2000

IARE

EDUCATION FOR LIBERATION

ENGINEERING CHEMISTRY

Course Code: AHSB03
Regulation: IARE-R18
B . TECH: I SEM
ENGINEERING CHEMISTRY

Institute of Aeronautical Engineering
Dundigal ,Hyderabad

MODULE - I

ELECTRO CHEMISTRY AND CORROSION

Introduction

- Electrochemistry is the branch of chemistry which deals with the transformation of electrical energy into chemical energy and vice versa.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.

Electro Chemistry

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) Electromotive → Electron + Motion

Conductors

- The substances which allow the passage of electric current are called conductors. Metals such as copper and silver are good conductors of electricity.
- Electrical conductors are of two types:

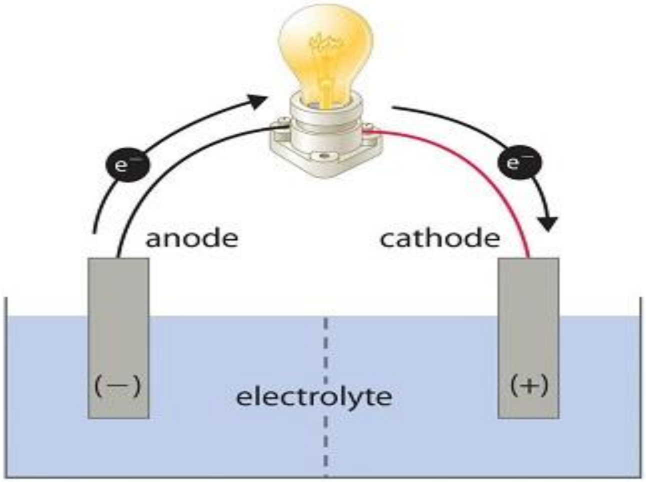
  1.Metallic conductors

  2. Electrolytic conductors.

Metallic And Electrolytic Conductors

Metallic conductors	Electrolytic conductors
1.Conductance is due to the flow of electrons. 2.It does not result any chemical change. 3.It does not involve any transfer of matter.	1. Conductance is due to the movement of ions in a solution. 2. Chemical reactions take place at the electrodes. 3. It involves transfer of matter.

Galvanic Cell And Electrolytic Cell



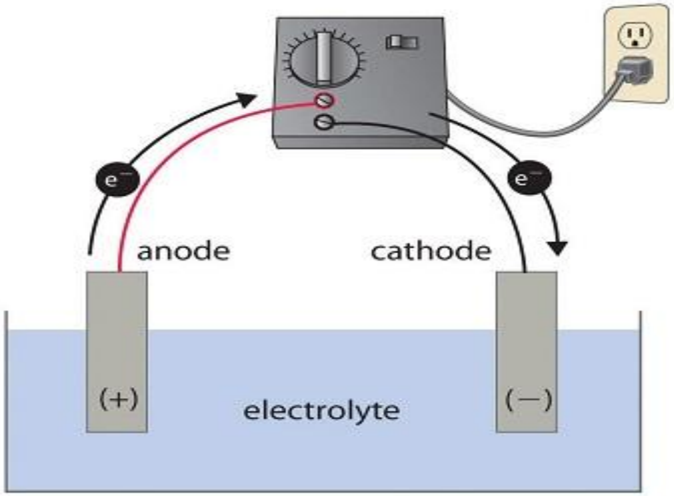
GALVANIC CELL

Energy released by spontaneous redox reaction is converted to electrical energy.

Oxidation half-reaction:
$Y \rightarrow Y^{+} + e^{-}$

Reduction half-reaction:
$Z^{+} + e^{-} \rightarrow Z$

Overall cell reaction:
$Y + Z \rightarrow Y^{+} + Z^{-}\ (G < 0)$



ELECTROLYTIC CELL

Electrical energy is used to drive nonspontaneous redox reaction.

Oxidation half-reaction:
$Z^{-} \rightarrow Z + e^{-}$

Reduction half-reaction:
$Y^{+} + e^{-} \rightarrow Y$

Overall cell reaction:
$Y^{+} + Z^{-} \rightarrow Y + Z\ (G > 0)$

Electrode Potential

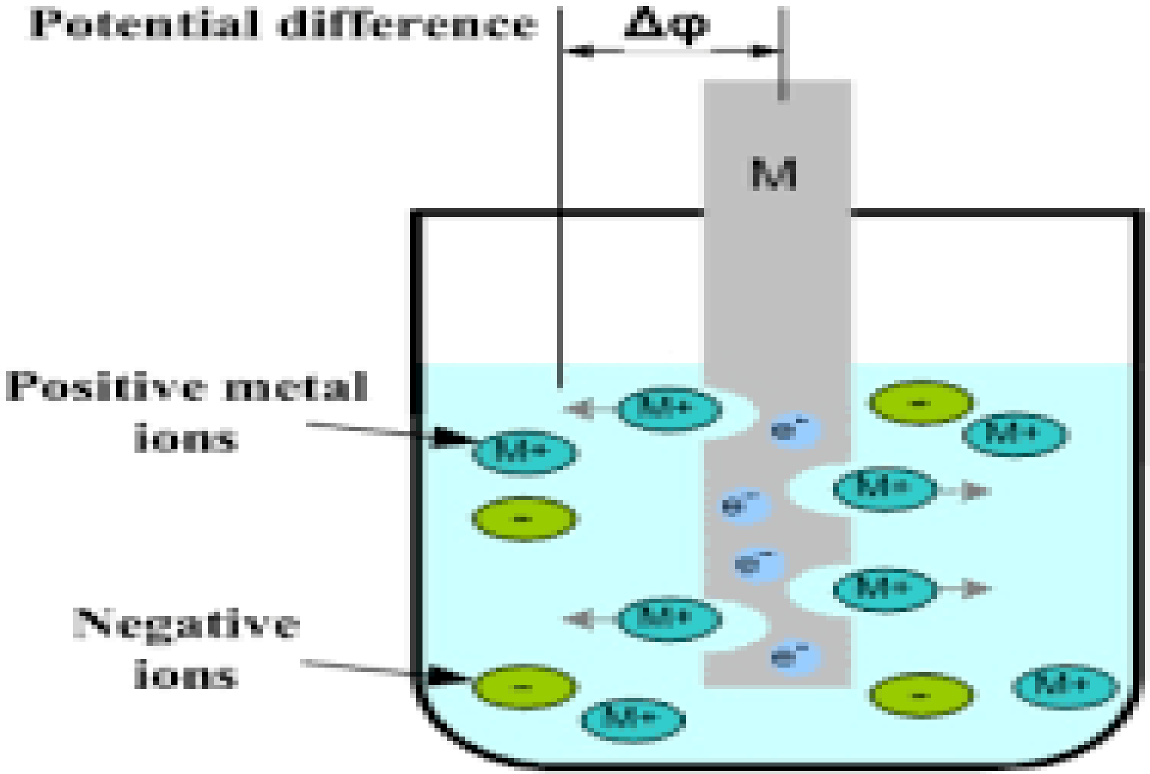
When a metal rod is dipped in its salt solution (electrolyte), the metal atom tends either to lose electrons (oxidation) or to accept electrons (reduction). The process of oxidation or reduction depends on the nature of metal. In this process, there develops a potential between the metal atom and its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

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

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

Electrode Potential

Single electrode cell (half-cell)



Electrode Potential

Electrode potential is the electric potential on an electrode component. In a cell, there is an electrode potential for the cathode and an electrode potential for the anode. The difference between the two electrode potentials equals the cell potential:

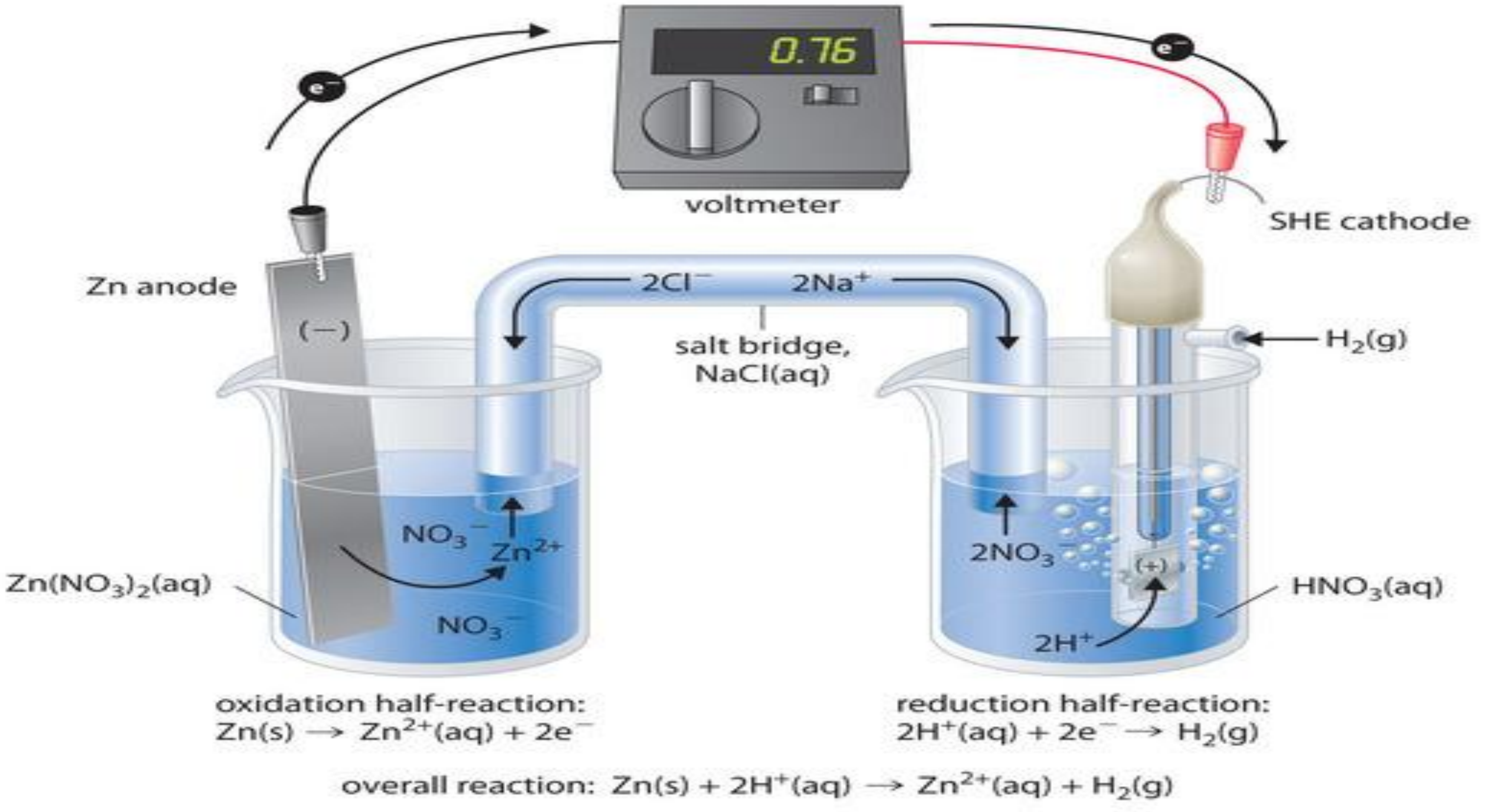
$$E_{\text{cell}} = E_{\text{cathode}} - E_{\text{anode}}$$

Standard Electrode Potential

The potential exhibited by single at unit concentration of its metal ion at 25^0C is called standard electrode potential (E^0)

Eg: E of Zn^{+2} / Zn = E^0 when concentration of Zn^{+2} is IM. E^0 value of single electrode is determined experimentally by combining the single electrode with standard hydrogen electrode.

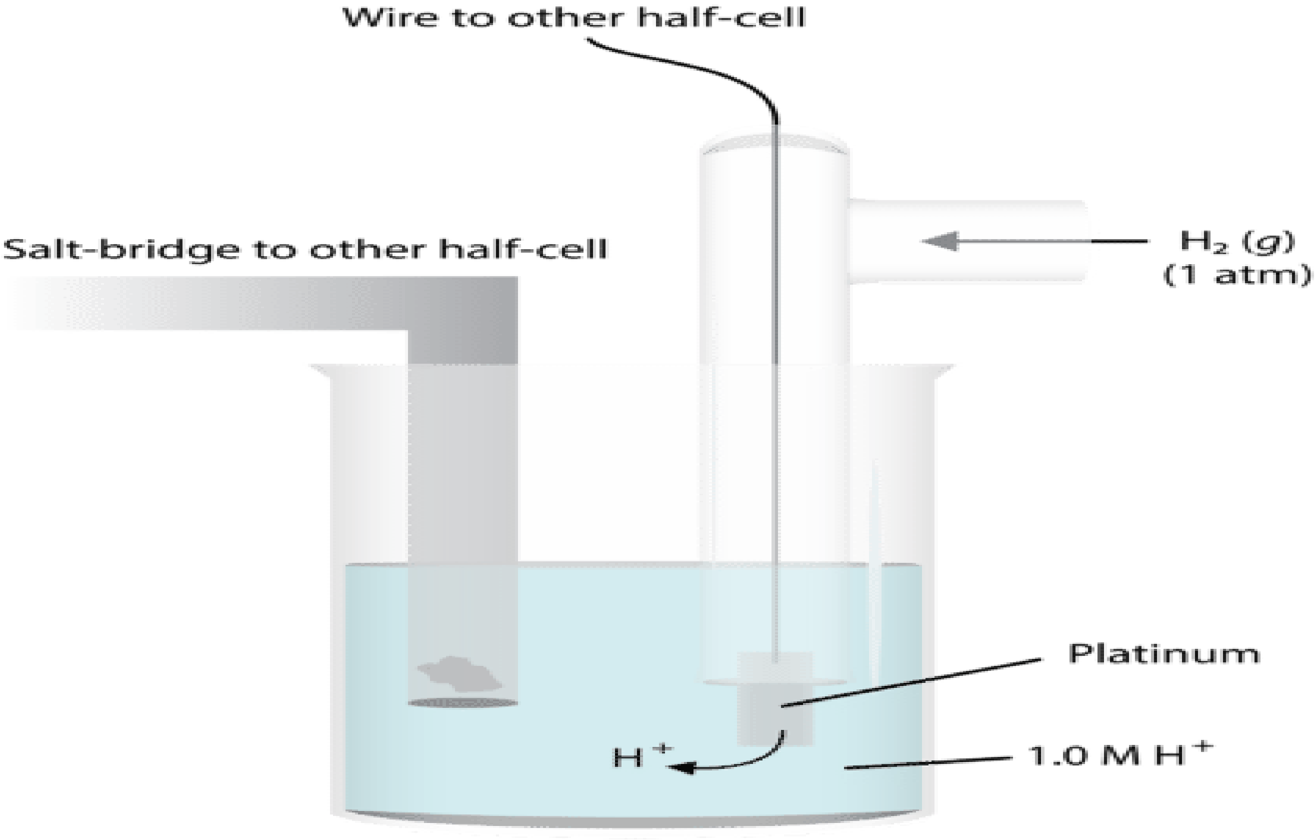
Electrode Potential



Standard 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.).

Standard Hydrogen Electrode



Electrochemical Series

The standard reduction potentials of a large number of electrodes have been measured using standard hydrogen electrode as the reference electrode. These various electrodes can be arranged in increasing or decreasing order of their reduction potentials. The arrangement of elements in order of increasing reduction potential values is called electrochemical series.

Electrochemical Series

i) The negative sign of standard reduction potential indicate that an electrode when joined with SHE acts as anode and oxidation occurs on this electrode.

For example, standard reduction potential of zinc is – 0.76 volt, When zinc electrode is joined with SHE, it acts as anode (–ve electrode)

i.e., oxidation occurs on this electrode. Similarly, the +ve sign of standard reduction potential indicates that the electrode when joined with SHE acts as cathode and reduction occurs on this electrode.

Electrochemical Series

i) The negative sign of standard reduction potential indicate that an electrode when joined with SHE acts as anode and oxidation occurs on this electrode.

For example, standard reduction potential of zinc is – 0.76 volt, When zinc electrode is joined with SHE, it acts as anode (–ve electrode)

i.e., oxidation occurs on this electrode. Similarly, the +ve sign of standard reduction potential indicates that the electrode when joined with SHE acts as cathode and reduction occurs on this electrode.

Electrochemical Series

ii) The substances, which are stronger reducing agents than hydrogen are placed above hydrogen in the series and have negative values of standard reduction potentials. All those substances which have positive values of reduction potentials and placed below hydrogen in the series are weaker reducing agents than hydrogen.

The substances, which are stronger oxidizing agents than H^+ ion are placed below hydrogen in the series.

Electrochemical Series

ii) The substances, which are stronger reducing agents than hydrogen are placed above hydrogen in the series and have negative values of standard reduction potentials. All those substances which have positive values of reduction potentials and placed below hydrogen in the series are weaker reducing agents than hydrogen.

The substances, which are stronger oxidizing agents than H^+ ion are placed below hydrogen in the series.

Electrochemical Series

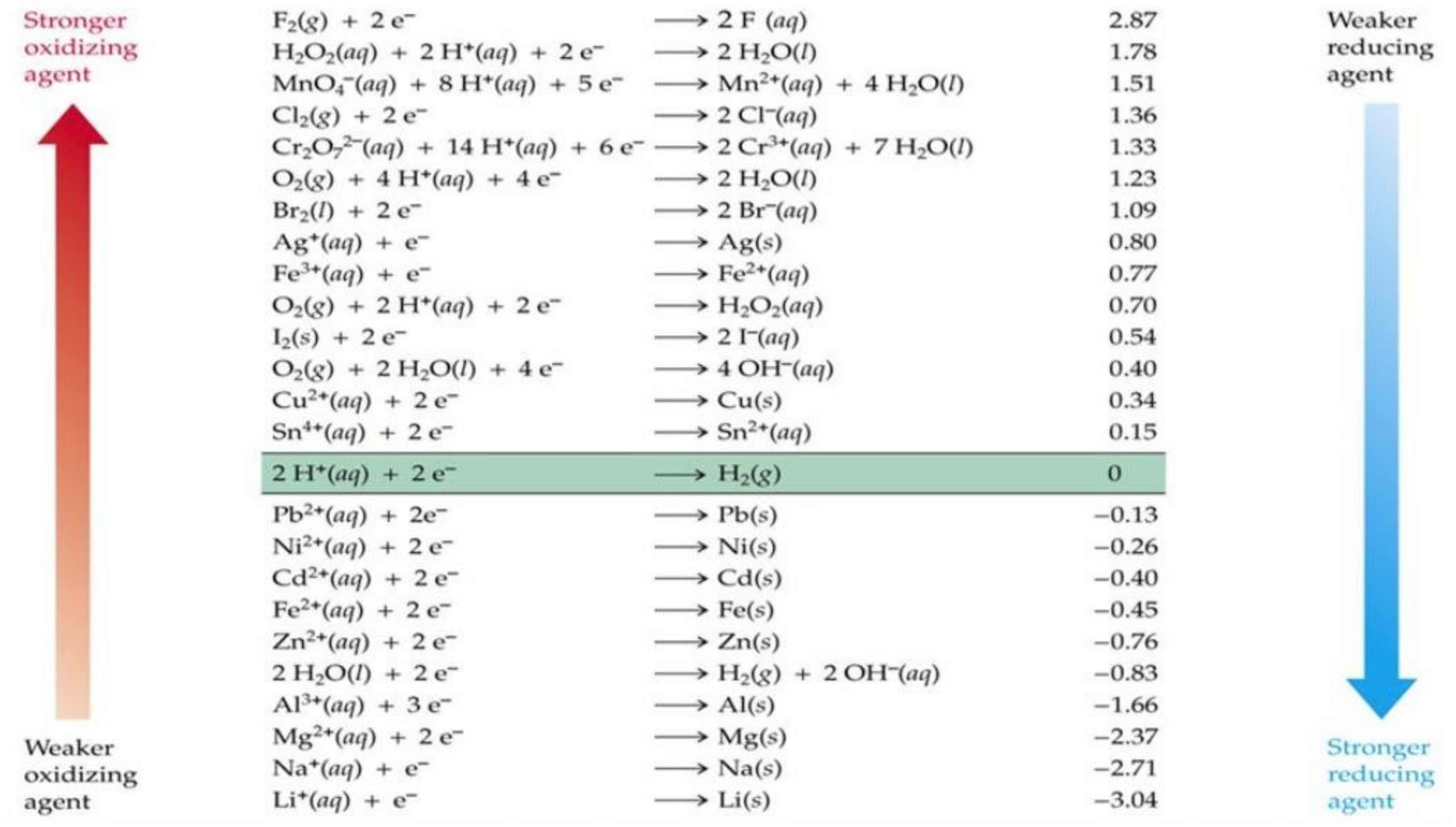
iii) The metals on the top (having high negative value of standard reduction potentials) have the tendency to lose electrons readily. These are active metals.

The activity of metals decreases from top to bottom.

The non-metals on the bottom (having high positive values of standard reduction potentials) have the tendency to accept electrons readily. These are active non-metals.

The activity of non-metals increases from top to bottom.

