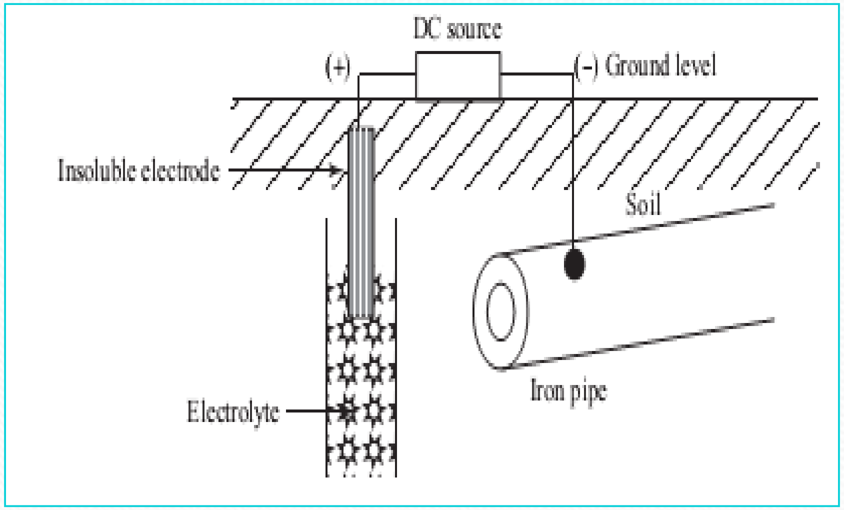
Underground steel pipes are protected from corrosion by this method. A magnesium rod is fixed near the metal under protection (Fe) and both are connected with a conducting wire. Magnesium is more positive than iron and, hence, in electrochemical cell it acts as anode and the iron acts as cathode. According to the principle of galvanic cell, it is anode that undergoes oxidation, and, hence, corrosion occurs at anode saving cathode (iron) from corrosion. Thus, magnesium sacrifies itself for saving the iron. Usually, buried pipes and storage tanks made of steel are connected to Mg blocks. Mg protects steel sacrificially; Zn or Mg sheets are hung around the ship hull to protect the steel or iron base of ship by sacrificial protection.

b) Impressed current cathodic protection:

This is another method for the cathodic protection of metals. The object or the metal to be protected (the metal is exposed to soil or other electrolyte) is made anode by connecting to an external battery. The battery contains an inert graphite anode which is buried in a back fill to maintain electrical contact.



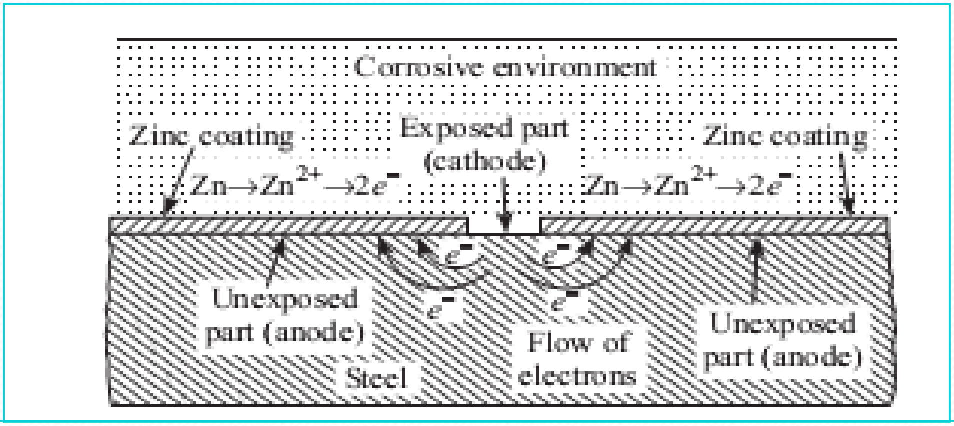
Sacrificial anodic protection



Impressed current cathodic protection

- **Methods of application of metal coatings:**

Metallic dipping causes a coat of metal over the base metal. It is of two types, anodic coating and cathodic coating.



Functioning of anodic coating. In galvanised steel, Zn serves as anode; while iron of steel serves as the cathode. Therefore, the iron is protected, even if it is exposed, when a part of the zinc coating is scrapped off

- **Hot dipping**

Galvanizing:

- Galvanizing is a process in which the iron article is protected from corrosion by coating it with a thin layer of zinc.
- Galvanizing is widely used for protecting iron exposed to the atmosphere (roofs, wire fences, pipes etc.) Galvanized metallic sheets are not used for keeping eatables because of the solubility of zinc.

Tinning:

- The process of coating tin over the iron or steel articles to protect them from undergoing corrosion is known as tinning.

- **Electroplating:**
- Electroplating is the process of coating metals and protects them from corrosion, wear and chemical attack.
- Electroplating is the method of electro-deposition of metal by means electrolysis over surface of metals and alloys.
- The base metal is first subjected to acid pickling to remove any scales, oxides etc. The base metal is made as cathode of the electrolytic cell and the coating metal is made as anode.
- Low temperature, medium current density, low metal ion concentration conditions are maintained for better electro-plating.

- **PASSIVITY**

- The process in which a metal exhibits higher corrosion resistance is called passivity. When a very thin, invisible and highly protective film is formed on the surface of a metal or an alloy, it is called passivity. This film is insoluble and non-passive. A metal is passive in a certain environment if its corrosion rate is very low. By the change of the environment, the passivity of a metal may change and may become active towards corrosion.
- The formation of a passive film on the metal surface in determined by the Pourbaix diagram, which depends on the electrode potential and pH of the medium. Low carbon steel does not corrode in conc. HNO_3 due to protection effect of passive film. However, in dil. HNO_3 it does not form a stable passive film and therefore dissolves steel. Passive film is formed on the surface of aluminium, Cr, Si, Ti in air, water and dilute acids.
- There is a good corrosion and oxidation resistance of stainless oxide passive layer. A damage of passive film may cause intensive localised corrosion (pitting corrosion). Passive oxide layers are dissolved in electrolytes containing $SO_4^{\ 2-}$ and chloride. Phosphate and chromate ions stabilise passive films, promoting the regain of its defects.

Paints:

- A paint is a mechanical dispersion of one or more pigments in medium (liquid, non-volatile) drying oil and thinner. When a metallic surface is painted, the thinner evaporates while the drying oil forms a dry pigmented film after oxidising itself.
- A paint has following qualities:

(i) it should be spread easily on the surface,
(ii) it should form a tough, uniform and adherent film,
(iii) the coating of paint should not crack after drying,
(iv) it should have high covering power,
(v) it should neither be oxidised nor reduced in environment and
(vi) the colour due to point should be shining and stable

- Constituents of a paint:

- **Pigment:** It is a solid substance which is of different colours depending upon the composition, e.g. zinc oxide, white lead, lithophone, titanium oxide (all are white in colour). Red lead, ferric oxide, chrome red are of red colour. Chromium oxide is green, while carbon black is black. Pigments provided (i) strength to point, (ii) protection to the film by reflecting harmful ultraviolet light, (iii) resistance against abrasion/wear, (iv) impermeability to moisture and (v) aesthetic appeal to the paint film. A good pigment should be (i) opaque, (ii) chemically inert, (iii) non-toxic so that there is no bad effect on the health of a painter as well as an inhabitant, (iv) cheap and (v) freely mixable with film forming constituent oils.
- **Drying oil:** It is also called vehicle. It is a film-forming constituent. They are glycerides of higher fatty acids (saturated or unsaturated), e.g.Drying oil may be vegetable oil. Drying oil absorbs oxygen and forms peroxides, hydroperoxides, etc. and forms tough, coherent, insoluble and highly cross-linked structure on the surface. They provide toughness, durability, adhesion and water proofness to the film. When paint is applied in the form of a film, the drying oil absorbs oxygen from air and forms peroxides and hydroperoxides at double bonds. These peroxides isomerise, polymerise condense to form tough, elastic, insoluble, infusible polymer film.

- **Thinner:** It is a highly volatile liquid, it reduces viscosity of the paint and increases its elasticity. It increases the penetration power of drying oil. The common thinner is turpentine oil. Other thinners are benzene, mineral spirit, xylol, kerosene, etc. Some other constituents of paint are—driers(oxygen carrier catalyst) helpful in drying, e.g. tungstate, linoleates of Co, Mn, Pb and Zn, turpentine, mineral spirit, naphtha, methylated naphthalene etc.
- **Extenders or fillers:** They reduce the cost and increase durability, e.g. barytes ($BaSO4$), talc, asbestos, gypsum ($CaSO4$)etc. They serve to fill voids in the film and act as carriers for pigment colour.
- **Plasticisers:** They are used to increase elasticity and to minimise cracking, e.g. dibutyl phosphate, tri-cresyl phosphate, dibutyl tartarate etc.
- **Anti-skinning agents** prevent skinning and gelling of paint film, e.g. polyhydroxyphenols.

- **THEORETICAL QUESTIONS**
- 1. What is corrosion? Why do metals corrode?
- 2. Why most of the metals are found in the ore form and not in the pure form? Explain.
- 3. Describe the electrochemical theory of corrosion.
- 4. Show the reactions involved in the hydrogen evolution and oxygen absorption types of corrosion.
- 5. Describe the factors on which corrosion depends.
- 6. Discuss various methods of protection corrosion.
- 7. Discuss the wet theory of corrosion.
- 8. Explain the rusting of iron with the help of electrochemical theory of corrosion.
- 9. Explain two methods to prevent from corrosion.
- 10. Define passivity with an example.
- 11. Explain the acid theory of corrosion.
- 12. Why rusting of iron is fast in saline water than in ordinary water?

- 13. What is differential aeration corrosion?
- 14. What is meant by passivity?
- 15. What is cementation?
- 16. Give the functions of pigments.
- 17. What is electrochemical series?
- 18. Explain sacrificial anodic and impressed current cathodic protection.
- 19. Give the characteristic features of paints and their functions.
- 20. Differentiate anodic and cathodic protection methods.
- 21. Differentiate galvanising and tinning.
- 22. Rusting of iron is quicker in saline water than in ordinary water. Why?
- 23. What is cathodic protection?
- 24. State the two conditions for wet corrosion

- **Multiple-Choice Questions**
- 1. Corrosion is a process of

  (a) reduction (b) oxidation(c) ozonolysis (d) electrolysis
- 2. In the wet theory of corrosion

  (a) dry cell is formed (b) galvanic cell is formed (c) concentration cell is formed(d) none
- 3. Which one of the following causes corrosion of iron?

  (a) oxygen (b) hydrogen(c) strong base (d) moisture and oxygen
- 4. The method in which the base metal is heated with another powdered metal to prevent corrosion is known as

  (a) electroplating (b) metal spraying (c) pack cementation (d) metal cladding
- 5. The method to prevent corrosion of iron by zinc coating is called

  (a) galvanisation (b) electrolysis (c) cathode protection (d) anode protection

- 6. The rusting of iron is catalysed by
  (a) Zn (b) Fe (c) Al (d) H_2O (H^+)
- 7. A process in which metal is protected from corrosion by dipping it in molten zinc is known as
  (a) tinning (b) galvanisation (c) cladding (d) electroplating
- 8. During wet corrosion
  (a) the anodic part undergoes reduction
  (b) the cathodic part undergoes oxidation
  (c) the anodic part undergoes corrosion
  (d) none
- 9. The chemical composition of rust is
  (a) $Fe_2O_3 \cdot H_2O$ (b) $Fe_3O_4 \cdot xH_2O$ (c) $Fe_2O_3 \cdot xH_2O$ *(d)* $Fe_3O_4 \cdot H_2O$
- 10. When the ratio of anodic to cathodic area decreases, the rate of corrosion
  (a) decreases (b) increases (c) has no effec

❖ *Characteristics of a Good Thermal Insulator*

- 1. Its thermal conductivity is extremely low.
- 2. It should be waterproof and fireproof.
- 3. It should be chemically stable to the surrounding conditions of high temperatures.
- 4. It should have low density.
- 5. It should be mechanically stable and capable of bearing the load applied on it during working.
- 6. It should be odourless during use.
- 7. Cost of the thermal insulator should be low.

UNIT 3

WATER TECHNOLOGY

- **INTRODUCTION**
- Water is a natural gift on the earth. It is essential for humans, animals and plants. Human beings use water for drinking, cooking, bathing, cleaning and washing.
- Chemically, water consists of two atoms of hydrogen and one atom of oxygen and hence have the molecular formula H2O. In several chemical reactions, water is formed along with the main product, e.g., acid reacts with a base to give salt and water. Alcohol and organic acids react to give ester and water.
- Water is found in three physical states: liquid (water), solid (ice) and gas (vapour). The freezing point of water is 0°C and the boiling point is 100°C. Several special behaviours found in water are due to the hydrogen bond present in it. In nature, water is present in abundance. About 96% of water forms the oceans, 2.2% forms the ice and snow, 1.2% forms the groundwater and only 0.003% of water is useful for human consumption. It is therefore essential to use available water carefully and economically, the rest forms the surface water and the water present in the atmosphere. The various sources of water are rivers, tanks, reservoirs, seas, oceans, w ells, tubewells, rain, glaciers, etc.

Hardness of Water

- Water is a very good solvent and even called as the universal solvent. Most of the inorganic salts are soluble in water. The water that has calcium and magnesium salts dissolved in it causes hardness of water. Water passes through rocks and flows on the ground. The calcium and magnesium salts that are present in the rocks are dissolved in water and make it hard. Hard water does not give lather with soap, while soft water easily gives lather with soap. Hence, the hardness of water is its characteristic which resists the lathering with soap. Chemically, it can be understood as follows:
- A soap is a sodium salt of higher fatty acid such as stearic acid (C17H35COOH). Soap in the absence of Ca2+ and Mg2+ gives lather with water easily, but in the presence of Ca2+ and Mg2+ reacts with them and forms insoluble soap that appears as precipitate (formation of scum).
- **Reaction**

$$\underset{\text{(soap)}}{2C_{17}H_{35}COONa} + Ca^{2+}/Mg^{2+} \rightarrow \underset{\text{(insoluble scum)}}{(Mg^{2+}/Ca^{2+})(C_{17}H_{35}COO)_2} + 2Na^{+}$$

- **Disadvantages of Hard Water**
- **In domestic use**

(a) **Washing**: When hard water is used for washing purposes, it does not produce lather freely with soap; rather it produces sticky precipitates of calcium and magnesium soaps. The precipitation continues to take place till all calcium and magnesium salts in water are precipitated. After that the soap gives lather with water.

$$C_{17}H_{35}COONa + H_2O \rightleftharpoons C_{17}H_{35}COOH + NaOH$$

$$C_{17}H_{35}COOH + C_{17}H_{35}COONa \longrightarrow \text{Lather}$$

As a result, wastage of soap takes place and in the presence of iron salts it may cause staining of cloth.

(b) **Bathing:** Hard water forms sticky precipitate with soap on bath tub and body. Thus, cleaning quality of soap is reduced and a lot of it is wasted.

(c) **Cooking:** Due to the presence of dissolved hardness producing salts, the boiling point of water is elevated. Hence, more fuel and time are required for cooking. The dissolved salts are deposited as carbonates on the inner walls of the utensils.

(d) **Drinking:** Hard water causes bad effect on our health. Calcium forms oxalate crystals in urinary tract.

- **In industrial use**

(a) **Textile industry:** Hard water produces precipitates of calcium and magnesium with soap. The fabrics when dyed later on do not produce exact shades of colour. Iron and magnesium salts containing water produces coloured spots on the fabric.

(b) Sugar industry: Water containing sulphates, nitrates, alkali carbonates if used in sugar refining causes difficulties in the crystallization of sugar. Moreover, the sugar so produced may be deliquescent.

(c) Dying industry: The dissolved calcium, magnesium and iron salts in hard water react with costly dyes forming undesirable precipitates, which yield impure shades and give spots on the fabric being dyed.

(d) Laundry: Hard water causes wastage of soap. Iron salts cause colouration of clothes.

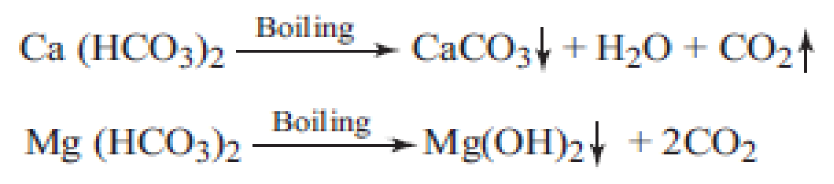
(e) Pharmaceutical industry: Hard water if used for the preparation of pharmaceutical products such as drugs injections, ointments may produce undesirable products in them.

f) Paper industry: Iron salts affect the colour of the paper.

❖ Types of Hardness

- Hardness in water is of two types:

  (i) Temporary hardness and (ii) Permanent hardness.
- Temporary hardness is due to the presence of bicarbonates of calcium and magnesium that can be removed by boiling. On boiling, soluble (Ca^{+2}/Mg^{+2}) ($HCO3)2$ is converted into insoluble carbonate that can be removed by filtration.



$$Ca\,(HCO_3)_2 \xrightarrow{\text{Boiling}} CaCO_3\downarrow + H_2O + CO_2\uparrow$$

$$Mg\,(HCO_3)_2 \xrightarrow{\text{Boiling}} Mg(OH)_2\downarrow + 2CO_2$$

- *Permanent Hardness*
- Permanent hardness cannot be removed by boiling. It is due to the dissolution of $CaCl2$, $CaSO4$, $MgCl2$ and $MgSO4$ in water. These salts cannot be removed by boiling. They are removed by different other methods. Fe^{+3}, Al^{+3} and Mn^{+7} also cause hardness in water but they are rarely found in hard water.

- **Meaurement of Hardness**
- To estimate hardness, it is essential to know the various units to measure it. The hardness of water is measured in terms of CaCO3 because it is highly insoluble in water and also its molecular weight is 100 that makes the calculation easier.
- *Units of Hardness*
- **Parts per million (ppm):** It is the number of parts of equivalent CaCO3 per 106 part of water. For example, 50 ppm hardness means 106 parts of water has 50 parts of equivalent CaCO3.
- **Milligram per litre (mg/L):** It is the number of milligrams of equivalent CaCO3 per litre of water. One milligram per litre hardness means 1 mg of equivalent CaCO3 per litre of hard water.

  1 kg of water = 1000 × 1000 mg = 106 parts

  1 ppm = 1 mg/L
- **Degree Clarke:** It is the number of grams of CaCO3 per gallon of water, i.e., the number of parts of calcium carbonate equivalent hardness per 70,000 part of water.

  Hardness 1°Clarke (1°Cl) means 1 gram equivalent CaCO3 present in 1 gallon of hard water.

  Degree French: It is the number of parts of CaCO3 per 105 parts of hard water. Hardness 1°French (1°Fr) means 1 part of equivalent CaCO3 per 105 parts of hard water.

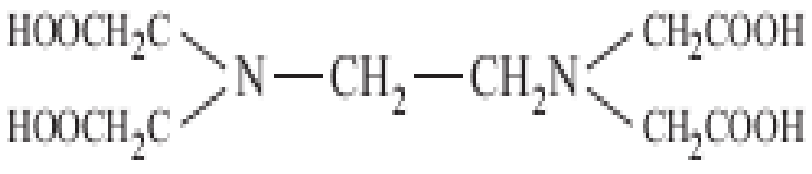
  Relationship among units of hardness:

  1 ppm = 1mg/L = 0.1°Fr = 0.07°Cl

  Any water sample with hardness less than 150 ppm is good and potable, while beyond 350 ppm is not suitable for consumption.

Methods to Determine Hardness:

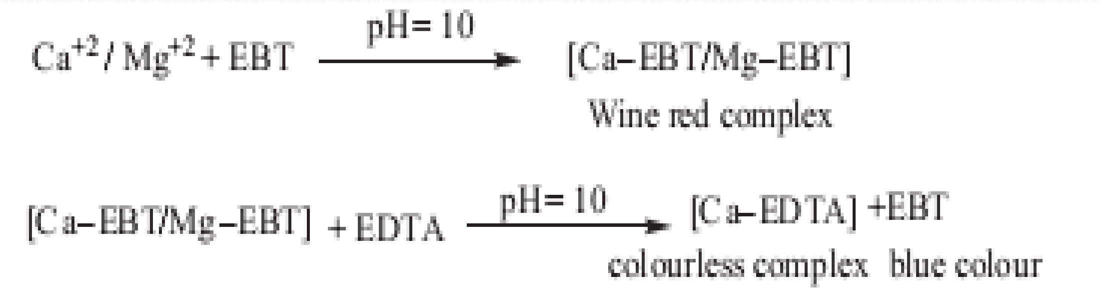
- Hardness of water is determined by the EDTA method, which involves the complexometric titration. EDTA is a strong complexing agent. EDTA (ethylene diamine theoretic acid) is a strong complexing agent whose structure is given as
- As such it is not very soluble in water; hence, disodium salt of EDTA is used in complexometry.



$[H_4Y]$

- **Principle:**

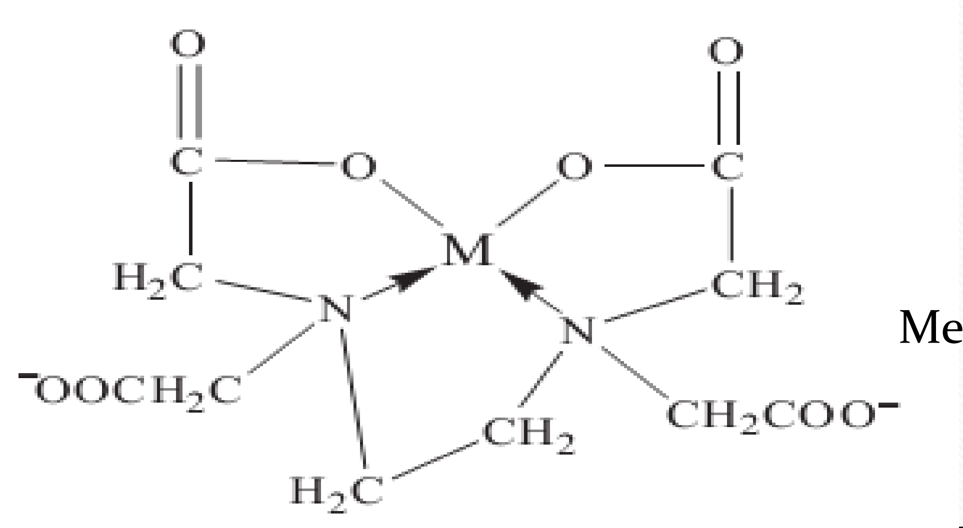
  The EDTA solution is standardized with a standard solution of calcium carbonate, prepared by dis-solving a known weight of calcium carbonate in dil. HCl and then making up the solution to a known volume with distilled water. The permanent hardness of water can be determined by titrating the water after boiling well to remove the temporary hardness as carbonates of calcium and magnesium. When hard water is treated with EBT at pH 10, Ca2+ /Mg 2+ ions form unstable wine red coloured complex. When it is titrated with EDTA under similar conditions, EDTA extracts metal ions from the complex and forms a stable colourless complex and releases EBT into the solution. Hence, the colour of the solution changes to blue at the end point



$$Ca^{+2}/Mg^{+2}+EBT \xrightarrow{pH=10} \underset{\text{Wine red complex}}{[Ca\text{–}EBT/Mg\text{–}EBT]}$$

$$[Ca\text{–}EBT/Mg\text{–}EBT]+EDTA \xrightarrow{pH=10} \underset{\text{colourless complex}}{[Ca\text{–}EDTA]}+\underset{\text{blue colour}}{EBT}$$

- EDTA forms complexes with different metal ions at different pH values (Fig below). Calcium and magnesium ions present in water form complexes with EDTA in a buffer solution of ammonium chloride and ammonium hydroxide at pH = 10



Metal–EDTA complex

- **Experimental Procedure:**

  100 ml of water sample is taken in a flask and two drops of phenolphthalein (pH > 10) is added to it. The colour will become pink due to pH > 10. This water sample of pink colour is titrated against N/50 HCl solu-tion. At the endpoint, pink colour disappears. This endpoint is termed as P-endpoint. Now add two drops of methyl orange indicator to the same water (pH falls below 7). At the endpoint, pink colour reappears. This endpoint is M-endpoint (methyl orange endpoint).

  REACTIONS:

$$CO_3^{-2} + H^+ \longrightarrow HCO_3^-$$
$$HCO_3^- + H^+ \longrightarrow H_2O + CO_2$$
$$OH^- + H^+ \longrightarrow H_2O$$

- **Calculation**

  At the phenolphthalein endpoint (at P ml), the alkalinity thus calculated is phenolphthalein alkalinity in terms of $CaCO_3$ and it is given by

$$\frac{P \times 50 \times 10^6}{50 \times 100 \times 1000} = (10P) \text{ ppm}$$

The alkalinity of methyl orange (at M ml) is given by

$$\frac{M \times 50 \times 10^6}{50 \times 100 \times 1000} = (10M) \text{ ppm}$$

- **Determination of Hardness of Water by Winkler's method:**
- The determination of dissolved oxygen is to bring about the oxidization of potassium iodide with the dissolved oxygen present in the water sample after adding MnSO4, KOH and KI. The basic manganic oxide formed acts as an oxygen carrier to enable the dissolved oxygen in the molecular form to take part in the reaction. The liberated iodine is titrated against standard hypo Solution using starch indicator.
- $MnSO_4 + 2KOH \rightarrow Mn(OH)_2 + K_2SO_4$
- $2Mn(OH)_2 + O_2 \rightarrow 2\,MnO(OH)_2$
- Basic manganic oxide (Brown precipitate)
- $MnO(OH)_2 + H_2SO_4 \rightarrow MnSO_4 + 2H_2O + [O]$
- $2KI + H_2SO_4 + [O] \rightarrow K_2SO_4 + H_2O + I_2$
- $I_2 + Na_2S_2O_3 \rightarrow Na_2S_4O_6 + 2NaI$
- Starch + $I_2 \rightarrow$ blue colored complex.

Boiler Feed water

- In several industries, boilers are used to produce steam. The water used for making steam must have the following
- Characteristics:

- 1. The pH value should be nearly 7.
- 2. It should have very low hardness (less than 0.2 ppm).
- 3. Caustic and soda alkalinity should not exceed 0.45 ppm and 1.00 ppm, respectively.

Boiler feedwater is treated to avoid

(i)carry over (priming and foaming),

(ii) caustic embrittlement,

(iii) boiler corrosion, and

(iv) scale and sludges formation.

- **Carry Over**
- The phenomenon of carrying of water along with impurities by steam is called carry over. This is due to priming and foaming. Carry over is undesirable because it decreases the efficiency and results in some practical difficulties in the successful operation of the boilers. Foaming of water makes it difficult to know the exact level of water in the boiler.
- Water takes grit along with it at high velocity and damages the walls of the cylinder. A considerable amount of heat is wasted by the removal of hot boiler water.
- ***Priming and Foaming***

During functioning of the boilers, some water droplets pass with steam. This process of wet steam formation is called priming. Priming in boilers is due to

- (i) the presence of the suspended and dissolved solids,
- (ii) high of water in boilers,
- (iii) faulty design of boilers and
- (iv) sudden steam demands.

Formation of priming reduces the efficiency of the boilers and causes damage to the system.

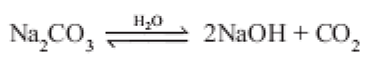
- *Priming can be controlled by*

1. proper evaporation and using adequate heating surfaces.
2. controlling rapid change in steam velocities.
3. proper design of boilers by maintaining low water levels in the boilers.
4. filtering water before feeding to boilers.
5. by blow down.

- Formation of stable, persistent foam or bubbles at the surface tension of water in the boiler is called foaming. Foaming is due to the presence of oil or alkali in boiler feed water. The oil and alkali react with water to form soap, as a result the surface tension of water decreases. More foaming will cause more priming. Oil is introduced into the boiler through lubricants. It results with the formation of wet steam that harms the boiler cylinder and turbine blades, etc. Foaming is due to the presence of oil drops, grease and some suspended solids. Silicic acid and aluminium hydroxide are used as clarifying agents to minimise foaming. Oil can be removed by sodium aluminate or alum. It can also be removed by cataphoresis. Polyamide and castor oil also act as anti-foaming agents.
- *Thus, foaming can be prevented by*
  1. adding anti-foaming agents which reduces the surface tension, e.g., castor oil, prevents foaming.
  2. blow down, removing the concentrated boiler water and replace the water by fresh feed water.

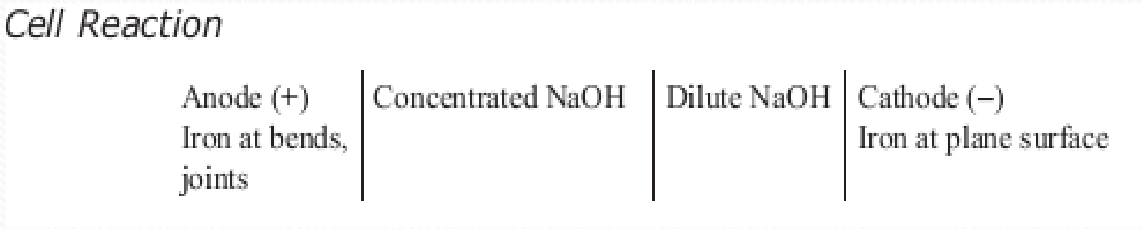
Caustic Embrittlement

- It is the brittlement of the boiler due to the increased concentration of caustic alkali in boiler water. It is a type of boiler corrosion caused when excess of caustic alkali is present in water. In high-pressure boilers, sodium carbonate is hydrolysed to yield NaOH.



$$Na_2CO_3 \overset{H_2O}{\rightleftharpoons} 2NaOH + CO_2$$

- The NaOH thus formed concentrates after long use. It causes inter-granular cracks on the boiler walls, especially at the stress points. The concentrated alkali is dissolved iron as sodium ferroate (NaFeO2) which enter through minute cracks and causes brittlement of the boiler parts, especially at the bends, joints and rivets, even causing failure of boiler. The formation of cracks in the boilers due to increased concentration of NaOH is called caustic embrittlement. Caustic cracking can be explained by the following concentration cell.



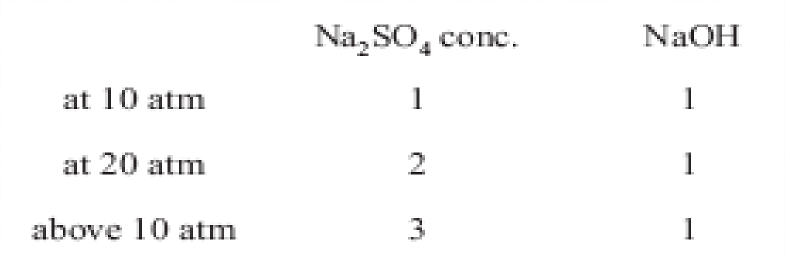
Cell Reaction

Anode (+)	Concentrated NaOH	Dilute NaOH	Cathode (–)
Iron at bends, joints			Iron at plane surface

- i.e., iron at bends and joints is in contact with concentrated alkali and causes corrosion. The iron at plane surface is in contact with dilute alkali and acts as cathode.

- *Caustic embrittlement can be prevented by*
- 1. using Na3PO4 as softening reagent instead of Na2CO3 in external treatment of boiler water.
- 2. adding tannin, lignin to boiler water, which blocks the hair cracks in the boiler walls.
- 3. adding Na2SO4 to boiler water to prevent caustic cracking in boiler.

  At different pressures, the proportions of sodium sulphate to NaOH as follows:



	Na_2SO_4 conc.	NaOH
at 10 atm	1	1
at 20 atm	2	1
above 10 atm	3	1

- 4. neutralizing alkali with very small quantity of acid

Sludge and Scale Formation

- In industries, boilers are continuously used for stream generation. As a result of continuous evaporation of water, the concentration of dissolved salts increases. When the ionic product of the salts exceeds the solubility product, the salts are thrown out of boiler. These salts may get deposited on the inner walls of the boiler to form scales or they may float on boiler water as loose and slimy precipitates called sludges. Scales are hard and sticky deposits formed on the inner walls of the boiler. They are very difficult to remove. Scales are formed due to the presence of MgCl2, CaSO4, Mg(OH)2, Ca(OH)2 and silica in water.

Formation of Scales

Decomposition of Ca(HCO3)2: Ca(HCO3)2 decomposes to an insoluble calcium carbonate salt. In low-pressure boilers, calcium carbonate causes scale formation. In high pressure boilers, it becomes soluble.

$$Ca(HCO_3)_2 \xrightarrow{\Delta} CaCO_3 + H_2O + CO_2\uparrow$$

$$CaCO_3 \longrightarrow CaO + CO_2$$

$$CO_2 + H_2O \longrightarrow Ca(OH)_2$$

- **Hydrolysis of magnesium salts:** Magnesium salts dissolved in water undergoes hydrolysis and form a precipitate of Mg(OH)2.

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

- **Presence of silica: Silica present in water gets deposited as CaSiO3. This is sparingly soluble in water.**
- **Decomposition of CaSO4: It is soluble in cold water but solubility decreases with rise in temperature. At** high temperature in boilers, CaSO4 gets deposited as hard scale which is very difficult to remove. The chemicals found in the sludges and scales are CaSO4, Ca(OH)2, Mg(OH)2, carbonates of Ca2+ and Mg2+, phosphates and silicates.

❖ **Disadvantages of scale formation:**

- 1. Wastage of fuel: Scales have poor thermal conductivity so the rate of heat transfer is reduced. In order to provide a steady supply of heat to water, overheating is done and this causes increase in fuel consumption.
- 2. Lowering of boiler safety: Due to overheating, to maintain steady supply of heat, the boiler material becomes soft and distortion of boiler tubes takes place.
- 3. Decrease in efficiency: Scales may get deposited in the valves and condensers of the boiler and choke them there by decreasing the efficiency.
- 4. Danger of explosion: When thick scales crack due to uneven expansion, water suddenly comes in contact with overheated walls and a large amount of steam is formed instantaneously. Sudden high pressure is developed and causes explosion of the boiler.

❖ **Removal of scales: Scales can be removed by mechanical and chemical methods.**

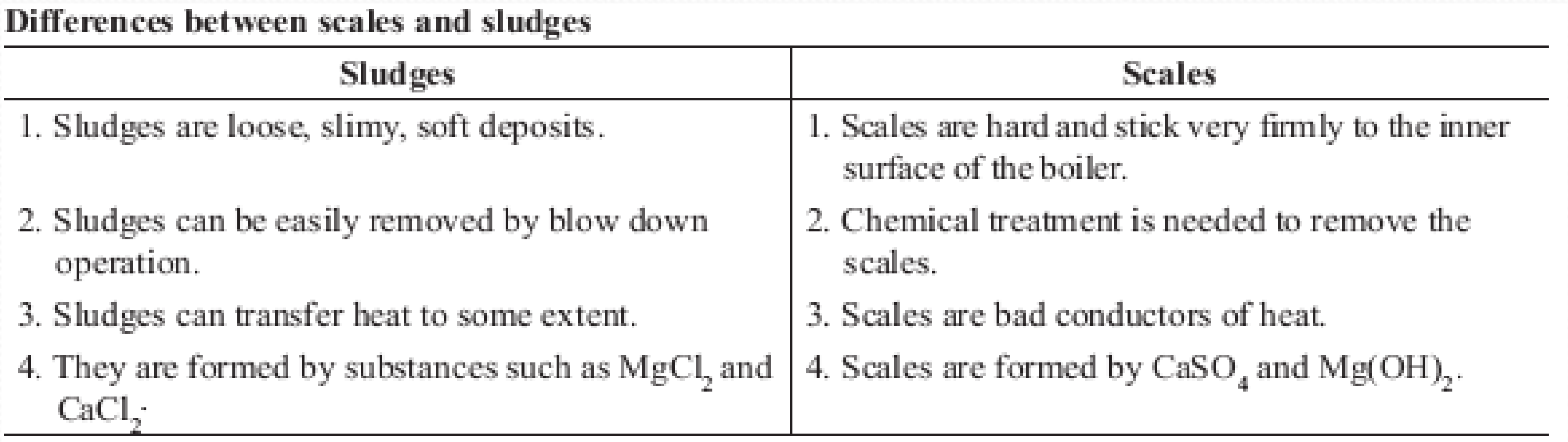
- 1. Mechanical methods: If scales are loosely adhering, they can be removed with a scraper or a piece of wood or wire brush. They can also be removed by blow down. If the scales are brittle, thermal shocks are to be given.
- 2. Chemical methods: If scales are hard and adhering, they can be removed by dissolving in chemicals.
- • Calcium carbonate scales are dissolved in 5–10% HCl.
- • Calcium sulphate complex is highly soluble by adding EDTA.
- • Ca–EDTA complex is highly soluble in water.

Formation of Sludges

- Sludges are loose and slimy precipitates. They do not stick to the walls of the boiler. They are formed by substances having more solubility in hot water. Examples, magnesium carbonate, magnesium sulphate, magnesium chloride, calcium chloride form sludges. The solubility of these salts increases with increase in temperature. Sludges are formed at comparatively colder portions of the boiler such as bends, joints, rivets, etc.

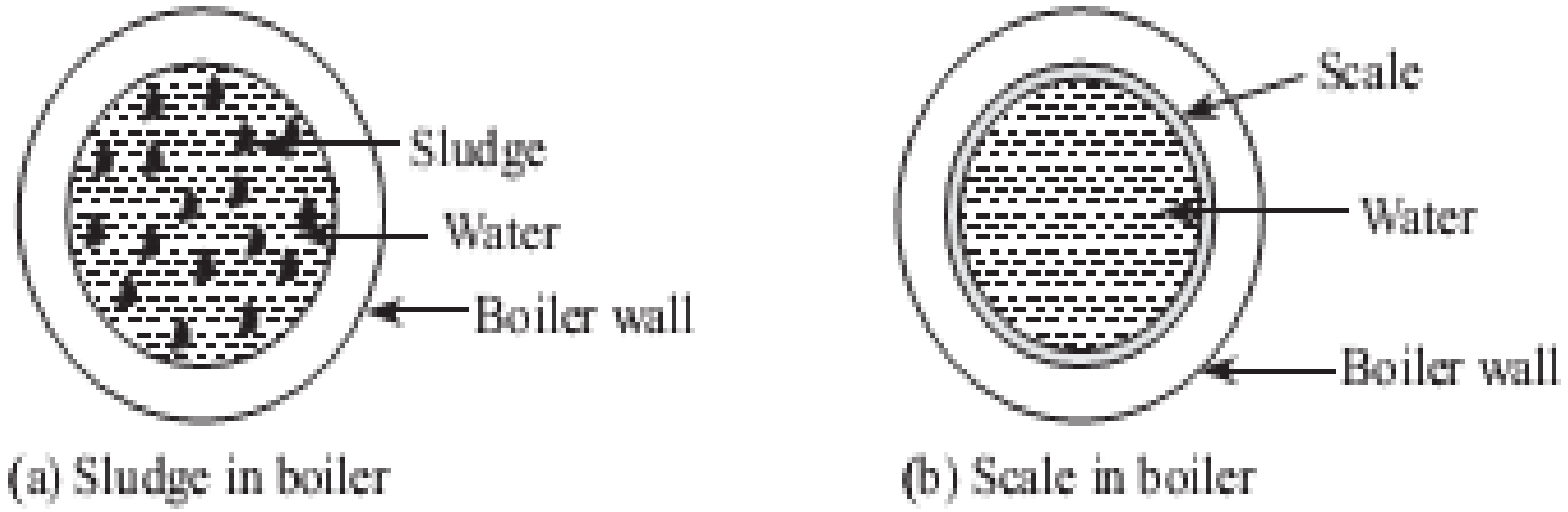
Disadvantages of sludges:

- 1. Sludges are poor conductors of heat. They tend to waste a portion of heat generated and decreases the efficiency of boiler.
- 2. Sludges settle in regions of poor water circulation such as pipe connections and plug openings, thereby causing chocking of the pipes.



Differences between scales and sludges

Sludges	Scales
1. Sludges are loose, slimy, soft deposits.	1. Scales are hard and stick very firmly to the inner surface of the boiler.
2. Sludges can be easily removed by blow down operation.	2. Chemical treatment is needed to remove the scales.
3. Sludges can transfer heat to some extent.	3. Scales are bad conductors of heat.
4. They are formed by substances such as $MgCl_2$ and $CaCl_2$.	4. Scales are formed by $CaSO_4$ and $Mg(OH)_2$.



Sludges and scales in boiler

Softening of Water

- The process of removing the hardness causing salts from water is called softening of water. Soft water is essential for many industries such as textiles, laundries, paper, ice, brewing, canning, etc. Water used for steam generation should be perfectly soft in boilers.
- 1. To minimize boiler troubles, the water used must be perfectly soft otherwise loss of efficiency and of boiler tube takes place.
- 2. Hardness causing salts are removed by external and internal treatment methods.

There are two treatment methods for preventing scale formation.

They are

- ***Internal treatment:*** *In this method, raw water is treated inside the boiler. Internal treatment means addition* of suitable chemicals to reduce scale and sludge formation. It is mainly based on the solubility product. If the product of the concentration of ions exceeds the solubility product, it precipitates.This is a corrective method to remove slight residual hardness and to remove corrosive nature of water.
- ***External treatment:*** *This treatment is given outside the boiler before the feed water enters in***.** External treatment methods include lime–soda process, permutit process, ion-exchange process.

Pre-heating: Feed water is heated before it enters the boiler. Hot flue gas leaving the boiler is also used for pre- heating. Water may be heated in a heat exchanger.

- ***Advantages of pre-heating is as follows:***

1. Fuel will be saved. Instead of feeding boiler with water at atmospheric temperature, it is fed with hot water.

2. A portion of temporary hardness may be removed

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

3. Dissolved O_2, CO_2 are removed when water is heated to 650C. As these gases have corrosive effect, their removal is advantageous.

- The main principle involved in internal condition is that scales formed are converted into sludges.

Internal Treatment Methods

- After feeding water to the boiler for steam generation, scale formation can be prevented by internal treatment method. The precipitation process applied includes carbonate conditioning, phosphate conditioning, colloidal conditioning, calgon process and treatment with sodium alluminate. These reduce the scale and sludge formation in the boilers.
- **Carbonate conditioning**: Scale formation in low pressure boilers can be avoided by adding sodium carbonate to boiler water, where $CaSO_4$ is converted into calcium carbonate, a sludge which can be removed by blow down operation.

  $CaSO_4 + Na_2CO_3 \; CaCO_3 + Na_4SO_4$
- By adding Na_2CO_3, the concentration ratio of carbonate ion to sulphate ion is made greater than the solubility product ratio of $CaCO_3$ to $CaSO_4$. $CaCO_3$ is a loose sludge which can be scraped off by blow down operation.
- $CO_3^{2-}/SO_4^{2-} > CaCO_3/CaSO_4$

  i.e., the concentration of carbonate ion is greater than concentration of sulphate. Precipitation of calcium carbonate occurs in preference to calcium sulphate. In high pressure boilers, excess of sodium carbonate may get hydrolysed to NaOH which causes caustic embrittlement.

- **Phosphate conditioning:** Phosphate conditioning is generally applied to high pressure boilers. When sodium phosphate in added to boiler water, it reacts with magnesium and calcium salt forming soft sludges of Mg3(PO4)2 and Ca3(PO)2.

$$3CaCl_2 + 2Na_3PO_4 \longrightarrow Ca_3(PO_4)_2\downarrow + 6NaCl$$

$$3MgCl_2 + 2Na_3PO_4 \longrightarrow Mg_3(PO_4)_2\downarrow + 6NaSO_4$$

- Trisodium phosphate is used when the alkalinity of boiler water in 9.5–10.5 and calcium gets precipitated at pH of 9.5. If alkalinity of boiler water is too high, NaH2PO4 (acidic) is used, and if the boiler water is slightly alkaline, Na2HPO4 is used.
- **Colloidal conditioning:** Colloidal substances like kerosene, tannin, agar-agar, etc. are added to low-pressure boilers. These substances gets adsorbed over the scale forming precipitates and yield non-sticky, loose deposits which can be easily removed by blow down.
- **Calgon conditioning process:** The word calgon means calcium gone, i.e. the removal of Ca2+. Sodium hexametaphosphate is called calgon. It reacts with calcium ion and forms a water-soluble compound. Calcium sulphate present in hard water forms sludge which on drying in boiler changes to scale and, hence, reduces the efficiency of the boiler.

$$Na_2[Na_4(PO_3)_6] + 2Ca^{2+} \rightarrow \underset{\text{(Soluble complex)}}{Na_2[Ca_2(PO_3)_6]}$$

- **Treatment with sodium aluminate:** When boiler water is heated with sodium aluminate, it gets hydrolysed to give sodium hydroxide and a gelatinous precipitate of

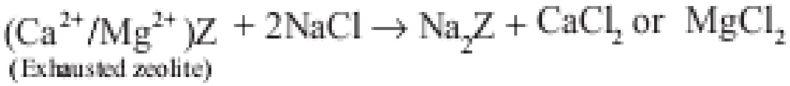
$$NaAlO_2 + 2H_2O \longrightarrow NaOH + Al(OH)_3$$

- The NaOH formed above reacts with MgCl2 to form another flocculant precipitate of Mg(OH)2. These two precipitate entrap colloidal impurities such as oil drops, sand and make them settle down at the bottom that can be easily removed.

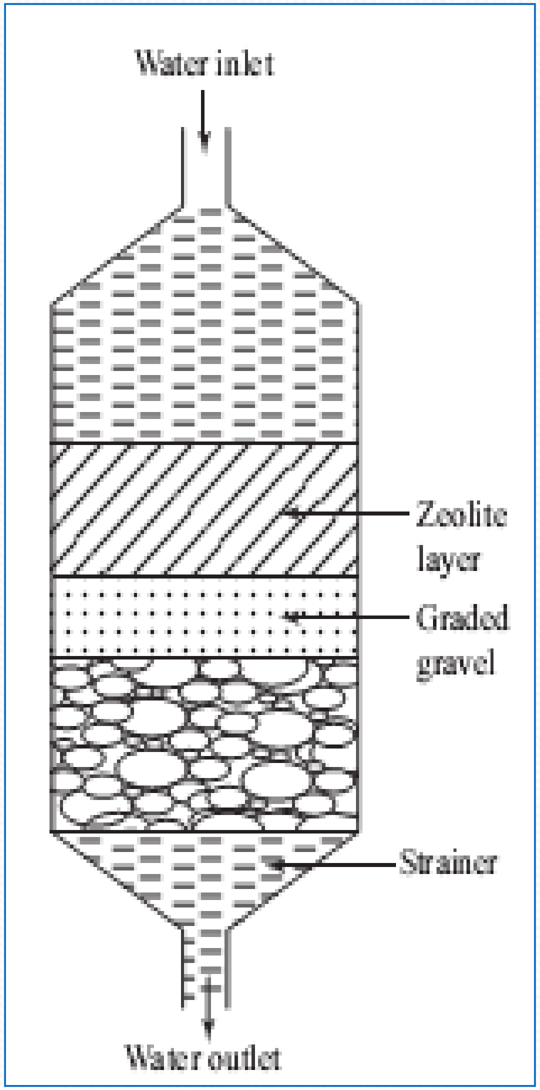
- **Zeolite Process**
- Zeolite is a three-dimensional silicate. In zeolite, Si (IV) atom is replaced by Al (III) atom and, hence, changes it into anion. Common zeolite is naturally occurring aluminosilicate with the general composition $Na_2O. Al_2O_3.xSiO_2.yH_2O$ (x= 2 to 10 and y= 2 to 6). Zeolite has a cage-like structure. It is derived from SiO_4 tetrahedron.
- Zeolites are of two types:
- Natural zeolite: They occur naturally and are porous. Example: natrolite $Na_2O·Al_2O_3·4SiO_2·2H_2O$.
- Synthetic zeolite: They can be prepared from feldspar china clay and soda ash. They are porous and possess gel structure. They possess high exchange capacity than natural zeolites.

- Besides natural zeolite, synthetic zeolite is also prepared with the help of soda ash, feldspar and china clay on heating.

The apparatus is made of cylindrical vessel inside it where zeolite salt is kept. Raw water bed percolated inside the apparatus through beds and, thus, ion-exchange reactions take place where Na^{-} ions is replaced by Ca^{+2}/Mg^{+2}ions. After the use of this process for a certain time, zeolite is exhausted, i.e. all Na^{+} of the zeolites are removed by Ca^{2+}/Mg^{2+}, and hard water will not be further softened.Exhausted zeolite can be regenerated or reactivated by heating it with brine solution (10% NaCl solution).



$$\underset{\text{(Exhausted zeolite)}}{(Ca^{2+}/Mg^{2+})Z} + 2NaCl \rightarrow Na_2Z + CaCl_2 \text{ or } MgCl_2$$

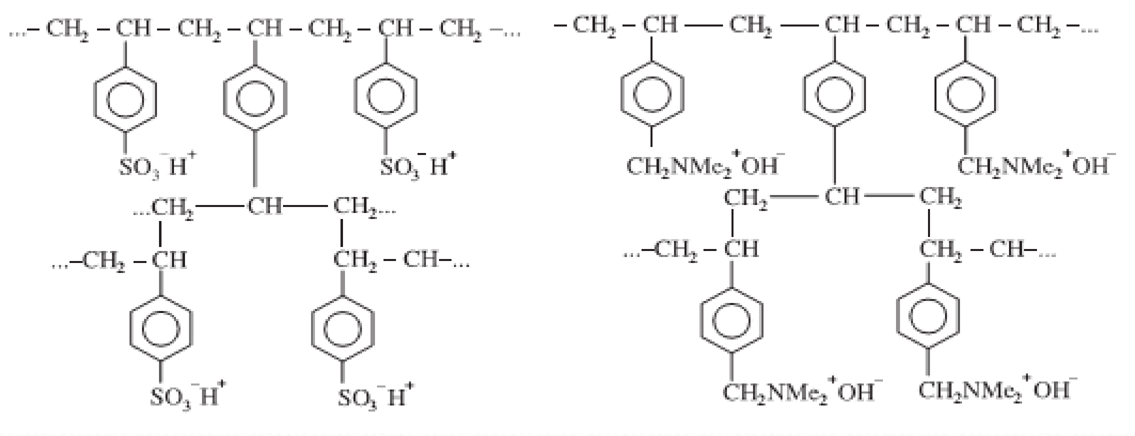


Zeolite softener

- **Advantages of zeolite process:**
- 1. Hardness of water is removed with residual hardness of about 10 ppm.
- 2. It is easy to operate.
- 3. It occupies less space.
- 4. The process can be made automatic and continuous.
- 5. This process is very cheap since regenerated permutit is used again.
- **Disadvantages of zeolite process:**
- 1. Since the process is an ion-exchange process in which 2Na+ is replaced by Ca2+/Mg2+ ion, the soft water obtained by this process has excess of Na+.
- 2. Hard water containing acid destroys the zeolite.
- 3. If suspended particles (turbidity) are present, the pores of the zeolite are blocked and softening is not possible.
- 4. Bicarbonate and carbonate ions, if present in water, are not removed and are present as sodium salt resulting in the alkalinity of water.
- 5. The colours present in hard water cannot be removed by this process

❖ Ion-exchange Process or Demineralisation Process

- Ion exchangers are of two types: anionic and cationic. They are copolymers of styrene and divinyl benzene. The polymers have two types of functional groups. The first group has (SO3H) or COOH group in which H+ ion is replaced by cations such as Mg^{2+}/Ca^{2+}. The second group contains substituted amino groups, such as $–NH^{+}{}_{2}$ OH or $>NH^{+}$ OH^{-}or $N^{+}OH^{-}$, in which $OH^{-}$is replaced by anions in water. General representation of cation and anion exchangers are H–R and R–OH, respectively. Structures of some cations and anions are shown in Fig.



Structures of (a) cation-exchange resins and (b) anion-exchange resins

Desalination

The process of removal of dissolved salts (NaCl, KCl) present in water is known as desalination. Water is divided into three categories on the basis of salinity:

(a) **Sea water:** The salinity is greater than 35000 mg/L.

(b) **Brakish water:** The salinity is in the range of 1000–35000 mg/L. It has peculiar salty taste.

(c) **Fresh water:** The salinity of water is less than 1000 mg/L.

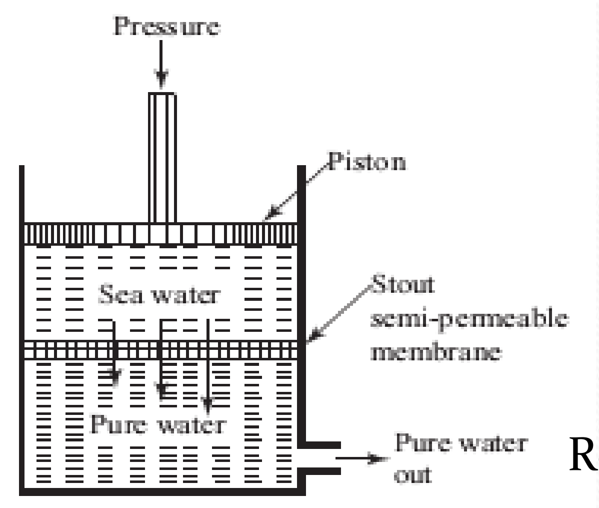
Brakish water and sea water are not fit for drinking as well as for industrial purposes. They can be subjected to desalination to make them suitable for drinking.

- Important desalination methods are:
- (i) reverse osmosis,
- (ii) electrodialysis and
- (iii) distillation.

Reverse Osmosis Process

Osmosis is the process in which the flow of solvent takes place from dilute to concentrated solution through a semi-permeable membrane. In this process, only solvent can flow but not the solute, which produces a pressure called osmotic pressure on the side of more concentrated solution.

When the flow of solvent under pressure from more concentrated solution to solvent or to the less concentrated solution through a semi-permeable membrane takes place is called reverse osmosis.



Reverse osmosis cell

- This method is applicable mainly for the desalination of sea water. Sea water and pure water are separated by a semi-permeable membrane made up of cellulose acetate fitted on both sides of a perforated tube. Inventions are in progress to search for better membrane. Polymethacrylate and polyamides have been proved to be better membranes.
- The process is very easy. It is used to make pure water. It removes the ionic and non-ionic substances in the water. It can also remove suspended colloidal particles. The life of a membrane is nearly two years, and it should be replaced after this period. By this process, sea water is made fit for drinking. Water obtained after being treated by this process is used in boilers.

- **Advantages of the process**
- 1. The process removes ionic as well as non-ionic dissolved salts easily.
- 2. It is effective in removing colloidal impurities in water.
- 3. The process is economical and convenient. The process can be carried out at a room temperature.
- 4. It is suitable for converting sea water into drinking water

Potable/Domestic/Municipal Water

The water supplied by municipality should be fit for human consumption. It should satisfy the following requirements:

- 1. It should be colourless, odourless, and pleasant to taste.
- 2. Turbidity should not exceed 10 ppm. TDS should not exceed 500 ppm. It should not be very alkaline (pH 8.0).
- 3. It should be free from dissolved gases.
- 4. It should be free from objectionable minerals such as Pb, As, Cs, Mn and dissolved gases such as $H_2S$and CO_2.
- 5. It should be free from pathogenic micro-organisms (coliform bacteria are used as indicator organisms,whose presence suggests water is contaminated.)

- **Treatment of municipal water involves the following:**
- 1. **Screening:** Water is allowed to pass through the mesh screens whereby large floating matters are removed
- 2. **Sedimentation:** Water is allowed to stand undisturbed for 2–5 h in big setting tanks**.** Suspended particles settle down due to gravity and clear water raises which can be drawn out with the help of the pumps.

  Disadvantages
  - It requires long big tanks. It takes a long time.
  - It removes 70–75% suspended matter.
  - If water contains clay and colloidal impurities, coagulants are added before sedimentation.
- 3. **Coagulation:** Colloidal particles from the water are removed by adding coagulants such as alum, $Al_2(SO_4)_3$, $NaAlO_2$, etc., which produces flocs. Smaller particles gather together to form bigger flocs. They can be easily removed by filtration. Some bacteria and colour are also removed.

$$Al_2\ (SO_4)_3 + 3\ Ca\ (HCO_3)_2 \rightarrow 2\ Al(OH)_3\downarrow + 3aSO_4 + 6\ CO_2$$

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

$$FeSO_4 + Mg(HCO_3)_2 \rightarrow Fe(OH)_2 + MgCO_3 + CO_2 + H_2O$$

$$4Fe(OH)_2 + O_2 + 2H_2O \rightarrow 4\ Fe\ (OH)_3$$

- 4. **Filtration:** Colloidal matter, bacteria, micro-organism are removed. Water is passed through a large area sand bed. The filter may be pressure filter or gravity filter.
- 5. **Sterilization/disinfection:** Water after passing through sedimentation, coagulation, and filtration still contains a small percentage of pathogenic micro-organisms such as bacteria. Its removal can be achieved by sterilization

- The chemicals used for killing bacteria are called disinfectants. Water can be sterilized by the following methods:

  (a)Boiling: Water is boiled for 10–15 min, where most of the pathogenic bacteria are killed.