Electrochemical Series



Stronger oxidizing agent

Weaker reducing agent

$F_2(g) + 2e^-$	$\longrightarrow 2\,F\,(aq)$	2.87
$H_2O_2(aq) + 2H^+(aq) + 2e^-$	$\longrightarrow 2H_2O(l)$	1.78
$MnO_4^-(aq) + 8H^+(aq) + 5e^-$	$\longrightarrow Mn^{2+}(aq) + 4H_2O(l)$	1.51
$Cl_2(g) + 2e^-$	$\longrightarrow 2Cl^-(aq)$	1.36
$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^-$	$\longrightarrow 2Cr^{3+}(aq) + 7H_2O(l)$	1.33
$O_2(g) + 4H^+(aq) + 4e^-$	$\longrightarrow 2H_2O(l)$	1.23
$Br_2(l) + 2e^-$	$\longrightarrow 2Br^-(aq)$	1.09
$Ag^+(aq) + e^-$	$\longrightarrow Ag(s)$	0.80
$Fe^{3+}(aq) + e^-$	$\longrightarrow Fe^{2+}(aq)$	0.77
$O_2(g) + 2H^+(aq) + 2e^-$	$\longrightarrow H_2O_2(aq)$	0.70
$I_2(s) + 2e^-$	$\longrightarrow 2I^-(aq)$	0.54
$O_2(g) + 2H_2O(l) + 4e^-$	$\longrightarrow 4OH^-(aq)$	0.40
$Cu^{2+}(aq) + 2e^-$	$\longrightarrow Cu(s)$	0.34
$Sn^{4+}(aq) + 2e^-$	$\longrightarrow Sn^{2+}(aq)$	0.15
$2H^+(aq) + 2e^-$	$\longrightarrow H_2(g)$	0
$Pb^{2+}(aq) + 2e^-$	$\longrightarrow Pb(s)$	−0.13
$Ni^{2+}(aq) + 2e^-$	$\longrightarrow Ni(s)$	−0.26
$Cd^{2+}(aq) + 2e^-$	$\longrightarrow Cd(s)$	−0.40
$Fe^{2+}(aq) + 2e^-$	$\longrightarrow Fe(s)$	−0.45
$Zn^{2+}(aq) + 2e^-$	$\longrightarrow Zn(s)$	−0.76
$2H_2O(l) + 2e^-$	$\longrightarrow H_2(g) + 2OH^-(aq)$	−0.83
$Al^{3+}(aq) + 3e^-$	$\longrightarrow Al(s)$	−1.66
$Mg^{2+}(aq) + 2e^-$	$\longrightarrow Mg(s)$	−2.37
$Na^+(aq) + e^-$	$\longrightarrow Na(s)$	−2.71
$Li^+(aq) + e^-$	$\longrightarrow Li(s)$	−3.04

Weaker oxidizing agent

Stronger reducing agent

Electrochemical Series

(i) Reactivity of metals

(ii) Electropositive character of metals

(iii) Displacement reactions

(iv) Reducing power of metals

(v) Oxidizing nature of non-metals

(vii) Extraction of metals

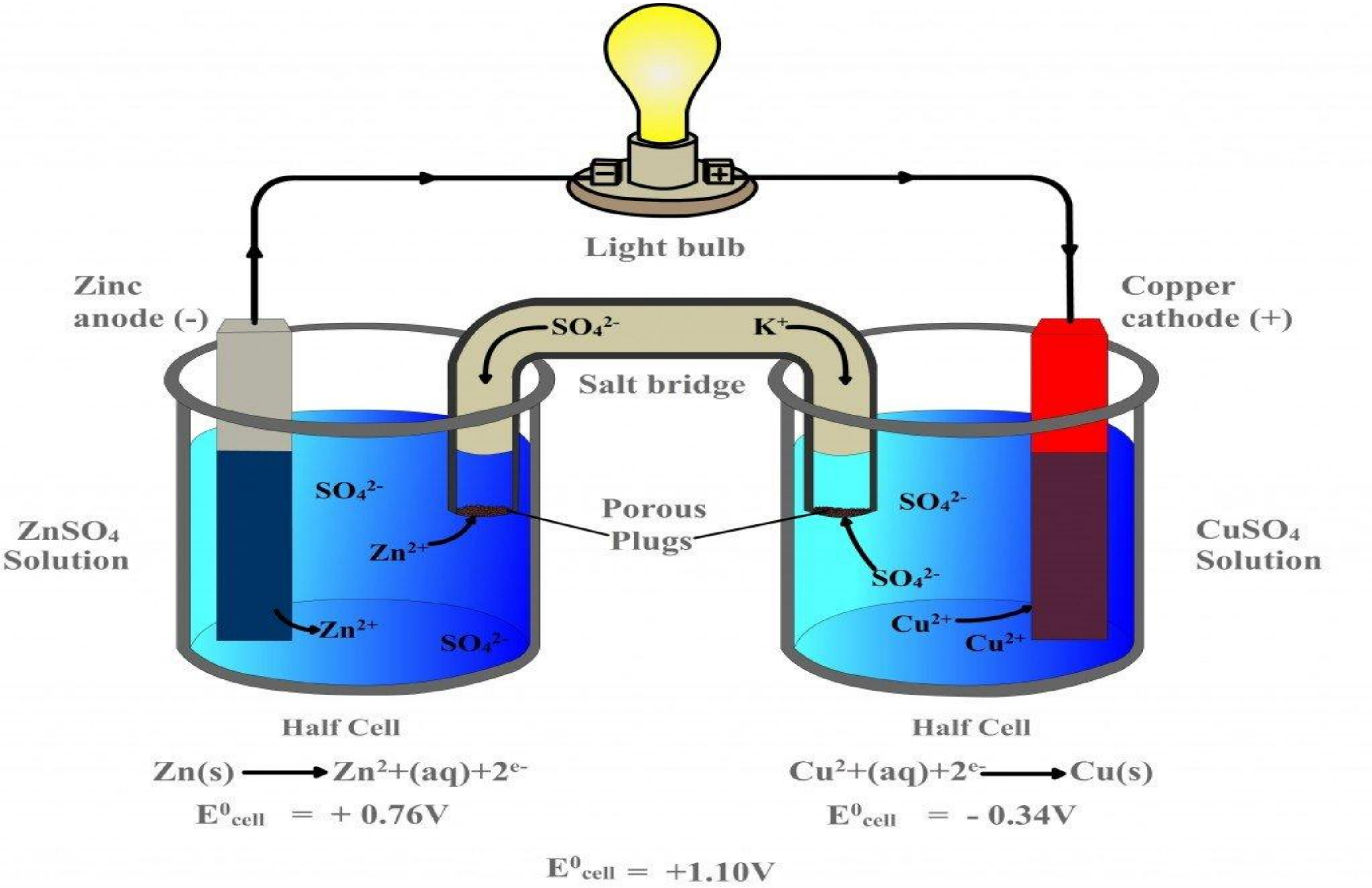
Galvanic Cell

- 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

Galvanic Cell

- The second half cell is made of copper electrode dipped in copper sulphate solution. Both half cells are connected externally by metallic conductor 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.

Galvanic Cell



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

$E^0_{cell} = +0.76V$

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

$E^0_{cell} = -0.34V$

$E^0_{cell} = +1.10V$

Nernst Equation

It tells us the effect of electrolyte concentration on electrode potential Consider a general electrode reaction

$Mn^{+} \ + \ ne^{-} \ \rightarrow \ M(s)$

For this electrode reaction ,free energy change (G) can be calculated provided standard free energy change (G^0)

Gas constant (R), temperature (T), activity of product and activity of reactant are known using the following equation.

$G = G^0 + RTl \ \ln ({}^{a}\text{product} / {}^{a}\text{reactant})$

Since $G = -nFE$ and $G^0 = -NFE^0$

Nernst Equation

Hence

$$E = E^0 - 2.303\ RT\ / nF\ \log\ ({}^{a}\text{product} / {}^{a}\text{reactant})$$

This is Nernst equation where

E = Electrode potential

E^0 = Standard electrode potential

F = faraday of electricity (96500 C)

T = temperature at 298k

R = Gas constant (8.314 k^{-1} mol^{-1})

a = activity

Nernst Equation

at 298k

- putting the value of F = faraday of electricity (96500 C) and R = Gas constant (8.314 k^{-1} mol^{-1}) we get

$$E = E^0 - 0.0591/n \quad \log ({}^{a}\text{product} / {}^{a}\text{reactant})$$

- In dilute solutions, activities may be replaced by molar concentrations terms,

$$E = E^0 - 0.0591 / n \quad \log ([M(s)] / [M^{n+}_{(aq)}])$$

- For pure solid ($[M(s)] = 1$

$$E = E^0 - 0.0591 / n \quad \log (1 / [M^{n+}_{(aq)}])$$

$$E = E^0 - 0.0591 / n \quad \log [M^{n+}_{(aq)}]$$

Nernst Equation

- The above equation is Nernst equation for the electrode at 298 k Nernst studied the theoretical relationship between electrode reaction and the corresponding cell e.m.f. This relationship generally Known as Nernst equation.

Consider a galvanic cell aA + bB cC +dD.

- Where a,b,c,d represents no. of moles respectively at equilibrium.

$$E = E^0 - 2.303\ RT\ /\ nF\ \log\ ([C]^c [D]^d / [A^a][B^b])$$

- Thus Nernst equation is applicable for the determination of Emf of cell

Similarly, for the cell reaction.

$$E = E^0 - 2.303\ RT\ /\ nF\ \log\ ([Zn^{+2}(1m) / Cu^{+2}(1m)])$$

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.

Standard Calomel Electrode

The calomel electrode consists of a glass tube having two side tubes. A small quantity of pure mercury is placed at the bottom of the vessel and is covered with a paste of Hg and Hg_2 Cl_2. KCl solution of known concentration is filled through side tube, Shown on the right side of the vessel. The KCl sol. is filled in the left side tube which helps to make a connection through a salt bridge with the other electrode, which potential has to be determined.

Standard Calomel Electrode

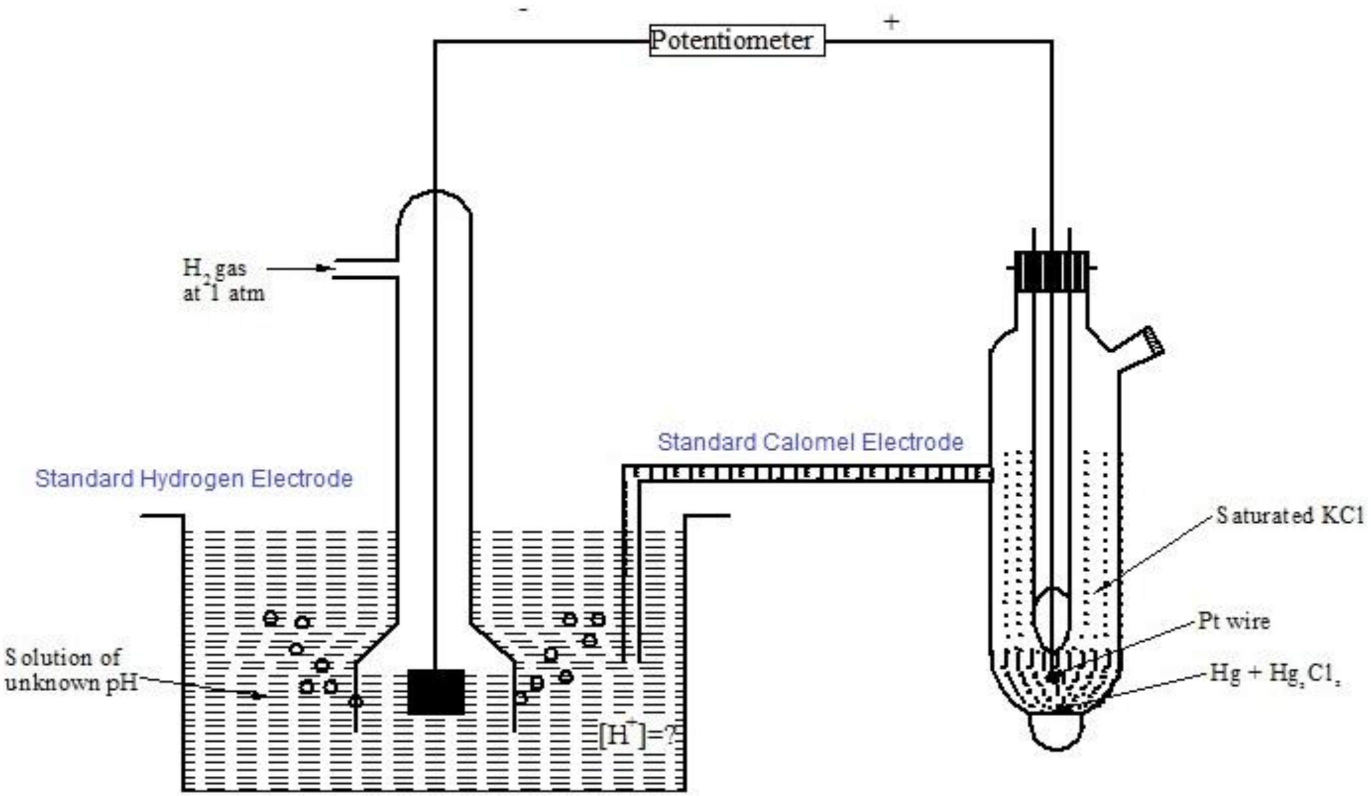
A ‘pt’ wire is sealed into a glass tube as shown in the fig which is in contact with Hg.

When the cell is set up it is immersed in the given solution. The concentration of KCl. The electrode potentials of calomel electrode of different concentrations at 25^0c are

0.1 M KCl/ Hg_2cl_2 (s) / Hg,pt 0.33v 1M KCl / H g_2cl_2 (s) / Hg,pt 0.28v Saturated kcl /Hg_2 cl_2 (s) /Hg, pt 0.24v The corresponding electrode reaction is

$Hg_2 Cl_2 + 2e^- \quad 2Hg + 2cl^-$

Standard Calomel Electrode

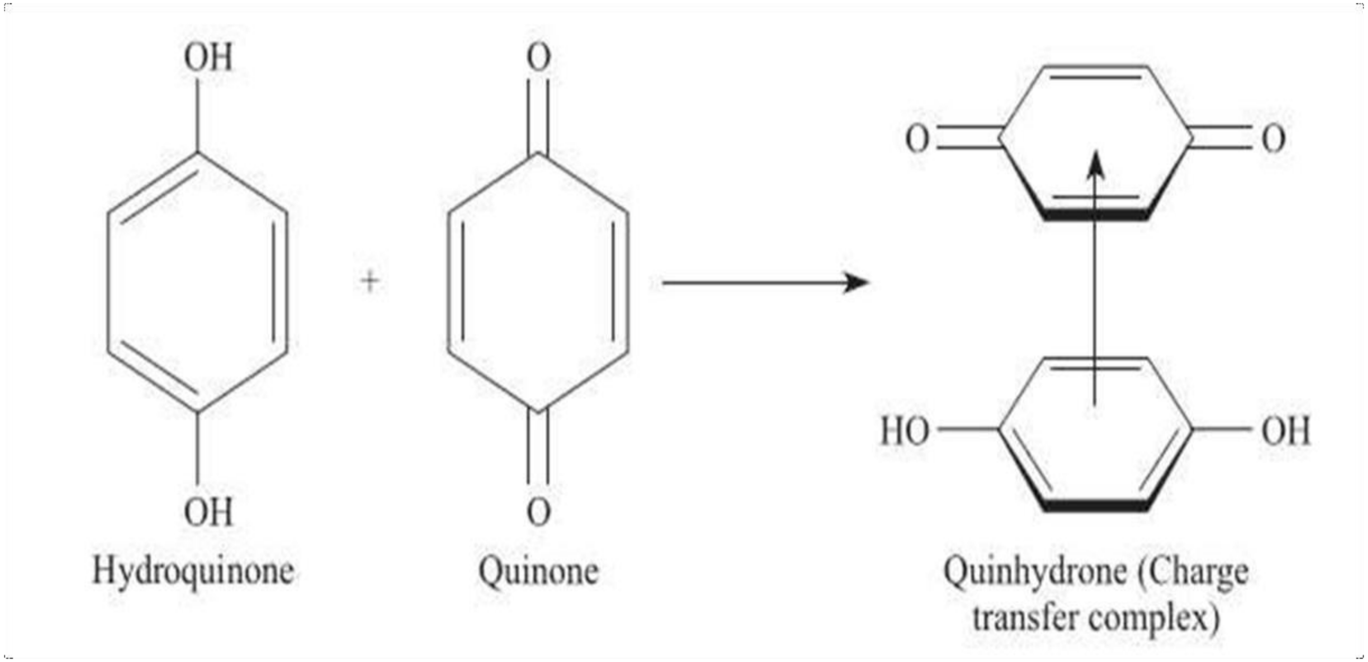


Finding Unknown pH USING Standard Calomel Electrode

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.

Quinhydrone Electrode



Batteries

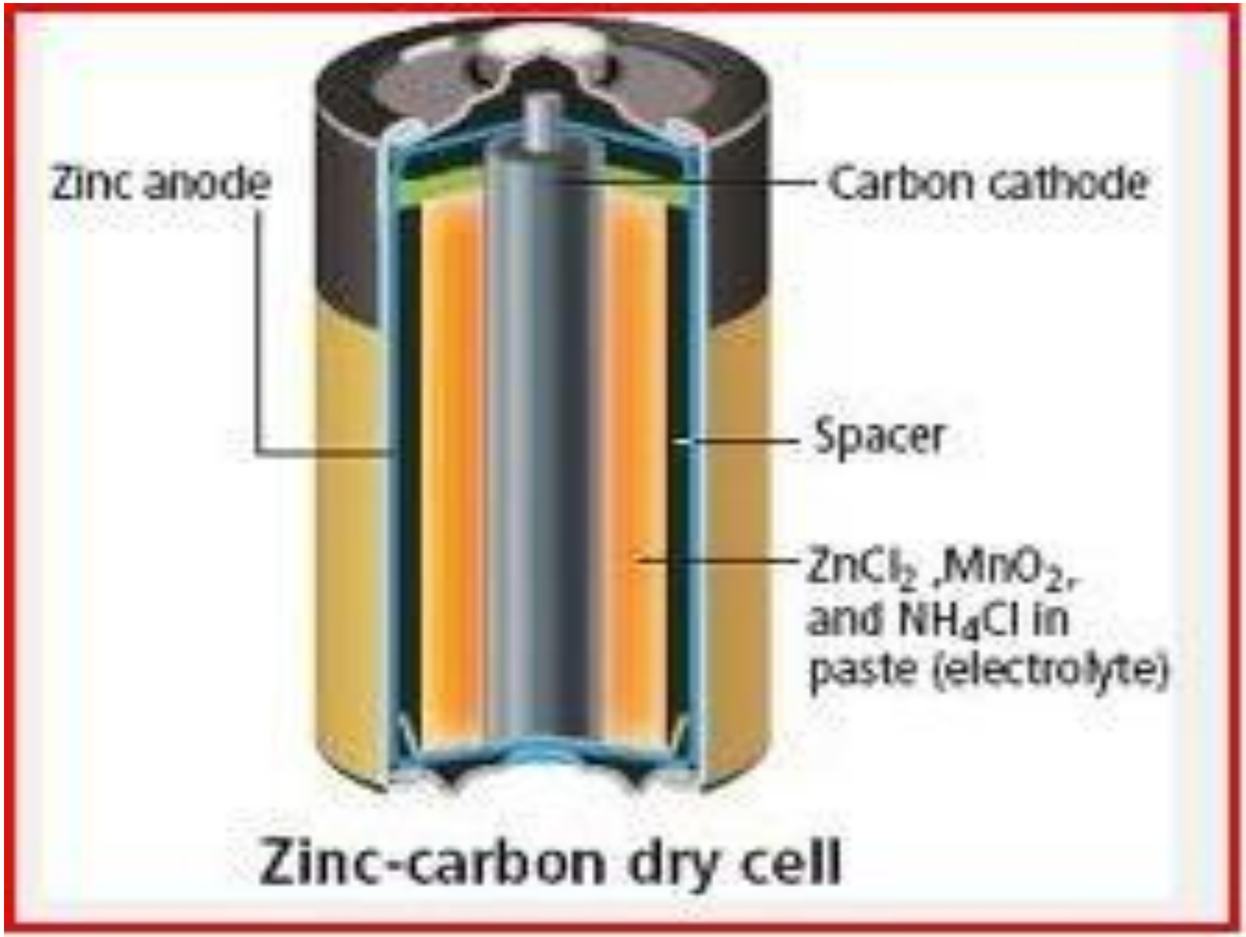
- When two or more electrochemical cells are electrically interconnected, each of which containing two electrodes and an electrolyte is called a Battery.
- Classification of batteries:
  - i) Primary batteries (or) primary cells
  - ii) Secondary batteries (or) secondary cells
  - iii) Flow batteries (or) Fuel 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.

- Examples of primary cells: Voltaic cells, Daniel cell, Leclanche cell, and lithium cell.

Primary Cell



Zinc-carbon dry cell

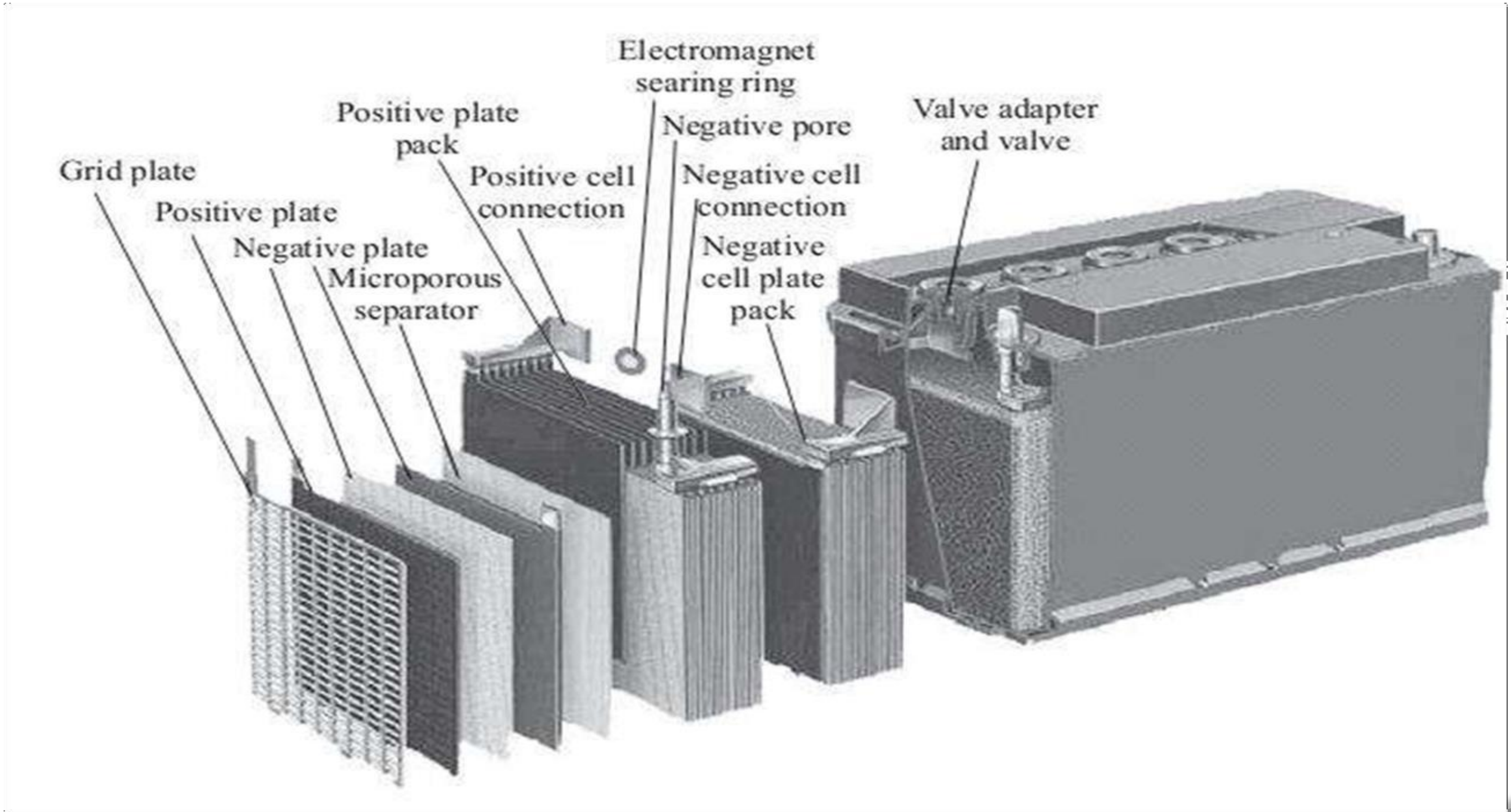
Secondary Cell

- 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,Lithium-ion cell battery

Secondary Cell

- 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. $H2SO4$(38%), which acts as an electrolyte. Hence, it is called lead-acid battery.

Secondary Cell



Secondary Cell

- 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 with 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. What is electrochemical series? Discuss its three important applications.
7. Describe the construction and working of a calomal electrode.
8. Describe the construction of a galvanic cell. Write down the electrode reactions and the formula for its EMF.
9. What are fuel cells? Explain the working of the hydrogen–oxygen fuel cell?

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.

Introduction

- 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

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.

Effect of corrosion

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:

O

What is an Ore?

Gold Ore — A rock with gold in it

Iron Ore — A rock with iron in it

Copper Ore — A rock with copper in it

A rock that contains enough metal or metal compounds so that it can be mined profitably

Effects 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.

Causes of corrosion

To understand the wet theory, let us take the example of corrosion of iron. Oxidation of metal takes placeat 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 type corrosion

(ii) Absorption of oxygen type corrosion

Dry Corrosion

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.