  (b)By adding bleaching powder. Bleaching powder in calculated amount is added to water and allowedto stand for several hours.

  - $CaOCl_2 + H_2O \rightarrow Ca(OH)_2 + Cl_2$
  - $Cl_2 + H_2O \rightarrow HCl + HOCl$
  - HOCl + Germs → germs are killed

  Disadvantages:

  Bleaching powder introduces Ca^{2+} hardness in water and adds lime residue.

  Excess of it gives bad smell and bad taste. Excess chlorine is irritating to mucous membrane.

- **(c)By chlorination**

  - $Cl_2 + H_2O \rightarrow HCl + HOCl$
  - Bacteria + HOCl → killed bacteria

  The quantity of chlorine to be added is important. The disinfection will not complete if chlorine is insufficient. If excess chlorine is added, it causes irritation, bad taste, and odour.

De-chlorination

Over chlolrinated water can be de chlorinatede by passing it through a bed of activated carbon. Excess chlorine can also be removed by adding SO_2 (or) $NaSO_3$.

- $SO_2 + Cl_2 + 2H_2O \rightarrow H_2SO_4 + 2HCl$
- $Na_2SO_3 + Cl_2 + H_2O \rightarrow Na_2SO_4 + 2HCl$

(d) **By using chloramine (NH_2Cl):** It is obtained by mixing chlorine and NH_3 in 2:1 ratio. It has better bactericidal action than chlorine. It is more stable and not producing any irritating odour.

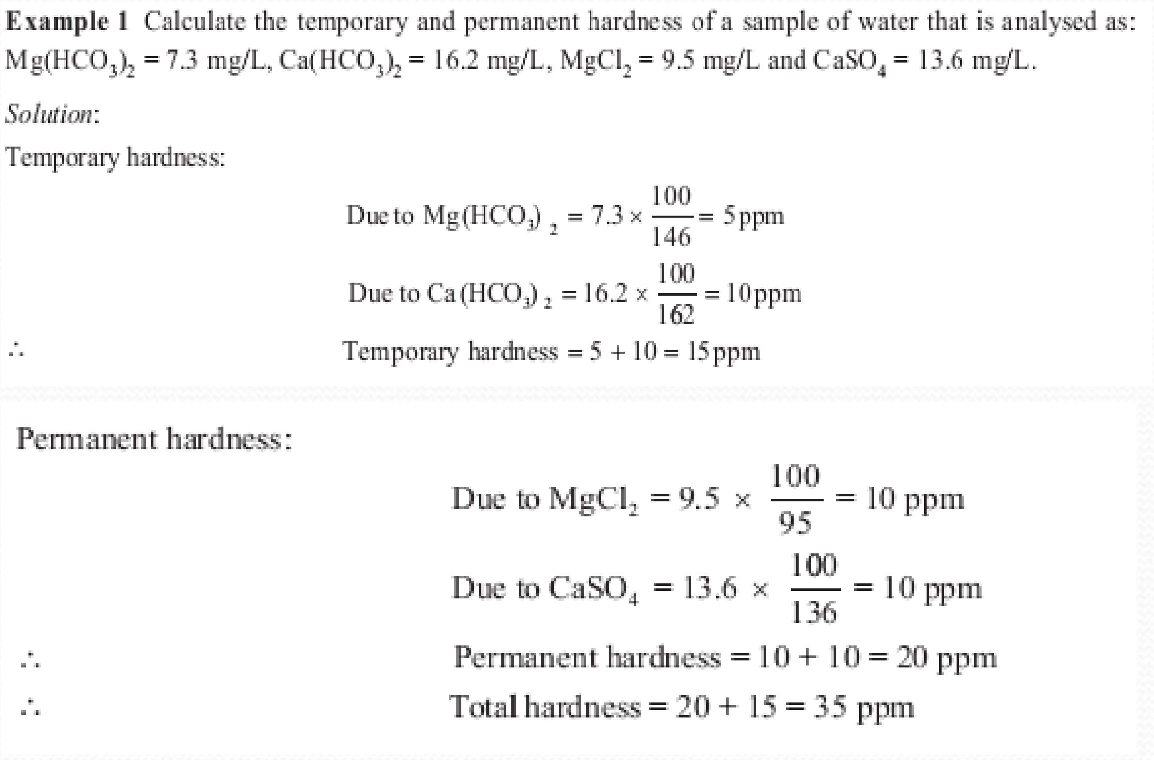
- $NH_3 + Cl_2 \rightarrow HCl + NH_2Cl$
- $NH_2Cl + H_2O \rightarrow NH_3 + HOCl$

(e) **Disinfection by ozone:** O_3 is prepared by passing silent electric discharge through cold, dry O_2. It is highly unstable.

- $O_3 \rightarrow O_2 + (o)$

O_3 is an excellent, harmless disinfectant. It is highly unstable and decomposes to give nacent oxygen (o). (o) is a powerful oxidizing agent. It oxidizes organic matter in water and also kills bacterias.

- **Solved Examples**
- Numerical problems based on this chapter can be solved using the table that gives the equivalence of different salts, ions and compounds in terms of CaCO3 which is also called the multiplication factor.



Example 1 Calculate the temporary and permanent hardness of a sample of water that is analysed as: $Mg(HCO_3)_2$ = 7.3 mg/L, $Ca(HCO_3)_2$ = 16.2 mg/L, $MgCl_2$ = 9.5 mg/L and $CaSO_4$ = 13.6 mg/L.

Solution:

Temporary hardness:

$$\text{Due to } Mg(HCO_3)_2 = 7.3 \times \frac{100}{146} = 5\,\text{ppm}$$

$$\text{Due to } Ca(HCO_3)_2 = 16.2 \times \frac{100}{162} = 10\,\text{ppm}$$

$$\therefore \quad \text{Temporary hardness} = 5 + 10 = 15\,\text{ppm}$$

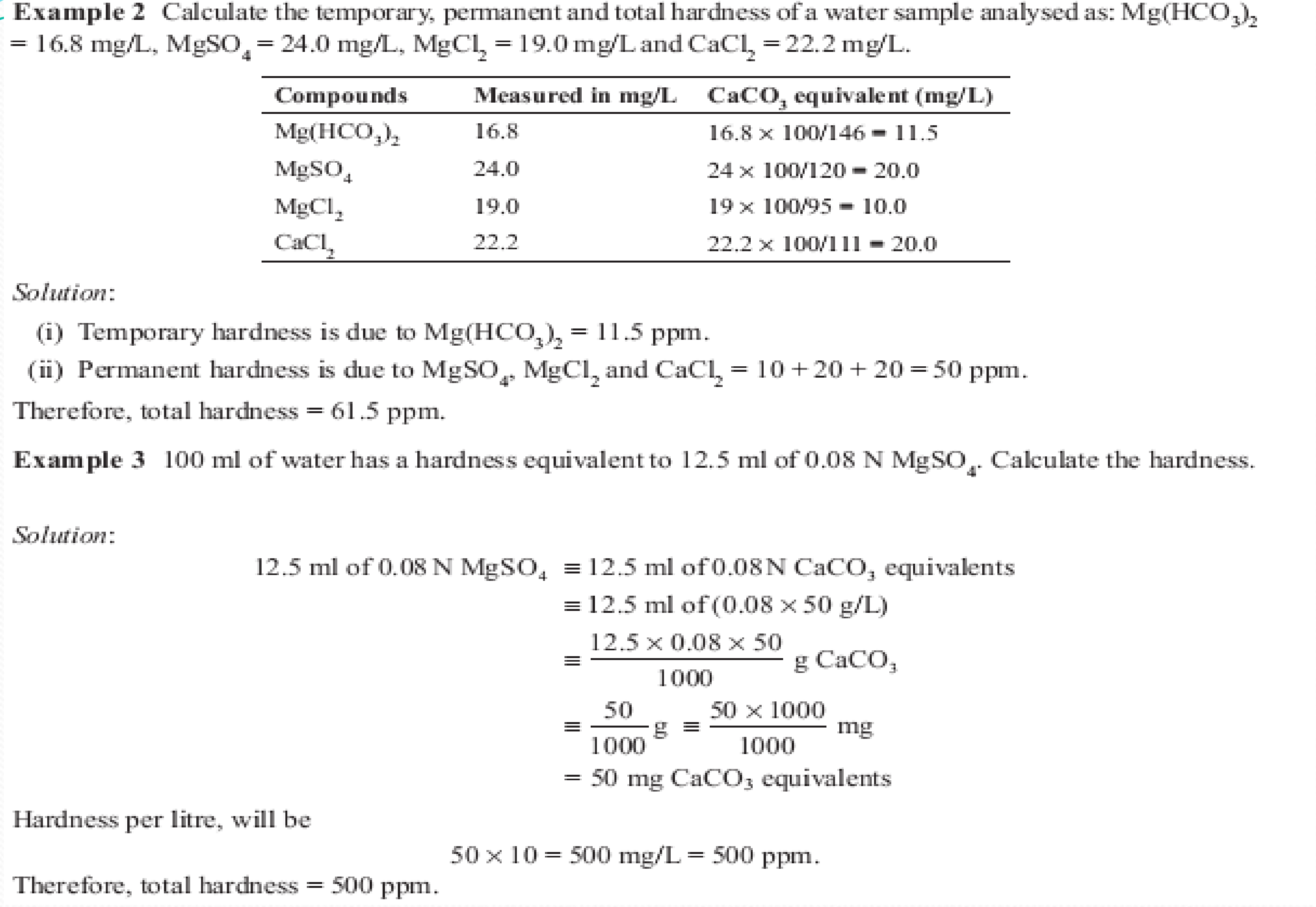
Permanent hardness:

$$\text{Due to } MgCl_2 = 9.5 \times \frac{100}{95} = 10\,\text{ppm}$$

$$\text{Due to } CaSO_4 = 13.6 \times \frac{100}{136} = 10\,\text{ppm}$$

$$\therefore \quad \text{Permanent hardness} = 10 + 10 = 20\,\text{ppm}$$

$$\therefore \quad \text{Total hardness} = 20 + 15 = 35\,\text{ppm}$$



Example 2 Calculate the temporary, permanent and total hardness of a water sample analysed as: $Mg(HCO_3)_2$ = 16.8 mg/L, $MgSO_4$ = 24.0 mg/L, $MgCl_2$ = 19.0 mg/L and $CaCl_2$ = 22.2 mg/L.

Compounds	**Measured in mg/L**	**$CaCO_3$ equivalent (mg/L)**
$Mg(HCO_3)_2$	16.8	$16.8 \times 100/146 = 11.5$
$MgSO_4$	24.0	$24 \times 100/120 = 20.0$
$MgCl_2$	19.0	$19 \times 100/95 = 10.0$
$CaCl_2$	22.2	$22.2 \times 100/111 = 20.0$

Solution:

(i) Temporary hardness is due to $Mg(HCO_3)_2$ = 11.5 ppm.

(ii) Permanent hardness is due to $MgSO_4$, $MgCl_2$ and $CaCl_2$ = 10 + 20 + 20 = 50 ppm.

Therefore, total hardness = 61.5 ppm.

Example 3 100 ml of water has a hardness equivalent to 12.5 ml of 0.08 N $MgSO_4$. Calculate the hardness.

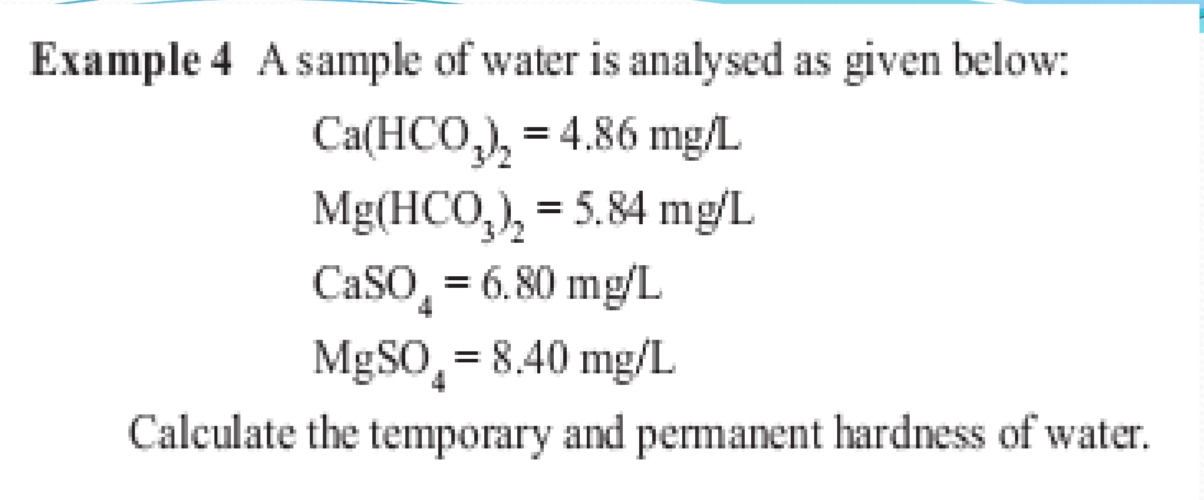
Solution:

$$\begin{aligned}
12.5 \text{ ml of } 0.08 \text{ N } MgSO_4 &\equiv 12.5 \text{ ml of } 0.08 \text{ N } CaCO_3 \text{ equivalents} \\
&\equiv 12.5 \text{ ml of } (0.08 \times 50 \text{ g/L}) \\
&\equiv \frac{12.5 \times 0.08 \times 50}{1000} \text{ g } CaCO_3 \\
&\equiv \frac{50}{1000} \text{ g} \equiv \frac{50 \times 1000}{1000} \text{ mg} \\
&= 50 \text{ mg } CaCO_3 \text{ equivalents}
\end{aligned}$$

Hardness per litre, will be

$$50 \times 10 = 500 \text{ mg/L} = 500 \text{ ppm}.$$

Therefore, total hardness = 500 ppm.



Example 4 A sample of water is analysed as given below:

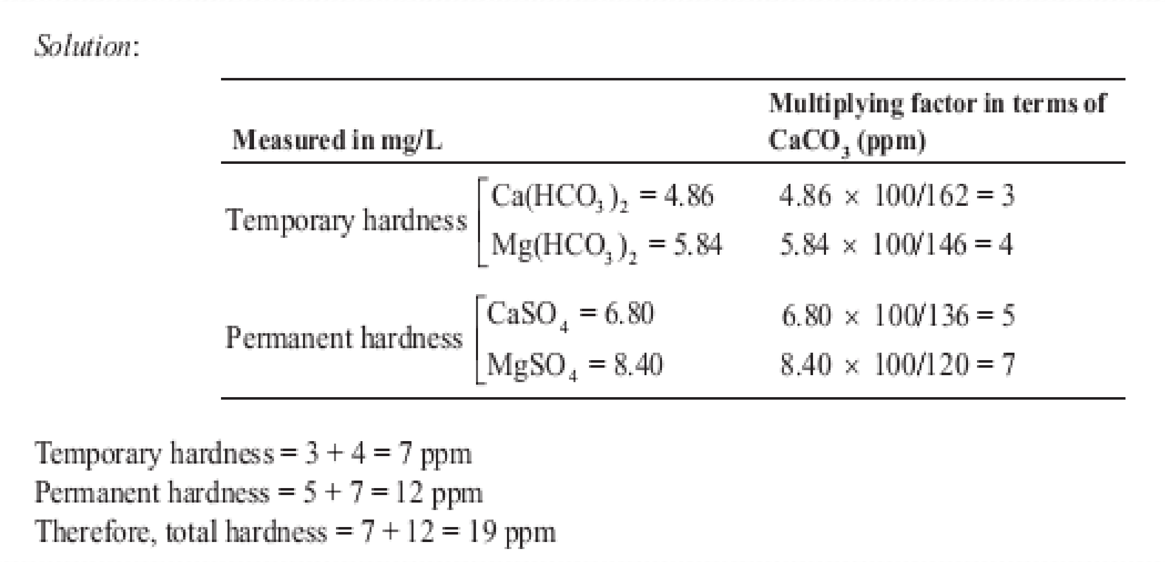
$Ca(HCO_3)_2$ = 4.86 mg/L

$Mg(HCO_3)_2$ = 5.84 mg/L

$CaSO_4$ = 6.80 mg/L

$MgSO_4$ = 8.40 mg/L

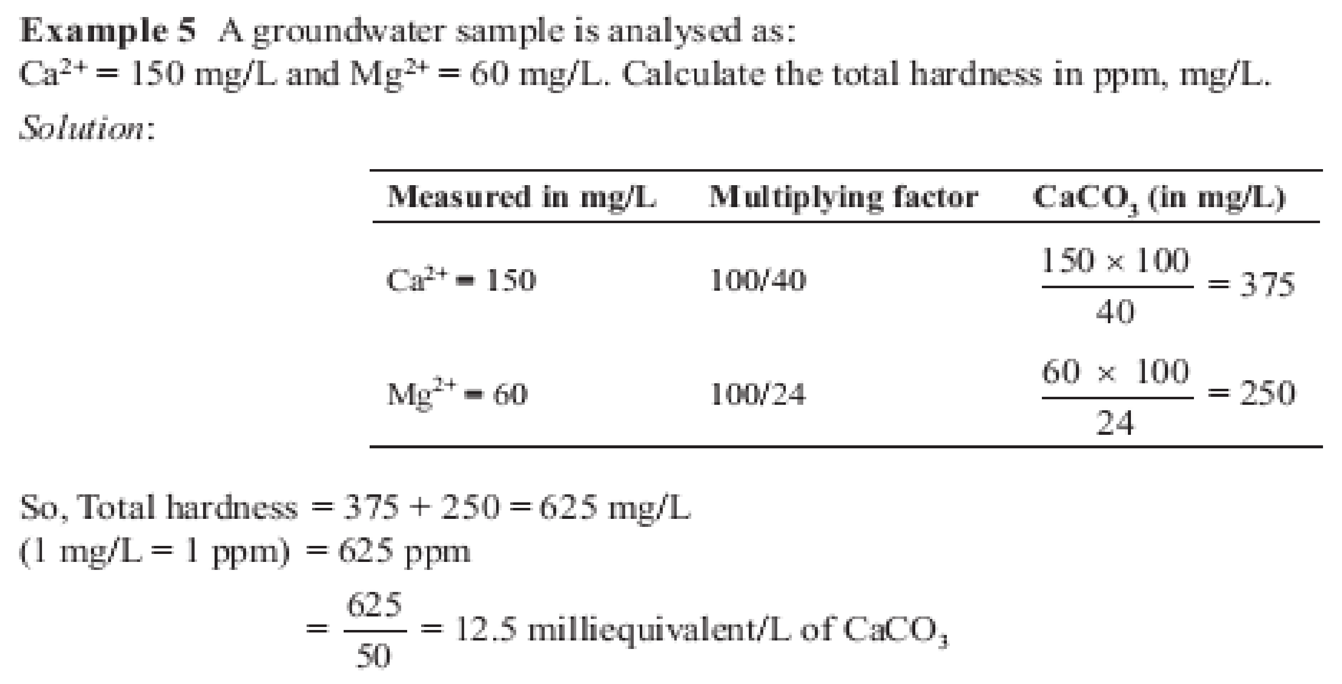
Calculate the temporary and permanent hardness of water.



Solution:

Measured in mg/L		Multiplying factor in terms of $CaCO_3$ (ppm)
Temporary hardness	$Ca(HCO_3)_2 = 4.86$	$4.86 \times 100/162 = 3$
	$Mg(HCO_3)_2 = 5.84$	$5.84 \times 100/146 = 4$
Permanent hardness	$CaSO_4 = 6.80$	$6.80 \times 100/136 = 5$
	$MgSO_4 = 8.40$	$8.40 \times 100/120 = 7$

Temporary hardness = 3 + 4 = 7 ppm
Permanent hardness = 5 + 7 = 12 ppm
Therefore, total hardness = 7 + 12 = 19 ppm



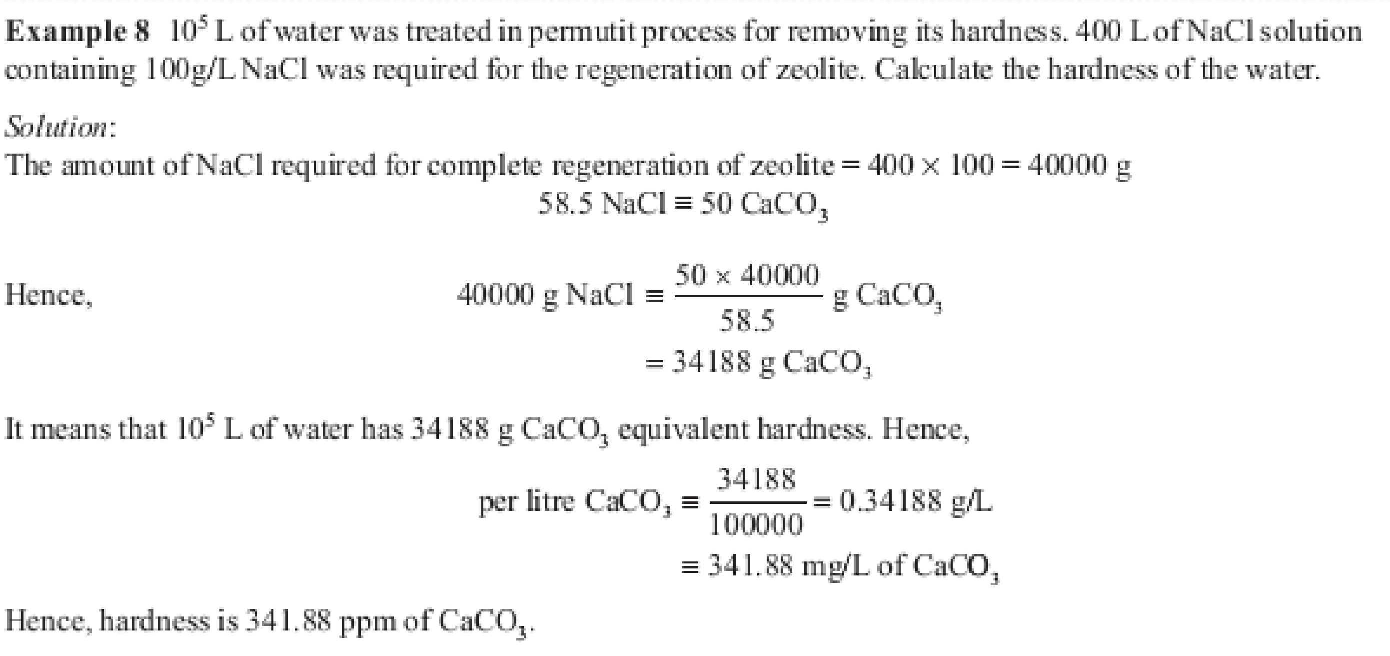
Example 5 A groundwater sample is analysed as:
Ca^{2+} = 150 mg/L and Mg^{2+} = 60 mg/L. Calculate the total hardness in ppm, mg/L.

Solution:

Measured in mg/L	Multiplying factor	$CaCO_3$ (in mg/L)
$Ca^{2+} = 150$	100/40	$\frac{150 \times 100}{40} = 375$
$Mg^{2+} = 60$	100/24	$\frac{60 \times 100}{24} = 250$

So, Total hardness = 375 + 250 = 625 mg/L
(1 mg/L = 1 ppm) = 625 ppm

$$= \frac{625}{50} = 12.5 \text{ milliequivalent/L of } CaCO_3$$



Example 8 10^5 L of water was treated in permutit process for removing its hardness. 400 L of NaCl solution containing 100g/L NaCl was required for the regeneration of zeolite. Calculate the hardness of the water.

Solution:
The amount of NaCl required for complete regeneration of zeolite = 400 × 100 = 40000 g

$$58.5 \text{ NaCl} \equiv 50\ CaCO_3$$

Hence,

$$40000 \text{ g NaCl} \equiv \frac{50 \times 40000}{58.5} \text{ g } CaCO_3$$
$$= 34188 \text{ g } CaCO_3$$

It means that 10^5 L of water has 34188 g $CaCO_3$ equivalent hardness. Hence,

$$\text{per litre } CaCO_3 \equiv \frac{34188}{100000} = 0.34188 \text{ g/L}$$
$$\equiv 341.88 \text{ mg/L of } CaCO_3$$

Hence, hardness is 341.88 ppm of $CaCO_3$.

Theoretical Questions

- 1. A water sample contains 408 mg of $CaSO_4$ per litre. Calculate the hardness of water in terms of $CaCO_3$ equivalent.
- 2. Why do we express hardness of water in terms of $CaCO_3$ equivalent?
- 3. Write various units of hardness and the relationship between them.
- 4. What are zeolites? How do they function in removing the hardness of water? What are the limitationsof this process?
- 5. What is the basic principle applied to remove the hardness of water by lime–soda process?
- 6. What are ion-exchange resins?
- 7. What do you understand by the hardness of water? What are its causes?
- 8. Distinguish between temporary and permanent hardness of water.
- 9. How is water softened by lime–soda process? Describe its types and suitable chemical reactions.
- 10. What is calgon? What is its application in water treatment?

- 11. What is meant by the exhaustion of cation and anion exchangers? How can they be regenerated?
- 12. Why is demineralisation process preferred over zeolite process for the softening of water for use in boilers?
- 13. How is water analysed for alkalinity? How the alkalinity due to various ions can be determined?
- 14. 250 ml of a sample of water on EDTA titration with EBT as indicator consumed 13 ml of 0.022 M EDTA till the endpoint is reached. Calculate the hardness of water in terms of ppm.
- 15. The hardness of 1000 L of a water sample was completely removed by passing it through a zeolite softener. The softener then required 30 L of NaCl solution containing 1.5 g/L of NaCl for regeneration. Calculate the hardness of the sample of water.

Multiple-choice Questions

- 1. Hardness of water is caused by
  (a) $CaCl_2$ (b) $NaCl$ (c) Na_2CO_3 (d) K_2SO_4

- 2. Hard water contains
  (a) $Na^{\oplus}$ (b) Mg^{2+} (c) Ca^{2+} (d) both (b) and (c)

- 3. The chemical formula of zeolite is
  (a) $FeSO_4.7H_2O$ (b) $Al_2(SO_4)_3.18H_2O$(c) $Na_2Al_2O_4$ (d) $Na_2O\ .\ Al_2O_3\ .\ xSiO_2\ .\ yH_2O$

- 4. Permanent hardness of water is due to
  (a) HCO_3^- (b) CO_3^- (c) Cl^- (d) $Na^{\oplus}$

- 5. Temporary hardness can be removed by
  (a) zeolite process (b) ion exchange (c) boiling (d) none
- 6. The demineralisation of water is called
  (a) zeolite process (b) ion-exchange process (c) lime–soda process (d) none
- 7. Which is not the unit of hardness of water?
  (a) ppm (b) epm (c) degree Clark (d) none of these
- 8. The relation between mg/L and ppm is
  (a) 1 mg/L = 1 ppm (b) 10 mg/L = 1 ppm (c) 1 mg/L = 10 ppm (d) 1 mg

- 9. In EDTA titration, the colour of the end point is

  (a) red (b) blue (c) yellow (d) no change
- 10. The colour of phenolphthalein in acidic medium is

  (a) colourless (b) pink (c) yellow (d) blue
- 11. Tannin, lignin are used for

  (a) phosphate conditioning (b) carbonate conditioning (c) colloidal conditioning (d) calgon conditioning
- 12. Blow down operation causes the removal of

  (a) sludges (b) scales (c) NaCl (d) acidity
- 13. Temporary hardness of water can be removed by

  a) filtration (b) screening (c) boiling (d) sedimentation
- 14. Purest form of natural water is

  (a) sea water (b) river water (c) rain water (d) lake water
- 15. Calgon is a trade name given to

  (a) sodium hexametaphosphate (b) magnesium phosphate

  (c) calcium silicate (d) sodium sulphate
- 16. The phenomenon of carrying of water along with impurities by steam is

  (a) priming (b) carry over (c) foaming (d) embrittlement
- 17. Brakish water mostly contains dissolved

  (a) KCl (b) $MgCl_2$ (c) $CaCl_2$ (d) NaCl
- 18. Water can be sterilized by using

  (a) Cl_2 (b) CCl_4 (c) $CaCO_3$ (d) NaOH
- 19. pH of alkaline water is

  (a) 7 (b) more than 7 (c) less than 7 (d) 0
- 20. Brakish water can be purified by using

  (a) lime–soda process (b) permutit process

  (c) filtration (d) reverse osmosis method

- 21. Hard water contains

  (a) Ca^{+2} and Mg^{+2} (b) K^+ and Na^+ (c) CO_2 and O_2 (d) NO_3^- and PO_4^{3-}
- 22. Water containing calcium chloride and magnesium sulphate causes

  (a) temporary hardness (b) permanent hardness (c) both (d) softness
- 23. Best method of removing hardness of water is

  (a) ion exchange (b) permutit (c) lime–soda (d) boiling
- 24. Hardness of water is expressed in terms of equivalents of

  (a) $MgCO_3$ (b) $CaCO_3$ (c) Na_2CO_3 (d) K_2CO_3
- 25. Caustic embrittlement is caused due to the presence of

  (a) NaCl (b) NaOH (c) $MgCO_3$ (d) KNO_3
- 26. Priming and foaming in boilers produce

  (a) wet steam (b) dry steam (c) soft steam (d) hard steam
- 27. The exhausted cation exchange resin can be regenerated by treating with

  (a) dil. NaOH (b) dil. HCl (c) distilled water (d) dil. NaCl
- 28. A hard sticky precipitate formed on the inner surface of the boiler is called

  (a) sludge (b) embrittlement (c) coating (d) scale
- 29. Which of the following is responsible for temporary hardness?