Dry Corrosion

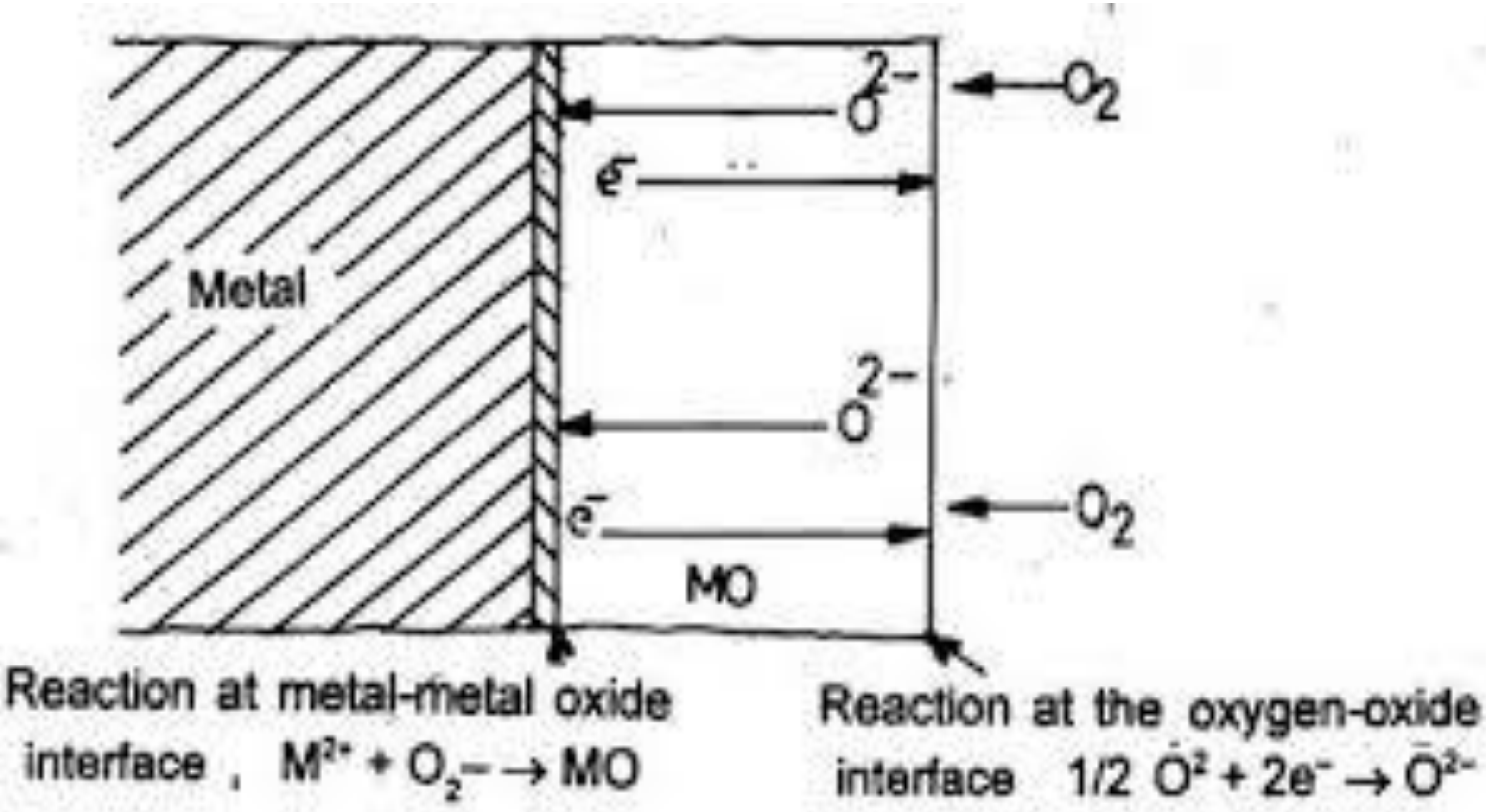
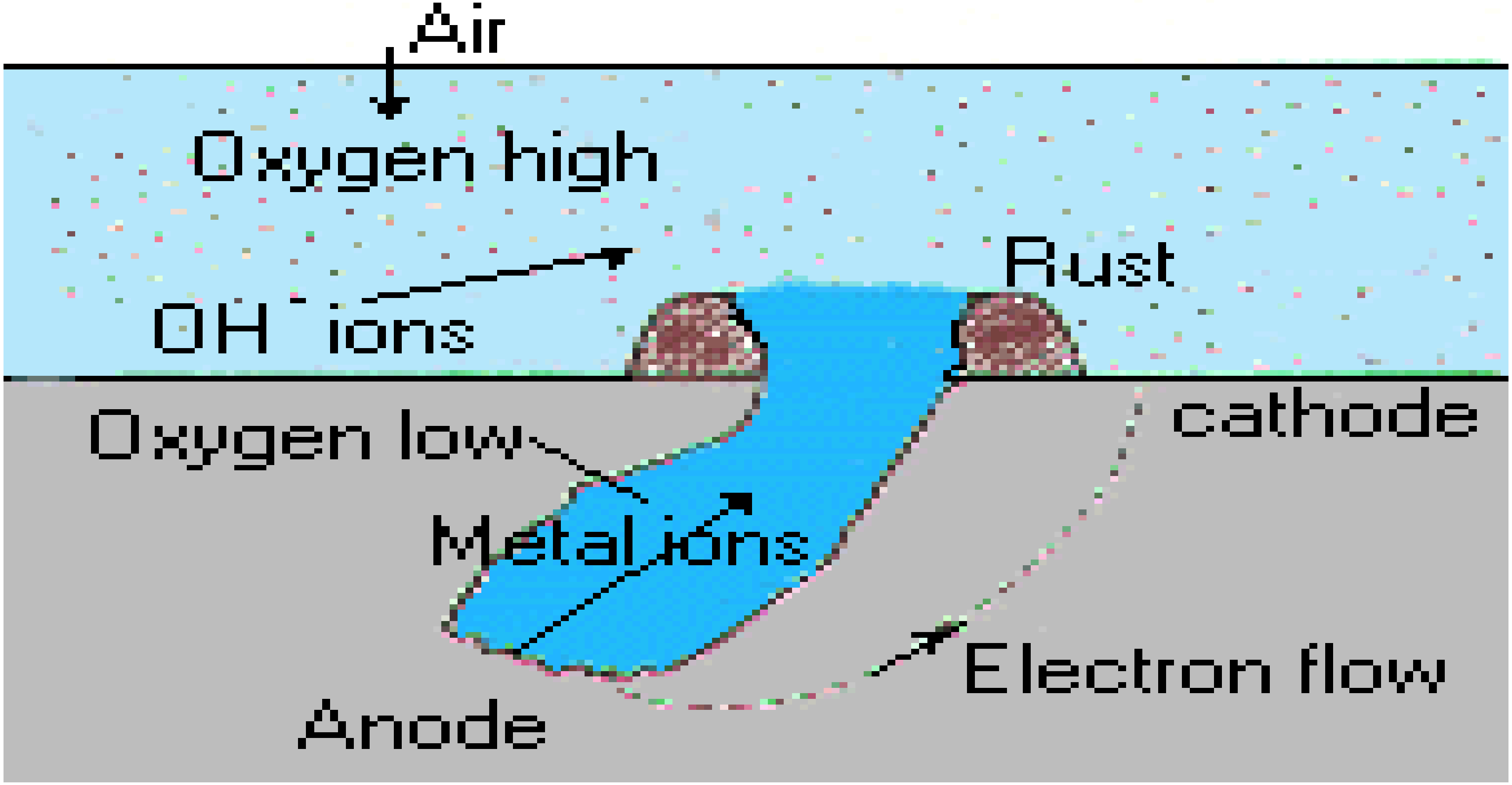


Fig. 14.6. Simplified picture of anion diffusion based oxidation.

Electrochemical Theory OfCorrosion

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.

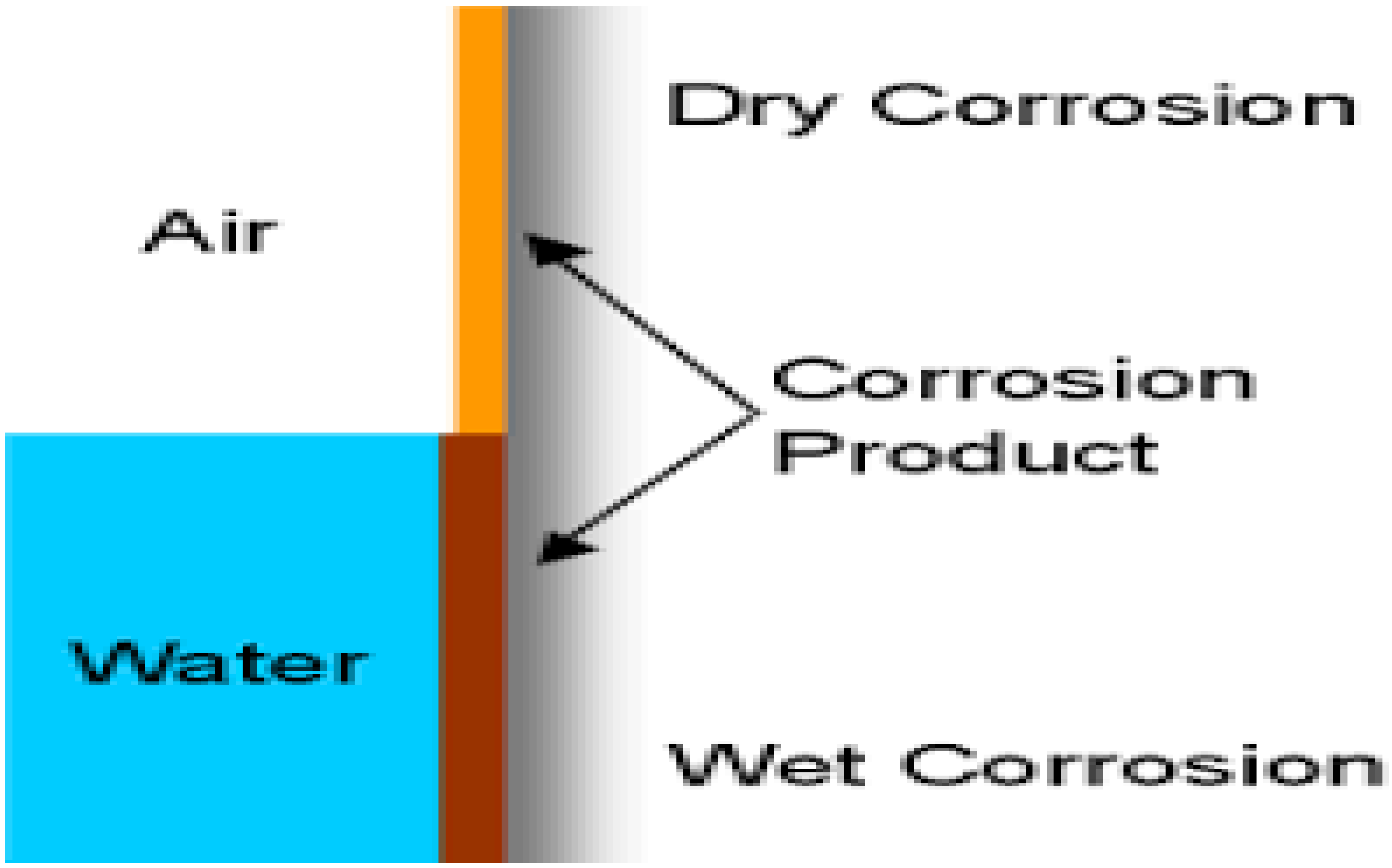
Electrochemical Theory OfCorrosion



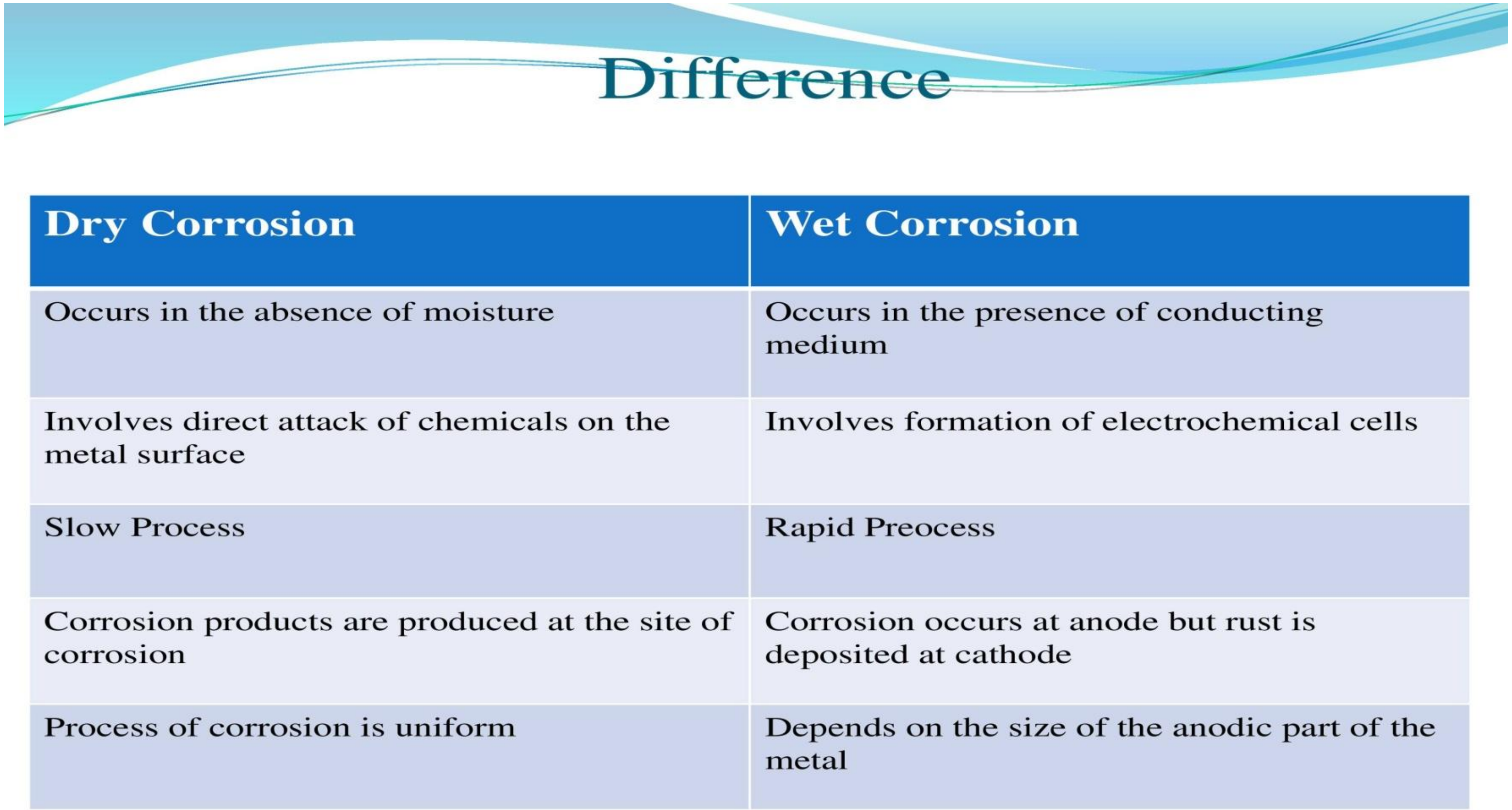
Electrochemical Theory OfCorrosion

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.

Electrochemical Theory OfCorrosion



Dry And Wet Corrosion



Difference

Dry Corrosion	Wet Corrosion
Occurs in the absence of moisture	Occurs in the presence of conducting medium
Involves direct attack of chemicals on the metal surface	Involves formation of electrochemical cells
Slow Process	Rapid Preocess
Corrosion products are produced at the site of corrosion	Corrosion occurs at anode but rust is deposited at cathode
Process of corrosion is uniform	Depends on the size of the anodic part of the metal

Types Of Corrosion

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

(a) Water-line corrosion

(b) Galvanic

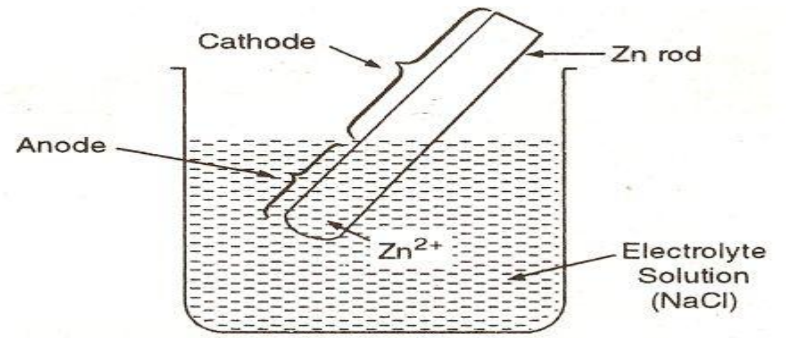
(c) Pitting

Water Line 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)

Water Line Corrosion

Corrosion



Water-line Corrosion :

When water is stagnant in a steel tank, the concentration of Oxygen above the water surface is greater than that under the surface. This generates an oxygen concentration cell. In this cell the metal just above the water level is cathodic w.r.t. the metal below the water level.

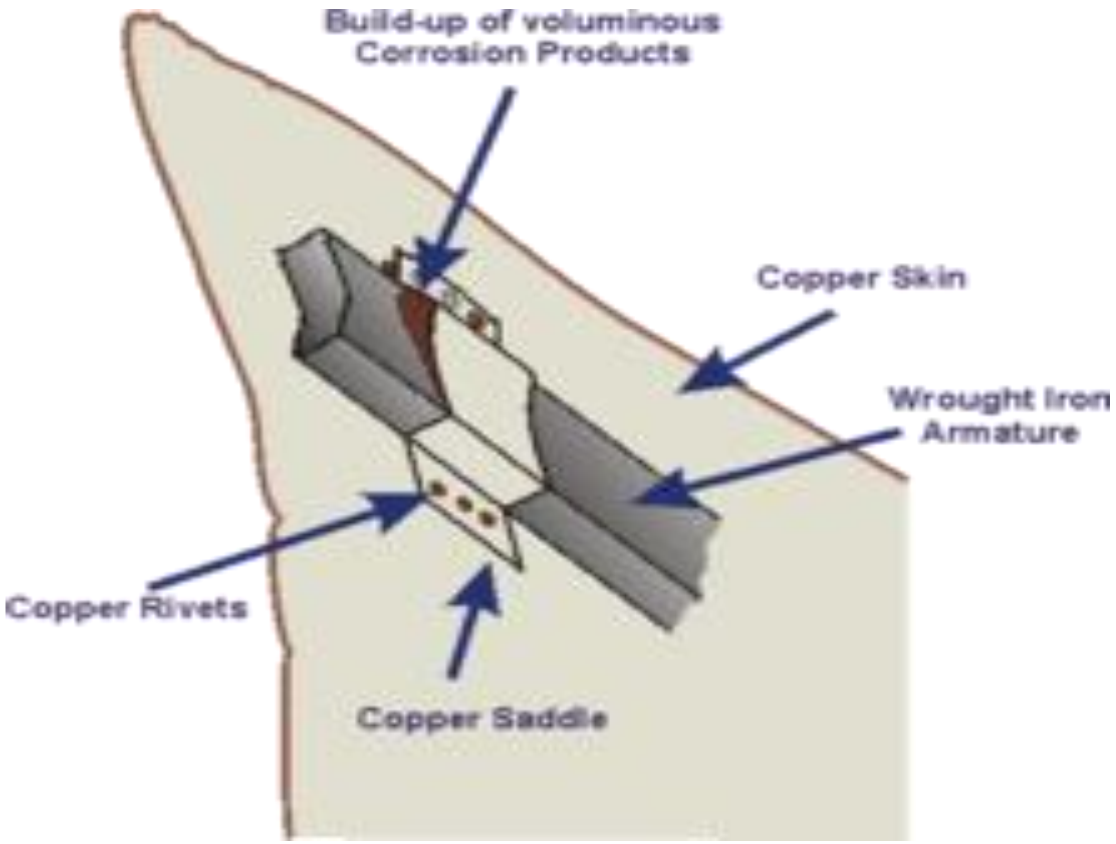
Galvanic Corrosion

- Dissimilar metals and alloys have different electrode potential, and when two or more come into contact in an electrolyte, one metal acts as anode and the other as cathode. If the electrolyte contains only metal ions that are not easily reduced (such as Na^+, Ca^{2+}, K^+, Mg^{2+}, or Zn^{2+}), the cathode reaction is reduction of dissolved H^+ to H_2 or O_2 to OH^-.

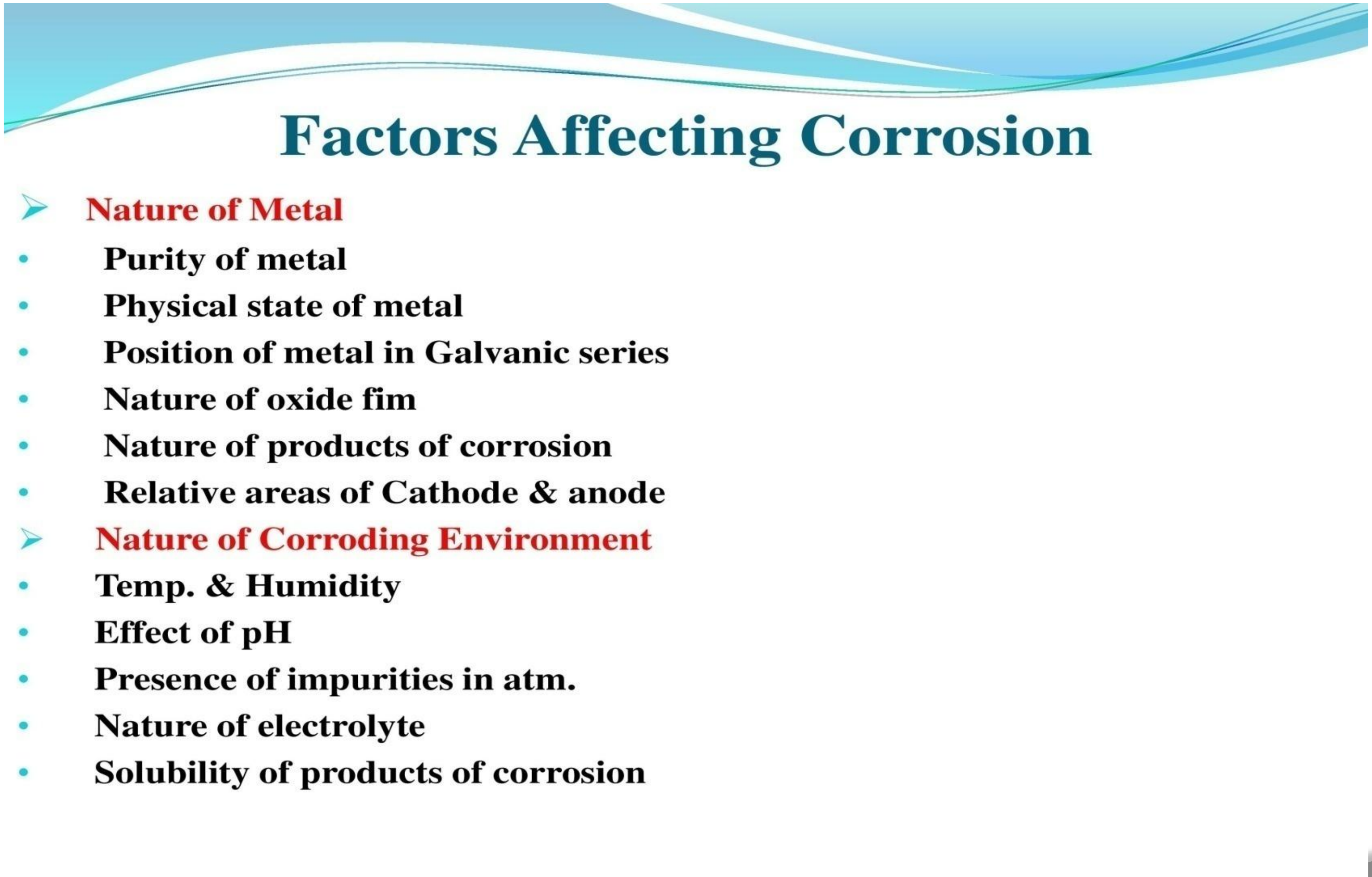
Galvanic Corrosion

- The electrode potential difference between the reactions at the two electrodes is the driving force for an accelerated attack on the anode metal, which dissolves into the electrolyte. This leads to the metal at the anode corroding more quickly than it otherwise would and corrosion at the cathode being inhibited. The presence of an electrolyte and an electrical conducting path between the metals is essential for galvanic corrosion to occur.