  (a) $MgCl_2$ (b) $NaHCO_3$ (c) $MgSO_4$ (d) $Mg(HCO_3)_2$
- 30. The water which is fit for drinking is called

  (a) hard water (b) brakish water (c) potable water (d) mineral water
- 31. Which of the following is a curdy precipitate?

  (a) sodium stearate (b) calcium stearate (c) potassium stearate (d) sodium carbonate
- 32. Which indicator is used for the determination of hardness by EDTA method?

  (a) methyl orange (b) methyl red (c) EBT (d) FSB-F
- 33. pH of purest water is

  (a) 7 (b) 14 (c) 10 (d) 0
- 34. Water shows hardness, when it contains

  (a) alkalinity (b) acidity (c) dissolved sodium salts (d) dissolved Ca and Mg salts
- 35. Loose and slimy precipitate formed within the boiler is called

  (a) scale (b) sludge (c) priming (d) corrosion

UNIT 4

MATERIAL CHEMISTRY

- Polymers are important engineering materials which have diversified uses in day-to-day life
- Natural polymers such as polysaccharides, cellulose, starch and proteins have been parts of every living being since the beginning of life. In addition, there are numerous man-made polymers, which have a wide range of applications.
- The term ‘Polymers’ is derived from two Greek words: ‘poly’ means many and ‘mers’ means unit or part.
- A polymer is a high molecular weight compound formed by the joining of a large number of small units.

- **CLASSIFICATIONS OF POLYMER**

  Polymers can be classified in several ways.

- Based on Structure of Polymers
- Based on Tacticity (Configuration)
- Based on Synthesis

- **Addition Polymerization:**
- Addition polymers are formed by adding monomer units without any loss of atoms or groups.
- E.g.:- (1) n CH_2 = CH2 [CH2 – CH_2] n
- Ethene polythene
- **Condensation polymerization:-** Condensation polymers are those in which two like or unlike monomers join each other by the elimination of small molecules such as H_2O, HCl, etc.
- When the same kind of monomers joins, the polymer is called homopolymer.
- E.g.:- <u>Nylon -6</u>
- n $H_2N – (CH_2)_6 – NH_2$ + n $HOOC – (CH_2)_4 – COOH$
- Hexa methylene di amine Adipic acid
- ↓
- $[NH\text{-}(CH_2)6\text{-} NH – CO – (CH_2)_4 \text{-} CO]$ n + ZnH_2O
-

Nylon 6, 6

❑ Based on Structure of Polymers

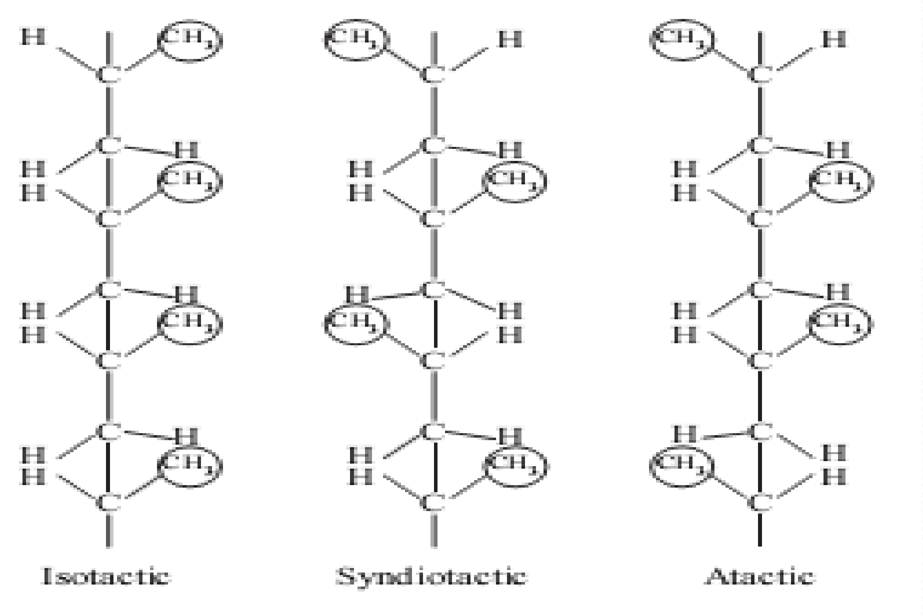
On the basis of the structures, polymers can be classified into three groups.

- **Linear chain polymer**: In these polymers, monomers are joined together in a chain. They have high density and high melting point due to a well-packed structure, e.g. polyethylene and nylon.
- **Branched chain polymer:** In these polymers, the chain of the polymer contains branches of monomers,which hinders the close packing of polymeric chains, and, hence, these are less tightly packed in comparison to the linear chain polymers. They have low melting points and less density in comparison to the linear chain.
- **Cross-linked polymers:** In the cross-linked polymers, monomers are cross-linked together in all the three dimensions, e.g. bakelite.

Based on Tacticity (Configuration)

There are three different types of polymers depending upon the relative geometric arrangement of the functional(side) groups.

- **Isotactic polymer:** All functional groups are on the same side of the polymer chain.
- **Syndiotactic polymer:** All the functional groups are arranged in regular on alternate sides of the polymeric chain.
- **Atactic polymer:** All the functional groups are arranged randomly on both sides of the polymeric chain



- **Based on Synthesis**

On the basis of synthesis, polymers are of two types:

- ***Addition polymers:*** *These are formed by the polymerisation of monomers without the elimination of atoms* or groups.
- ***Condensation polymers:*** *These are formed by the polymerisation of monomers with the elimination of small* molecules such as NH3, H2O, CH3 and OH.

On the basis of **Thermal processing behaviour,** polymers may be classified further into two groups-

- **Thermoplastic polymers:** Thermoplastics are polymers that soften on heating and become hard on cooling. These are the polymers in which inter-molecular forces of attraction are moderate and there are no cross-links between the chains, e.g. polyethylene, polypropylene, PVC and nylon-66.
- **Thermosetting polymer:** On heating, extensive cross-link is formed in these polymers between the polymeric chains and, thus, they become hard, e.g. Bakelite, urea–formaldehyde resin, terylene.

- **Polytetrafluoroethylene (Teflon) (PTFE):** It is prepared by the polymerisation of tetrafluoroethylene under pressure in the presence of free radical initiator (benzoyl peroxide).

  Teflon is also known as fluon.

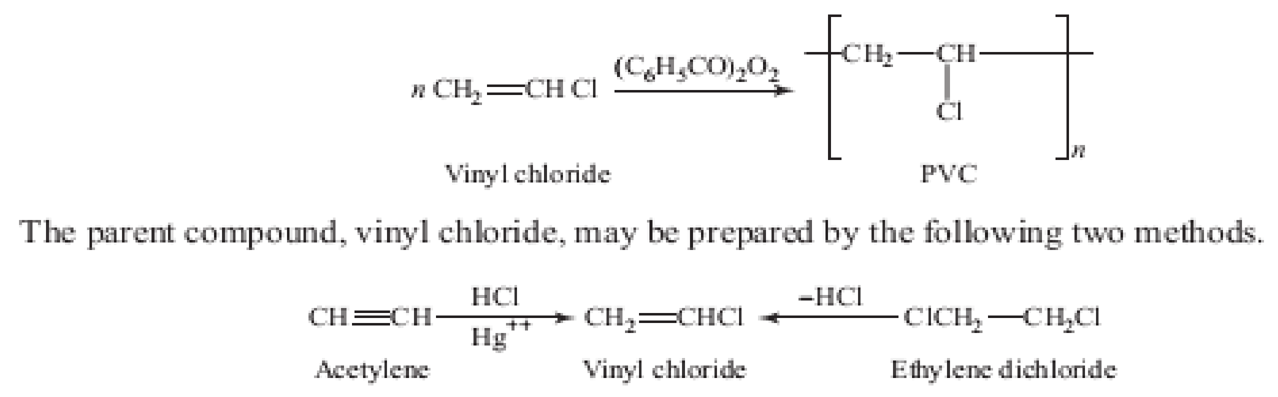
- ***Properties:***

  Because of the presence of highly electronegative fluorine atoms, there are strong attractive forces between different chains in the teflon molecules. This strong attractive force is responsible for high toughness and high chemical resistance towards all chemicals except hot alkali metal and hot fluorine.

- ***Engineering applications***:

  It is used in making seals and gaskets, stopcock for burettes and impregnating glass fibre, asbestos fibre, etc. which have to withstand high temperature. It is also used for insulation of electrical items and for making non-sticky surface coating, particularly for cooking utensils. It is used for storing corrosive chemicals.

- **Polyvinyl chloride (PVC):** It is obtained by heating vinyl chloride in an inert solvent in the presence of benzoyl peroxide.



$$n\,CH_2{=}CHCl \xrightarrow{(C_6H_5CO)_2O_2} \left[-CH_2-\underset{\underset{Cl}{|}}{CH}-\right]_n$$

The parent compound, vinyl chloride, may be prepared by the following two methods.

$$CH{\equiv}CH \xrightarrow[Hg^{++}]{HCl} CH_2{=}CHCl \xleftarrow{-HCl} ClCH_2-CH_2Cl$$

PVC is also known as **Koroseal.**

- ***Properties:***
  1. *It is due to the presence of electronegative chlorine atom on alternative carbon atoms,* and attraction between different strands takes place due to difference in polarity. Hence,the polymer will have high softening temperature and is very hard.
  2. It is colourless, odourless and non-inflammable.
  3. It is resistant to weather, chemicals and oil.
  4. Its plasticity can be increased by the addition of a plasticizer (ester of phthalic acid).
- ***Uses:*** *It is used in making sheets, pipes, raincoats, handbags, table clothes, plastic dolls, floor covering,*electrical insulation and coating on electrical cables. It is used in preparing bottles to pack food stuff, water and cosmetics.
- **PVC is of two types:** Rigid PVC and Placticized PVC.

- **Nylon 6, 6:-**
- It is prepared by condensation polymerization of adipic acid and hexamethylene diamine in the absence of air.
- H
- $HOOC - (CH_2)_4 - CO\,OH + n\,H\,N - (CH_2)_6\,NH_2$ ----→
- Adipic acid $-H_2O$
- Hexamethylene diamine
- $[OC\,(CH_2)_4\,CO - NH\,(CH_2)_6 - NH]n$
- Nylon 6, 6
- **Applications:-**
- The major application is in textile industry.
- Because of its high thermal & abrasion resistance nylons are used in mechanical engineering applications like gears, bearings, machine parts where greater friction is there.
- Flexible tubing's for conveying petrol etc are made from nylons

- **RUBBER (ELASTOMER)**

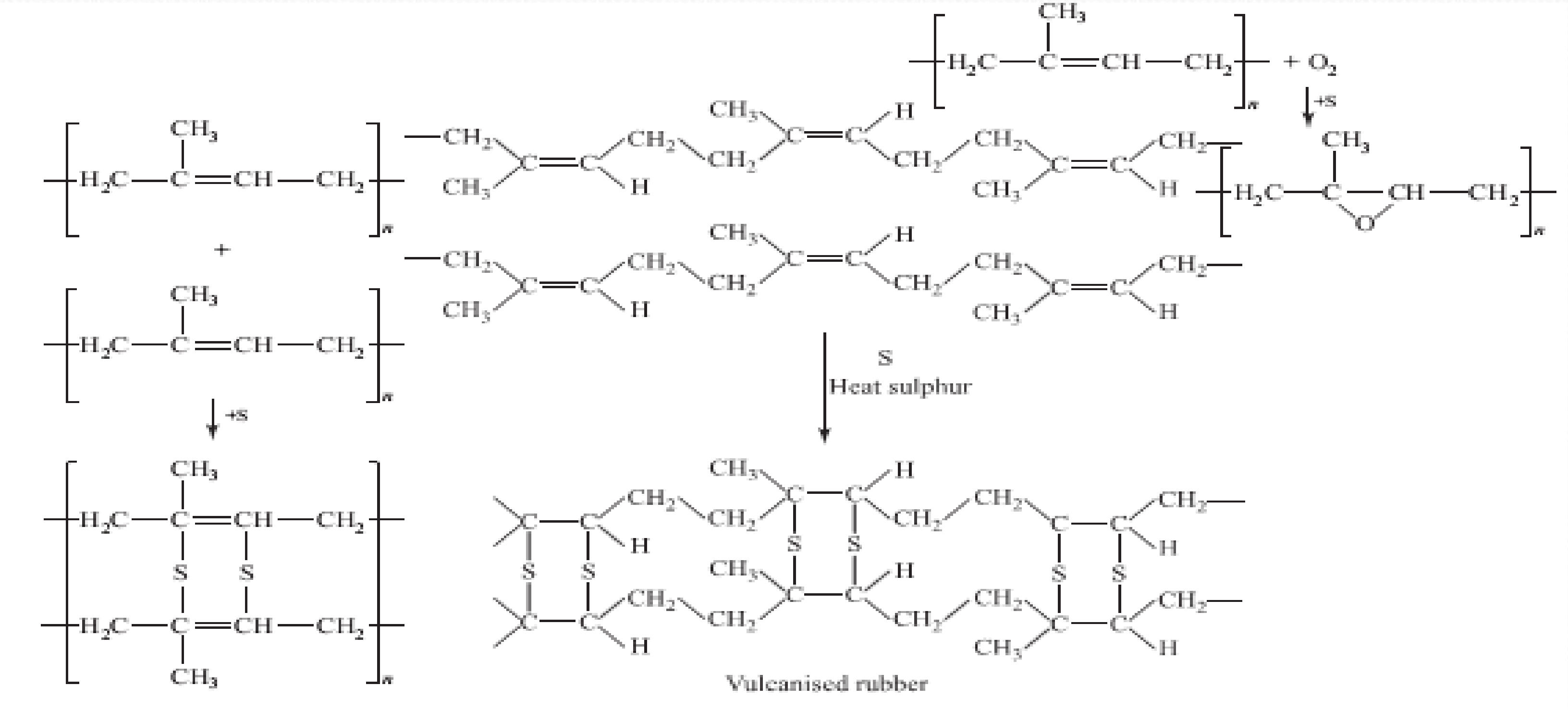
  Rubbers are high polymers capable of returning to their original length, shape or size after being stretched or deformed. Rubber is also known as elastomer. The rubber obtained from natural sources is called natural rubber, and the polymers prepared in the laboratory, which are similar to natural rubber, are known as synthetic rubber. About 200 plants and shrubs have been found to produce latex on tapping. Sapotaceae latex gives trans-isomer of isoprene; it is called Gutta percha.

- **Natural Rubber**

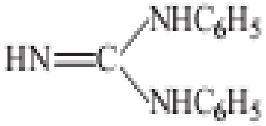
- Natural rubber is obtained from nearly 500 different plants, but the main source from which the commercial natural rubber is obtained is the tree *Hovea braziliansis. It is in cis form known as natural rubber. The rubber* is obtained from latex (milky sap) collected from the cuts made in the bark of the tree. The latex is diluted to 15–20% and filtered to remove impurities such as leaves, pieces of bark, etc. The obtained latex contains hydrocarbon with impurities such as fatty acids, proteins and resins in an emulsified form. The latex is then coagulated with acetic acid or formic acid. The crude or raw rubber is composed of 95% hydrocarbons, 4% protein and 1% of resins. The latex is diluted to 15–20% and filtered to remove suspended impurities such as bark, leaves, dirt, etc. It is treated with acetic acid or formic acid. The rubber coagulates as white coagulum. It is washed with water and passed between two rollers where rubber comes out as a sheet resembling crepe paper. It is called crepe rubber, which can be dried and used. In the second type of process, the rubber sheets are hung in smoked chamber for 3–4 days at 40–50°C. This rubber is called smoked rubber. Destructive distillation of natural rubber gives isoprene as the main product.

❖Vulcanisation of Rubber

- The raw or crude rubber is of very little use because it has very undesirable properties such as low tensile strength, possesses elasticity only over a limited range of temperature and becomes softer, more plastic and sticky on heating and brittle on cooling. Its solubility in organic solvents (such as $CHCl_3$,benzene and petrol) is of advantage for preparing rubber derivatives and adhesive solutions. It swells in water and attacked by acids, bases O_2. It reacts with O_2 to give epoxide with bad smell.
- In order to give more strength and more elasticity, natural rubber is heated with sulphur or sulphur compounds at 150°C temperature for a few hours.

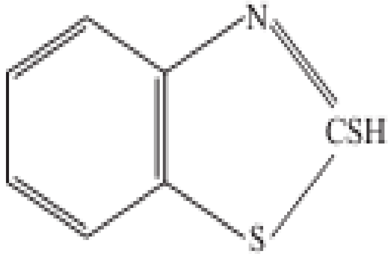


- The sulphur combines chemically at double bonds of different rubber springs and a cross-linked network is formed. This process is known as vulcanisation of rubber. The vulcanisation process was invented by Charles Goodyear in 1839. The vulcanisation can also be accomplished with certain peroxides, gamma radiation and several other organic compounds. The vulcanisation process can be enhanced in the presence of certain organic substances known as accelerators. The common accelerators contain nitrogen, sulphur or both.



$$\mathrm{HN{=}C}\genfrac{}{}{0pt}{}{\diagup\mathrm{NHC_6H_5}}{\diagdown\mathrm{NHC_6H_5}}$$

Diphenylguanidine



Mercaptobenzothiazole

- **Advantages of vulcanised rubber**

1. Vulcanised rubber has good tensile strength.
2. The working temperature of vulcanised rubber is enhanced up to 100°C. The temperature range of raw rubber is 10–60°C.
3. The elasticity of vulcanised rubber is very low.
4. It has good resistance to organic solvents.
5. It acts as good electrical insulator.
6. It has low water absorption tendency.
7. It has good impact resistance.
8. It possesses good resistance, i.e., articles made from it return to original shape when load is removed.

- **Application of natural rubber**

1. It is used in tank lining in chemical plant for storing corrosive chemical.
2. It is used in the manufacture of tyres, toys, sport items etc.
3. In used as sandwitching material between metal surface to prevent liberation in machine parts.

Thiokol (polysulphide rubber or GR-P):

- Polysulphide rubbers are the condensation products of ethylene dichloride and sodium tetrasulphide. Polymers | 109 Thiokol (yellow solid)
- ***Properties***

The properties of polymers depend on the length of the aliphatic groups and the number of sulphur atoms present. The polymer behaves like elastomer when four sulphur atoms are present per monomer and it does not behave as elastomer if only two sulphur atoms are present per monomer. Thus, in case of thiokol, four methylene groups should be present in the dihalide to induce elastic properties. Some of the important properties are:

(i) Thiokol is resistant to the action of oxygen and ozone.

(ii) It is also resistant to the action of petrol lubricants and organic solvents.

(iii) Thiokols show outstanding resistance to swelling by organic solvents, but benzene and its derivatives cause some swelling.

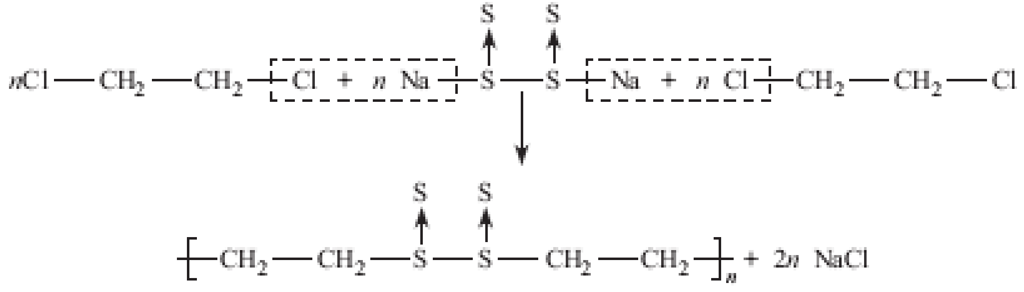
(iv) Thiokol films are impermeable to gases to a large extent.

(v) Thiokols are vulcanised with metal oxides such as zinc oxide.

(vi) Thiokol has poor heat resistance and low tensile strength. The odour of thiokol is very bad. It tends to lose its shape under continuous pressure.

- ***Uses***

- Thiokol mixed with oxidising agents is used as a fuel in rocket engine.
- It is used in engine gaskets and other such products that come into contact with oil.
- Thiokols are used for hoses and tank lining for the handling and storage of oils and solvents



$$n\,Cl-CH_2-CH_2-Cl + n\,Na-\overset{\overset{S}{\uparrow}}{S}-\overset{\overset{S}{\uparrow}}{S}-Na + n\,Cl-CH_2-CH_2-Cl \longrightarrow \left[-CH_2-CH_2-\overset{\overset{S}{\uparrow}}{S}-\overset{\overset{S}{\uparrow}}{S}-CH_2-CH_2-\right]_n + 2n\,NaCl$$

Thiokol (yellow solid)

- Bu Na S Rubber:
- It is a copolymer of butadiene (75%) and styrene (24%). In the early days of its synthesis sodium was used as the catalyst.

  Hence the name bu (butadiene), na (symbol Nafor sodium) and S (for styrene). It is also called GRS (government rubber styrene) or SBR (styrene butacliene Rubber).
- **Properties:-**
- It is a strong & tough polymer.
- The rubber can be vulcanized similar to natural rubber using either sulphur ot sulphur mono chloride.
- **Applications:-**
- Major application of styrene rubber is in manufacture of tyres.
- It is used in foot wear industry for making shoe soles and footwear components
- It is also used for making wires and cable, insulators.

- **Dacron:**
- **Preparation:-**
- Terylene is a polyestar fiber made from ethylene glycol and terephthalic acid. Terephthalic acid required for the manufacture of terylene is produced by the catalytic atmospheric oxidation of P-xylene.
- **Properties:-**

1)This occurs as a colourless rigid substance.

2)This is highly resistant to mineral & organic acids but is less resistant to alkalies. This is hydrophobic in nature. This has high melting point due to presence of aromatic ring.

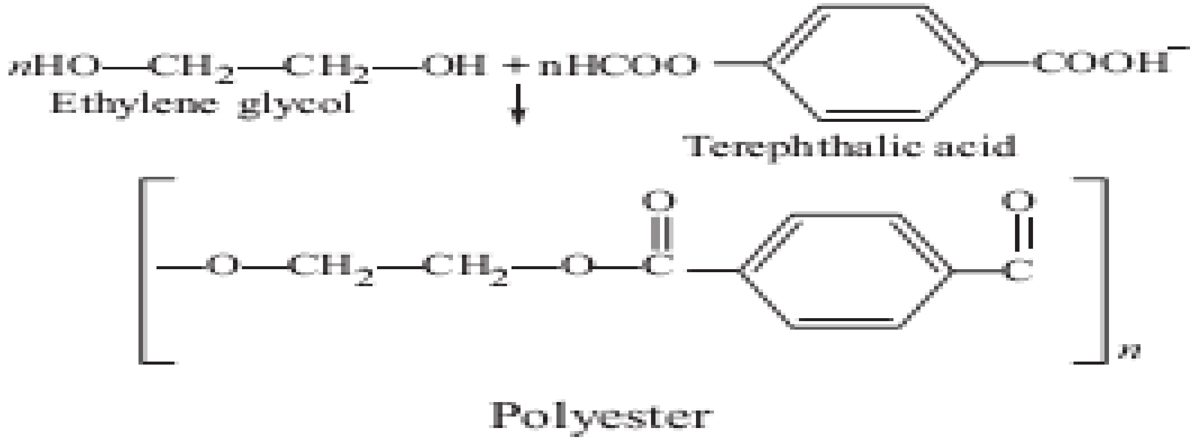
- **Uses:-**

1)It is mostly used for making synthetic fiber.

2)It can be blended with wool, cotton for better use and wrinkle resistance.

- **Fibres**-:

- Fibres are thin ,long ,thread like materials which are extremely long compared to its width, atleast hundred times longer than its width.
- Fibres can be classified into two groups
- Natural Fibre = Natural Fibre naturally occurs in plants and animals e.g. wood ,silk,cotton
- Manufactured Fibre = It is further classified in to two groups
- Regenerated Fibre = These are made from natural fibres.e.g. rayon (made from cellulose), cellulose acetate (made from cellulose)
- Synthetic Fibre = These are made from chemicals e.g. nylons (polyamide) ,terylene , polyester etc



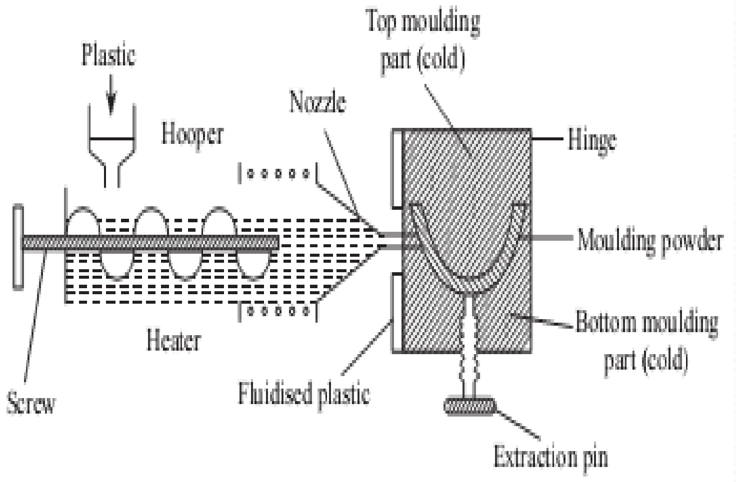
COMPOUNDING OF PLASTICS

- The pure material obtained from the process of polymerisation is known as polymer. The usefulness of long chain pure polymer is very little. After adding some materials, polymer becomes useful and termed as *plastic.*
- These additives improve the workability of plastics and change the properties of plastics.
- The following types of additives are found to be present in plastic:

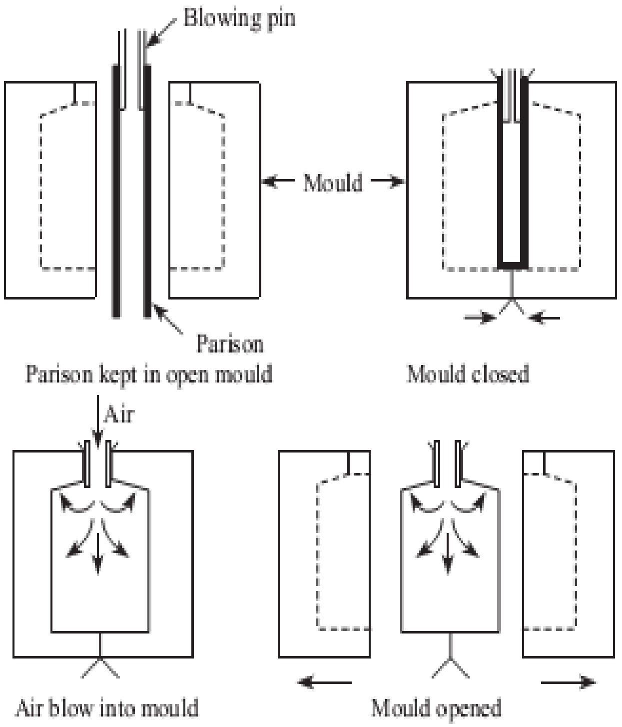
- **Fillers:** These are substances that increase hardness, tensile strength and the mechanical properties of plastics. Some important fillers are carbon-black (C-black), chalk, china clay, cellulose fillers, metallic oxide (ZnO, PbO, etc.), metal powders (Al, Cu, Pb, etc.), carborundum, quartz, etc. Fillers also reduce the cost of final compounds.
- **Binder (resin):** In plastics, binder holds different constituents together. They are generally low-molecularweight materials and withstand high temperature.
- **Plasticisers:** Plasticisers are generally small liquid molecules that are chemically similar to the polymer and create gaps between polymer chains for greater mobility and reduced inter-chain interactions. Commonly used plasticisers are camphor, some phosphate esters (dioctyl phthalate), etc.

- **Stabilisers:** Stabilisers are used to improve the thermal stability of plastics, e.g. polyvinyl chloride.
- At moulding temperature, PVC undergoes decomposition and decolourisation. So during their moulding, stabilisers are used. The commonly used stabilisers are white lead, lead chromate, red lead, etc.
- **Colouring materials:** Organic dyestuffs and inorganic pigments are used as colouring materials. They give bright transparent colours. For example, carbon black—black, anthraquinone—yellow and phthalocyanine

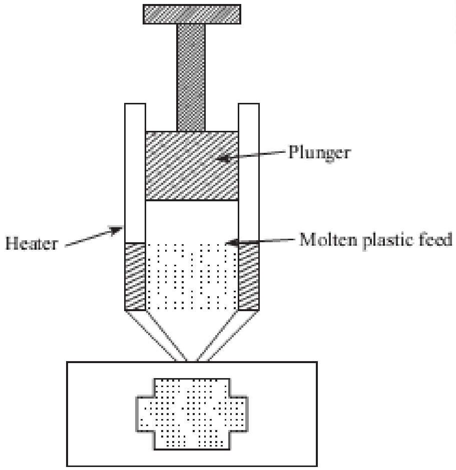
- **Moulding Process:** The commonly used methods are
- Injection moulding
- Compression moulding
- Transfer moulding
- Blow moulding



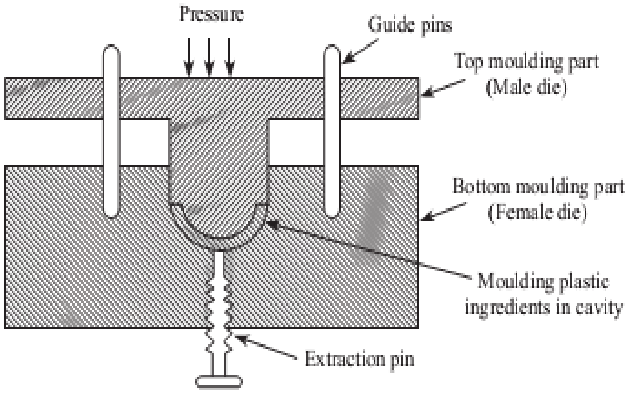
Injection moulding



Blow moulding



Transfer moulding



Compression moulding

Fibre-Reinforced Plastic (FRP)

- Fibre-reinforced plastics are a category of plastics that specifically use fibrous material to mechanically enhance the strength and elasticity of plastics. The plastic material without fiber reinforcement is known as matrix. Enhanced strength and elasticity in a fiber-reinforced plastic depends on the mechanical properties of both the fibre and the matrix, as well as the fibre length and orientation within the matrix.
- Mainly fibre-reinforced plastics are classified into two groups:

- **Carbon fibre reinforced plastics (CFRP)**
- **Glass-fibre reinforced plastics (GFRP)**

- There are various methods for producing fibre-reinforced plastic such as continuous lamination, pultru-sion, rotational moulding, injection moulding, hand lay up, etc.
- **Application of FRP:** They find extensive use in space crafts, aeroplanes, acid storage tanks, motorcars, and building materials. Melamine FRP is used for insulation and in making baskets.
- **Advantages of FRP:**

1. They are non-inflammable and resistant to corrosion, chemicals, etc.
2. The cost of production of FRPs is low.
3. They possess low coefficient of thermal expansion

THEORETICAL QUESTIONS

- 1. What is corrosion? Why do metals corrode?
- 2. Why most of the metals are found in the ore form and not in the pure form? Explain.
- 3. Describe the electrochemical theory of corrosion.
- 4. Show the reactions involved in the hydrogen evolution and oxygen absorption types of corrosion.
- 5. Describe the factors on which corrosion depends.
- 6. Discuss various methods of protection corrosion.
- 7. Discuss the wet theory of corrosion.
- 8. Explain the rusting of iron with the help of electrochemical theory of corrosion.

UNIT 4

MATERIALS CHEMISTRY

❖Introduction

- The term engineering materials is used to include a wide variety of materials used in construction and fabrication.
- Engineering materials include cementing materials or binding materials such as lime, cement, gypsum and ceramics.
- Ceramics includes a variety of materials such as glass, refractories, clay products, lubricants, rocket propellants, etc.

Cement

- Cement is a construction material which possesses adhesive and cohesive properties and is used for binding building blocks, bricks, stones, etc.
- Cements are classified into four types based on the chemical composition. The essential constituents of cement used for construction are the compounds of calcium (calcareous and argillaceous; calcium + silicon).

Classification of Cements-Cements are classified into various types as follows:

- 1. Natural cement
- 2. Puzzalona cement
- 3. Slag cement
- 4. Portland cement

Chemical Composition of Cement:

- Cement contains silica, lime and alumina. The proportion of these constituents in cements should be main-tained to get good quality cements.

$$\frac{\%SiO_2}{\%Al_2O_3} = 2.5\text{–}4.0$$

$$\frac{\%CaO - \%SO_3}{\%SiO_2 + \%Al_2O_3 + \%Fe_2O_3} = 1.9\text{–}2$$

- (1) MgO should be less than 6%.
- (2) Sulfur content should always be less than 2.75%.
- (3) The ratio of alumina to iron oxide should be 0.65.
- (4) Total loss on ignition should be less than 4%.

Setting and Hardening of Portland Cement

- The hydration of cement followed by gelation is called setting and the subsequent crystallisation is called hardening. The strength of cement depends on the amount of gelation and the extent of crystallisation.
- Cement is mixed with water to produce a plastic cement paste. The paste is subjected to hydration and gelation and finally crystalline products are formed.
- 1. Initial setting of cement involves hydration of tricalcium aluminate.

$$3CaO\cdot Al_2O_3 + 6H_2O \longrightarrow 3CaOAl_2O_3\cdot 6H_2O + 880\ kJ/kg$$

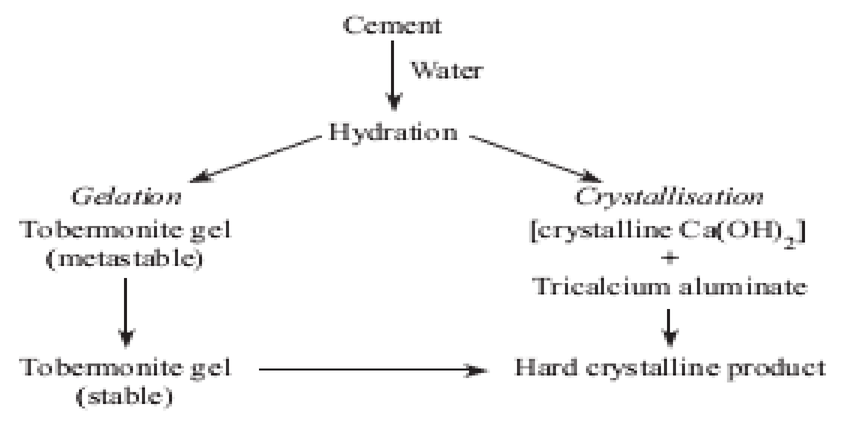
- 2. Second step of the reaction involves gelation in which tobermonite gel is formed. It also produces calcium hydroxide and hydrated tricalcium aluminate.

$$2(2CaO\cdot SiO_2) + 4H_2O \longrightarrow \underset{\text{Tobermonite gel}}{3CaO\cdot 2SiO_2\cdot 3H_2O} + Ca(OH)_2 + 250\ kJ/kg$$

- 3. Crystallisation of tricalcium aluminate takes place. Even though initial reaction involves the formation of tetracalcium alumiate, hardening of tricalcium aluminate takes place finally through crystallisation.

$$4CaO\cdot Al_2O_3\cdot Fe_2O_3 + 7H_2O \longrightarrow \underset{\text{Tricalcium aluminate crystal}}{Ca_3Al_2O_6\cdot 6H_2O} + CaO\cdot Fe_2O_3\cdot H_2O + 420\ kJ/kg$$

- Final setting and hardening of cement paste may be due to the formation of tobermonite gel with the
- crystallisation of calcium hydroxide and hydrated calcium aluminate.
- Mentioned below is the flow chart representing setting and hardening of cement.



- Complete setting and hardening of cement takes place in 20 days.

1. Hydration of cement takes place in one day

$$\text{Cement} + \text{Sand} + \text{Water} \xrightarrow[\text{1 day}]{\text{Hydration}} \text{Hydration of } C_3A \text{ and } C_4AF$$

2. Next hydration of C3S is completed in seven days

$$\begin{array}{c} C_3A \\ \text{and} \\ C_3AF \end{array} \xrightarrow{\text{7 days}} \begin{array}{c} \text{Gelation of } C_3S \text{ and} \\ \text{crystallisation of} \\ Ca(OH)_2 \end{array} \xrightarrow{\text{28 days}} \begin{array}{c} \text{Gelation of} \\ C_2S,\ C_3S \text{ and} \\ \text{crystallisation of} \\ Ca(OH)_2 \end{array}$$

- The gel of C3A crystallises and dicalcium silicate (C2S) begins to hydrate in 7–28 days. The strength of cement is increased in 7–28 days due to the gelation of both dicalcium silicate and tricalcium silicate. Initial setting and final setting are recognised based on the ability of the penetration of vicat needle into the mass. Initial set takes place when the needle does not penetrate the paste beyond certain depth; final set takes place when the needle does not penetrate the mass at all.
- For ordinary cements, initial setting should be less than 45 minutes to allow sufficient time for mixing, transportation and placing between the aggregates. Final setting should not be more than 10 hours. Quick setting cement requires 5 minutes for initial setting and less than 30 minutes for final setting.
- Hardening involves increasing strength of cement. It depends on the chemical combination of cement and water and occurs faster in the beginning and goes on decreasing gradually. It is a relatively slow process.
- The heat of hydration of cement constituents is useful in the formulation of cements for different purposes. Information regarding heat of hydration helps in preventing freezing water in the cement paste in winter. It is used in controlling the speed of setting and hardening of cement. The liberated heat should be quickly dis-sipated, otherwise serious stress crackings occur in concrete constructions.

- **Special Cements**
- **1. Water-proof cement:** This cement makes the concrete impervious to water and resist absorption of water. This type of cement is prepared by adding water proofing agents like calcium stearate, aluminum stearate, gypsum and tannic acid to Portland cement during grinding and powdering process.
- **2. High alumina cement:** High alumina cements are made by fusing bauxite and limestone mixture at 1500–1600ºC in rotary kiln and the resulting mass is subjected to grinding .Setting time is similar to portland cement but hardening is very rapid. It also has superior resistance to chemicals.
- **3. Acid-resistant cements:** They are produced by mixing finely ground quartzite with silicon in suitable proportions. Sodium silicon fluoride, or ethyl acetate are used as setting agents; silica gel gets precipitated. On drying, it becomes very porous and permeable to liquids. Hence, it should be always kept wet to prevent shrinking of gel.
- **4. Barium strontium cements:** The calcium in Portland cement is replaced by barium or strontium.Tribarium and dibarium silicates offer more resistance to radioactive rays. Hence, they are used in concrete shields for atomic piles.

Lubricants

- When one solid surface is sliding past over another solid surface, friction and wear is developed due to the relative motion of two contacting surfaces which results in the loss of energy as heat. As the equipment gets heated up, it is damaged and sometimes result in welding or seizure.
- Any substance introduced between the two moving and sliding surfaces with a view to reduce frictional resistance is known as 'lubricant'. 'Lubrication' may be defined as the reduction of friction between two relatively moving surfaces by the interposition of some other substance (lubricant) between them.

Functions of Lubricants

- 1. Lubricants help in reducing frictional forces between two sliding surfaces. Even highly polished and extremely smooth surfaces show many irregularities and peaks called asperities when viewed under a microscope; when pressed together they exhibit high friction and wear. Even highly polished surfaces can be welded together by the application of pressure. But when a lubricant is placed, the separation of two surfaces takes place and interlocking of peaks and valleys does not occur, and sliding takes place conveniently.
- 2. It reduces wear and tear and surface deformation. When a lubricant is placed between the two sliding surfaces, direct contact between them is avoided. Without lubricant, small peaks would be sheared which results in wear and tear and surface deformation; excessive wear in machinery or any part result in malfunctioning of entire unit.

- **3**. It prevents the loss of heat energy produced by frictional forces between two sliding surfaces and acts as a coolant. In a machine, frictional heat is produced at the point of contact between the rubbing parts. Cool oil which is flowing on a heated surface carries away the heat.
- **4**. It reduces running cost and maintenance cost of machines and tools. A lubricant prevents corrosion and rusting of machine parts. The rust inhibitor in lubricant protects the machine parts.
- **5**.It acts as a seal. In internal combustion engines, lubricant is used as a seal between the wall of the cylinder and piston and prevents the leakage of gases under high pressure from the cylinder.
- **6**. It prevents the accumulation of dirt and foreign matter entering the bearing.

- **Classification of Lubricants**
- Lubricants are classified according to the state of aggregation as liquid, semi-solid and solid lubricants. Their use in machinery depends on its working conditions. They contain 90% base (usually petroleum fractions called mineral oils) and less than 10% additives.
- **1. Liquid lubricants:** Lubricating oils are widely used for the lubrication of machine tools. They act as sealing agents, corrosion inhibitor and cooling medium. Majority of them are of petroleum origin; some of them are of vegetable or animal origin.

➢ **Examples:**

✓ *Animal oils: whale oil, lard oil, tallow oil, seal oil, etc.*

✓ *Vegetable oils: mustard oil, sunflower oil, cotton seed oil, etc.*

- **2. Semi-solid lubricants:**
- When a liquid lube oil cannot be maintained, lubrication is done by a semi-solid lube. Greases are very good semi-solid lubricant. An automotive wheel bearing is best lubricated by grease. A semi-solid lubricant is obtained by combining lubricant oil with thickening agent.
- They are special soaps of sodium, calcium, baricum, aluminium, etc. Non-soap thicknes are carbon-black, silica gel, poly urea, etc. They have high resistance to friction than oils and can support heavier loads at low speeds.
- Semi-solid lubricant are used (a) where oil is not suitable for machines, (b) when machines are working with heavy load at low speed and (c) where sealing is required without dust particles and moisture and contamination is not acceptable.

- **3. Solid Lubricants:**
- In certain aero-space devices and some other environments, liquid and semi-solid lubes cannot be used. Solid lubricates such as MoS_2, mica, chalk, wax, soap, graphite, which can with stand heavy load and low speed can be used. They consist of a number of layers of atoms held together by weak van der Waals forces which makes them soft and smooth to act as lubricant. Because of its slippery touch, non-inflammability and resistance to oxidation, graphite is a widely used solid lubricant. It can be used as powder or as colloidal dispersion in water (aqua dag) oil (oil dag). Graphite is used in IC. engines, lathes, and air compression engines, but is ineffective in vacuum conditions and above 370ºC. MoS_2 can be used upto 800ºC. It possess very low coefficient of friction. Hence, it can be used in air frame lubrication and wire drawing. Other organic solid lubes are copper phthalocyanine and teflon.

➢ **Gases:**

- In recent times, gases have also been used as lubes in precious spindles, fans, compressors, etc., because of their low viscosity which is independent of temperature. Hence, the viscous resistance is minimum and there is no effect of variation in temperature on lubrication. There is no risk of contamination of gas if enclosed system is used as lubricant.

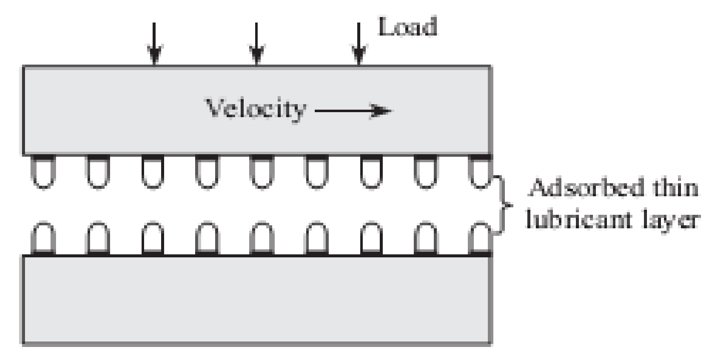
Mechanisms of Lubrication

Three mechanisms have been proposed to explain the action of lubricants. They are:

- *1. Thin film or boundary lubrication*
- *2. Fluid film or hydrodynamic lubrication*
- *3. Extreme pressure lubrication*

1. Thin film or boundary lubrication:

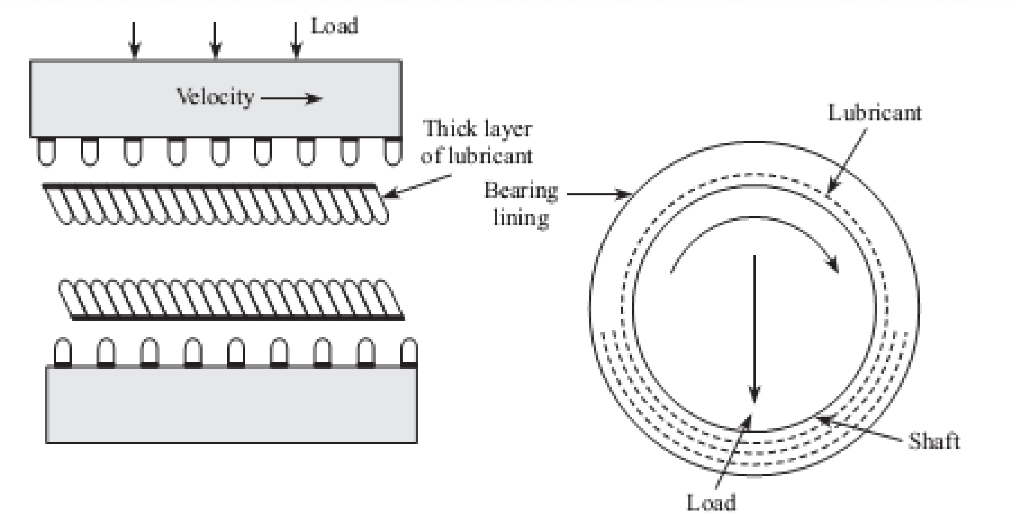
In this type of lubrication, a thin film of lubricant is adsorbed on the surface and held by van der Waals forces. When the lubricant is not viscous enough to generate a film of sufficient thickness for the separation of surfaces under heavy loads, friction is reduced by thin film lubrication. Thin film lubrication is applied when (a) the speed in very low, (b) the shaft moves from rest position to operation, (c) the load in heavy and (d) the oil has low viscosity. Some peaks or asperities may have higher thickness than the film of lubricant which results in wearing and tearing. Hence, the chemical or physical forces on some metal surfaces would avoid the direct contact of metals and absorb a thin layer of lubricating oil. In such conditions, lubricant forms a thin layer and gets adsorbed.



Boundary film lubrication

2. Fluid film or hydrodynamic lubrication

This type of lubrication is also known as thick film lubri-cation. It is carried out with the help of liquid lubricants. In fluid film lubrication, the two sliding sur-faces are separated by a thick film of about 1000 Å which is applied to prevent direct surface-to-surface contact. Wearing and tearing of metals is minimised.



Fluid film lubrication

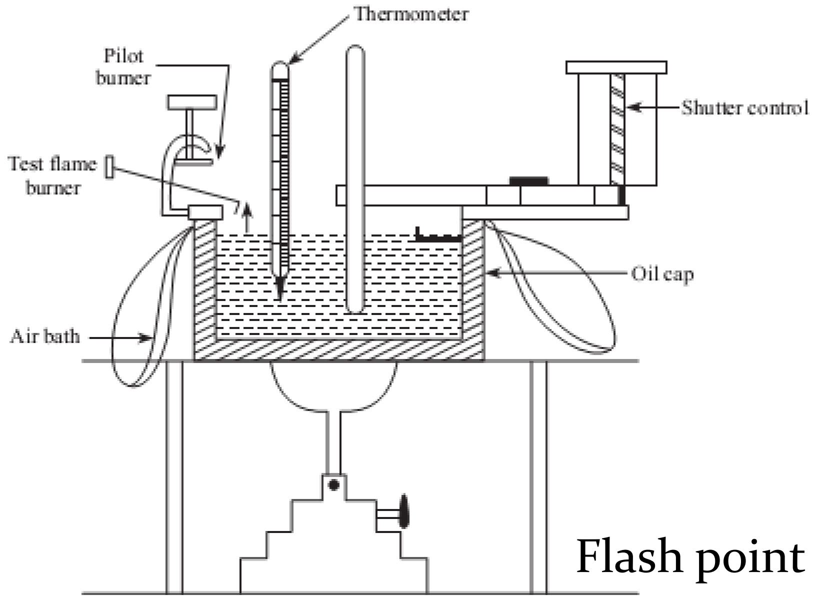
3. Extreme pressure lubrication

It involves chemical action on the part of lubricant Under heavy load and high speed conditions, high local temperature is generated. The liquid film may not stick, it may decompose and vapourise. Hence, special additives called extreme pressure additive are blended with lubricating oils to form more durable film to withstand high temperature and pressure. Chlorinated esters, sulfurised oils and tricresyl phosphates are used as extreme pressure additives.

- **Properties of Lubricants:**
- **Cloud Point:** The temperature at which the impurities being to separate from the solution and lubricating oil becomes cloudy or hazy in appearance is called cloud point.
- **Pour Point:** The temperature at which the oil ceases to flow and pour is called pour point.
- **Viscosity:**
- Viscosity is the property of a fluid that determines its resistance to flow. It is an indicator of flow ability of lubricating oil. The lower viscosity greater the flow ability. If temperature increases viscosity of the lubricating oil decreases and pressure increases viscosity of lubricating oil increases.

Flash and Fire Point

- Flash point is defined as the minimum temperature at which the lubricating oil gives off its vapours that ignite for a moment when a flame is brought near it. Fire point is the lowest temperature at which the vapours of the oil burn continuously for at least 5 seconds, when a flame is brought near it.
- The flash point of the lubricating oil is above the operating temperature, because a good lubricating oil should not volatalise under the working conditions usually. The fire points are 5 to 40°F higher than flash points. But the flash and fire points do not have any relation with the lubricating property of oil. Flash and fire points indicate the occurrence of fire accident. Before fire occurs flash appears.



Flash point apparatus

Application of Lubricants

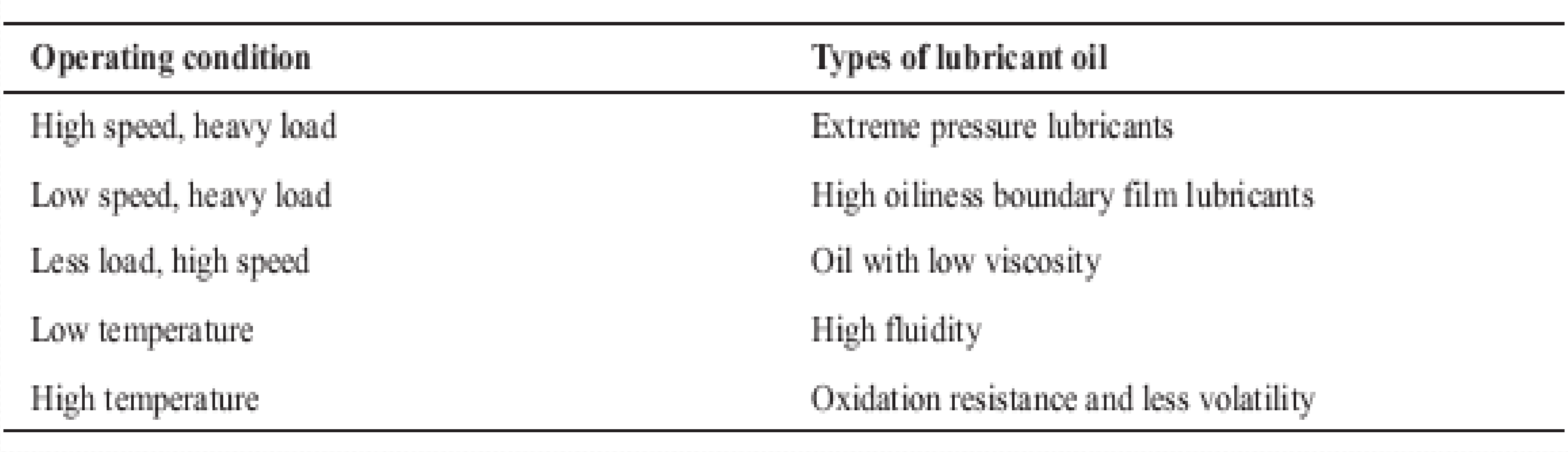
- Selection of lubricants for few typical applications is given under.

- **Lubricants for IC engines:** In internal combustion (IC) engines, the lubricants are generally exposed to high temperatures. Therefore, they should possess high viscosity index and should be thermally stable. Hence, petroleum oils containing additives which produce high VI and oxidation stability are used in IC engines.
- **Lubricants for refrigerators**: For refrigeration, the selected lubricant must possess low pour point, low viscosity and low cloud point. Maximum limit of pour point is –40ºF for lighter grade and –13ºF for heaviest grade oils, and viscosity should be 85–325 say bolt universal seconds at (545) 100ºF. Naphthalene base oils satisfy these conditions and hence are suitable for refrigeration.

- **Lubricants for very high pressure and low speed**: Concrete mixers, lathes, railway joints, tractor rollers, etc. are exposed to very high temperature and move at low speed. A film of oil or grease is difficult lathes, railway joints, tractor rollers, etc. are exposed to very high temperature and move at low speed. A film of oil or grease is difficult to maintain. Hence, a dry power of solid lubricants such as graphite, mica is used.
- **Lubricants for gears:** The lubricants used in gears are exposed to extreme pressures, hence thick mineral lubricating oils are used so that they should stick to the gear teeth. The oil also should possess high resistance to oxidation and high tensile strength. Lubricants should possess good lubricating properties, non-corrosive nature, and chemical stability.

- **Selection of a Lubricant**
- The selection of a lubricant depends on the operating conditions. Many conventional lubricants do not work at lower temperatures, and at higher temperatures, they may break down. The type of lubricating oil suitable for different conditions is given in Table.

- **Table :** *Types of lubricating oil suitable for different conditions*



Operating condition	Types of lubricant oil
High speed, heavy load	Extreme pressure lubricants
Low speed, heavy load	High oiliness boundary film lubricants
Less load, high speed	Oil with low viscosity
Low temperature	High fluidity
High temperature	Oxidation resistance and less volatility

- **Operating condition Types of lubricant oil**
- High speed, heavy load Extreme pressure lubricants
- Low speed, heavy load High oiliness boundary film lubricants
- Less load, high speed Oil with low viscosity
- Low temperature High fluidity
- High temperature Oxidation resistance and less volatility

Refractories

- Refractories are inorganic materials which can withstand very high temperatures without softening or suffering deformation. Therefore, they are used for the construction of kilns, ovens, crucibles, retarts, furnaces, etc. The main function of refractories varies depending on the purpose to which they are subjected like confining heat within the furnace, transmitting or storing heat in regenerators. The selection of a refractory for a particular purpose depends on the service conditions, like working temperature to which it is exposed, the nature of the materials which come into contact with it, temperature fluctuations, load applied and the nature of chemical reactions which occur.

Characteristics of a Refractory

A good refractory materials should possess

(1) high-temperature resistance under working conditions,

(2) good abrasion resistance by dusty gases and molten metals,

(3) low permeability or ability to contain heat,

(4) high mechanical strength, structural strength and crack resistance to withstand overlying load,

(5) thermal strength to withstand thermal shock due to rapid and repeated temperature fluctuations and

(6) high resistance to change in physical, chemical and mechanical properties.

- If a given refractory, materials does not have the above-mentioned characteristic properties, it will fail in service.

Classification of Refractories

Refractories are broadly classified into three categories.

- **1. On the basis of their chemical nature**

a. Acidic refractories: *They are made from acidic materials such as alumina (Al_2O_3) and silica (SiO_2).* They are resistant to acid slags, but attacked by basic materials such as CaO and MgO.

Examples: Silica, alumina and fire clay refractories (fire clay refractories contain silicate mineral kaolinite. Silicate refractories which rank next to fireclay refractories are produced from quartzite and quartz pebbles).

b. Basic refractories: *Basic refractories are those which consist of basic materials. They are not attacked* by basic materials, but attacked by acidic materials. They find extensive use in steel-making open hearth furnaces.

Example: Magnesite, dolomite, chrome magnesite refractories.

c. *Neutral refractories*: *They are not completely neutral in chemical sense. They consist of weakly basic*/ acidic materials such as carbon, zirconia (ZrO_2), chromite ($FeOCrO_2$), graphite and silicon carbide.