Galvanic Corrosion



Factors Effecting Rate of Corrosion



Factors Affecting Corrosion

- **Nature of Metal**
  - **Purity of metal**
  - **Physical state of metal**
  - **Position of metal in Galvanic series**
  - **Nature of oxide fim**
  - **Nature of products of corrosion**
  - **Relative areas of Cathode & anode**
- **Nature of Corroding Environment**
  - **Temp. & Humidity**
  - **Effect of pH**
  - **Presence of impurities in atm.**
  - **Nature of electrolyte**
  - **Solubility of products of corrosion**

Factors Effecting Rate of Corrosion

The rate and extent of corrosion depends upon various factors due to nature of metal and nature of corroding environment.

Factors due to nature of metal

1. Purity of the metal*:* Heterogeneity of the metal is due to the presence of impurities which form tiny electrochemical cells at the exposed parts.

2. Electrode potentials***:*** metals with higher reduction potentials do not corrode easily. Whereas the metals with lower reduction potentials readily undergo corrosion (eg. Zn, Mg, Al etc.).

Factors Effecting Rate of Corrosion

3. Position of metal in galvanic series*:* Metals which possess low reduction potentials and occupy higher end of galvanic series undergo corrosion easily.

4. Metals which possess high reduction potentials and occupy lower end of galvanic series do not undergo corrosion and they get protected.

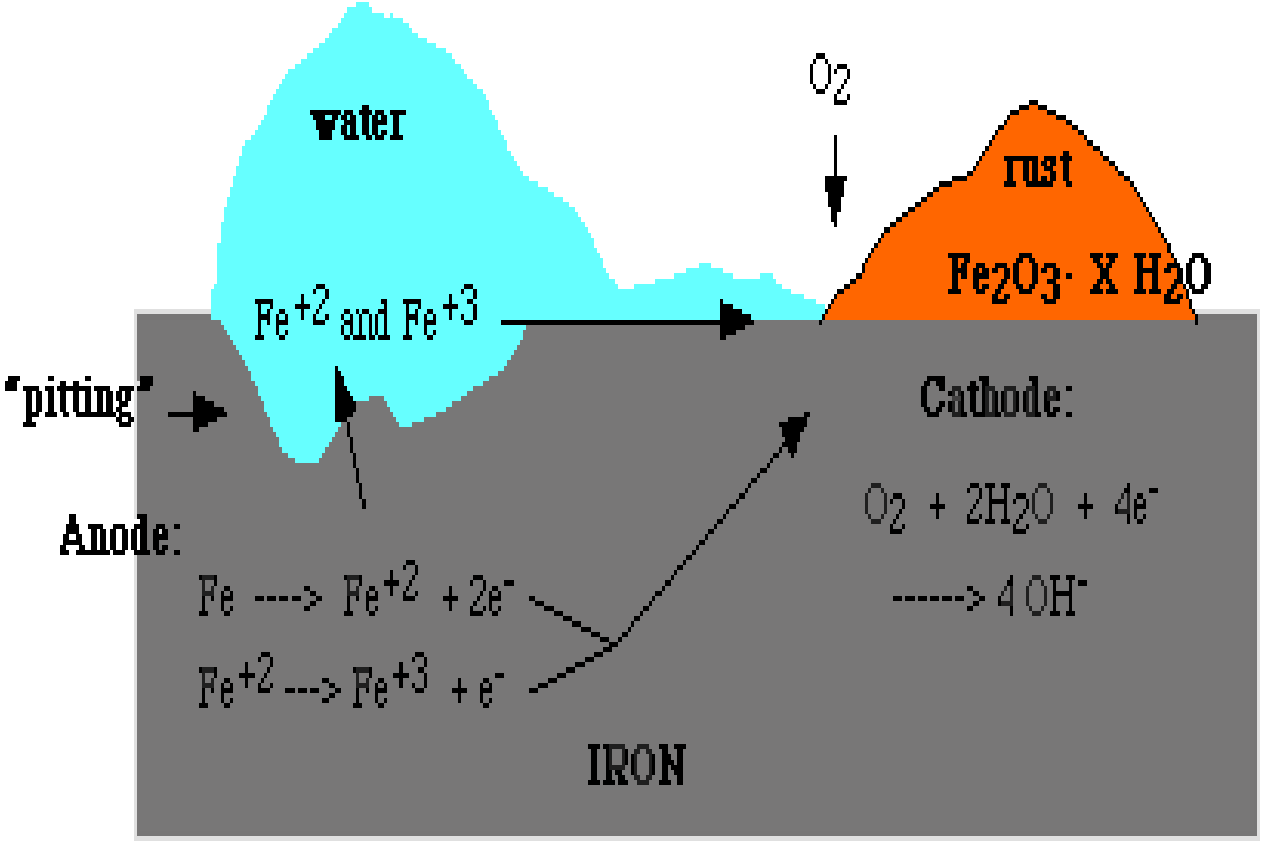
Greater the difference more will be the extent of corrosion at anode.

Factors Effecting Rate of Corrosion

5.Relative areas of anodic and cathodic cells*:* the relative areas o of corrosion is influenced by cathodic to anodic cells.

If the metal has small anodic and large cathodic area, the rate of corrosion is very high. This is because the electrons are liberated at anode which is consumed at cathode. If the cathodic area is larger, the liberated electrons are rapidly consumed at cathode. This further enhances the anodic reaction leading to increase the rate of corrosion.

Electrode Potential



Factors Effecting Rate of Corrosion

6.Physical state of metal: Metals with small grain size have more tendencies to undergo corrosion. Metal with more stress/strain also undergoes corrosion easily.

7. Nature of surface film: If the corrosion product formed is more stable, insoluble and nonporous, it acts as protective layer and prevents further corrosion (Eg. Ti, Al and Cr). If the corrosion product is porous, volatile and soluble, it further enhances the corrosion (Fe, Zn and Mg).

Factors Effecting Rate of Corrosion

Factors due to nature corrosive environment

1. Temperature*:* the rate of corrosion reactions increases with increase in temperature.

2. Humidity in air*:* the moisture or humidity present in atmosphere furnishes water to the electrolyte which is essential for setting up of an electrochemical cell.

3. Presence of impurities*:* Atmosphere is contaminated with gases like CO_2, SO_2, H_2S; fumes of H_2SO_4, HCl etc.

Factors Effecting Rate of Corrosion

4.P^H value*:* pH value of the medium has the greater effect on corrosion. Acidic pH increases the rate of corrosion.

5. Amount of oxygen in atmosphere: As the percentage of oxygen in atmosphere increases, the rate of corrosion also increases due to the formation of oxygen concentration cell. The decay of metal occurs at the anodic part and the cathodic part of the metal is protected.

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

Cathodic Protection

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

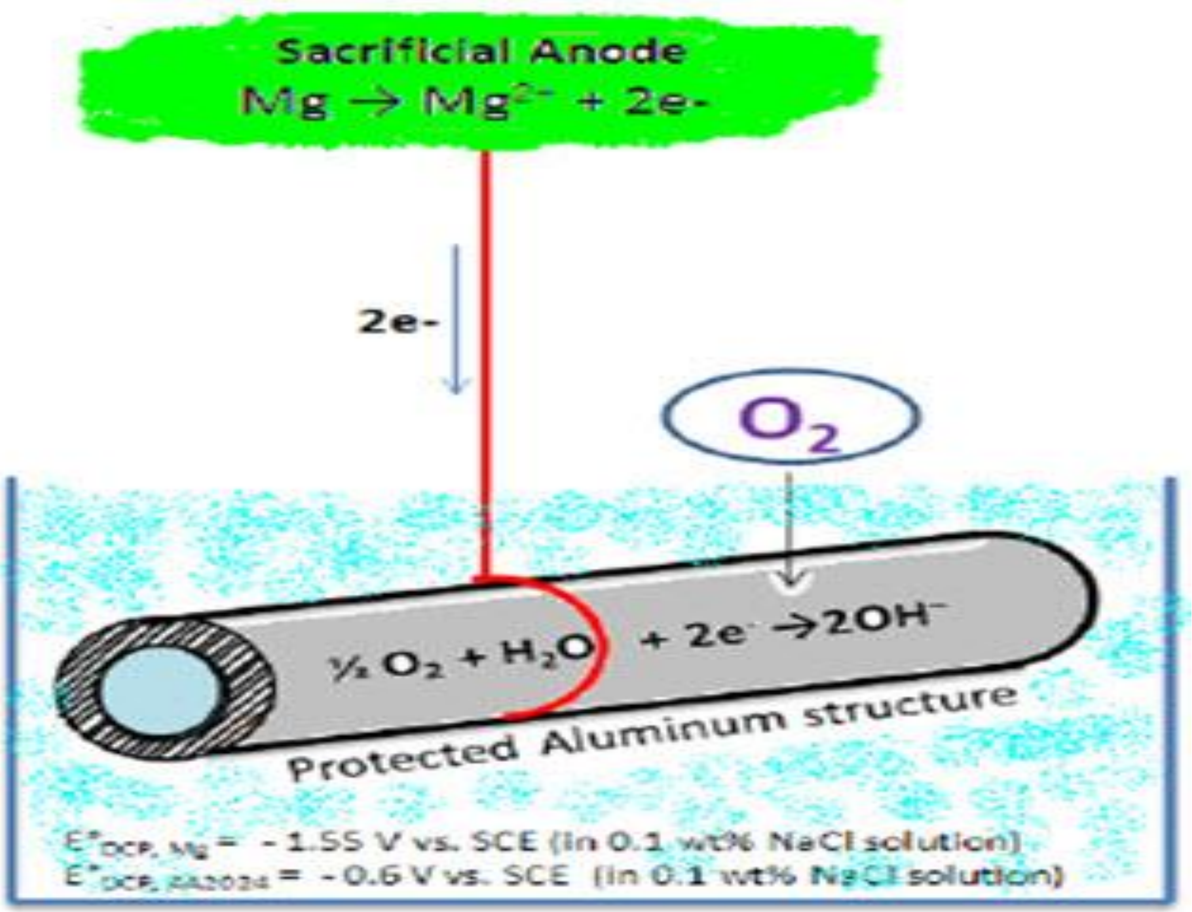
a)Sacrificial anodic protection:

b)Impressed current cathodic protection:

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.

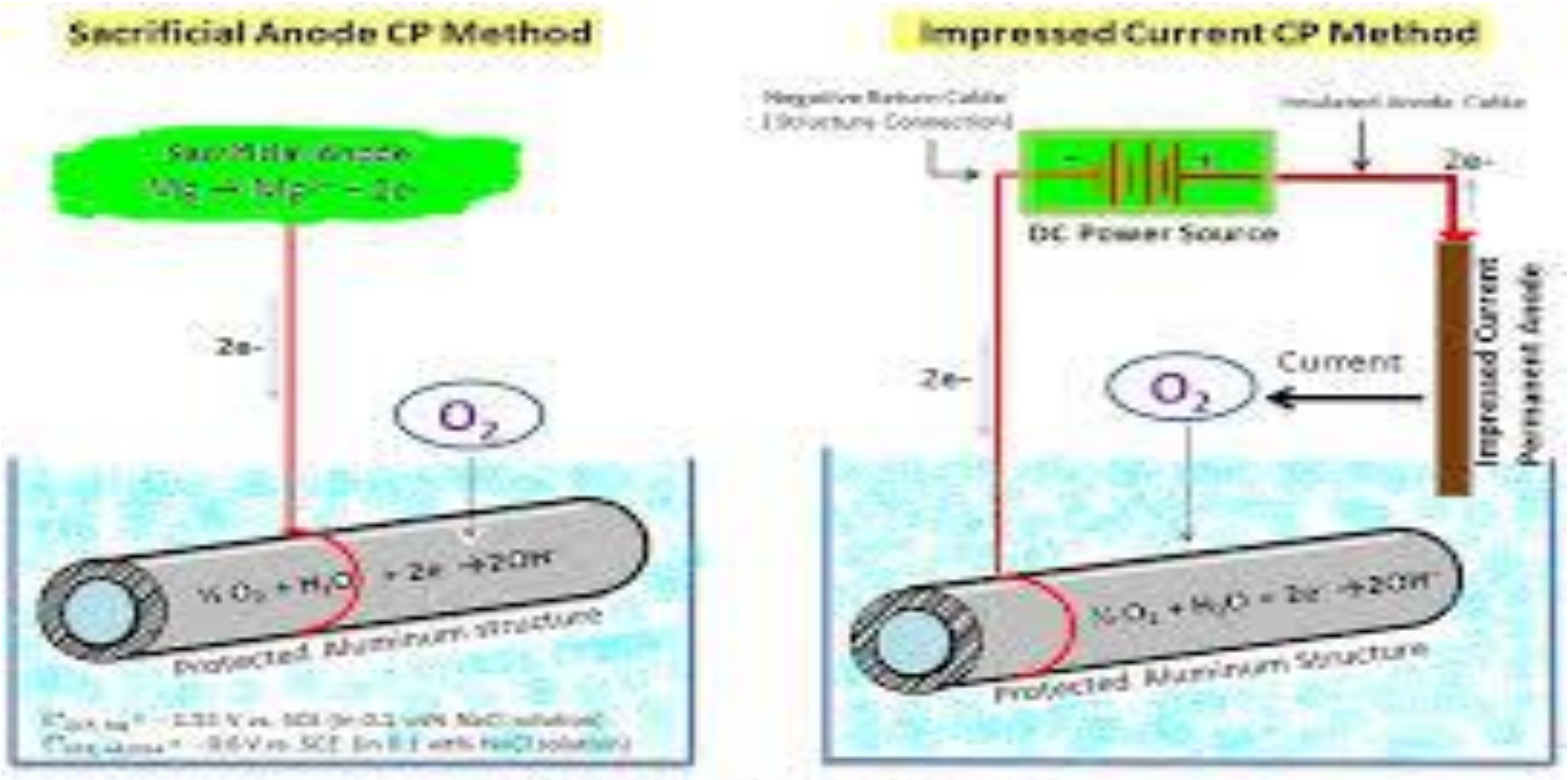
Sacrificial Anodic Protection



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.

Impressed Current cathodic Protection

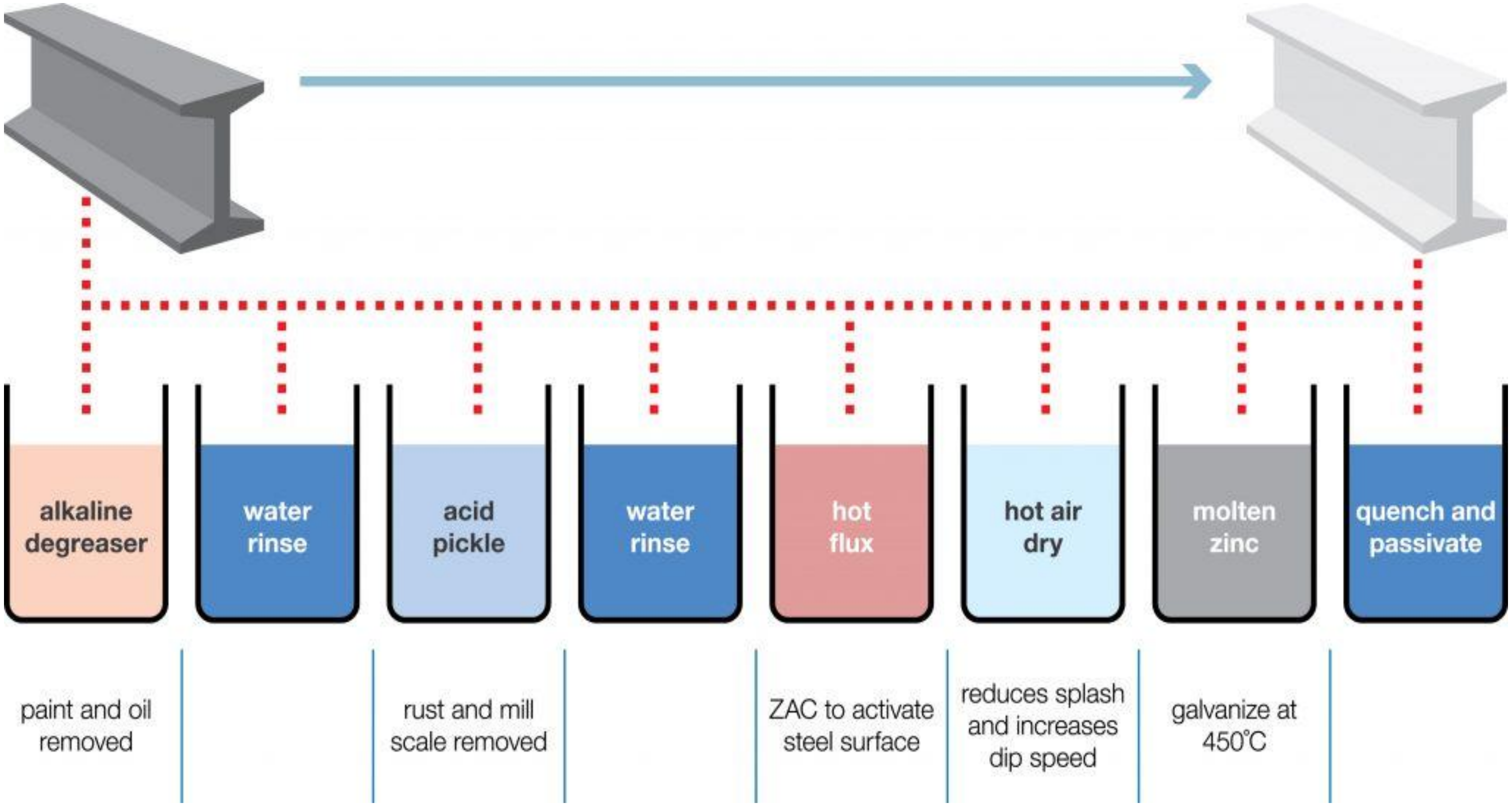


Cathodic Protection (CP) Methods

Galvanizing

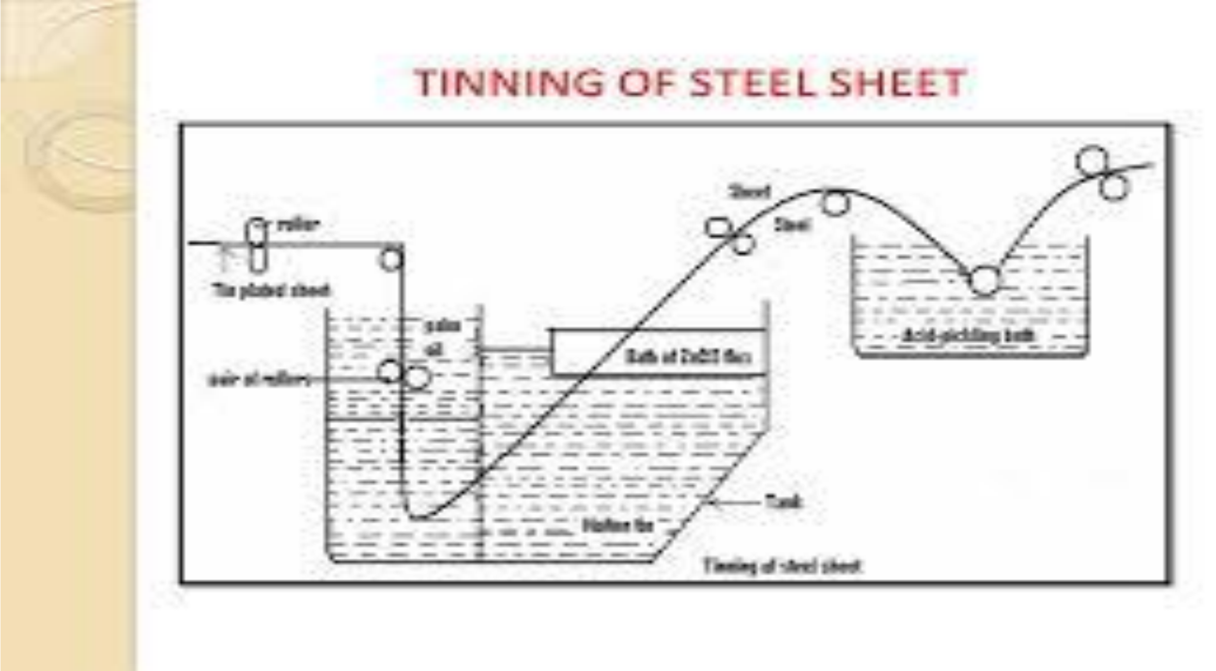
- Galvanizing is a process in which the iron article is protected from corrosion by coating it with a thin layer of zinc.
- Galvanizing is widely used for protecting iron exposed to the atmosphere (roofs, wire fences, pipes etc.) Galvanized metallic sheets are not used for keeping eatables because of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

Galvanizing



Sacrificial Anodic Protection

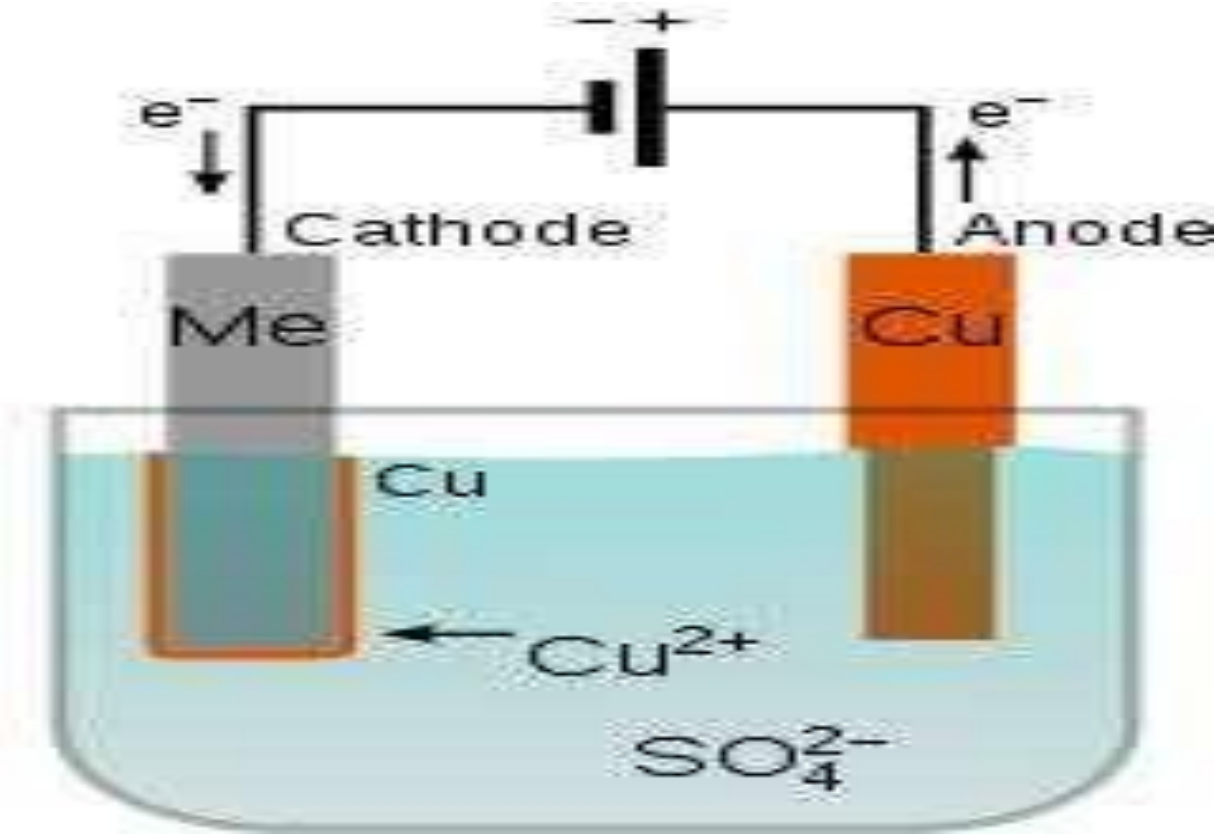
Tinning:The process of coating tin over the iron or steel articles to protect them from undergoing corrosion is known as tinning.