- **2. On the basis of fusion temperature**

a. Normal refractory: *Fusion temperature is 1580–17800C.*

Example: Fire clay refractory

b. High refractory: *Fusion temperature is 1780–20000C.*

Example: Chromite refractory

c. *Super refractory:* *Fusion temperature is above 20000C.*

Example: Zirconia

3. On the basis of oxide content

a. Single oxide refractory

Examples: Alumina, magnesia and zirconia refractory

b. Mixed oxide refractory

Example: Spinel and mullite

c. *Non-oxide refractory*

Example: Borides, carbides and silicates

Properties of Refractories

- **Chemical inertness**:

The refractory materials used as lining for furnace should be chemically inert. It should not react with slags, reagents, furnace gases, fuel ashes and products produced inside the furnace. Acidic refractories should not be in contact with alkaline product, vice-versa.

Example: Silica bricks being acidic cannot be used in a basic furnace and magnesite bricks being basic can-not be used in acidic furnace.

- **Refractoriness:**

It indicates the ability of a refractory to bear its own weight at high temperature. The refrac-tory materials should not undergo deformation with increase in temperature. Higher the softening tempera-ture, more valuable is the refractory.

Refractoriness is expressed in pyrometric cone equivalents (PCE). The materials whose refractoriness is to be tested is taken in the form of cone and a similar sized standard cone is also taken. Then both the cones are heated uniformly at 10°C per minute. The standard cones possess definite softening temperature. Standard cones are given the number 22 to 42 with increasing softening temperature. When the test cone gets softened and loses its shape, one of the standard cones whose refractoriness is close to that of the test cone will also soften. The serial number of that standard cone is noted and this number is the PCE of test cone. The soften-ing temperature range of this pair is also noted. For example, silica brick has PCE of 33 with a softening temperature range of 1700–1750°C. This indicates that particular refractory can be used in the temperature range of 1700°C.

- **Thermal expansion and contraction**:

  The expansion and contraction of a good refractory should be negligible with change in temperature. Repeated contractions and expansions of a refractory materials will lead to the breakdown of refractory materials. The lower the thermal expansion and contraction, the better the quality of the refractory.

- **Porosity:**

  Combustible materials like sawdust when used as raw materials for making bricks make them po-rous. Certain foaming agents are added to make the refractory porous. The porosity of a refractory is the ratio of its pore volume to the total or bulk volume. Porosity influences the strength of a refractory. If it is highly porous, molten reactants, gases, slags, etc., penetrate and damage the brick. As a result, its abrasion resistance and mechanical strength decreases. Contrary to it, in a porous brick the pores act as an insulator for the furnace. Porosity decreases thermal spalling.

- **Thermal spalling**: The breaking, cracking, peeling of a refractory can be reduced by (1) using materials with low porosity and low coefficient of expansion, (2) avoiding sudden changes in temperatures and (3) avoiding overfiring during construction and finishing of internal lining of refractories

UNIT 5

FUELS AND COMBUSTION

Introduction

- A fuel is a combustible substance which on proper burning produces a large amount of heat energy. The heat evolved during combustion can be used economically for industrial and other uses.
- For example, coal is used in locomotives and as reducing agent in blast furnace. Petrol is mainly used in internal combustion engines and for doing mechanical work. There are solid, liquid, and gaseous fuels that are available for firing in boilers, furnaces, and other combustion equipment. Right type of fuel can be selected depending on various factors such as storage, availability, handling, pollution, and landed cost of fuel. Combustion is the process of chemical reaction between fuel and oxygen. During combustion heat and products of combustion are released. The combustion process is an exothermic chemical reaction, i.e., a reaction that releases energy as it occurs. Symbolically, combustion can be represented as
- Fuel + Oxidizer (Oxygen) → Products of combustion + Energy
- Heating value of a fuel is the amount of energy or heat released per unit mass during combustion of that fuel. The main elements of combustion are carbon, hydrogen, sulphur, oxygen and nitrogen. With the advent of nuclear fuels, which generate heat by nuclear reaction, the common fuels may be termed as chemical fuels.

Classification of Fuels

Classification of fuels is based on two factors:

- (i) based on occurrence (natural or primary and artificial or secondary)
- (ii) physical state of the fuel (solid, liquid, gas) or state of aggregation. Nuclear fuels are nowadays used for power generation. It includes 92U235 and 94Pu239.

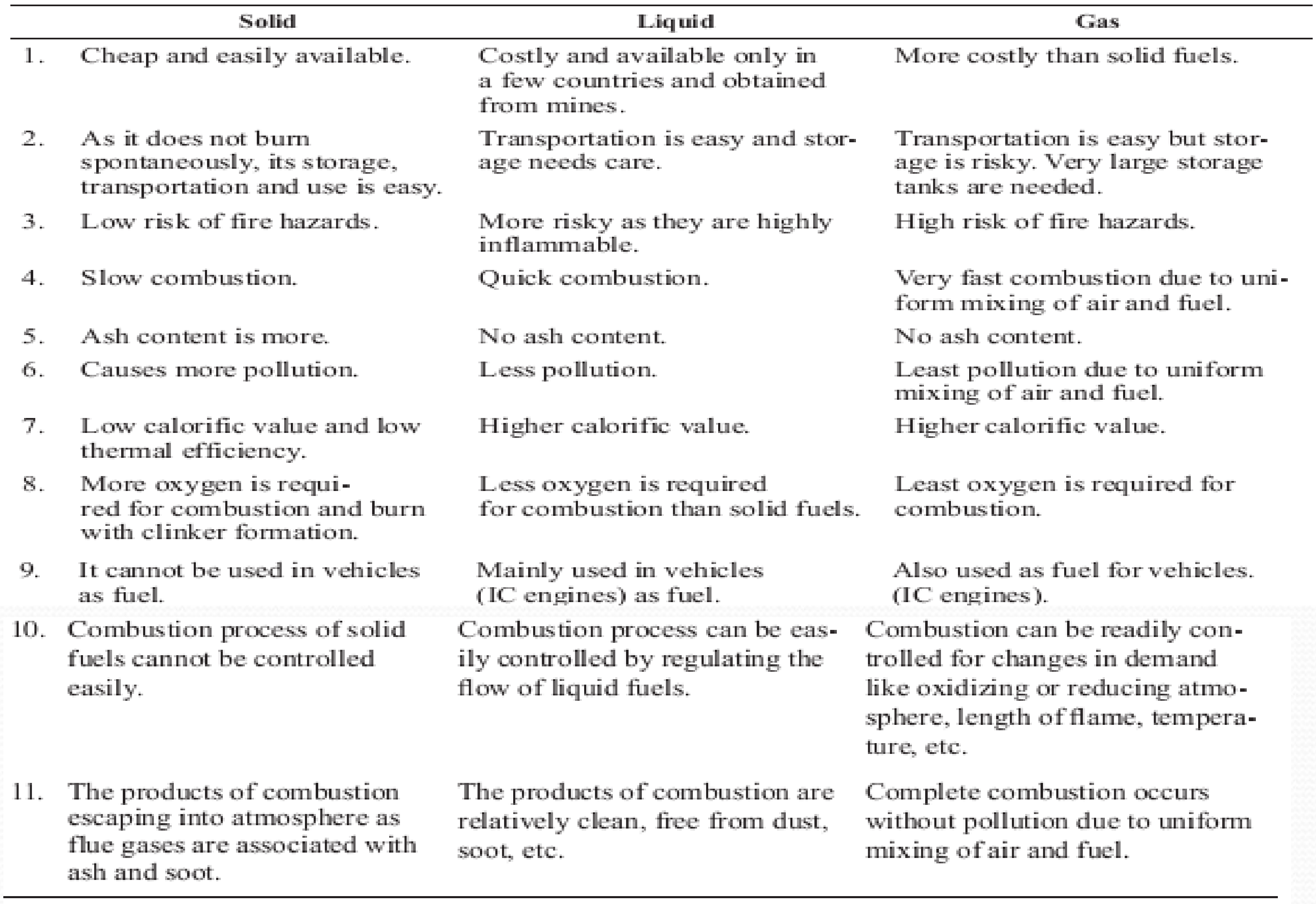
Natural Fuels (Primary Fuels)

Some fuels are found in nature and are used in the same form. These are called natural fuels, e.g. wood, coal, natural gas and petroleum.

Artificial Fuels (Secondary Fuels)

The fuels that are derived from natural fuels (primary) are called artificial or secondary fuels, e.g. petrol, producer gas and charcoal.

Comparison of solid, liquid and gaseous fuels: advantages and disadvantages



	Solid	Liquid	Gas
1.	Cheap and easily available.	Costly and available only in a few countries and obtained from mines.	More costly than solid fuels.
2.	As it does not burn spontaneously, its storage, transportation and use is easy.	Transportation is easy and storage needs care.	Transportation is easy but storage is risky. Very large storage tanks are needed.
3.	Low risk of fire hazards.	More risky as they are highly inflammable.	High risk of fire hazards.
4.	Slow combustion.	Quick combustion.	Very fast combustion due to uniform mixing of air and fuel.
5.	Ash content is more.	No ash content.	No ash content.
6.	Causes more pollution.	Less pollution.	Least pollution due to uniform mixing of air and fuel.
7.	Low calorific value and low thermal efficiency.	Higher calorific value.	Higher calorific value.
8.	More oxygen is required for combustion and burn with clinker formation.	Less oxygen is required for combustion than solid fuels.	Least oxygen is required for combustion.
9.	It cannot be used in vehicles as fuel.	Mainly used in vehicles (IC engines) as fuel.	Also used as fuel for vehicles. (IC engines).
10.	Combustion process of solid fuels cannot be controlled easily.	Combustion process can be easily controlled by regulating the flow of liquid fuels.	Combustion can be readily controlled for changes in demand like oxidizing or reducing atmosphere, length of flame, temperature, etc.
11.	The products of combustion escaping into atmosphere as flue gases are associated with ash and soot.	The products of combustion are relatively clean, free from dust, soot, etc.	Complete combustion occurs without pollution due to uniform mixing of air and fuel.

Characteristics of a Good Fuel

A good fuel has the following features:

- 1. It should be cheap and easily available.
- 2. It should be dry and should have less moisture content. Dry fuel increases its calorific value.
- 3. It should be easily transportable, otherwise cost of fuel will increase.
- 4. It must have high calorific value.
- 5. It must leave less ash after combustion. In case of more ash, the fuel gives less heat.
- 6. The combustion speed of a good fuel should be moderate, otherwise it will not solve the problem of heating.
- 7. It must have moderate ignition temperature. Low (burning)/ignition temperature can cause fire accident.
- 8. It should not burn spontaneously to avoid fire hazards.
- 9. It should not give harmful gases after combustion.
- 10. Its handling should be easy.
- 11. The combustion of a good fuel should not be explosive.
- 12. The combustion of a good fuel should not result in the release of toxic gases such as CO, CO2, CH4,etc

- **Calorific Value of a Fuel**
- The calorific value of any fuel is a very important property. It measures the heat produced by the fuel. The higher the calorific value, the better will be the quality of fuel. Calorific value is defined as *“the amount of heat produced by the combustion of unit mass or unit volume of a fuel”. It is characteristic of every substance* and is important for thermodynamic design and calculation of combustion system.
- The calorific value is measured in several units of heat; they are calorie, kilocalorie, British thermal unit and Centigrade thermal unit (Centigrade heat unit).
- **Calorie:** The amount of heat which increase the temperature of one gram of water by 1°C in known as 1 calorie.
- **Kilocalorie:** The amount of heat that increases the temperature of 1 kg of water by 1°C (i.e., 15°C to 16°C) is called kilocalorie.

- **British thermal unit (BTU)**: The amount of heat required to raise the temperature of one pound of water by
- 1°F (60°F to 61°F) is BTU.
- 1 BTU = 252 cal = 0.252 kcal
- 1 kcal = 3.968 BTU
- **Centigrade heat unit (CHU):** It is the amount of heat required to raise the temperature of one pound of water through 1°C.
- 1 kcal = 3.968 BTU = 2.2 CHU

  Relationship among all the above units of heat is given as follows:
- 1 kcal = 1000 cal = 3.968 BTU = 2.2 CHU
- Joule is also a unit of energy.
- 1 cal = 4.18 J

- There are two types of calorific values of a fue

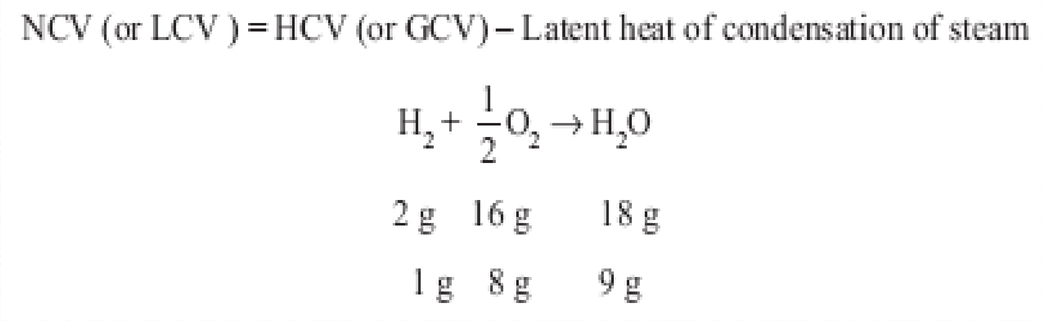
- **High Calorific Value (HCV) or Gross Calorific Value (GCV)**

  It is defined as the amount of heat energy produced by the combustion of unit mass (unit volume) of a fuel when the combustion products are allowed to cool at the room temperature. Generally, fuels contain hydrogen. When the calorific value of hydrogen-containing fuels is determined experimentally, hydrogen is oxidized to steam; when the products are cooled to room temperature, steam undergoes condensation to produce water and releases the latent heat of condensation of steam which must be included in the measured heat which is called GCV. Actually, during combustion, the products are not allowed to escape into the atmosphere and they are cooled to the room temperature. Hence, the net heat energy recovered on the combustion of fuel is lower.

- **Low Calorific Value (LCV) or Net Calorific Value (NCV)**

  It is defined as the amount of heat energy produced by the combustion of unit mass (unit volume) of fuel when the combustion products are allowed to escape out into the atmosphere. LCV does not include the latent heat of steam or water vapour formed.

- *Relationship Between HCV and LCV*



NCV (or LCV) = HCV (or GCV) – Latent heat of condensation of steam

$$H_2 + \frac{1}{2}O_2 \rightarrow H_2O$$

2 g   16 g   18 g

1 g   8 g   9 g

- If hydrogen is present in a fuel, the above-mentioned chemical reaction will take place and 2 g of hydrogen will produce 18 g of H2O or 1 g of hydrogen will produce 9 g of H2O. If *x gram hydrogen is present in* a fuel, it will produce 9*x g of water and 9x g of water vapour that will release 9x × L cal heat on cooling (L* cal/g is the latent heat of water vapour). So,

  LCV = HCV – latent heat of water vapour

  LCV = HCV – (mass of hydrogen × 9 × latent heat of steam)

  = HCV – (9 × H /100× 587)

  = HCV – (0.09 H × 587)

  where *H is the percentage of hydrogen in the fuel and latent heat of steam is 587 kcal/kg.*

Solid Fuels

- Because of environmental hazards, trees were buried inside the earth. By the action of temperature, pressure and bacterial actions over a period of thousands of years, they converted into a brown-black solid named coal.

$$\text{Wood} \xrightarrow[\text{Bacterial action}]{\text{Temperature/pressure}} \text{Coal}$$

- Since wood contains higher carbon percentage in the form of cellulose, lignocelluloses, they are transformed into the form of coal. The process of conversion of wood into coal is called coalification. Depending upon the percentage of carbon, hydrogen, moisture and calorific value, four different types of coals exist. It is called the ranking of coal.
- Dry wood has the following composition: carbon (48–50%), oxygen (42–44%), hydrogen (5–6%) and traces of minerals. The calorific value of wood is 4000–4500 kcal/kg and, thus, is used as a domestic fuel.
- Wood can be converted into charcoal by a process called carbonization (destructive distillation of wood). Charcoal is used as absorbent of gases and for de colourisation of sugar.

Coal

- It is a carbonaceous matter produced by the decomposition of vegetable and animal matter buried inside the earth's crust or under oceans. It is a non-renewable energy source formed by the decomposition of accumulated vegetation over a period of millions of years. Coal is one of the major source of energy in many industries such as steel, cement and paper, because of its easy availability and least risk of fire hazards.
- **Ranking of Coal**
- During coalification of wood, the first stage of coal is peat. It is ranked the lowest among coals. Other coals are lignite, bituminous and anthracite. It has been reported that graphite is also the final stage of coalification.

  Wood → Peat → Lignite → Bituminous → Anthracite

Analysis of Coal

- The analysis of coal is helpful in its ranking. The assessment of the quality of coal is carried out by these two types of analyses:

  (i) proximate analysis and (ii) ultimate analysis.

  Proximate Analysis

- Proximate analysis gives information regarding the practical utility of coal. In this analysis, the percentage of carbon is indirectly determined. This analysis includes percentage of moisture, volatile substance, ash content and carbon.
- **Moisture**: A known mass of finely powdered air-dried coal is taken in a crucible. It is heated up to 110°C for an hour and cooled to room temperature in a desiccator. The moisture is removed as water vapour and the process is repeated. The weight of coal is reported on moisture% basis till the constant weight is obtained.

  Percentage of moisture=Loss of weight of coal/Weight of coal taken×100

- **Volatile matter:** Dried sample of coal left in the crucible is covered with a lid and placed in a muffle furnace maintained at 950°C exactly for 7 minutes. The crucible is then taken out, cooled in the air and then in desiccator and weighed. The loss in weight is reported as the percentage of volatile matter

Percentage of volatile matter =

Loss in weight due to removal of volatile matter/Weight of coal taken×100

- **Ash content:** Coal, free from moisture and volatile matter, is heated in a crucible at about 700°C in a mufflef urnance in the presence of air. It undergoes combustion and results in the formation of ash. Crucible is cooled to room temperature and weighed. Heating, cooling, weighing is repeated to get constant weight of the residue. The residue is reported as as h. The mass of ash is then determined.

Percentage of ash=Mass of ash × 100/Mass of coal

- **Carbon:** Since the main component of coal is carbon, it can be determined by subtracting the sum of the percentage of moisture, volatile substance and ash content from 100.

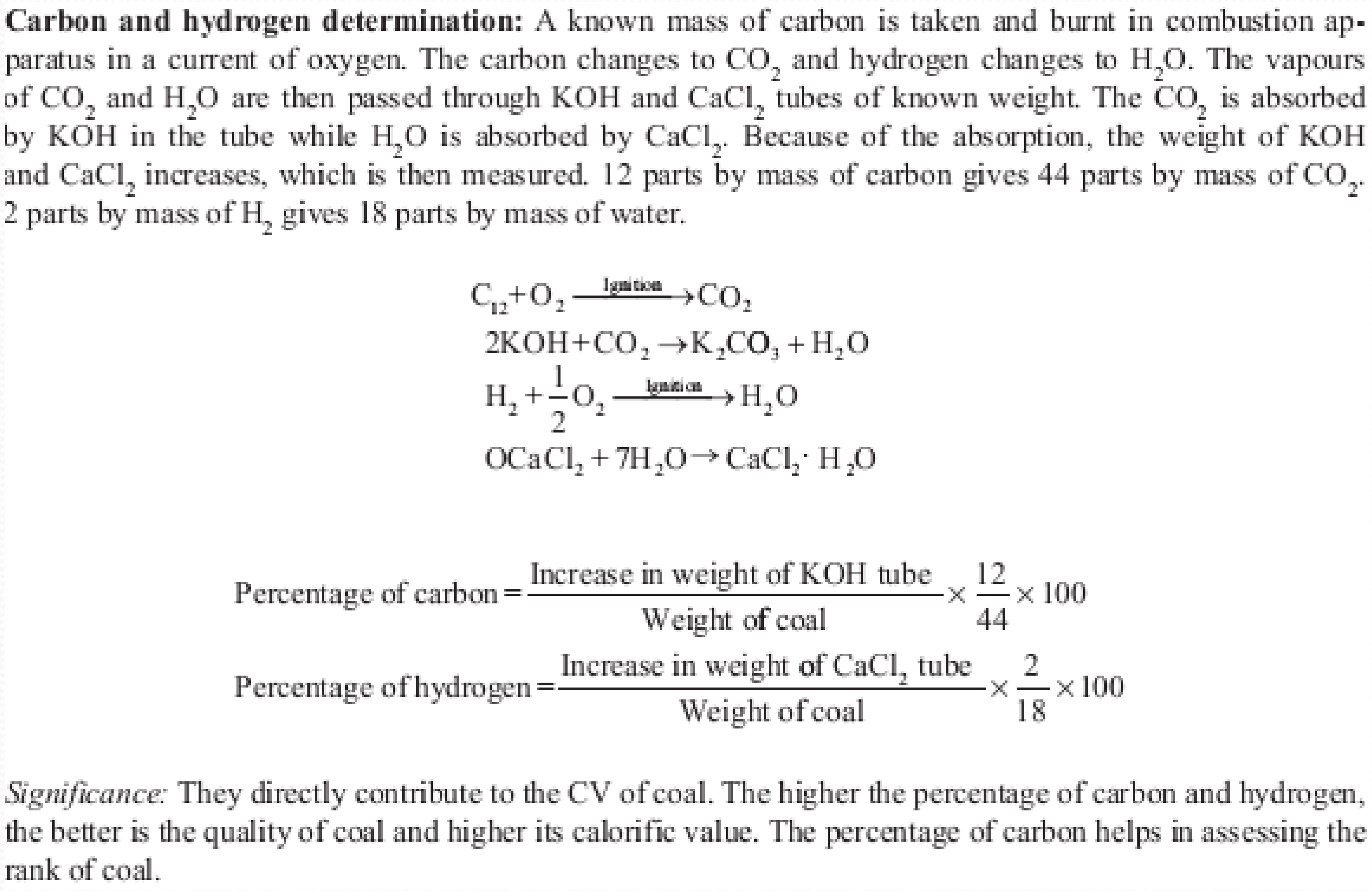
Carbon % = 100 – (% of moisture + % of volatile matter + % of ash)

- **Significance of analysis:** Proximate analysis gives quick and valuable information regarding commercial classification and suitability of coal for industrial use. It consists of a complex mixture of gaseous and liquid products resulting from the thermal decomposition of coal. The amount of decomposition and yield of V.M. depends on the conditions of heating, particularly temperature.
- *Moisture: A high moisture content in the fuel takes some heat liberated in the form of latent heat, reduces the* calorific value, increases the cost of transportation and causes wastage of heat. Hence, the lesser the moisture content, the better is the quality of a fuel. But moisture up to 10% produces a uniform fuel bed and less of fly ash.
- *Volatile matter: It is due to combustible and non-combustible gases. A coal containing high volatile matter* burns with long flame, high smoke and low calorific value. volatile matter also influences the design of the furnace since the higher the volatile matter, the larger is the combustion space required.
- *Ash: Ash is a residual, incombustible matter produced by burning of coal. It creates cleaning and disposal* problem. Ash adds impurities in metallurgical operations. It obstructs the flow of air and heat.

- 1. Ash reduces heating value of coal.
- 2. Ash content increases the cost of transportation, handling, storage and disposal.
- 3. It determines the quality of coal. hence, the lesser the percentage of ash, the better is the quality of coal.

➢ **Fixed carbon**: *The higher the fixed carbon in a coal, the greater is its calorific value and better is the quality of* coal. It helps in designing the furnace and shape of fire box. It increases from low ranking coals such as lignite to high ranking coals such as anthracite. It helps in designing furnace and fire box.

- **Ultimate Analysis**
- It is the elemental analysis of coal. This analysis includes percentages of C, H, O, S, N and ash content in coal and better quality of CO. The two components can be determined in a single experiment.



Carbon and hydrogen determination: A known mass of carbon is taken and burnt in combustion apparatus in a current of oxygen. The carbon changes to CO_2 and hydrogen changes to H_2O. The vapours of CO_2 and H_2O are then passed through KOH and $CaCl_2$ tubes of known weight. The CO_2 is absorbed by KOH in the tube while H_2O is absorbed by $CaCl_2$. Because of the absorption, the weight of KOH and $CaCl_2$ increases, which is then measured. 12 parts by mass of carbon gives 44 parts by mass of CO_2. 2 parts by mass of H_2 gives 18 parts by mass of water.

$$C_{12}+O_2 \xrightarrow{\text{Ignition}} CO_2$$

$$2KOH+CO_2 \rightarrow K_2CO_3 + H_2O$$

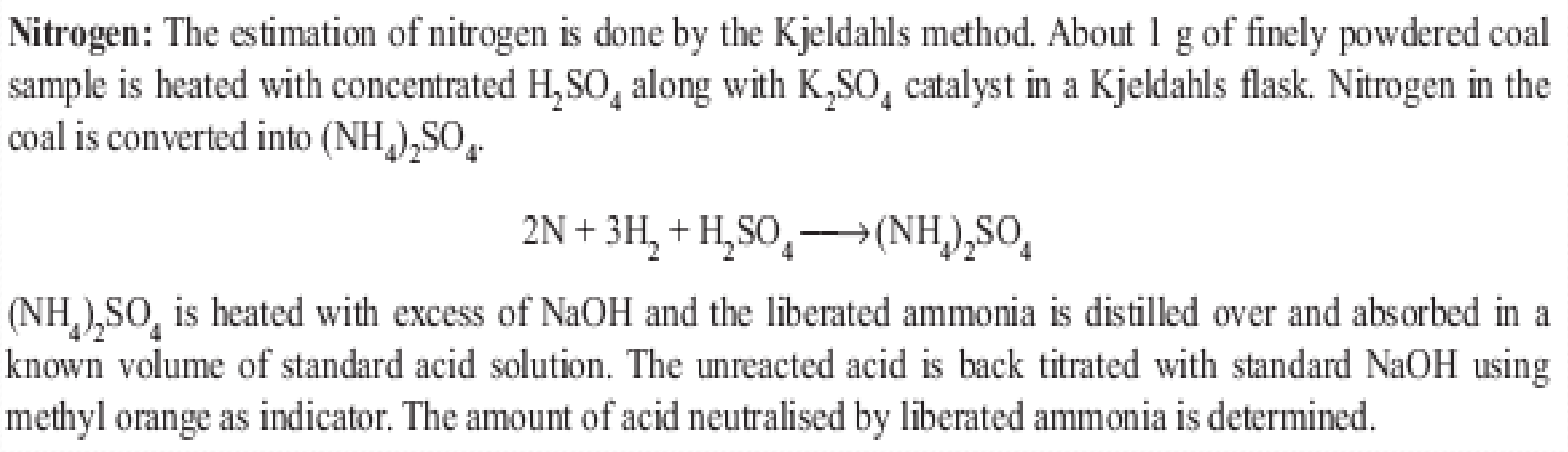
$$H_2 + \frac{1}{2}O_2 \xrightarrow{\text{Ignition}} H_2O$$

$$OCaCl_2 + 7H_2O \rightarrow CaCl_2 \cdot H_2O$$

$$\text{Percentage of carbon} = \frac{\text{Increase in weight of KOH tube}}{\text{Weight of coal}} \times \frac{12}{44} \times 100$$

$$\text{Percentage of hydrogen} = \frac{\text{Increase in weight of } CaCl_2 \text{ tube}}{\text{Weight of coal}} \times \frac{2}{18} \times 100$$

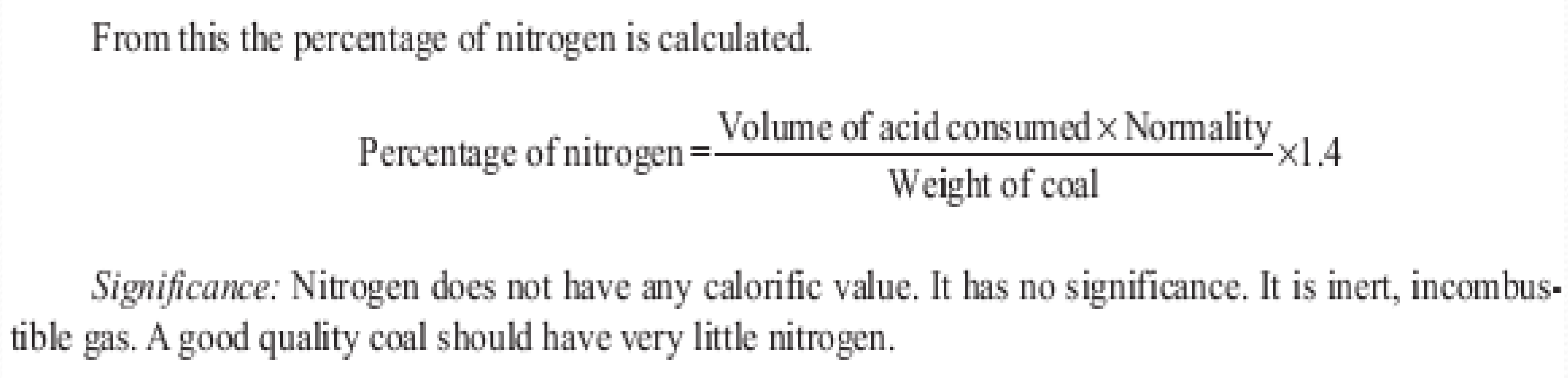
Significance: They directly contribute to the CV of coal. The higher the percentage of carbon and hydrogen, the better is the quality of coal and higher its calorific value. The percentage of carbon helps in assessing the rank of coal.



Nitrogen: The estimation of nitrogen is done by the Kjeldahls method. About 1 g of finely powdered coal sample is heated with concentrated H_2SO_4 along with K_2SO_4 catalyst in a Kjeldahls flask. Nitrogen in the coal is converted into $(NH_4)_2SO_4$.

$$2N + 3H_2 + H_2SO_4 \longrightarrow (NH_4)_2SO_4$$

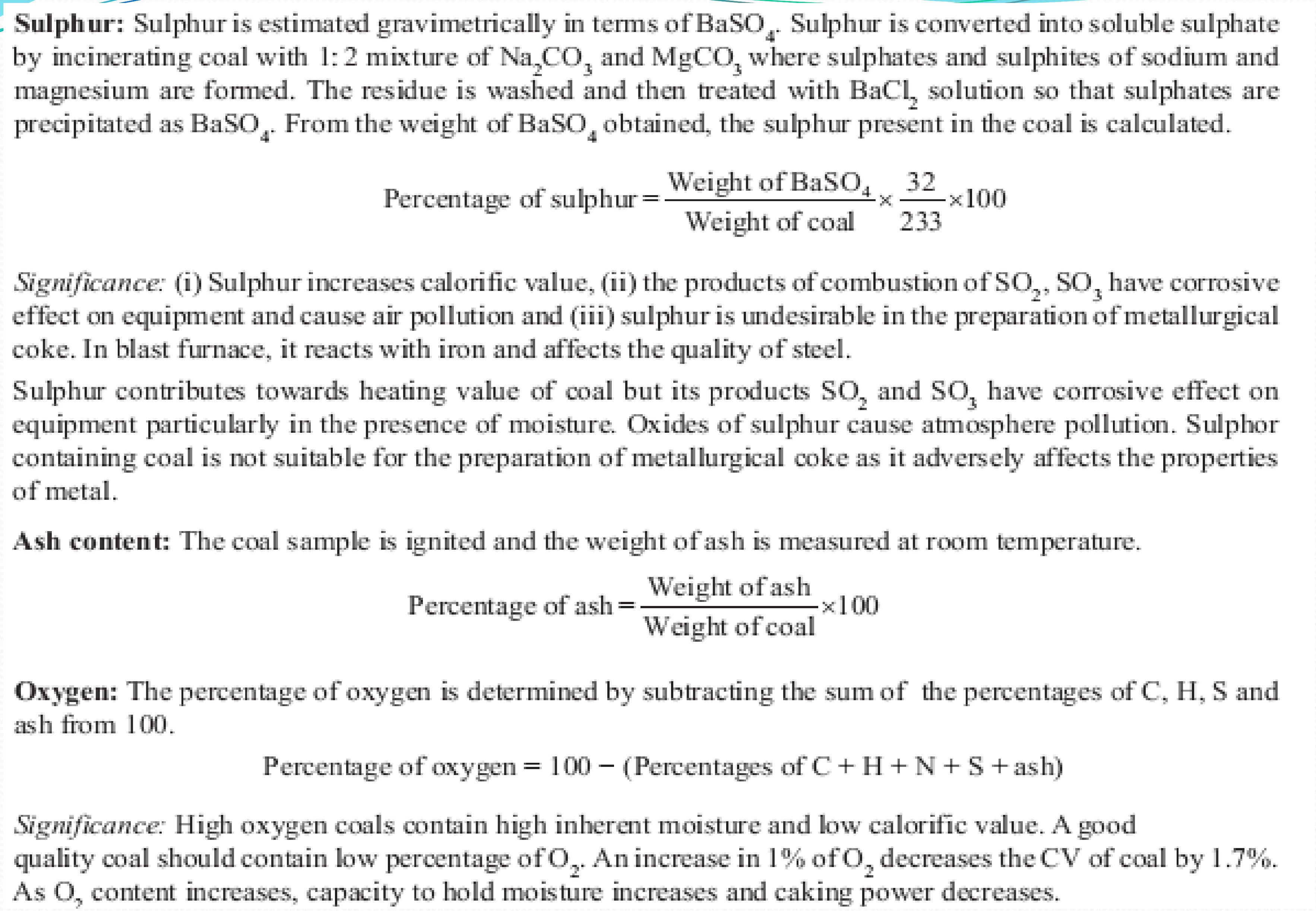
$(NH_4)_2SO_4$ is heated with excess of NaOH and the liberated ammonia is distilled over and absorbed in a known volume of standard acid solution. The unreacted acid is back titrated with standard NaOH using methyl orange as indicator. The amount of acid neutralised by liberated ammonia is determined.



From this the percentage of nitrogen is calculated.

$$\text{Percentage of nitrogen} = \frac{\text{Volume of acid consumed} \times \text{Normality}}{\text{Weight of coal}} \times 1.4$$

Significance: Nitrogen does not have any calorific value. It has no significance. It is inert, incombustible gas. A good quality coal should have very little nitrogen.



Sulphur: Sulphur is estimated gravimetrically in terms of $BaSO_4$. Sulphur is converted into soluble sulphate by incinerating coal with 1: 2 mixture of Na_2CO_3 and $MgCO_3$ where sulphates and sulphites of sodium and magnesium are formed. The residue is washed and then treated with $BaCl_2$ solution so that sulphates are precipitated as $BaSO_4$. From the weight of $BaSO_4$ obtained, the sulphur present in the coal is calculated.

$$\text{Percentage of sulphur} = \frac{\text{Weight of } BaSO_4}{\text{Weight of coal}} \times \frac{32}{233} \times 100$$

Significance: (i) Sulphur increases calorific value, (ii) the products of combustion of SO_2, SO_3 have corrosive effect on equipment and cause air pollution and (iii) sulphur is undesirable in the preparation of metallurgical coke. In blast furnace, it reacts with iron and affects the quality of steel.

Sulphur contributes towards heating value of coal but its products SO_2 and SO_3 have corrosive effect on equipment particularly in the presence of moisture. Oxides of sulphur cause atmosphere pollution. Sulphor containing coal is not suitable for the preparation of metallurgical coke as it adversely affects the properties of metal.

Ash content: The coal sample is ignited and the weight of ash is measured at room temperature.

$$\text{Percentage of ash} = \frac{\text{Weight of ash}}{\text{Weight of coal}} \times 100$$

Oxygen: The percentage of oxygen is determined by subtracting the sum of the percentages of C, H, S and ash from 100.

$$\text{Percentage of oxygen} = 100 - (\text{Percentages of C} + \text{H} + \text{N} + \text{S} + \text{ash})$$

Significance: High oxygen coals contain high inherent moisture and low calorific value. A good quality coal should contain low percentage of O_2. An increase in 1% of O_2 decreases the CV of coal by 1.7%. As O_2 content increases, capacity to hold moisture increases and caking power decreases.

❖ Liquid Fuels (Petroleum)

Petroleum is one of the best primary liquid fuel. It is also known as crude oil. Petrol, diesel, kerosene are main liquid fuels. They are secondary liquid fuels derived from petroleum. These fuels are used for domestic works, auto vehicles and power generation.

The word meaning of petroleum is ‘rock oil’ (petra = rock, oleum= oil).

Petroleum is dark-brown viscous liquid. Petroleum is a mineral found deep in earth’s crust. It is a mixture of number of hydrocarbons (paraffins, olefins, aromatics and naphthalene), nitrogen, sulphur, oxygen containing optically active compounds along with traces of compounds of heavy metals such as Fe, Co, Ni and V. The unpleasant odour of petroleum is due to the presence of some foul smelling sulphur compounds.

Petroleum does not have definite composition. Its composition varies with the place of origin. It is a complex mixture of various hydrocarbons and a small quantity of optically active compounds of S, N, O and traces of Fe, Cu, V, etc. Composition of petroleum is given as:

C = 80 to 87.1 %, H = 11.1 to 15.0 %, S = 0.1 to 3.5 %, O = 0.1 to 0.9 %, N = 0.4 to 0.9 %.

- **Origin of petroleum**

There are two theories to explain the origin of petroleum.

- **Carbide theory:** This theory is also called inorganic theory or Mendeleev's theory. Metals inside the earth react with carbon and form metal carbides. These carbides are converted into hydrocarbons in the presence of moisture or steam which on further hydrogenation polymerize to give a complex mixture of paraffin's, olefins, and aromatic hydrocarbons.

Drawbacks: This theory was unable to explain the presence of nitrogen, sulphur and optically active compounds found in petroleum.

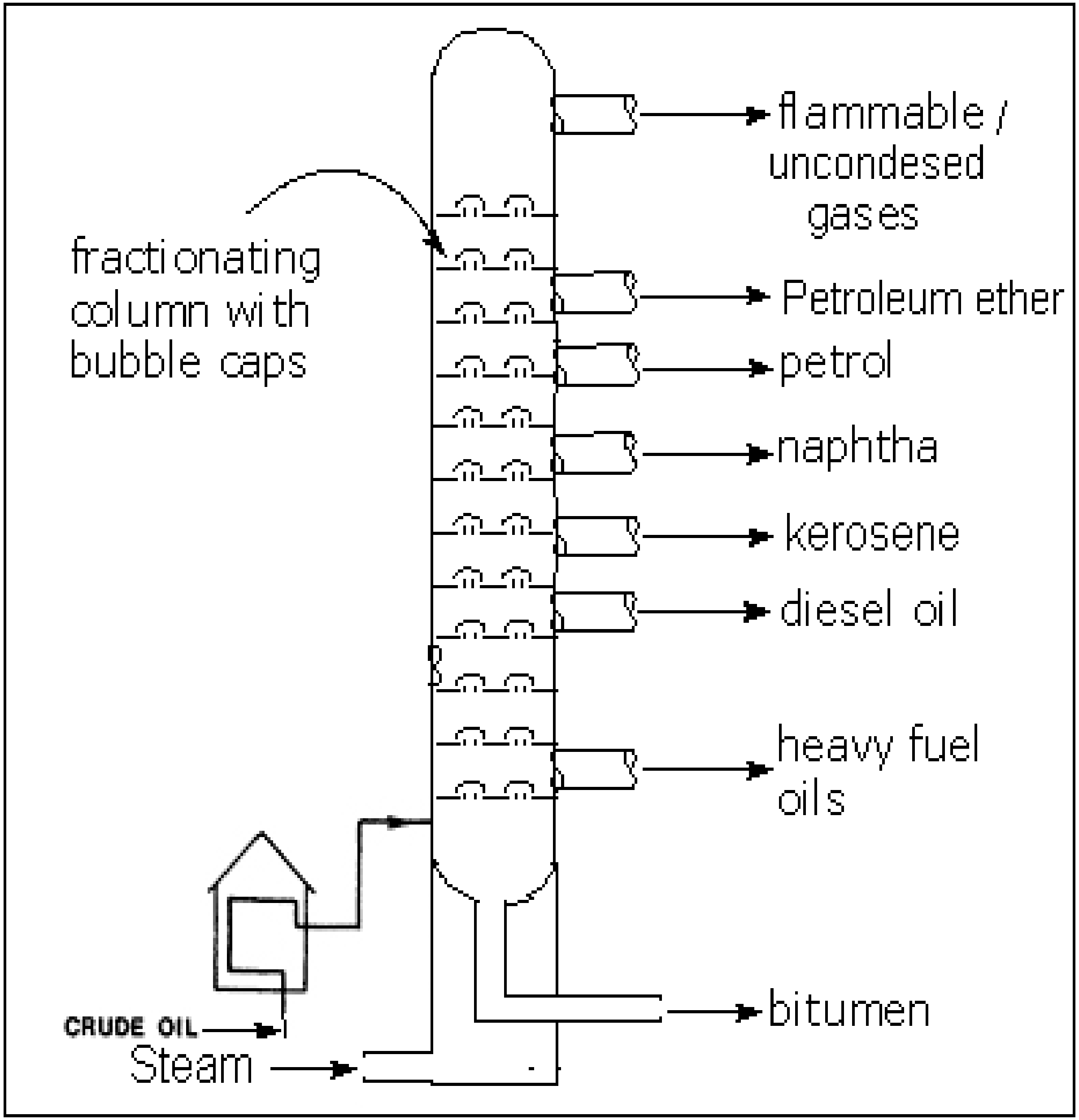
- **Engler's theory or organic theory:** According to this theory, organic matters, animals, vegetation and marine animals died and accumulated in sea. There, they were decomposed under high temperature and pressure by anaerobic bacteria to give a dark viscous liquid called petroleum. This theory is better accepted. The presence of optically active compounds in petroleum favours Engler's theory.

❖ Classification of crude oil

There are three types of petroleum.

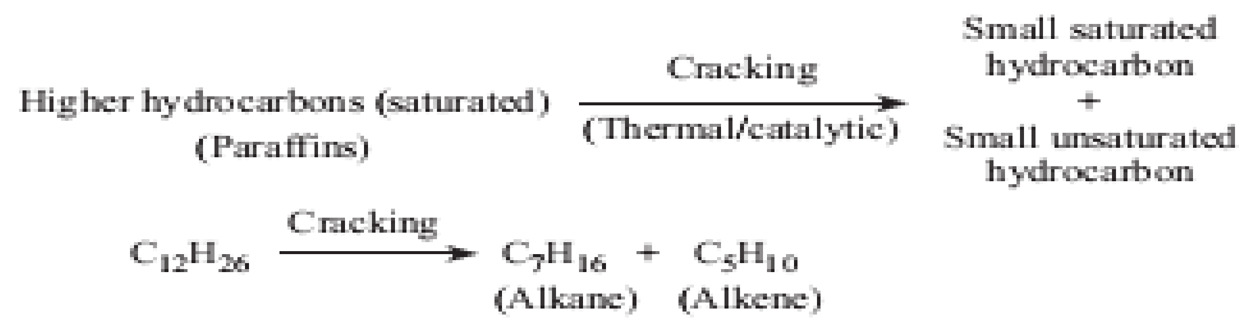
- **Paraffinic base type crude oil:** It has main saturated hydrocarbons $C_nH_{2n} + 2(n = 1 \text{ to } 35)$ *alongwith naphthalene* and aromatics hydrocarbons from $C_{18}H_{38}$ to $C_{35}H_{72}$ are solids, called waxes.
- **Asphaltic base type crude oil:** It has mainly naphthalene and cycloparaffins with a small quantity of aromatic and saturated hydrocarbons. These oils on distillation leave asphalt as residue.
- **Mixed base type**: This type of crude oil is a mixture of above two, paraffinic base type and asphaltic type. It has high percentage of semisolid waxes.

- **Refining of petroleum:**
- **Removal of water (Cottrell's process):** The crude oil obtained from the earth's crust is in the form of stable emulsion of oil and brine. This mixture when passed between two highly charged electrodes will destroy the emulsion films and the colloidal water droplets coalesce into bigger drops and get separated out from the oil.
- **Fractional distillation:** Heating of crude oil around 400°C in an iron retort, produces hot vapor which is allowed to pass through fractionating column. It is a tall cylindrical tower containing a number of horizontal stainless trays at short distances and is provided with small chimney covered with loose cap. As the vapors go up they get cooled gradually and fractional condensation takes place. Higher boiling fraction condenses first later the lower boiling fractions.


flammable / uncondesed gases
fractionating column with bubble caps
Petroleum ether
petrol
naphtha
kerosene
diesel oil
heavy fuel oils
bitumen
CRUDE OIL
Steam

❖Cracking

- The quality and yield of petrol produced by the fractionation of petroleum is low. Hence, the middle oil and heavy oil fractions are cracked to give petrol.
- Cracking is the process of conversion of bigger hydrocarbon molecules into smaller hydrocarbons of lower molecular weights.



$$\underset{\text{(Paraffins)}}{\text{Higher hydrocarbons (saturated)}} \xrightarrow[\text{(Thermal/catalytic)}]{\text{Cracking}} \begin{matrix}\text{Small saturated}\\ \text{hydrocarbon}\\ +\\ \text{Small unsaturated}\\ \text{hydrocarbon}\end{matrix}$$

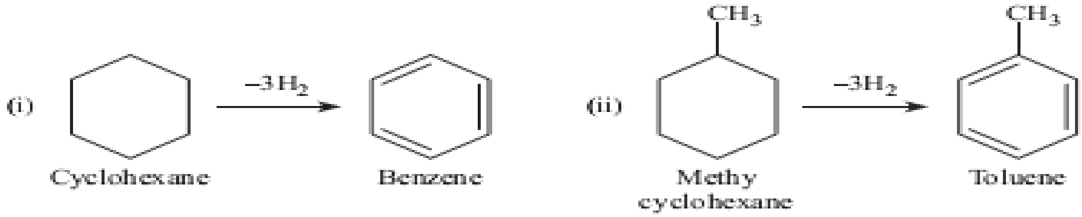
$$C_{12}H_{26} \xrightarrow{\text{Cracking}} \underset{\text{(Alkane)}}{C_7H_{16}} + \underset{\text{(Alkene)}}{C_5H_{10}}$$

Catalytic cracking

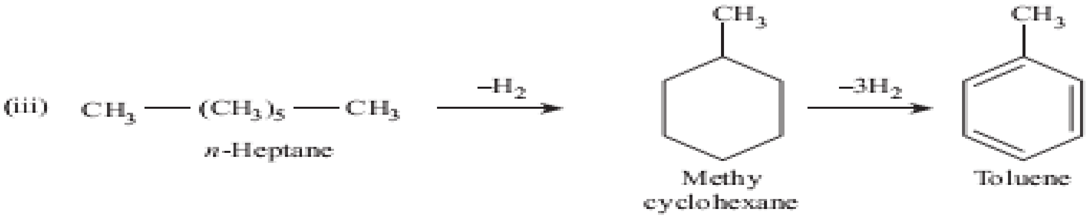
In this type of cracking catalysts are used. The best one is aluminosilicate with some metal oxides (oxides of Ca, Mg, Fe, Cr, Na). This process completes at lower temperature and lower pressure compared to the thermal process (300–450°C temperature; 1–5 kg/cm^2 pressure). Catalytic cracking is also of two types: (i) Fixed-bed cracking and (ii) Fluid-bed cracking.

Following chemical reactions take place in catalytic cracking.

(a) Dehydrogenation:

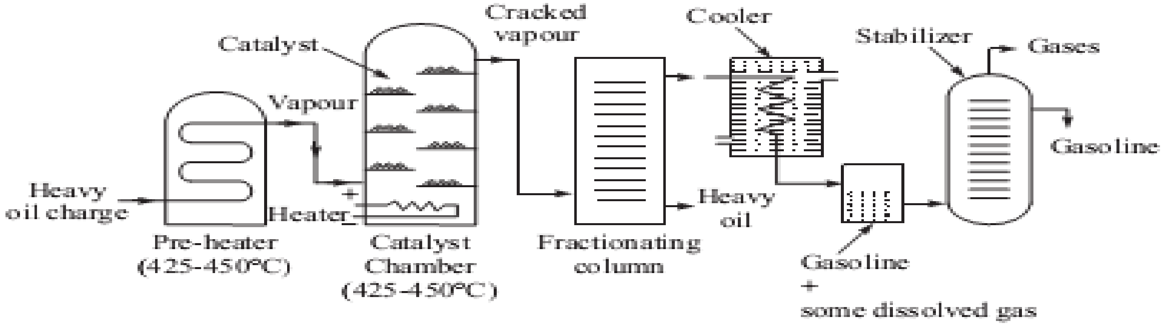


(b) Dehydrocyclization:



Flowchart of catalytic cracking (retaining) is given in Fig. 6.9.

Catalytic cracking can be brought about by (i) fixed bed catalytic cracking and (ii) moving bed and fluid bed catalytic cracking.



Knocking

- In internal combustion engines, diesel or gasoline mixed with air is used as fuel and ignited in the cylinder. The ignition is brought about by an electric spark (in petrol engines) and compressing air in diesel engines. After the ignition is initiated by a spark, the fuel air mixture must burn smoothly and rapidly and the flame should spread uniformly throughout the gaseous mixture. The expanding gas drives the piston down the cylinder due to high pressure and provides power stroke. The four strokes in petrol engine are:

1. *Suction stroke: Here the fuel–air mixture is drawn into the cylinder during induction.*
2. *Compression stroke: Fuel–air mixture is compressed in the cylinder.*
3. *Power stroke: Fuel–air mixture is ignited by electric spark. The hot gases produced due to combustion* increase the pressure and push the piston down the cylinder.
4. *Exhaust stroke: The piston ascends and expels exhaust gas from the cylinder and the next cycle starts* again. The efficiency of an engine is directly related to compression ration (CR)

- CR is the ratio of the volume of gas in the cylinder at the end of suction stroke to the volume of gas at the end of compression stroke. Compression ratio directly governs the efficiency of an engine. More the CR value, better will be efficiency of the engine. CR depends upon the type of constituents in gasoline. But in certain circumstances, the smooth burning of fuel is interrupted due to the presence of certain impurities. The last portion of the fuel ignites instantly and produces shock waves. it results in rattling sound in the engine called knocking. it results in rattling sound in the engine called knocking.
- Knocking decreases the efficiency of engine. The tendency of knocking is based on chemical structure of hydrocarbons. Branched chain alkenes burn more easily than straight chain alkenes. Lower alkenes (e.g., C_4H_{10}) burn easily than higher alkenes, e.g. C_7H_{16}. Also alkenes are better than alkanes and aromatic hydrocarbons; they burn more easily than cycloalkenes. Alternatively, the order of knocking tendencies is straight chain alkenes > cycloalkene > olefins > aromatics. For internal combustion engine, *n-alkanes are not fit for* modification. Knocking is the measure of octane number. Hence, for *n-heptane, octane number is 0, and that* of isooctane is 100.

- **Octane number or Octane rating**
- The anti-knocking value of fuel can be increased by adding tetraethyl lead (TEL). The oxides of lead formed as combustion products inhibit freeradical chain reaction responsible for knocking. Additives like ethylene dibromide and ethylene dichloride are also added to petrol to avoid the contamination of atmosphere by vapours of lead and PbO2. They form lead halides which escape into the atmosphere. They are not eco-friendly.
- Other additives tricresyl phosphate, 2,4-ditertiarybutyle-4-methyl phenols act as lead scavengers to prevent the oxidation of lead. The small quantity of methyl cyclopentadienyl manganese tercarbonyl (MMT) is also used nowadays in Canada and European countries in place of TEL, but results in Mn pollution in air and soil. Nowadays leaded petrol is used as aviation fuel known as avgas.

Prevention of Knocking -Knocking can be prevented by using:

(i) Good quality fuel with higher octane number.

(ii)By adding anti-knocking agents like tetraethyllead, methyl cyclopentadienyl manganese tricarbonyl (MMT) isooctane, diethyl telluride, etc.

(iii) By retarding spark plug ignition.

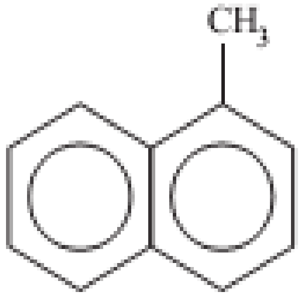
- It has been observed that maximum knocking is from a straight chain alkane *n-heptane and hence its* octane number (anti-knocking values) is assigned as zero while isooctane knocks minimum (say zero), its octane number has been given hundred. Hence, the octane number of gasoline is the percentage of isooctane in the mixture of isooctane and *n-heptane which has the same knocking as the gasoline itself. Therefore,* octane number 60 of a gasoline sample means, the mixture of 60% isooctane and 40% *n-heptane which* passees same knocking as the gasoline. The higher the octane number, the lower it is knocking. There are certain compounds which are used as anti-knock compounds. Tetraoctyl lead $(C_7H_5)_4Pb$ is better anti-knock but lead is dangerous for health. Methyl cyclopentadicyl manganese is also used as anti-knock but manganese is also harmful. Organic compounds like methanol, ethanol, methyl *t-butylether, etc. are also* inserted as anti-knocking agent blended with gasoline. Aviation gasoline has octane number even more than 100. The fuel marked 100 + 2 means a mixture of isooctane (100 ml) + TEL (2 ml).

Cetane Number or Rating

- The knocking characteristics of diesel oils are usually expressed in terms of cetane number. It is a measure of ignition lag or delay of the fuel. It is the time period between the start of ignition and start of combustion of the fuel. For the determination of cetane number, *n-hexadecane and a-methyl naphthalene are taken as* standard. (C16H34) *n-hexadecane is a saturated hydrocarbon having a short ignition lag as compared to any* commercial diesel fuel. Its cetane number is 100. It ignites below compression temperature. α-Methyl naphthalene has a very long ignition lag as compared to any commercial diesel oil. Its cetane number is taken as zero.

$CH_3—(CH_2)_{14}—CH_3$

n-hexadecane (cetane)



α-methylnapthalene

- In diesel engine, fuel is exploded not by spark but by temperature and pressure. The suitablity of diesel fuel is determined by its cetane number.
- Cetane number is the percentage of n-hexadecane in n-hexadecane and α-methyl naphthalene which has the same ignition characteristics as that of the sample under test. Cetane number 60 means, it has the same ignition characteristics as that of 60 parts of cetane and 40 parts of α-methyl naphthalene. The order of cetane number for the following is given as

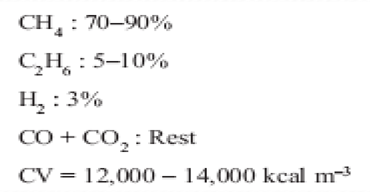
  n-alkanes > napthalenes > alkenes > branched alkanes > aromatics
- Thus, it is inferred that the hydrocarbons which are poor gasoline fuels are good diesel fuels. Alkyl and nitrites and di-tertiary peroxides are used as additives to increase the cetane number of fuel. They are called pre-ignition dopes.

Gaseous Fuels

- Natural gas is the primary gaseous fuel. A variety of secondary fuels are obtained from coal or petroleum. They include coal gas, producer gas, water gas derived from coal, and LPG, CNG derived from natural gas and oil gas formed by cracking of kerosene oil.

Natural Gas

- Natural gas is primarily methane gas. It is a fossil fuel. It is formed in coal beds (coal bed methane). Other sources are town gas and biogas. The main source of natural gas is oil fields, and the gas is called associated natural gas. (The gas formed in natural gas field is called associated gas.) Also, natural gas formed with petroleum and diesels is called wet gas and that formed with crude ore is called dry gas. The calorific value of wet gas is higher than the dry gas because of higher percentage of heavy unsaturated molecules. Composition of natural gas:



CH_4 : 70–90%

C_2H_6 : 5–10%

H_2 : 3%

$CO + CO_2$: Rest

$CV = 12{,}000 – 14{,}000$ kcal m^{-3}

- Natural gas contains ethane, propane, butane and pentane alongwith main component methane Before the use of natural gas, other heavier hydrocarbon, CO 2, N2, He, and H2O are removed. Commercially natural gas is produced from oil fields and natural gas fields. The gas obtained from oil wells is also called casing head gas. Town gas is a mixture of city and other gases mainly CO. It is used similar to the natural gas. The gas is used for cooking and lighting purposes. The waste product coaltar is used for road making. Biogas is also methane-rich and widely used as domestic fuel.
- The approximate composition of natural gas is

$$CH_4 = 70–90\%,\ C_2H_6 = 5–10\%,\ H_2 = 3\%,\ CO + CO_2 = 0.7\%.$$

- The calorific value of natural gas is 12000 to 14000 kcal/m^3. Sometimes harmful H_2S gas flows in traces which can be removed by 2-amino ethanol

- Natural gas has several applications:
- 1. It is used as a very good domestic fuel.
- 2. It is used in the preparation of ammonia (used for urea manufacturing).
- 3. It is used to prepare carbon-black which is used as filler for rubber industry.
- 4. It is used to prepare synthetic proteins for animal feed. (Methane on fermentation gives synthetic proteins used as animal feed.) Natural gas is being sent to thousands of kilometres through pipes.