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.

Electroplating



Electroless Plating

The first step in the plating process is the chemical deposition of a very thin layer of copper on the hole walls. The operator clamps the production panels into the jigs. The line is fully computer controlled and the panels are carried through a series of chemical and rinsing baths by the overhead crane. Almost all PCBs with 2 or more copper layers use plated through holes to connect the conductors between the layers.

Electroless Plating

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.

MODULE - II

WATER AND ITS TREATMENT

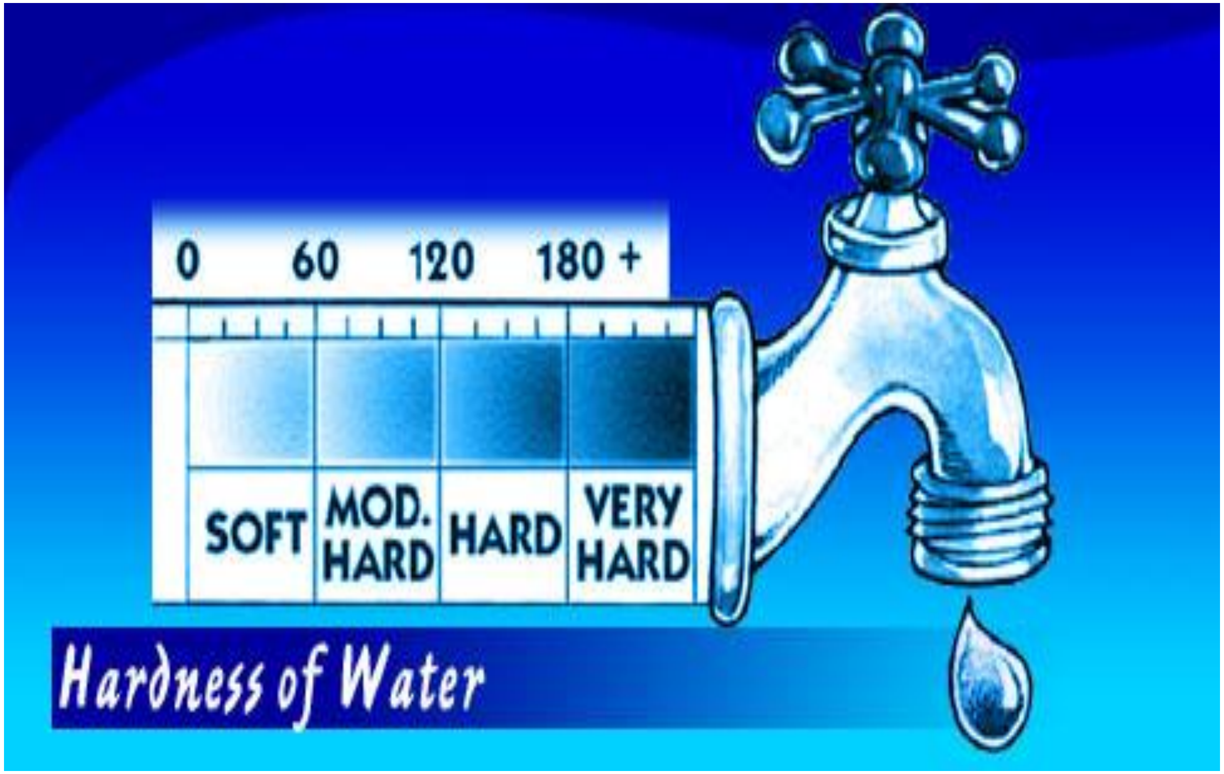
Introduction

- 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.

Introduction

Introduction



Hardness of Water

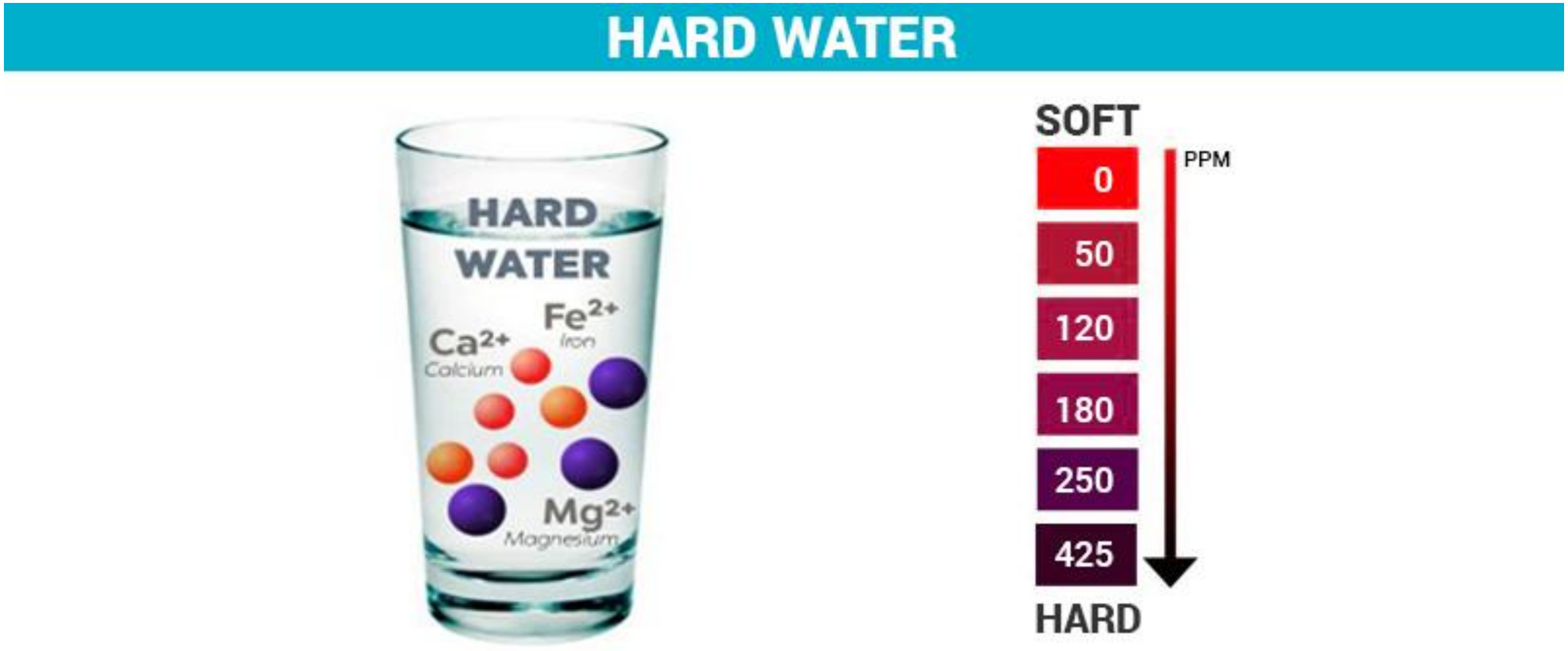
Water is a very good solvent and even called as the universal solvent. Most of the inorganic salts are soluble in water. The water that has calcium and magnesium salts dissolved in it causes hardness of water. Water passes through rocks and flows on the ground.

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

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

Hardness of Water



Hardness of Water

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.

Disadvantages of Hard Water

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.

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.

Drinking: Hard water causes bad effect on our health.

Calcium forms oxalate crystals in urinary tract.

Disadvantages of Hard Water

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.

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.

Disadvantages of Hard Water

(a)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.

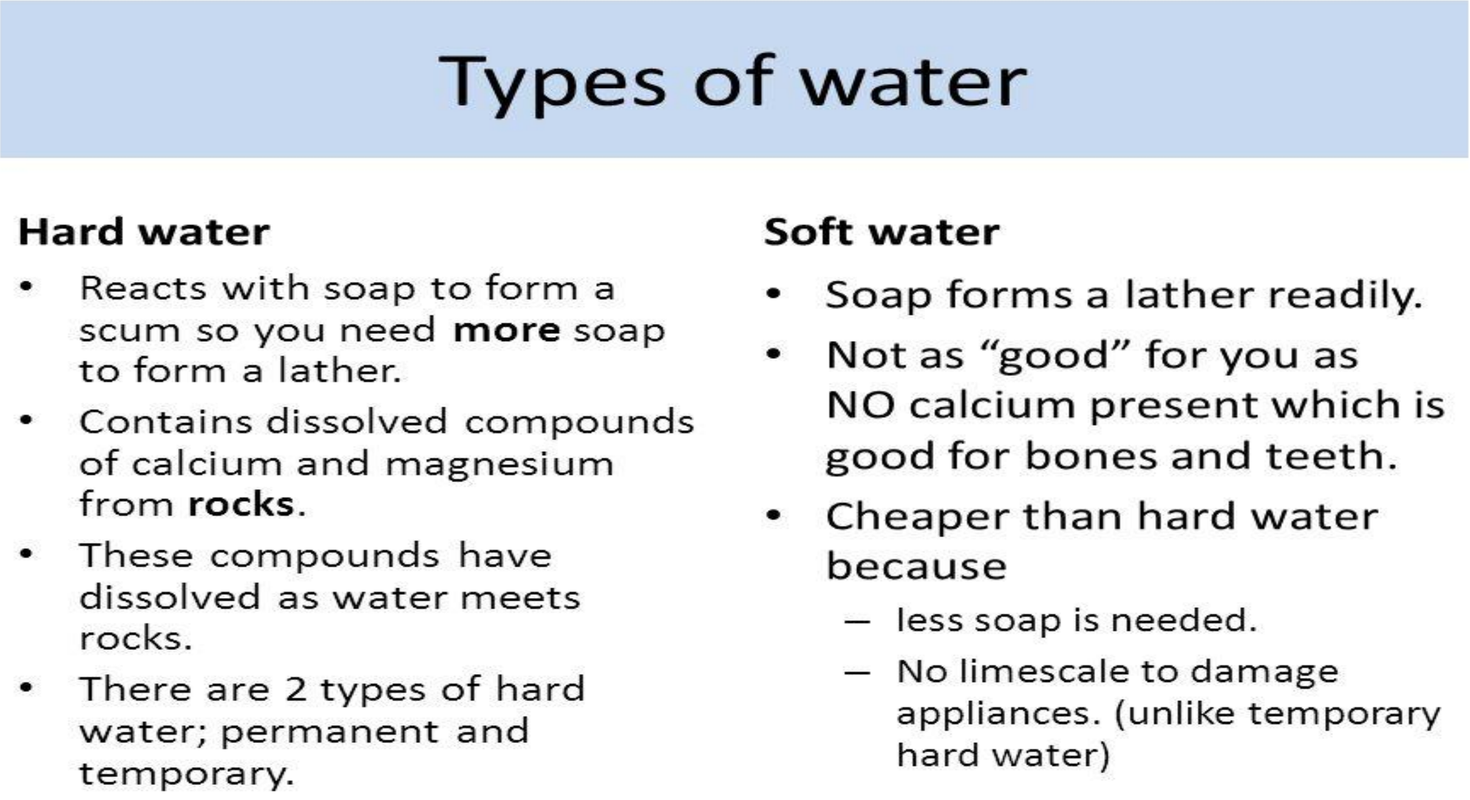
(b)Laundry: Hard water causes wastage of soap. Iron salts cause colouration of clothes.

Disadvantages of Hard Water

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

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

Disadvantages of Hard Water



Types of water

Hard water

- Reacts with soap to form a scum so you need **more** soap to form a lather.
- Contains dissolved compounds of calcium and magnesium from **rocks**.
- These compounds have dissolved as water meets rocks.
- There are 2 types of hard water; permanent and temporary.

Soft water

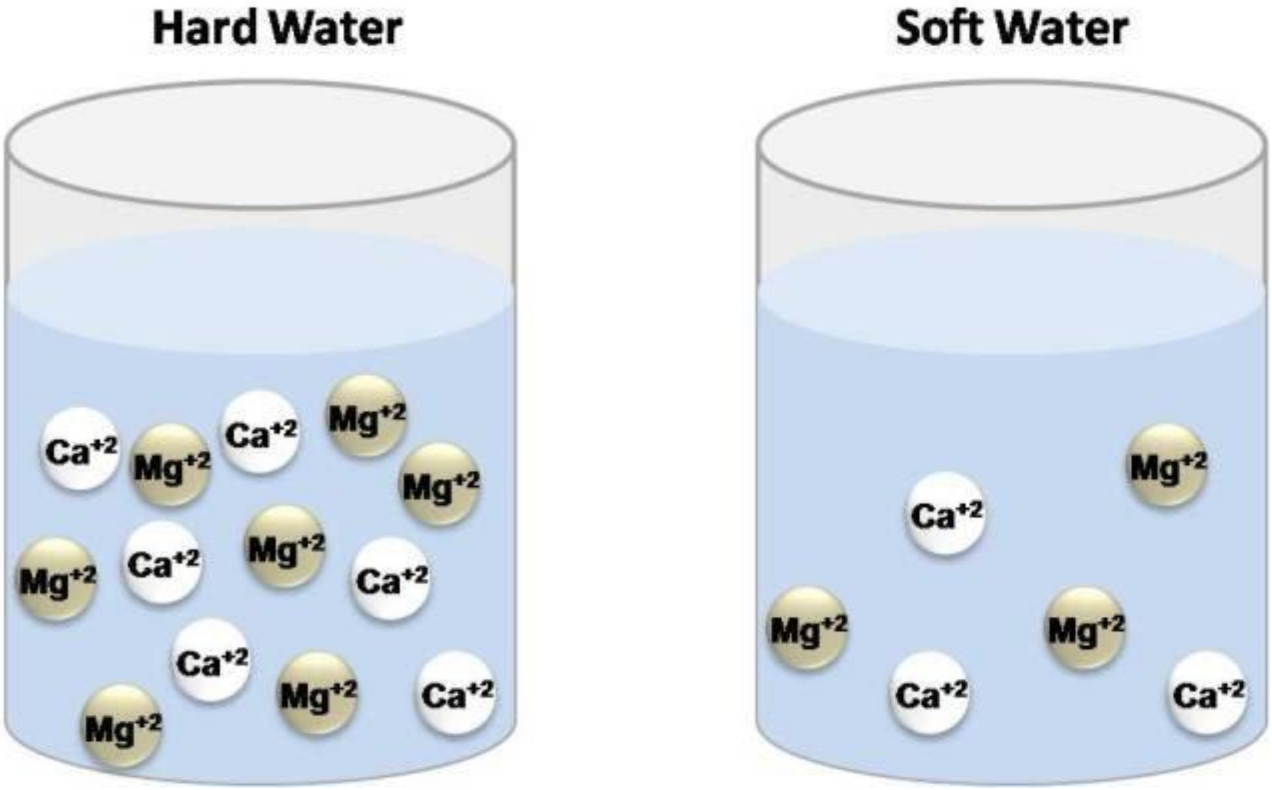
- Soap forms a lather readily.
- Not as “good” for you as NO calcium present which is good for bones and teeth.
- Cheaper than hard water because
  - less soap is needed.
  - No limescale to damage appliances. (unlike temporary hard water)

Hardness of Water

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

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

Hardness of Water



Hardness of Water

- 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 $(Ca^{+2}/Mg^{+2})(HCO_3)_2$ is converted into insoluble carbonate that can be removed by filtration

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

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

Hardness of Water

Hardness of Water

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).

Hardness of Water

Permanent hardness cannot be removed by boiling. It is due to the dissolution of $CaCl_2$, $CaSO_4$, $MgCl_2$ and $MgSO_4$ 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.

Units 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 $CaCO_3$ 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 $CaCO_3$ per 106 part of water. For example, 50 ppm hardness means 106 parts of water has 50 parts of equivalent $CaCO_3$.

Units of Hardness

- **Milligram per litre (mg/L):** It is the number of milligrams of equivalent $CaCO_3$ per litre of water. One milligram per litre hardness means 1 mg of equivalent $CaCO_3$ per litre of hard water.

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

1 ppm = 1 mg/L

Units of Hardness

Degree Clarke: It is the number of grams of $CaCO_3$ 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 $CaCO_3$ present in 1 gallon of hard water.

Units of Hardness

Degree French: It is the number of parts of $CaCO_3$ per 105 parts of hard water. Hardness 1°French (1°Fr) means 1 part of equivalent $CaCO_3$ per 105 parts of hard water.

Relationship among units of hardness:

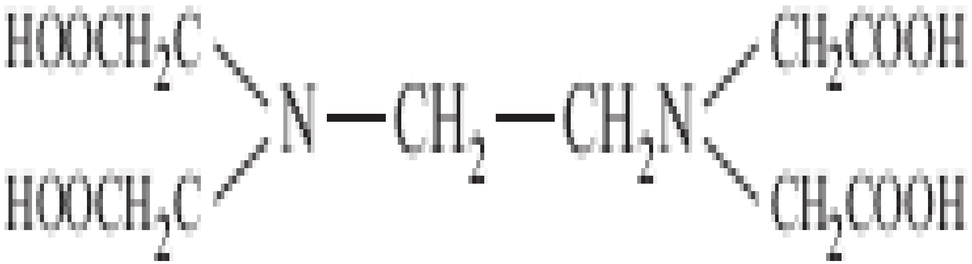
1 ppm = 1mg/L = 0.1°Fr = 0.07°Cl

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

Hardness of water by EDTA method

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 incomplexometry.



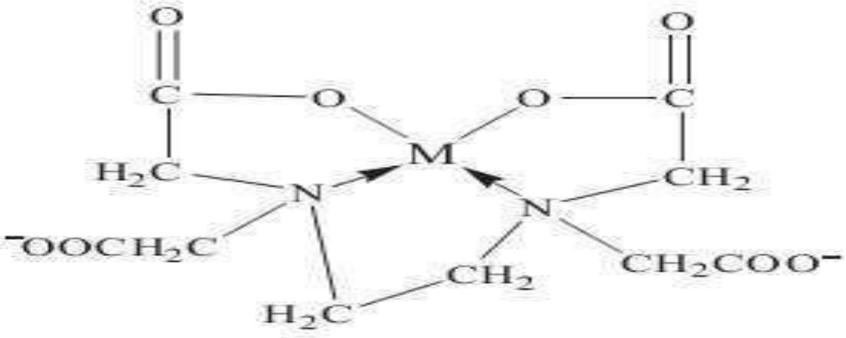
$[H_4Y]$

Hardness of water by EDTA method

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,

Hardness of water by EDTA method

Ca^{2+} /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



Hardness of water by EDTA method

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

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

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

Internal Treatment of Water

- 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.

Internal Treatment of Water

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

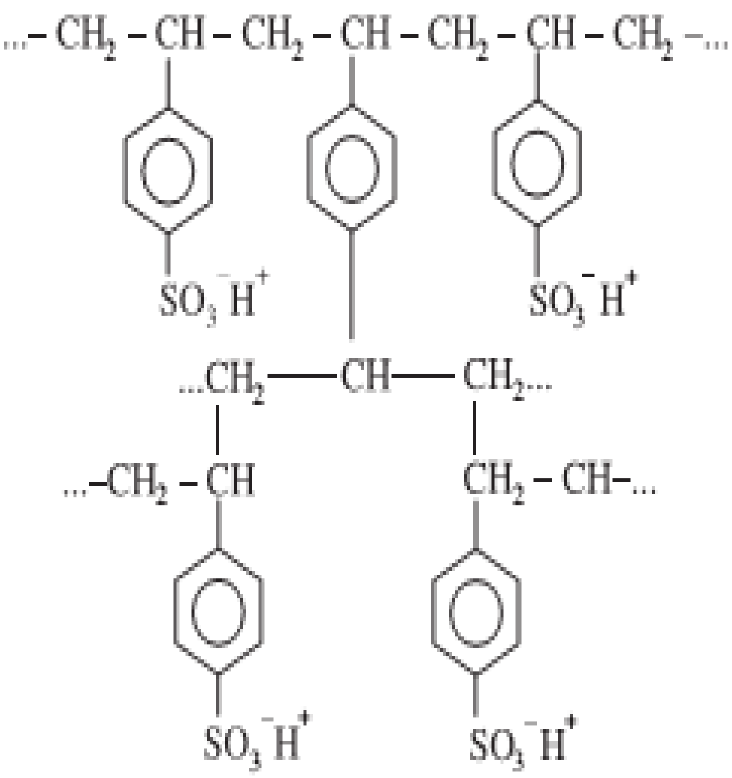
$$3MgCl_2 + 2Na_3PO_4 \longrightarrow Mg_3(PO_4)_2\downarrow + 6NaSO_4$$

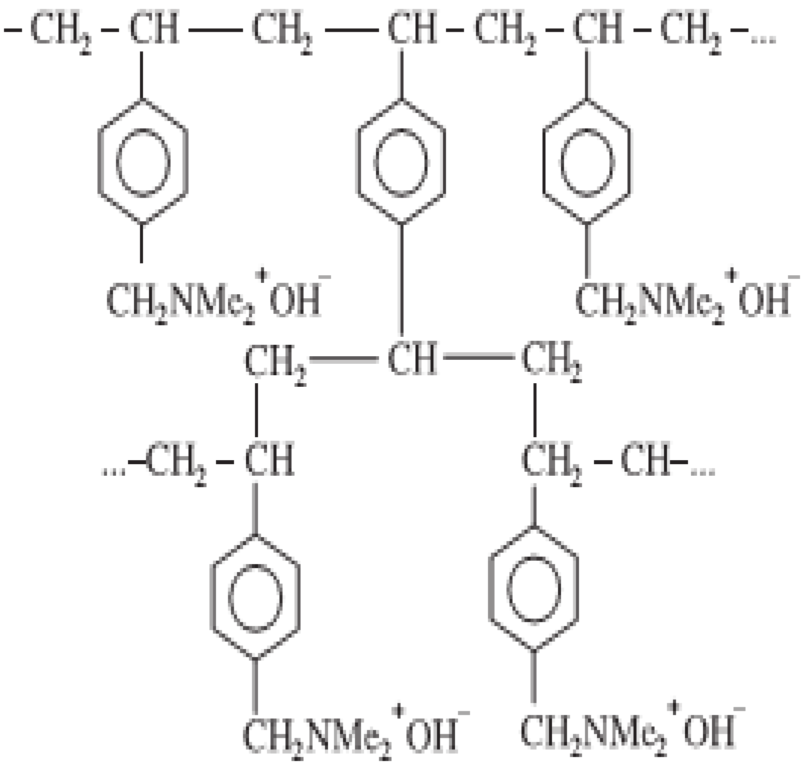
$$Na_2[Na_4(PO_3)_6] + 2Ca^{2+} \rightarrow \underset{\text{(Soluble complex)}}{Na_2[Ca_2(PO_3)_6]}$$

Ion Exchange 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 (SO_3H) 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 .

Cation and Anion Exchangers





Hardness of water by EDTA method

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 isgreater than 35000 mg/L**.**

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

Hardness of water by EDTA method

(a)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:

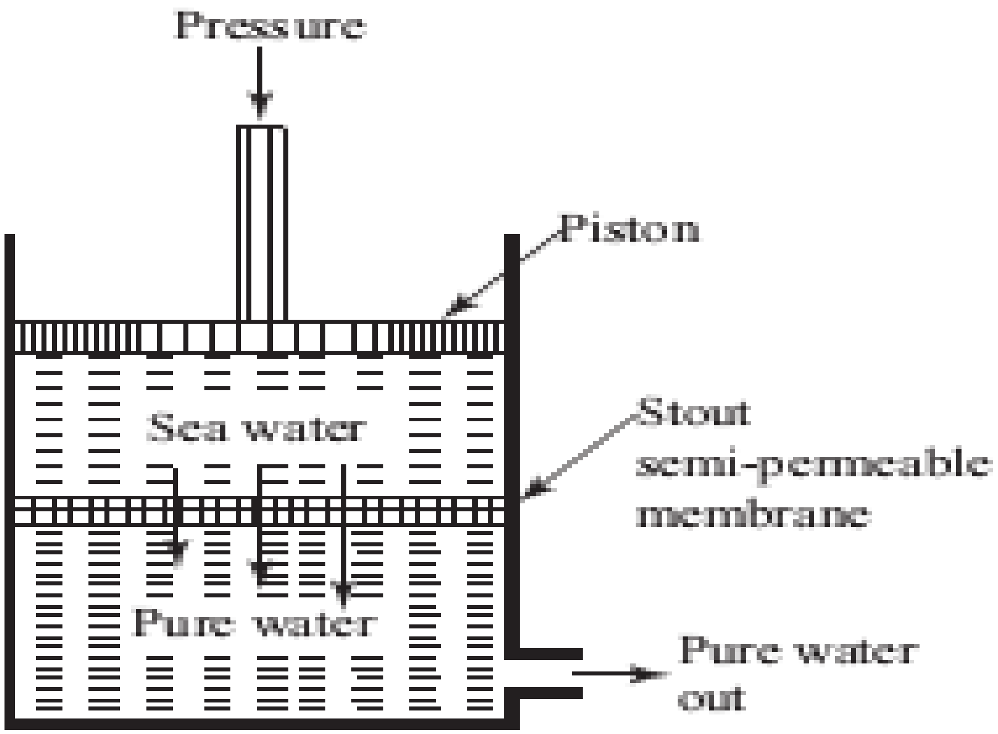
i) Reverse osmosis,
ii) Electrodialysis and
iii) Distillation

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 Process



Reverse Osmosis Process

- 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.
- 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 obtainedafter being treated by this process is used inboilers.

Advantages Of The Reverse Osmosis

- 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

- 1. It should be colourless, odourless, and pleasant to taste.
- 2.Turbidity should not exceed 10ppm.TDS shouldnot exceed 500 ppm. It should not be very alkaline (pH 8.0).
- 3. It should be free from dissolvedgases.
- 4. It should be free from objectionable minerals such as Pb, As, Cs, Mn and dissolved gases such as H_2SandCO_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

- **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.

Chlorination

- 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 allowed to stand for several hours.

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

Chlorination

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

$$Cl_2 + H_2O \rightarrow HCl + HOCl$$

$$\text{Bacteria} + HOCl \rightarrow \text{killed bacteria}$$

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.

Disinfection By Ozone

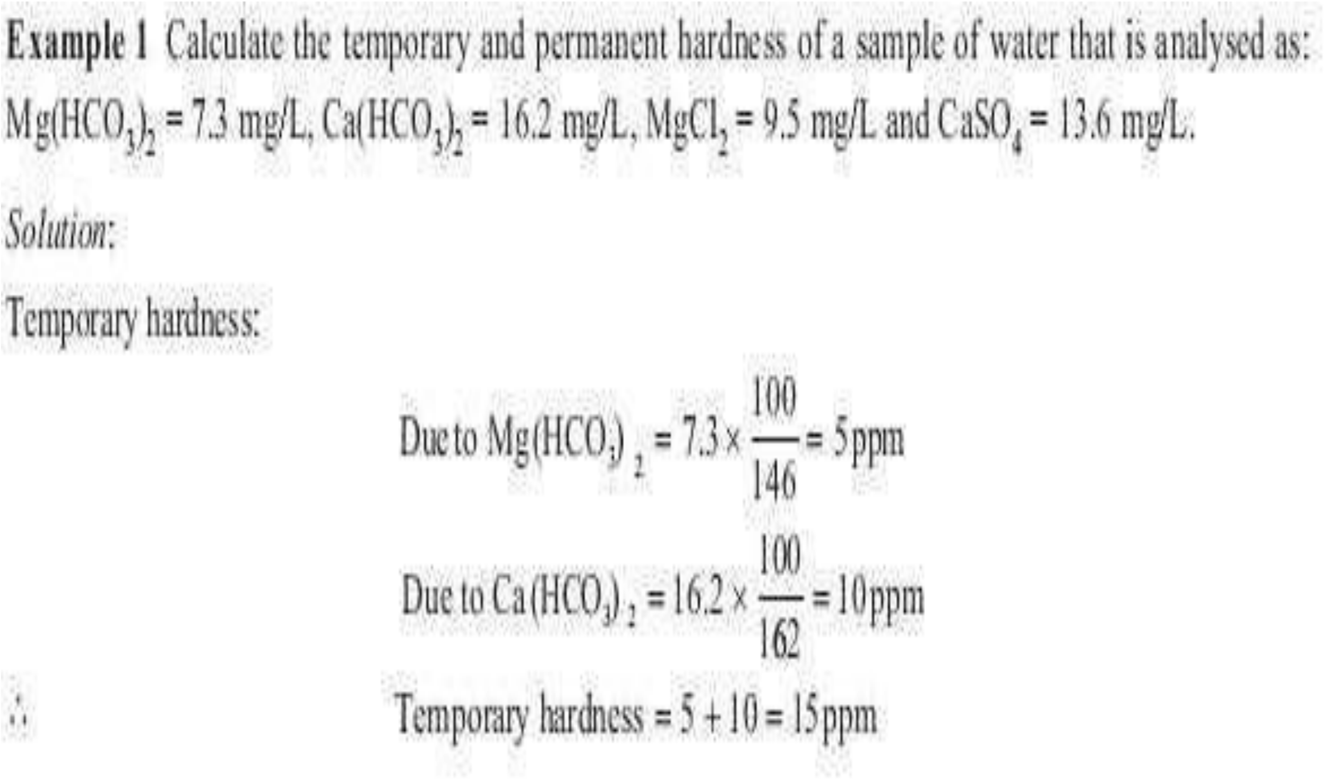
(e)Disinfection by ozone: O_3 is prepared by passing silent electric discharge through cold, dry O_2. It is highlyunstable.

- $O_3 \rightarrow O_2 + (o)$

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 $CaCO_3$ 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:

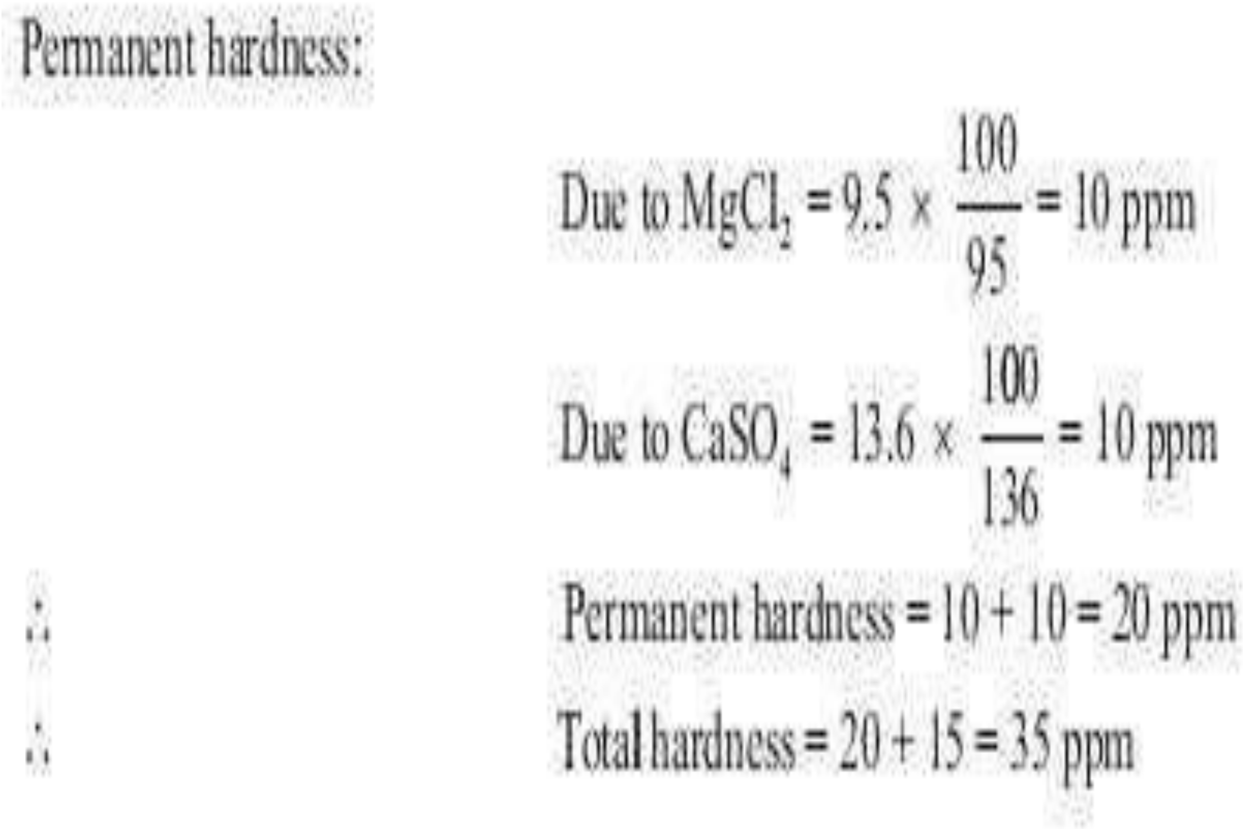
Temporary hardness:

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

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

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

Solved Examples



Permanent hardness:

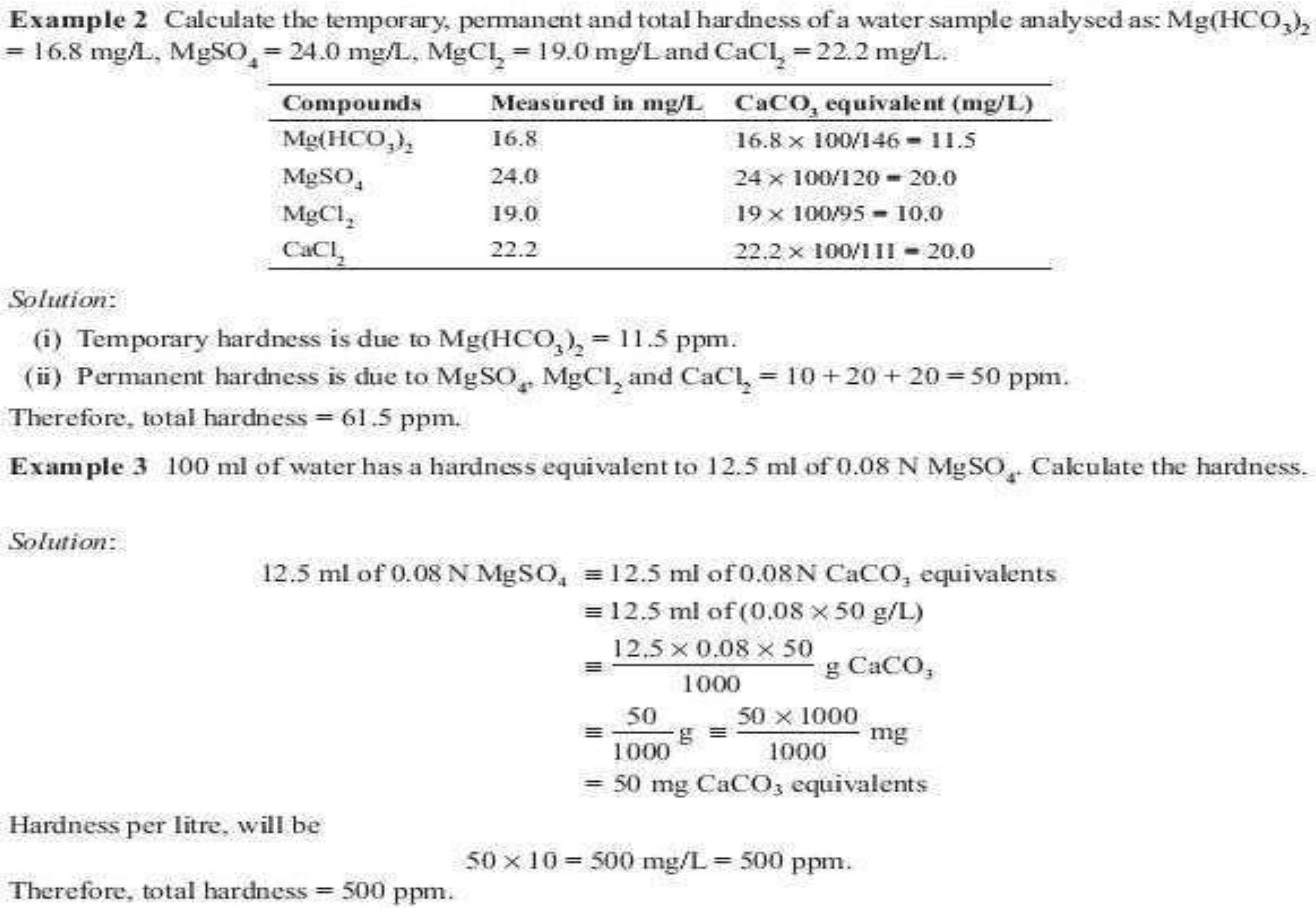
$$\text{Due to } MgCl_2 = 9.5 \times \frac{100}{95} = 10 \text{ ppm}$$

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

$\therefore$ Permanent hardness = 10 + 10 = 20 ppm

$\therefore$ Total hardness = 20 + 15 = 35 ppm

Solved Examples



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:

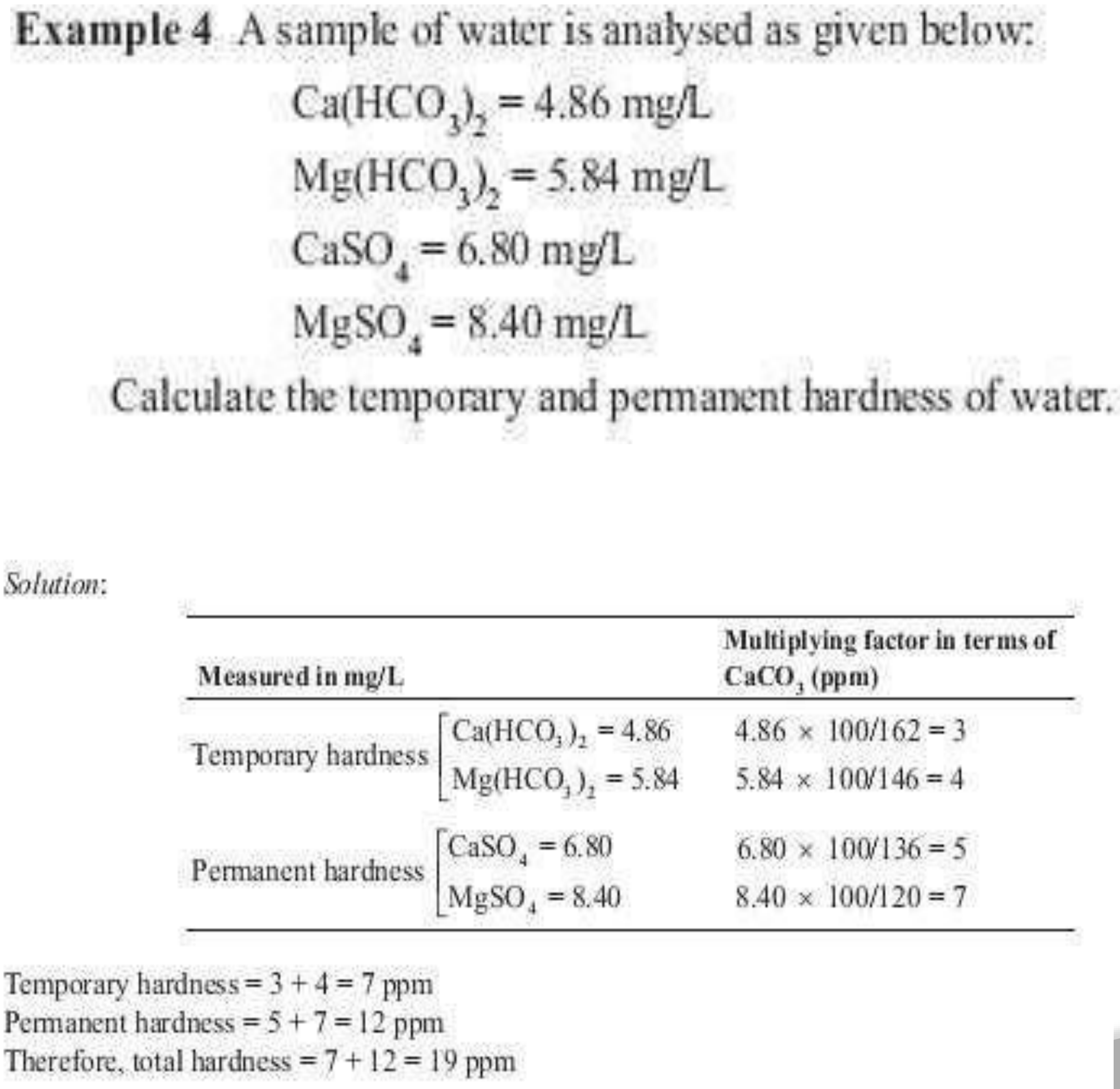
$$
\begin{aligned}
12.5 \text{ ml of } 0.08 \text{ N } MgSO_4 &\equiv 12.5 \text{ ml of } 0.08\text{N } CaCO_3 \text{ equivalents} \\
&\equiv 12.5 \text{ ml of } (0.08 \times 50 \text{ g/L}) \\
&\equiv \frac{12.5 \times 0.08 \times 50}{1000} \text{ g } CaCO_3 \\
&\equiv \frac{50}{1000} \text{ g} \equiv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

Hardness per litre, will be

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

Therefore, total hardness = 500 ppm.

Solved Examples



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

$$Ca(HCO_3)_2 = 4.86 \text{ mg/L}$$

$$Mg(HCO_3)_2 = 5.84 \text{ mg/L}$$

$$CaSO_4 = 6.80 \text{ mg/L}$$

$$MgSO_4 = 8.40 \text{ mg/L}$$

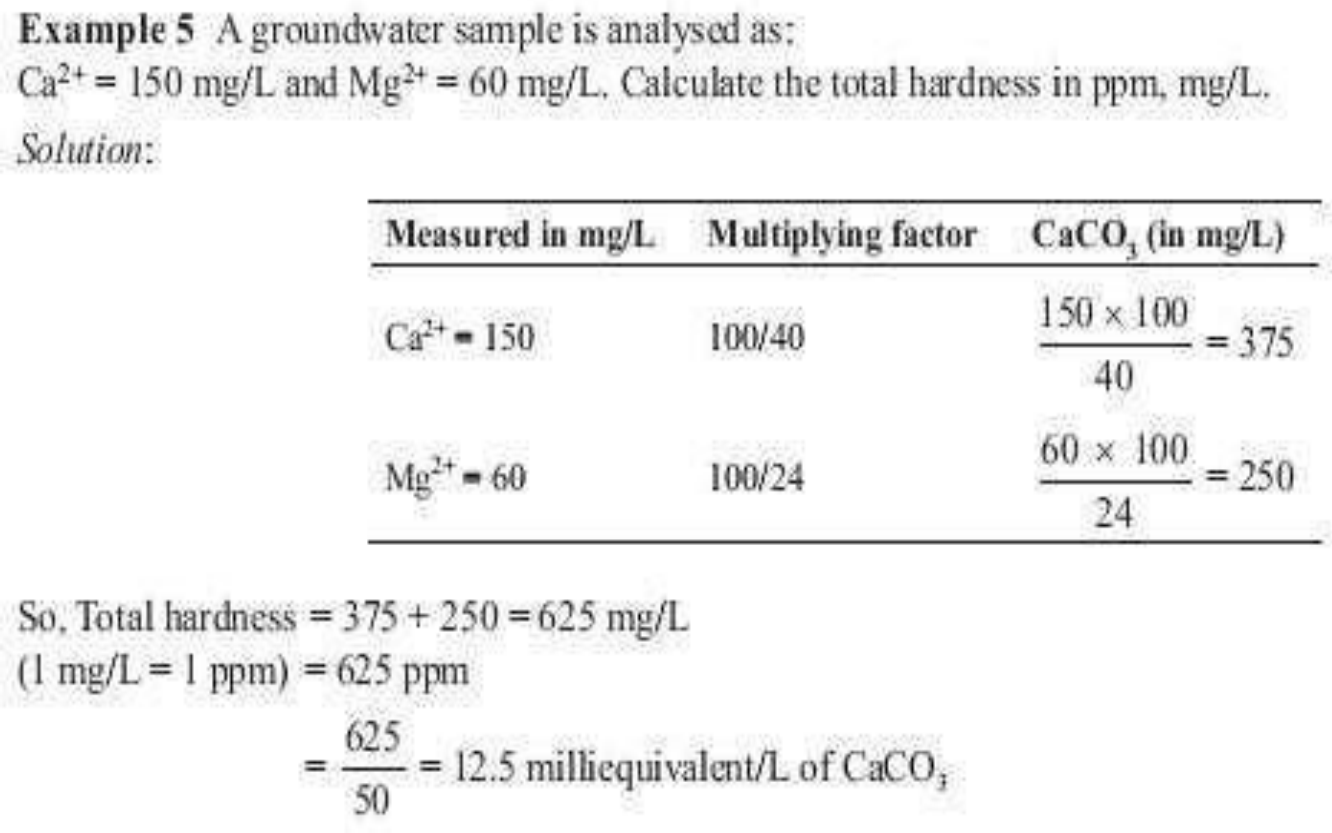
Calculate the temporary and permanent hardness of water.

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

Solved Examples



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.