❖ LPG (liquified Petroleum Gas)

- Nowadays LPG has been a common fuel for domestic work and also in most of the industries. The main components of LPG or cooking gas are *n-butane, isobutane, butylene and propane (traces of propene and ethane).*
- The hydrocarbon are in gaseous state at room temperature and at atmospheric pressure but can be liquified under higher pressures (Fig. 6.13A). The gas can be compressed under pressure in containers and sold under trade names like Indane, Bharat Petroleum gas, HP gas, etc.
- LPG is kept in metallic cylinder attached with burner through pipe. It has two stoppers, one at the cylinder and other at burner. LPG has special odour due to the presence of organic sulphides which are added specially for safety measure. The gas can be compressed under pressure in containers and sold under trade names like Indane, Bharat Petroleum gas, H. P. gas etc. The gas is obtained from natural gas or as a byproduct in refineries during cracking of heavy petroleum products.

- *Characteristics of LPG*
- 1. It has high calorific value: 27800 kcal/m3.
- 2. It gives less CO and least unburnt hydrocarbons. So it causes least pollution.
- 3. It gives moderate heat which is very good for cooking.
- 4. Its storage is simple. It is colourless.
- 5. It has the tendency to mix with air easily.
- 6. Its burning gives no toxic gases though it is highly toxic.
- 7. It neither gives smoke nor ash content.
- 8. It is cheaper than gasoline. It burns with little air pollution and leaves no solid residue. Hence, it is used as fuel in auto vehicles also.
- 9. It is dangerous when leakage is there. It is highly knock resistant.
- 10. LPG can be extracted from natural gases and also from refining of crude oil. Cryogenic process is best for the extraction for natural gas.
- *Advantages of LPG*
- 1. LPG is used as domestic fuel and as a fuel for internal combustion engines.
- 2. It is used as feedstock for the manufacture of various chemicals and olefins by pyrolysis.
- 3. LPG in used in industries as portable blow lamps, welding, annealing, hardening, steel cutting, etc.
- *Disadvantages*
- 1. It is difficult to handle as fuel.
- 2. Engines working at low compression ratio cannot use LPG as fuel.

CNG (Compressed Natural Gas)

- Natural gas contains mainly CH_4. When natural gas is compressed at high pressure (1000 atm) or cooled to –160°C, it is converted into CNG. It is stored in cylinder made of steel (Fig. 6.13B). It is now replacing gasoline as it releases less pollutants during its combustion. It is environmentally clean alternative to those fuels which produce toxic pollutants. In some of the metro cities, CNG-vehicles are used to reduce pollution. LNG (liquified natural gas) is different from CNG. LNG is costlier than CNG.

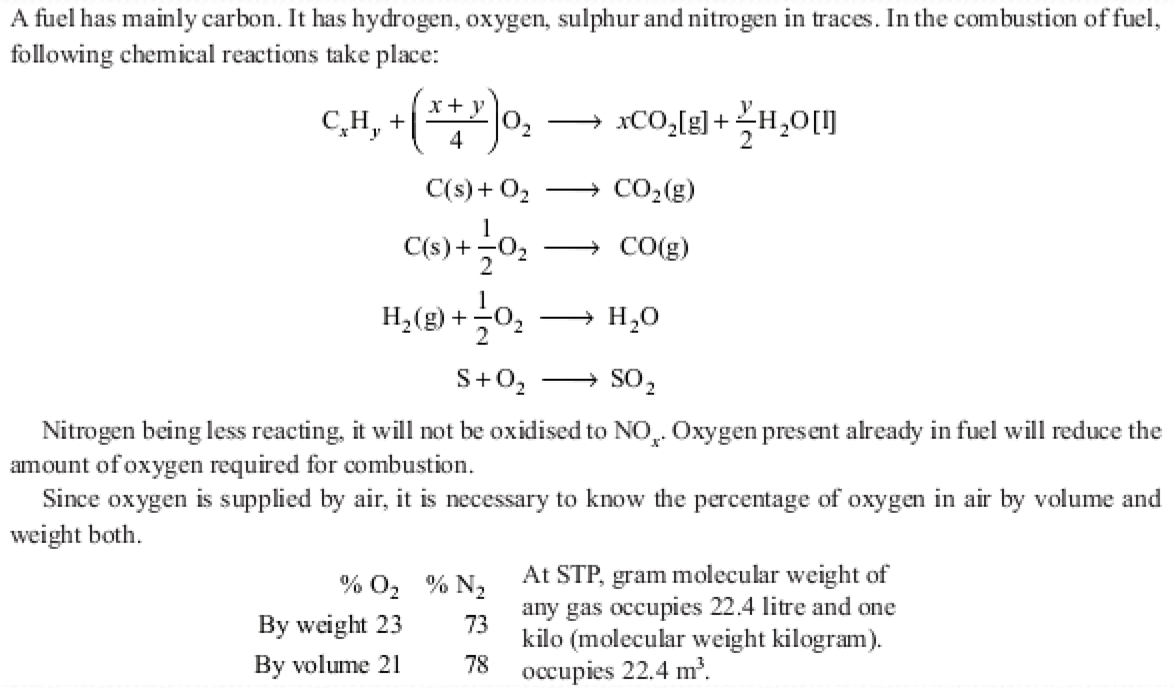
Advantages of CNG

- 1. Due to higher temperature of ignition, CNG is better fuel than petrol and diesel.
- 2. Operating cost of CNG is less. Cost of production is less. It can be easily stored.
- 3. It releases least pollutants like CO and unburnt hydrocarbons.
- 4. Spark plug of CNG-engines are not carbonified.
- 5. It undergoes regular combustion.

Disadvantages

- 1. Response to blending is poor.
- 2. Faint odour; leakage cannot be detected easily.
- 3. CNG tanks require a large tank space.
- 4. Refueling network for CNG is very expensive.

Combustion Problems



A fuel has mainly carbon. It has hydrogen, oxygen, sulphur and nitrogen in traces. In the combustion of fuel, following chemical reactions take place:

$$C_xH_y + \left(\frac{x+y}{4}\right)O_2 \longrightarrow xCO_2[g] + \frac{y}{2}H_2O[l]$$

$$C(s) + O_2 \longrightarrow CO_2(g)$$

$$C(s) + \frac{1}{2}O_2 \longrightarrow CO(g)$$

$$H_2(g) + \frac{1}{2}O_2 \longrightarrow H_2O$$

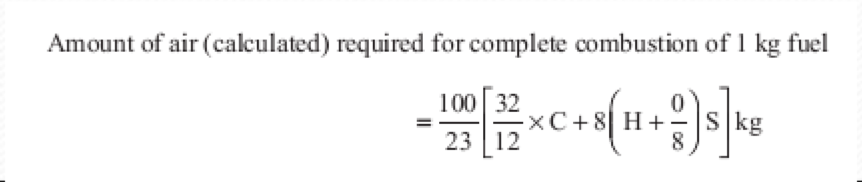
$$S + O_2 \longrightarrow SO_2$$

Nitrogen being less reacting, it will not be oxidised to NO_x. Oxygen present already in fuel will reduce the amount of oxygen required for combustion.

Since oxygen is supplied by air, it is necessary to know the percentage of oxygen in air by volume and weight both.

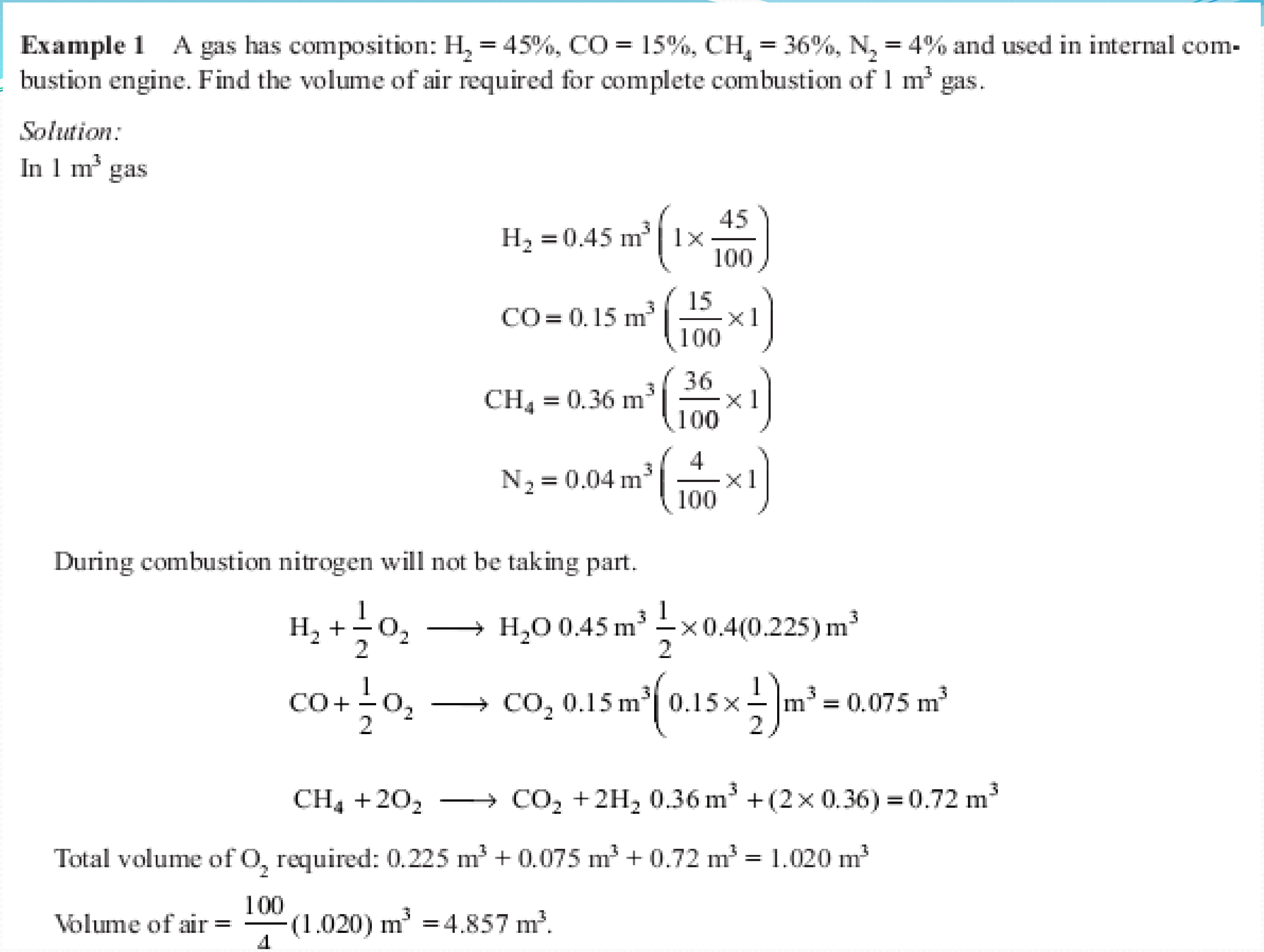
	% O_2	% N_2
By weight	23	73
By volume	21	78

At STP, gram molecular weight of any gas occupies 22.4 litre and one kilo (molecular weight kilogram). occupies 22.4 m^3.



Amount of air (calculated) required for complete combustion of 1 kg fuel

$$= \frac{100}{23}\left[\frac{32}{12}\times C + 8\left(H + \frac{0}{8}\right)S\right] \text{kg}$$



Example 1 A gas has composition: H_2 = 45%, CO = 15%, CH_4 = 36%, N_2 = 4% and used in internal combustion engine. Find the volume of air required for complete combustion of 1 m^3 gas.

Solution:

In 1 m^3 gas

$$H_2 = 0.45\ m^3 \left(1 \times \frac{45}{100}\right)$$

$$CO = 0.15\ m^3 \left(\frac{15}{100} \times 1\right)$$

$$CH_4 = 0.36\ m^3 \left(\frac{36}{100} \times 1\right)$$

$$N_2 = 0.04\ m^3 \left(\frac{4}{100} \times 1\right)$$

During combustion nitrogen will not be taking part.

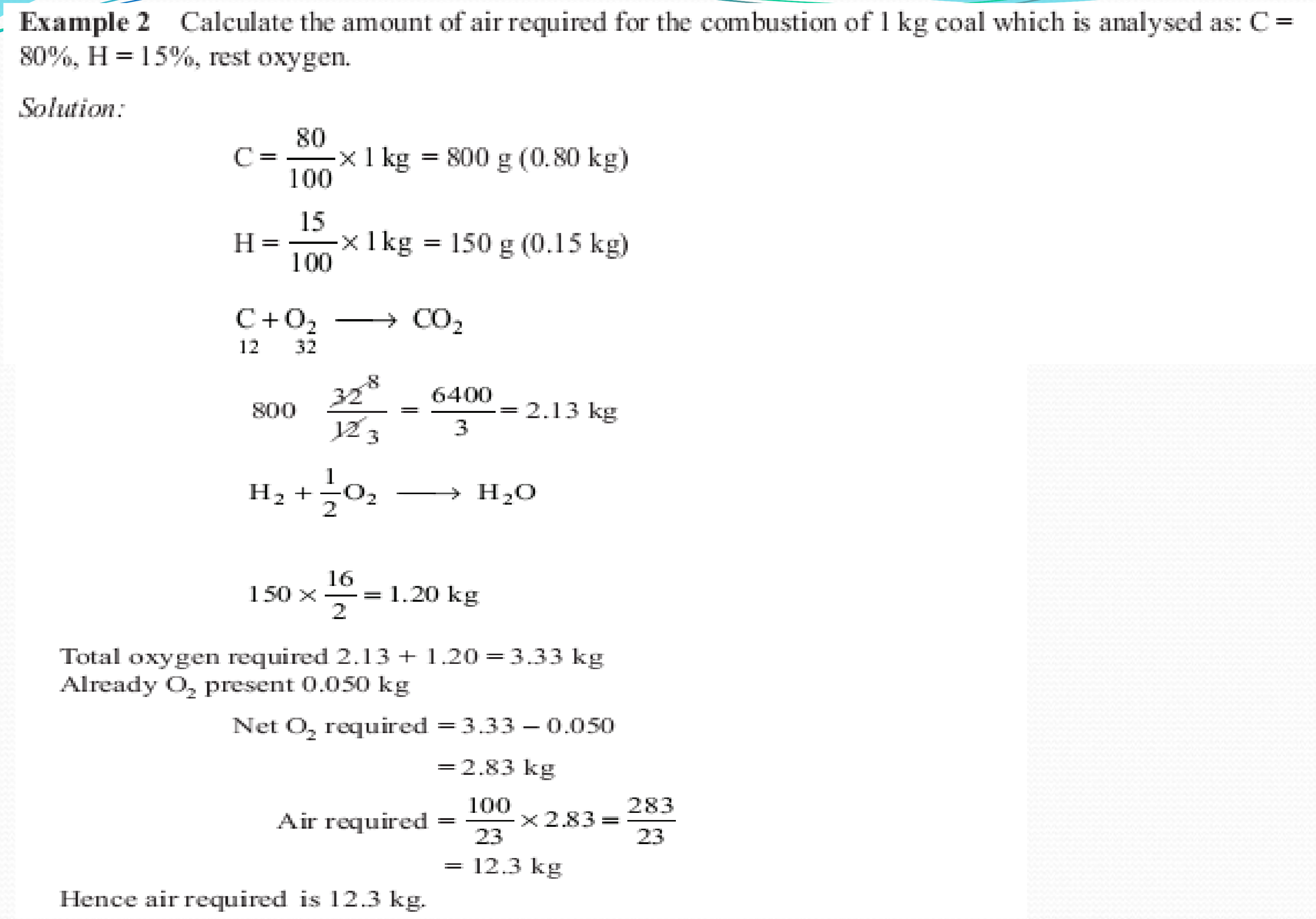
$$H_2 + \frac{1}{2} O_2 \longrightarrow H_2O\ 0.45\ m^3\ \frac{1}{2} \times 0.4(0.225)\ m^3$$

$$CO + \frac{1}{2} O_2 \longrightarrow CO_2\ 0.15\ m^3 \left(0.15 \times \frac{1}{2}\right) m^3 = 0.075\ m^3$$

$$CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2\ 0.36\ m^3 + (2 \times 0.36) = 0.72\ m^3$$

Total volume of O_2 required: 0.225 m^3 + 0.075 m^3 + 0.72 m^3 = 1.020 m^3

Volume of air = $\frac{100}{4}(1.020)\ m^3 = 4.857\ m^3$.



Example 2 Calculate the amount of air required for the combustion of 1 kg coal which is analysed as: C = 80%, H = 15%, rest oxygen.

Solution:

$$C = \frac{80}{100} \times 1\ \text{kg} = 800\ \text{g}\ (0.80\ \text{kg})$$

$$H = \frac{15}{100} \times 1\ \text{kg} = 150\ \text{g}\ (0.15\ \text{kg})$$

$$\underset{12}{C} + \underset{32}{O_2} \longrightarrow CO_2$$

$$800 \quad \frac{\cancel{32}^{8}}{\cancel{12}_{3}} = \frac{6400}{3} = 2.13\ \text{kg}$$

$$H_2 + \frac{1}{2}O_2 \longrightarrow H_2O$$

$$150 \times \frac{16}{2} = 1.20\ \text{kg}$$

Total oxygen required 2.13 + 1.20 = 3.33 kg

Already O_2 present 0.050 kg

$$\text{Net } O_2 \text{ required} = 3.33 - 0.050$$
$$= 2.83\ \text{kg}$$

$$\text{Air required} = \frac{100}{23} \times 2.83 = \frac{283}{23}$$
$$= 12.3\ \text{kg}$$

Hence air required is 12.3 kg.

Example 3 A gas was analysed and result by volume is: $H_2 = 19.4\%$, $CO = 20.5\%$, $N_2 = 50\%$, $CH_4 = 4.2\%$, $CO_2 = 6.0\%$. Calculate the dry product obtained, assuming 30% excess air is supplied for complete combustion of 1 m^3 gas.

Solutions:

(i) $H_2 = \frac{19.4}{100} \times 1 = 0.194\ m^3$,

(ii) $CO = \frac{20.5}{100} \times 1 = 0.205\ m^3$,

(iii) $CH_4 = \frac{4.2}{100} \times 1 = 0.042\ m^3$,

(iv) $CO_2 = \frac{6}{100} \times 1 = 0.06\ m^3$.

Volume of air required for combustion 1 m^3

$$= \frac{100}{21} \times (\text{Volume of oxygen for combustion})$$

(i) $H_2 + \frac{1}{2} O_2 \longrightarrow H_2O$

$(0.194) \times \frac{1}{2} = 0.097\ m^3$ (volume of O_2)

(ii) $CO + \frac{1}{2} O_2 \longrightarrow CO_2$

$\left(0.205 \times \frac{1}{2}\right) = 0.10253\ m^3$ (volume of O_2)

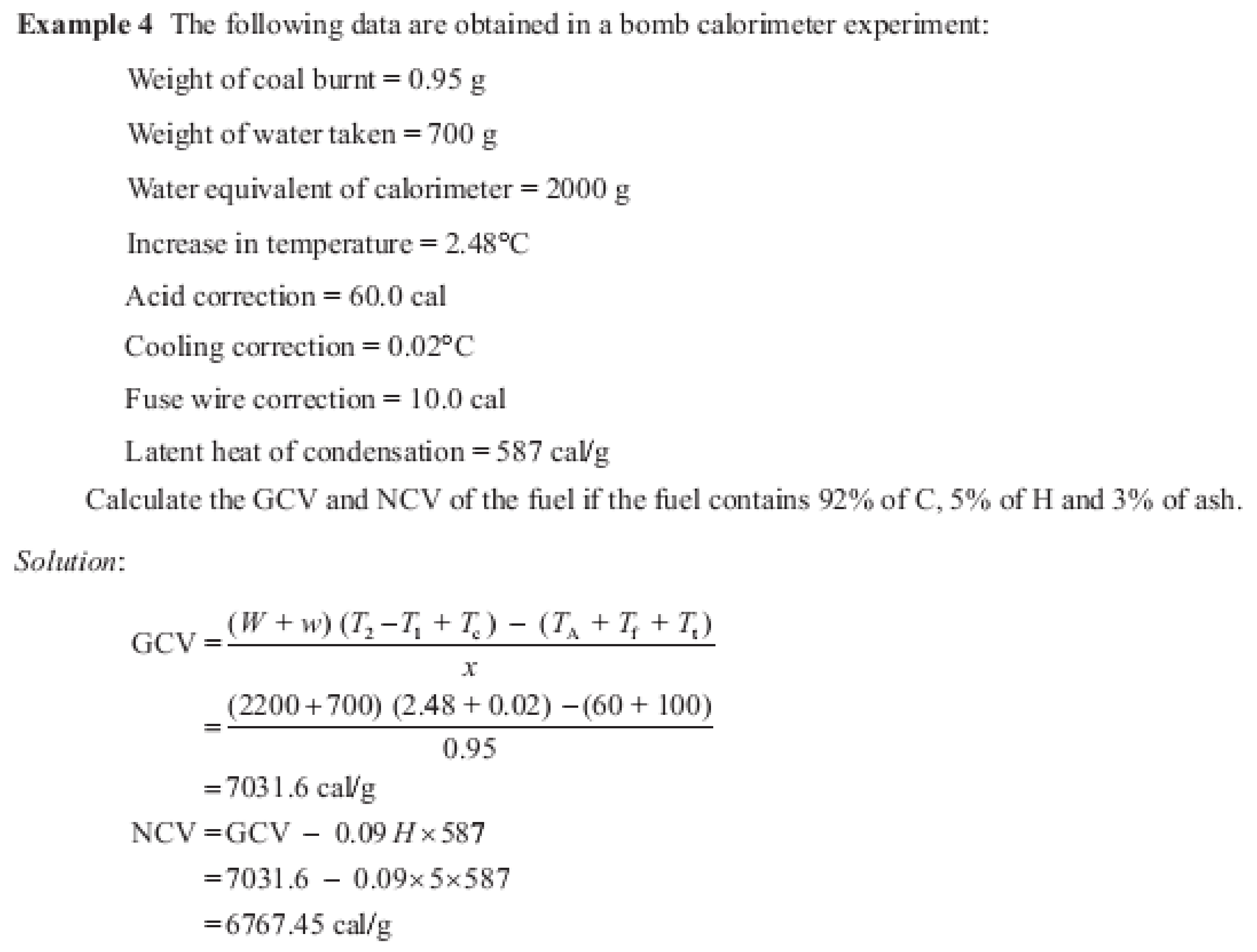
(iii) $CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O$

$(0.042 \times 2) = 0.084\ m^3$ (volume of O_2)

(iv) CO_2 will not require O_2.

Hence volume of O_2 required for (i), (ii) and (iii) $= (0.097 + 0.1025 + 0.084)\ m^3$
$= 0.2835\ m^3$

$$\text{Volume of air} = \frac{100}{21}(0.2835) = \frac{28.35}{21}\ m^3$$
$$= 1.35\ m^3$$



Example 4 The following data are obtained in a bomb calorimeter experiment:

Weight of coal burnt = 0.95 g

Weight of water taken = 700 g

Water equivalent of calorimeter = 2000 g

Increase in temperature = 2.48°C

Acid correction = 60.0 cal

Cooling correction = 0.02°C

Fuse wire correction = 10.0 cal

Latent heat of condensation = 587 cal/g

Calculate the GCV and NCV of the fuel if the fuel contains 92% of C, 5% of H and 3% of ash.

Solution:

$$\text{GCV} = \frac{(W + w)\,(T_2 - T_1 + T_c) - (T_A + T_f + T_t)}{x}$$

$$= \frac{(2200 + 700)\;(2.48 + 0.02) - (60 + 100)}{0.95}$$

$$= 7031.6 \text{ cal/g}$$

$$\text{NCV} = \text{GCV} - 0.09\,H \times 587$$

$$= 7031.6 - 0.09 \times 5 \times 587$$

$$= 6767.45 \text{ cal/g}$$

Theoretical Questions

- 1. Define fuel. What are the characteristics of a good fuel?
- 2. What is meant by calorific value of fuel? Explain the method of determination of calorific value of liquid and gaseous fuels.
- 3. How do you analyse coal by (a) proximate and (b) ultimate analysis? Give their significance.
- 4. What is octane number?
- 5. Explain Fischer–Tropsch's and Bergius methods for the synthesis of petrol.
- 6. What are the advantages of gaseous fuels?
- 7. How do you analyse flue gas by Orsat's methods?
- 8. Why tetraethyl lead is mixed with gasoline?
- 9. Write notes on LPG, CNG and biogas.
- 10. Give an account of the advantages and disadvantages of solid fuels over gaseous fuels.
- 11. What is LCV and HCV of fuel? Describe Junker's method for the determination of calorific value of gaseous fuels.
- 12. Give an account of the classification of the fuels with suitable examples.
- 13. Define octone number of gasoline. What is its significance and how is it measured? Why is ethylene dibromide added when TEL is used as an antiknock reagent?
- 14. What is biodiesel? How is it obtained? What are its advantages?
- 15. What is petroleum? How is it refined? What are the fractions obtained and their uses?
- 16. What is cracking? How gasoline is obtained from fixed bed cetelytic cracking

- **Multiple-Choice Questions**
- 1. A good fuel should possess
  (a) high ignition temperature (b) moderate ignition temperature (c) high calorific value (d) both (b) and (c)
- 2. Ignition temperature of a fuel is the
  (a) temperature at which the fuel ignites for a moment but does not burn after heat.
  (b) temperature attained when the fuel is burnt.
  (c) lowest temperature at which the fuel must be pre-heated so that it starts burning smoothly.
  (d) temperature at which the fuel can be stored safely.
- 3. An example of a secondary fuel is
  (a) wood (b) coal (c) natural gas (d) gobar gas
- 4. Purest form of coal is
  (a) lignite (b) bituminous (c) peat (d) anthracite
- 5. Gobar gas contains
  (a) CO_2 (b) H_2 (c) CH_4 (d) all of these
- 6. Biogas contains
  (a) CO_2 (b) CH_4 (c) C_2H_4 (d) C_2H_2
- 7. Power alcohol is an example of
  (a) liquid fuel (b) artificial fuel (c) secondary fuel (d) all of these
- 8. Gross calorific value is also known as
  (a) high calorific value (b) low calorific value (c) net calorific value (d) none
- 9. The correct relationship between HCV and LCV is
  (a) $LCV = HCV + 0.9\ HL$ (b) $LCV = HCV - 0.09\ HL$ (c) $HCV = LCV - 0.09\ HL$ (d) $HCV = LCV + 0.9\ HL$
- 10. The most impure form of coal is
  (a) anthracite (b) peat (c) wood (d) lignite

- 11. One kilogram of cattle dung produces biogas which gives

  (a) 1000 kJ of heat (b) 10 kJ of heat (c) 800 kJ of heat (d) 500 kJ of heat
- 12. Bomb calorimeter is used for the determination of calorific value of

  (a) solid fuel (b) liquid fuel (c) gaseous fuel (d) both (a) and (b)

  (e) both (b) and (c)
- 13. The fuel which has the highest calorific value is

  (a) wood (b) petrol (c) methane (d) hydrogen
- 14. The optimum temperature for fermentation in biogas plant is

  (a) 10–20°C (b) 25–35°C (c) 35–50°C (d) 55–75°C
- 15. The calorific value of biogas is

  (a) 1500 kcal/m3 (b) 2500 kcal/m3 (c) 5300 kcal/m3 (d) 43 kcal/m3

- 16. The other name of biogas is
  (a) producer gas (b) gobar gas (c) natural gas (d) none
- 17. The highest ranking coal is
  (a) lignite (b) peat (c) anthracite (d) bituminous
- 18. Natural fuel among the following is
  (a) oil gas (b) coke (c) petrol (d) coal
- 19. Major constituent of LPG is
  (a) methane (b) ethane (c) benzene (d) butane
- 20. The calorific value of a fuel is expressed as
  (a) kcal/m (b) kcal/kg (c) cal/cm3 (d) kcal/g
- 21. The calorific value of a fuel can be theoretically calculated by __________ formula.
  (a) Dulong's (b) Newton's (c) Avagadro's (d) Raman's
- 22. Compressed natural gas mainly contains
  (a) CO (b) N_2 (c) CH_4 (d) SO_2
- 23. The jet engine fuel is _____________.
  (a) kerosene (b) petrol (c) diesel (d) petroleum ether
- 24. Calorific value of diesel is
  (a) 11250 kcal/kg (b) 11000 kcal/kg (c) 11200 kcal/kg (d) 10000 kcal/kg
- 25. The greases used for lubrication can be obtained by fractionation of
  (a) diesel oil (b) kerosene oil (c) vegetable oil (d) heavy oil