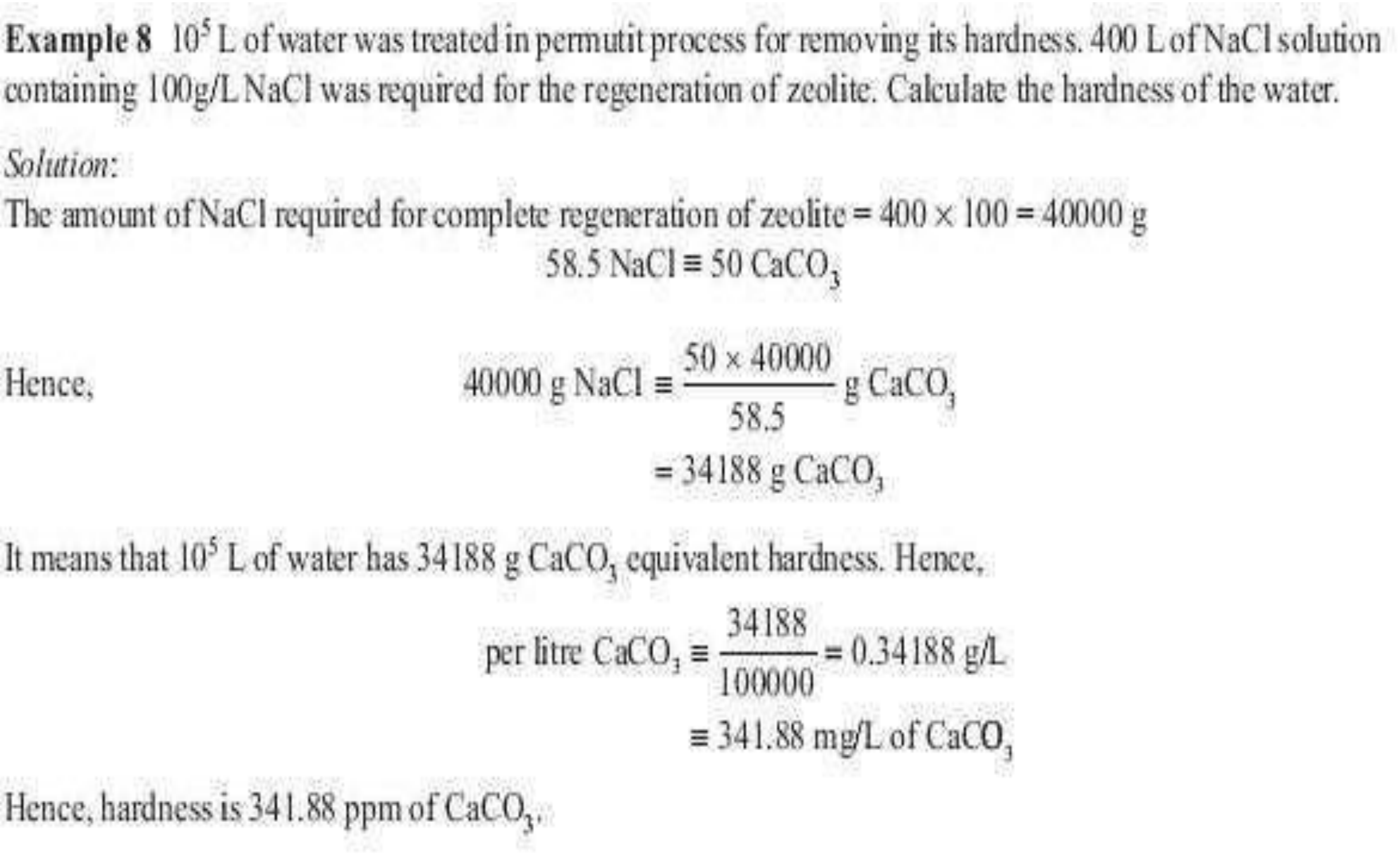
Solution:

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

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

Solved Examples



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

$$58.5 \text{ NaCl} \equiv 50 \text{ CaCO}_3$$

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 ion-exchange resins?
- 5. What do you understand by the hardness of water? What are its causes?
- 6. Distinguish between temporary and permanent hardness of water.
- 7. How is water softened by lime–soda process? Describe its types and suitable chemical reactions.

Theoretical Questions

- 8. What is calgon? What is its application in water treatment?
- 9.What is meant by the exhaustion of cation and anion exchangers? How can they be regenerated?
- 10. Why is demineralization process preferred over the zeolite process for softening of water for use in boilers?
- 11. How is water analyzed for alkalinity? How the alkalinity due to various ions can be determined?
- 12. 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.
- 13. 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.

MODULE - III

MOLECULAR STRUCTURE AND THEORIES OF BONDING

Molecular Structure and Theories of bonding

- ❖Atom is the smallest indivisible particle which aggregates to form matter. The word atom has been derived from Greek word ‘atomos’, meaning indivisible.
- ❖Atomic orbital is the region having the highest probability of finding an electron in an atom.
- ❖The energy levels about the nucles contain group of these atomic orbitals.
- ❖Each orbital (designated as s,p,d, and f) has a unique energy associated with it, can contain a maximum of two electrons and varies in shape and spatial orientation.

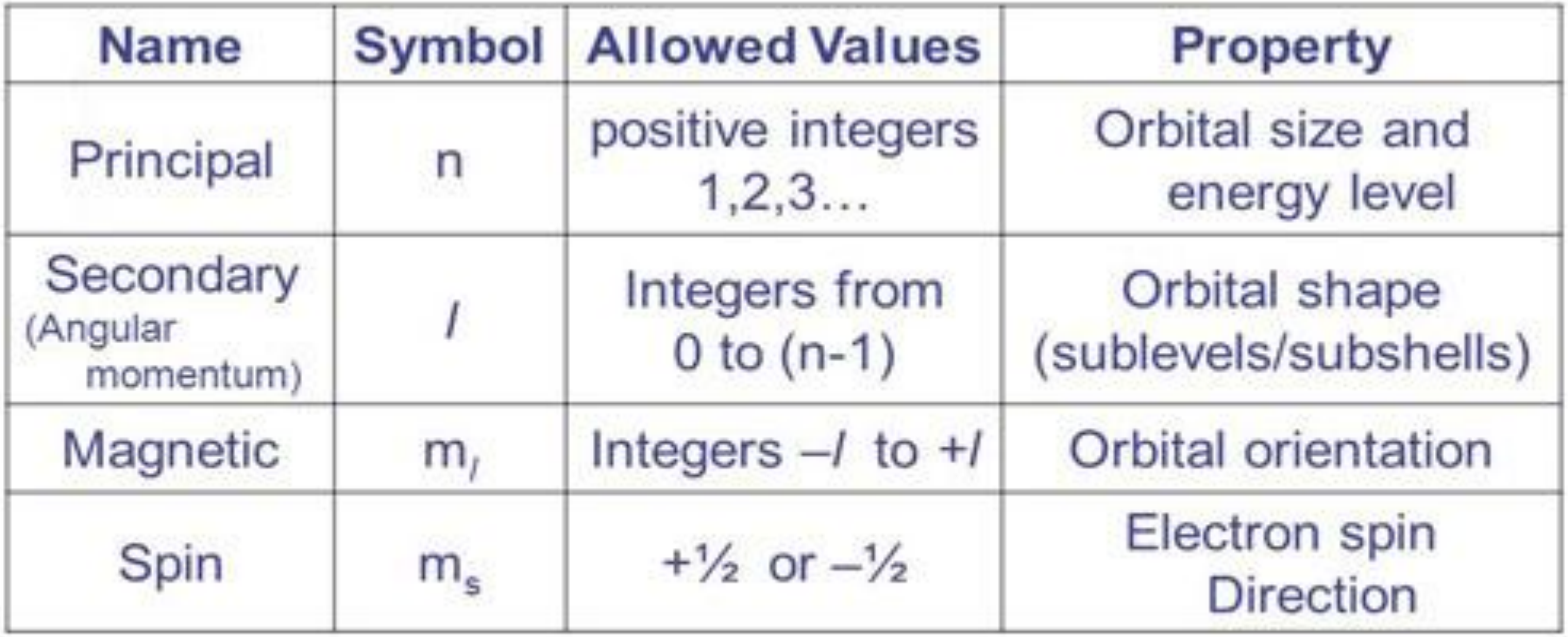
Molecular Structure and Theories of bonding

- We are mainly concerned with the s and p orbitals since most of the elements found in organic molecules have their electrons in the 1s, 2s and 2p orbitals
- The S orbital is in spherical shape. Each P orbital is in dumbbell shape.
- Molecular orbital is the region having the highest probability of finding an electron of a molecule.
- Molecular orbitals results from the combination of atomic orbitals.

Molecular Structure and Theories of bonding

- Atomic orbitals can be explained by quantum no.rs.
- Quantum no.rs can be classified by four
    - i. Principal Quantum Number(n)
    - ii. Azimuthal Quantum Number(l)
    - iii. Magnetic Quantum Number(m)
    - iv. Spin Quantum Number(s)

Molecular Structure and Theories of bonding



Name	Symbol	Allowed Values	Property
Principal	n	positive integers 1,2,3…	Orbital size and energy level
Secondary (Angular momentum)	l	Integers from 0 to (n-1)	Orbital shape (sublevels/subshells)
Magnetic	m_l	Integers –l to +l	Orbital orientation
Spin	m_s	+½ or –½	Electron spin Direction

Molecular Structure and Theories of bonding

Principal Quantum Number(n):

Principal quantum number can be explained by Niels Bhore.

It s mainly describe the energy level of an orbital.

n indicates the relative size of the orbital.

An increase in n also means increase in the energy of the electron in orbital.

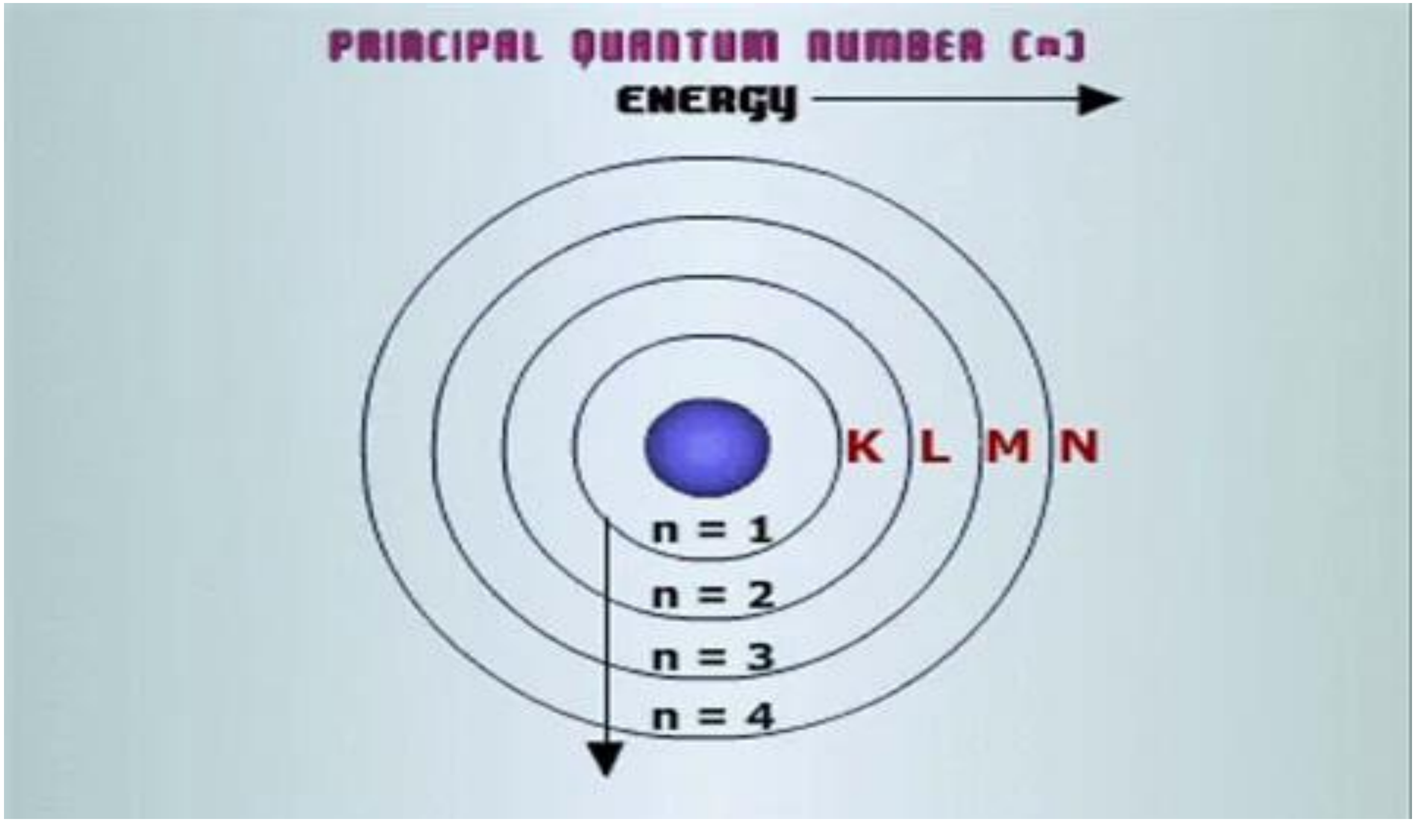
n = 1,2,3

The maximum number of electrons present in an orbit given by 2n2

Principal Quantum number (n) = 1,2,3,4 etc

Letter designation = K,L,M,N…

Maximum number of electrons (2n2)= 2,8,18,32


PRINCIPAL QUANTUM NUMBER (n)
ENERGY
K
L
M
N
n = 1
n = 2
n = 3
n = 4

Molecular Structure and Theories of bonding

Azimuthal Quantum Number(l):

Azimuthal quantum number also called as angular momentum number.

Azimuthal quantum number defines the shape of an atomic orbital.

An orbital with a principal quantum number n, can have an angular momentum, quantum number l from the integers 0 to n-1.

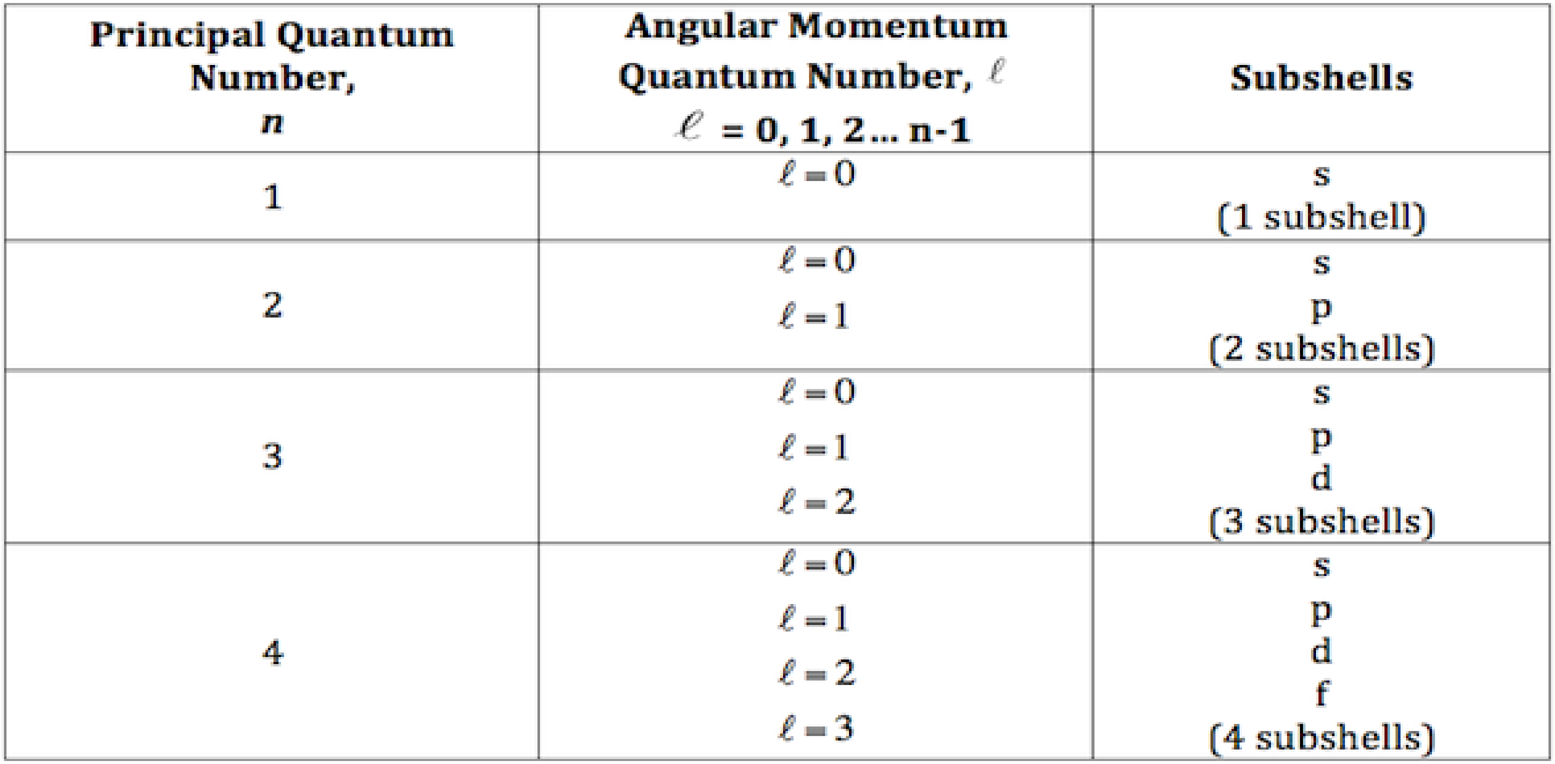
For example, we would call an orbital with $n=2$ and $l=1$ a 2p orbital. 2 designates the shell and p describes the subshell shape.

With in each shell there are different orbital's called subshell.

If $n=1$ then $l=0$, and $n=2$ then $l=0,1$.

Each number of l refers to a specific subshell shape and usually the number 0, 1, 2, 3… are replaced with the letters s, p, d, f… respectively

Molecular Structure and Theories of bonding



Principal Quantum Number, *n*	**Angular Momentum Quantum Number, ℓ** **ℓ = 0, 1, 2… n-1**	**Subshells**
1	$\ell = 0$	s (1 subshell)
2	$\ell = 0$ $\ell = 1$	s p (2 subshells)
3	$\ell = 0$ $\ell = 1$ $\ell = 2$	s p d (3 subshells)
4	$\ell = 0$ $\ell = 1$ $\ell = 2$ $\ell = 3$	s p d f (4 subshells)

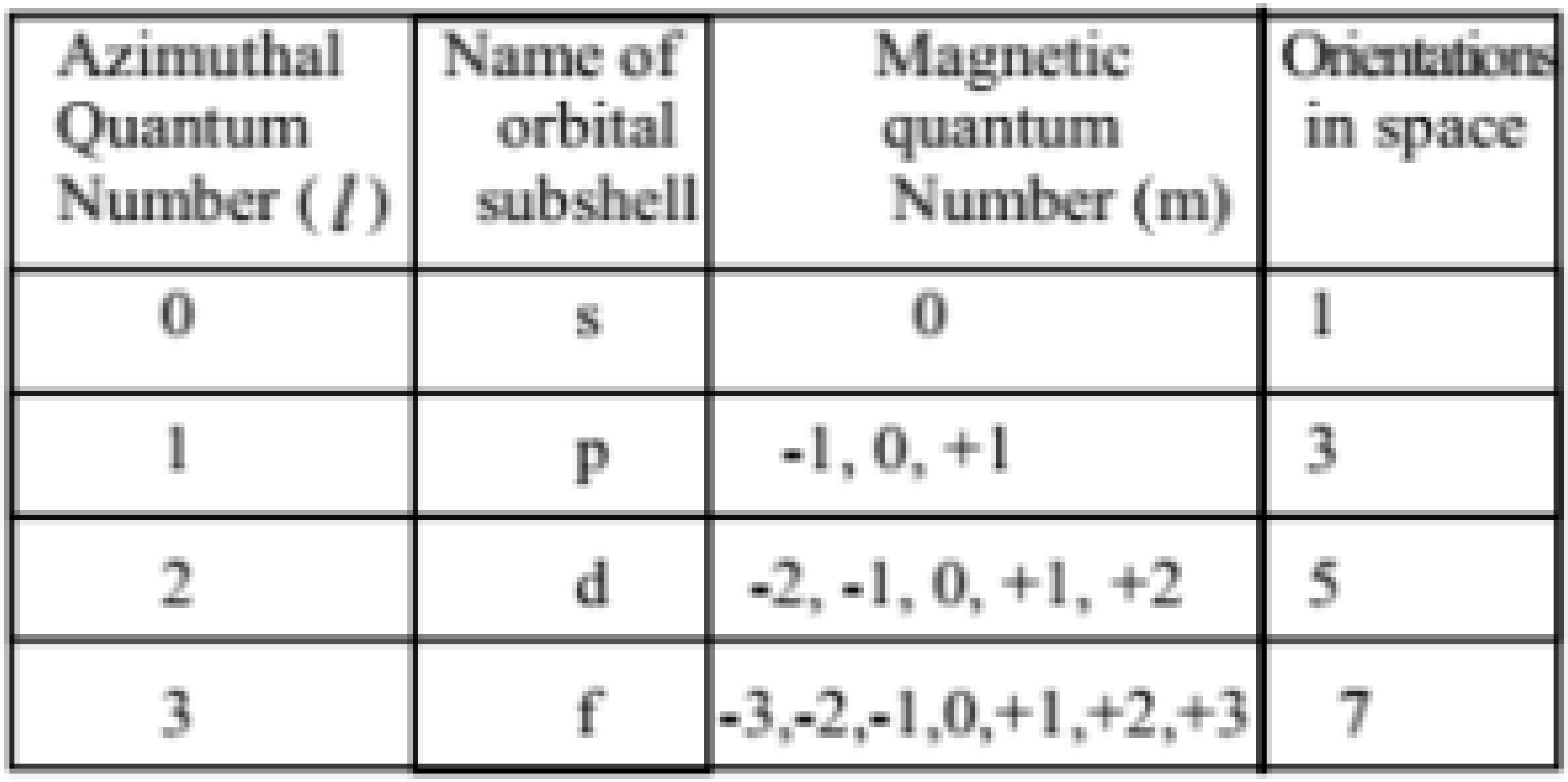
Molecular Structure and Theories of bonding

Magnetic quantum number (m):

m describes the orientation of the orbital in space.

m has integer values –l to +l including 0.

For azimuthal quantum number l possible values of magnetic quantum number are -1 to +1 through 0 i.e. m = -1,0,+1. This quantum number gives possible orientation of the orbital in the space.



Azimuthal Quantum Number (*l*)	Name of orbital subshell	Magnetic quantum Number (m)	Orientations in space
0	s	0	1
1	p	-1, 0, +1	3
2	d	-2, -1, 0, +1, +2	5
3	f	-3,-2,-1,0,+1,+2,+3	7

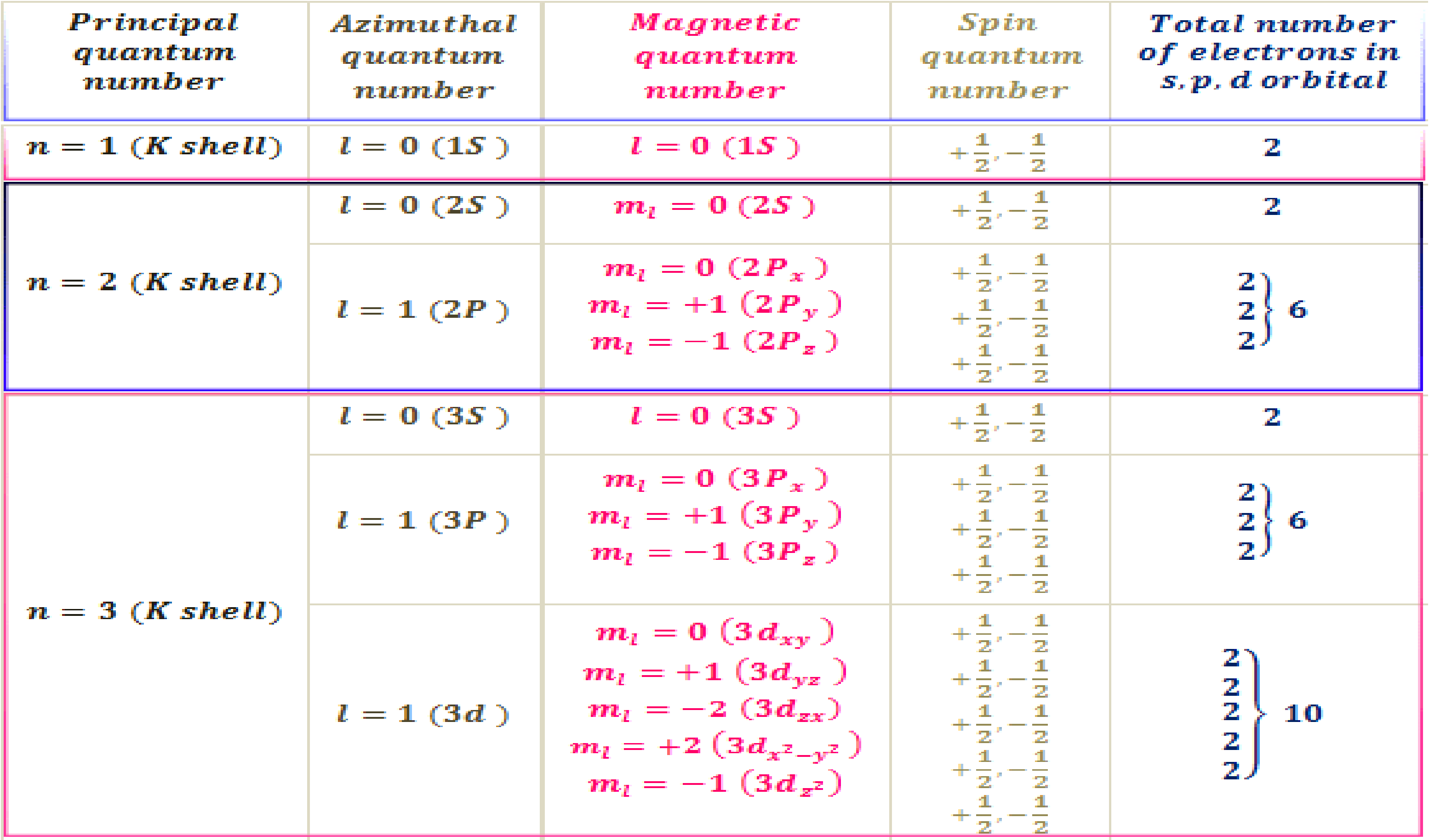
Molecular Structure and Theories of bonding

Spin Quantum Number(s):

The electron in orbital motion can spin clock wise or anti clock wise in its own axis. Hence two values of quantum number are possible.

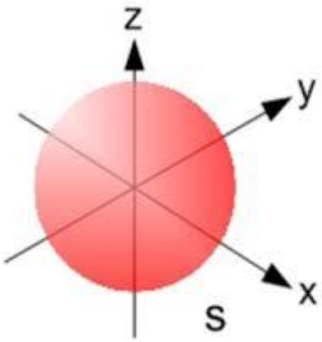
These values are taken as +1/2 or -1/2.

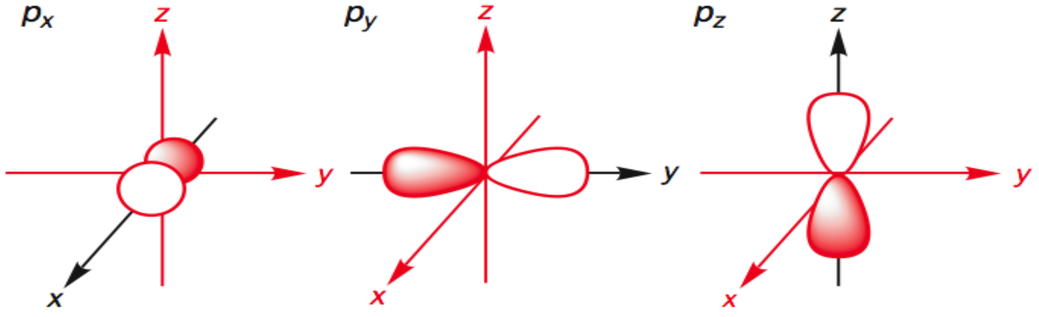
Spin Quantum number indicates magnetic moment associated with the electron.



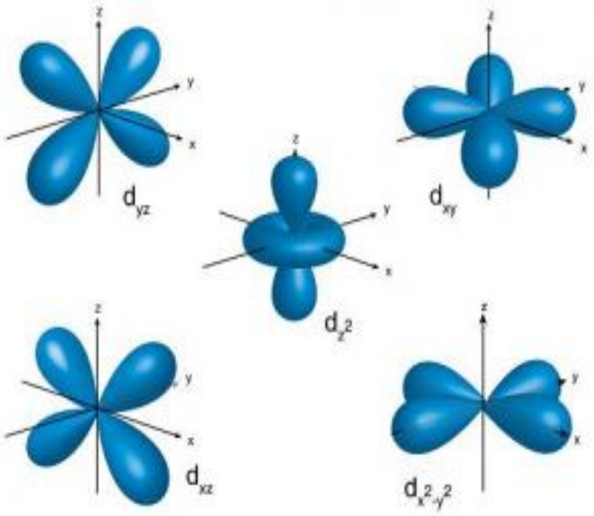
Principal quantum number	Azimuthal quantum number	Magnetic quantum number	Spin quantum number	Total number of electrons in s, p, d orbital
$n = 1$ (K shell)	$l = 0$ (1S)	$l = 0$ (1S)	$+\frac{1}{2}, -\frac{1}{2}$	2
$n = 2$ (K shell)	$l = 0$ (2S)	$m_l = 0$ (2S)	$+\frac{1}{2}, -\frac{1}{2}$	2
	$l = 1$ (2P)	$m_l = 0$ $(2P_x)$ $m_l = +1$ $(2P_y)$ $m_l = -1$ $(2P_z)$	$+\frac{1}{2}, -\frac{1}{2}$ $+\frac{1}{2}, -\frac{1}{2}$ $+\frac{1}{2}, -\frac{1}{2}$	$\left.\begin{matrix}2\\2\\2\end{matrix}\right\} 6$
$n = 3$ (K shell)	$l = 0$ (3S)	$l = 0$ (3S)	$+\frac{1}{2}, -\frac{1}{2}$	2
	$l = 1$ (3P)	$m_l = 0$ $(3P_x)$ $m_l = +1$ $(3P_y)$ $m_l = -1$ $(3P_z)$	$+\frac{1}{2}, -\frac{1}{2}$ $+\frac{1}{2}, -\frac{1}{2}$ $+\frac{1}{2}, -\frac{1}{2}$	$\left.\begin{matrix}2\\2\\2\end{matrix}\right\} 6$
	$l = 1$ (3d)	$m_l = 0$ $(3d_{xy})$ $m_l = +1$ $(3d_{yz})$ $m_l = -2$ $(3d_{zx})$ $m_l = +2$ $(3d_{x^2-y^2})$ $m_l = -1$ $(3d_{z^2})$	$+\frac{1}{2}, -\frac{1}{2}$ $+\frac{1}{2}, -\frac{1}{2}$ $+\frac{1}{2}, -\frac{1}{2}$ $+\frac{1}{2}, -\frac{1}{2}$ $+\frac{1}{2}, -\frac{1}{2}$	$\left.\begin{matrix}2\\2\\2\\2\\2\end{matrix}\right\} 10$

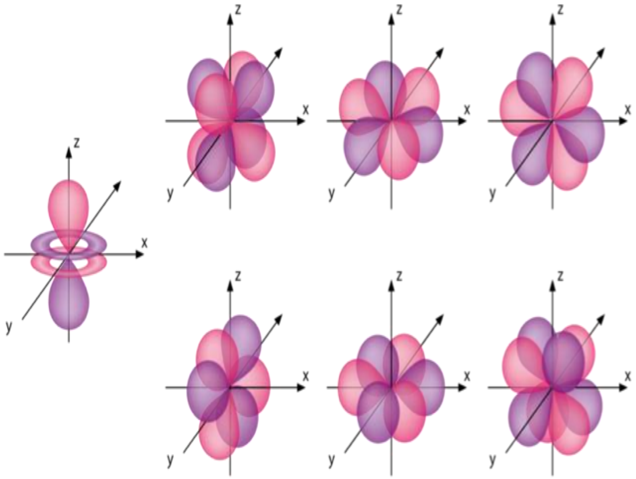
Shapes of Atomic Orbitals





the three degenerate p orbitals are aligned along perpendicular axes



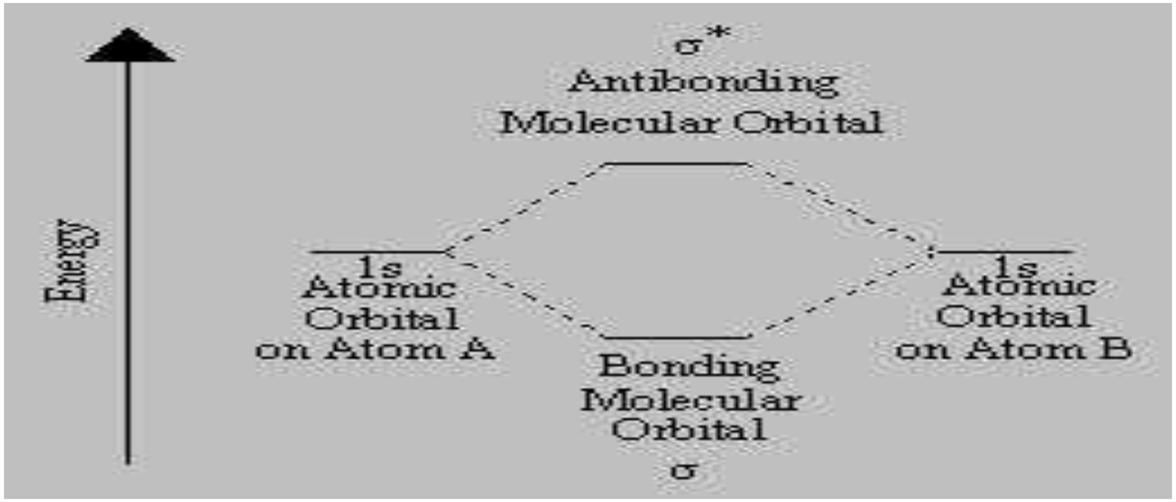


Linear combination of orbitals

- Molecular orbitals of a molecule,, i.e solutions to the molecular Schrodinger equation can be obtained by a method known as linear combination of atomic orbitals (LCAO). As per this method the formation of orbitals is because of addition or subtraction of atomic orbital wave function. For diatomic molecules, such a wave function takes the form, $\Psi = N (C_A\Psi_A \pm C_B \Psi_B)$
- Where Ψ is the wave function of MO; Ψ_A , Ψ_B are wave functions bbelonging AOs for atom A and atom B respectively; $C_{A,}$ C_B are adjustable coefficients and N is normalizing factor.

Molecular Structure and Theories of bonding

This high energy molecular orbital is termed the anti-bonding orbital since electrons placed in this kind of orbital decrease the stability of the bond. The anti-bonding orbital's are represented by super script asterisks (ex: σ*, π*). The lower energy molecular orbital is called bonding orbital. Since electrons placed in such an orbital increase the stability of the bond.



Molecular Structure and Theories of bonding

Bonding and anti-bonding orbital’s:

Two atomic orbital’s, one from each bonded atom, whose energies are comparable in value and which possess a large amount of overlap, coalesce to form two molecular orbital’s. One of these molecular orbital’s lower in energy than either of the atomic orbitals from which it was formed and hence gives rise to a repulsive state.

Energy Level Diagram of O2

O_2 :

$(1s^2)\ \sigma^*(1s^2)\ \sigma(2s^2)\ \sigma^*(2s^2)\ \sigma(2p_z{}^2)\pi(2p_x{}^2)\ \pi(2p_y{}^2)$

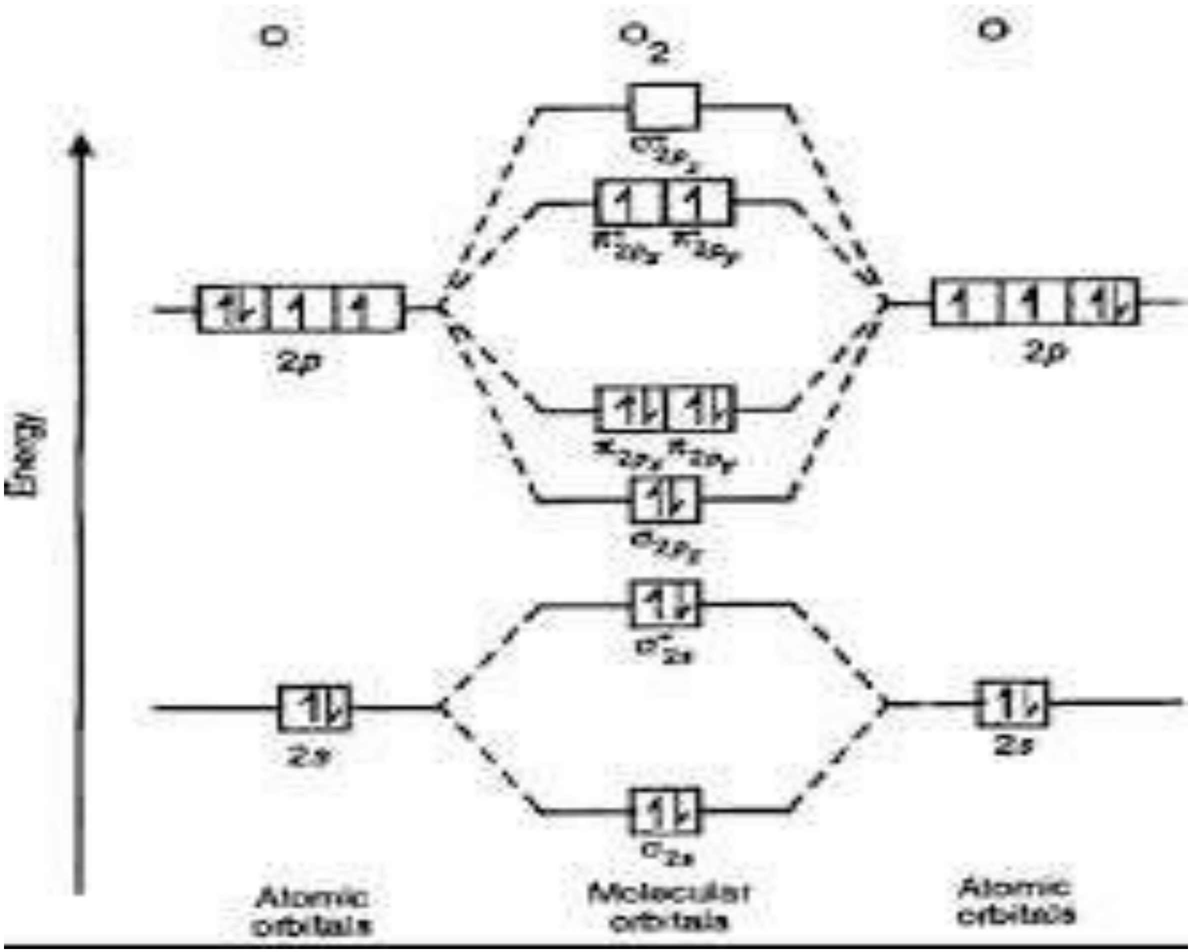
$\pi^*(2p_x{}^1)\quad \pi^*(2p_y{}^1)$

Bond order = 1/2 [10-6] = 2

The number of covalent bonds in Oxygen is two.

Presence of unpaired electron indicates it to be paramagnetic.

Energy Level Diagram of O2



Energy Level Diagram of N2

Nitrogen(N2):

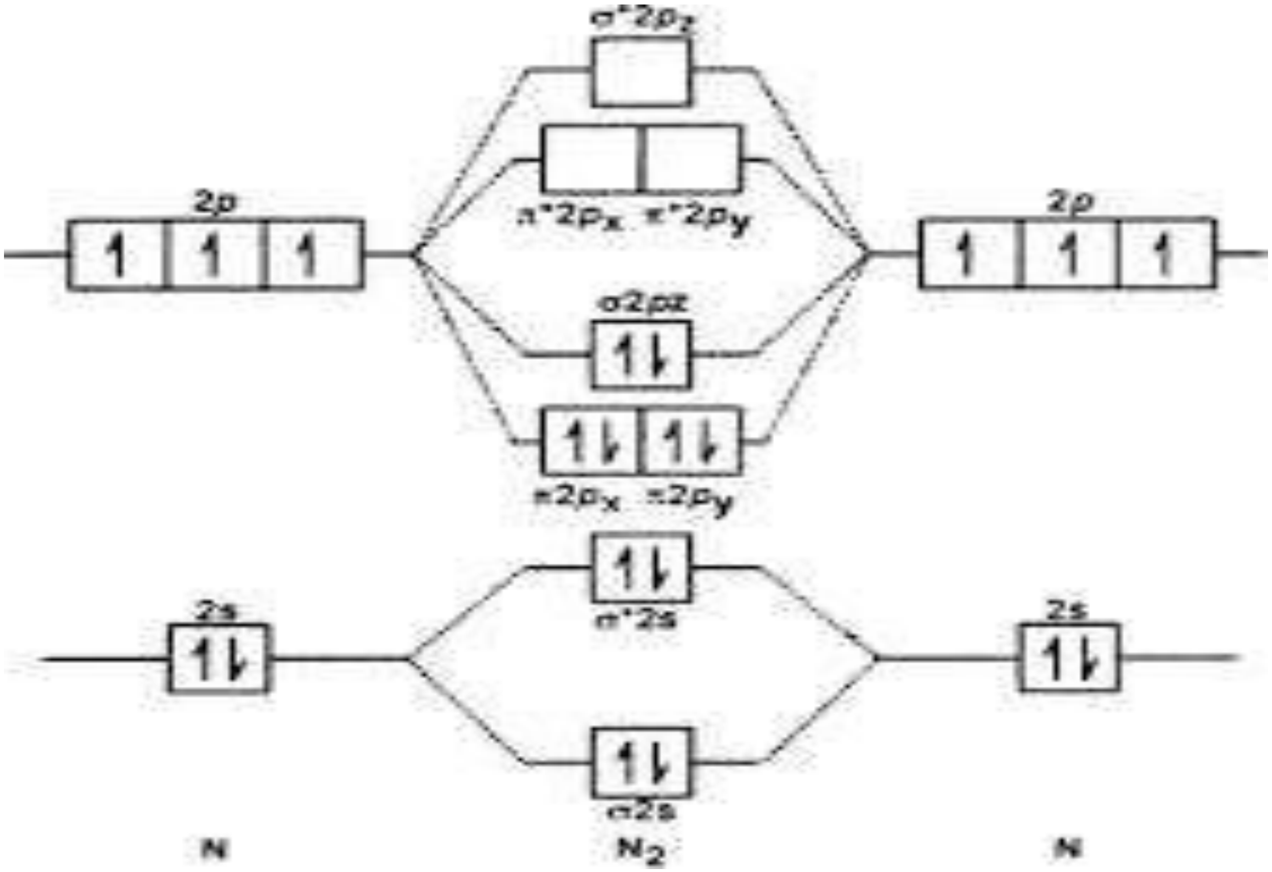
$(1s^2)\ \sigma^*(1s^2)\ \sigma(2s^2)\ \sigma^*(2s^2)\ \pi(2p_x{}^2)\ \pi(2p_y{}^2)\sigma(2p_z{}^2)$

Bond order = 1/2 [10-4] = 3

The number of covalent bonds in Nitrogen is three.

Presence of no unpaired electron indicates it to be diamagnetic.

Energy Level Diagram of N2



Energy Level Diagram of F2

F_2 :

$\sigma\,(1s^2)\ \sigma^*(1s^2)\ \sigma(2s^2)\ \sigma^*(2s^2)\ \sigma(2p_z^{\,2})\pi(2p_x^{\,2})\ \pi(2p_y^{\,2})\pi^*(2p_x^{\,2})\ \pi^*(2p_y^{\,2})$

Bond Order = 1/2 [10-8] = 1

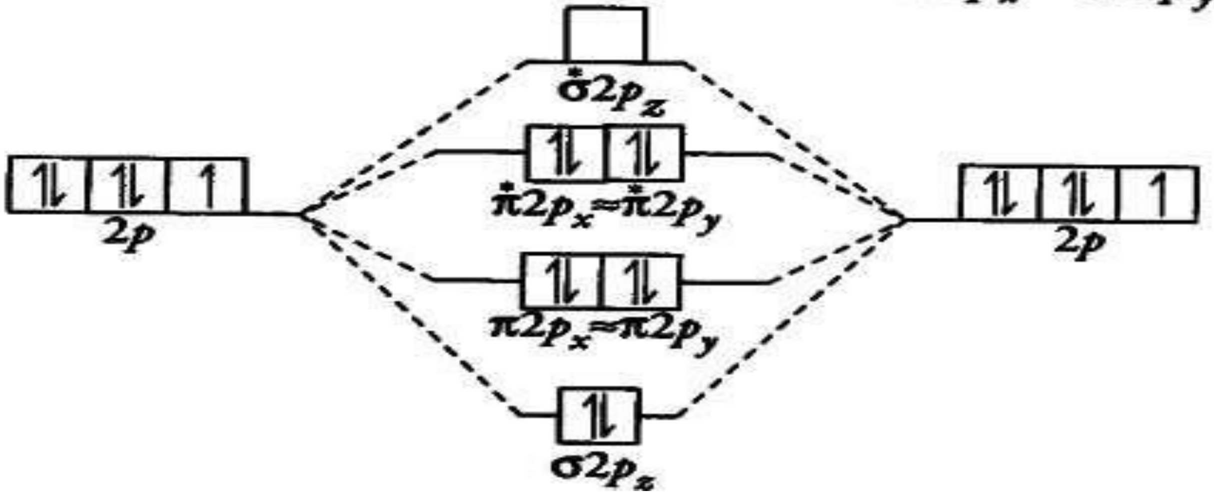
Number of covalent bond in Fluoride is 1.

Presence of no unpaired electron indicates it to be diatomic.

Energy Level Diagram of F2

Formation of F_2 molecule $_9F = 1s^2, 2s^2, 2p_x^2, 2p_y^2, 2p_z^1$

$F_2 = \sigma 1s^2, \overset{*}{\sigma} 1s^2, \sigma 2s^2, \overset{*}{\sigma} 2s^2, \sigma 2p_z^2, \pi 2p_x^2 \approx \pi 2p_y^2,$
$\overset{*}{\pi} 2p_x^2 \approx \overset{*}{\pi} 2p_y^2$



Energy Level Diagram of CO

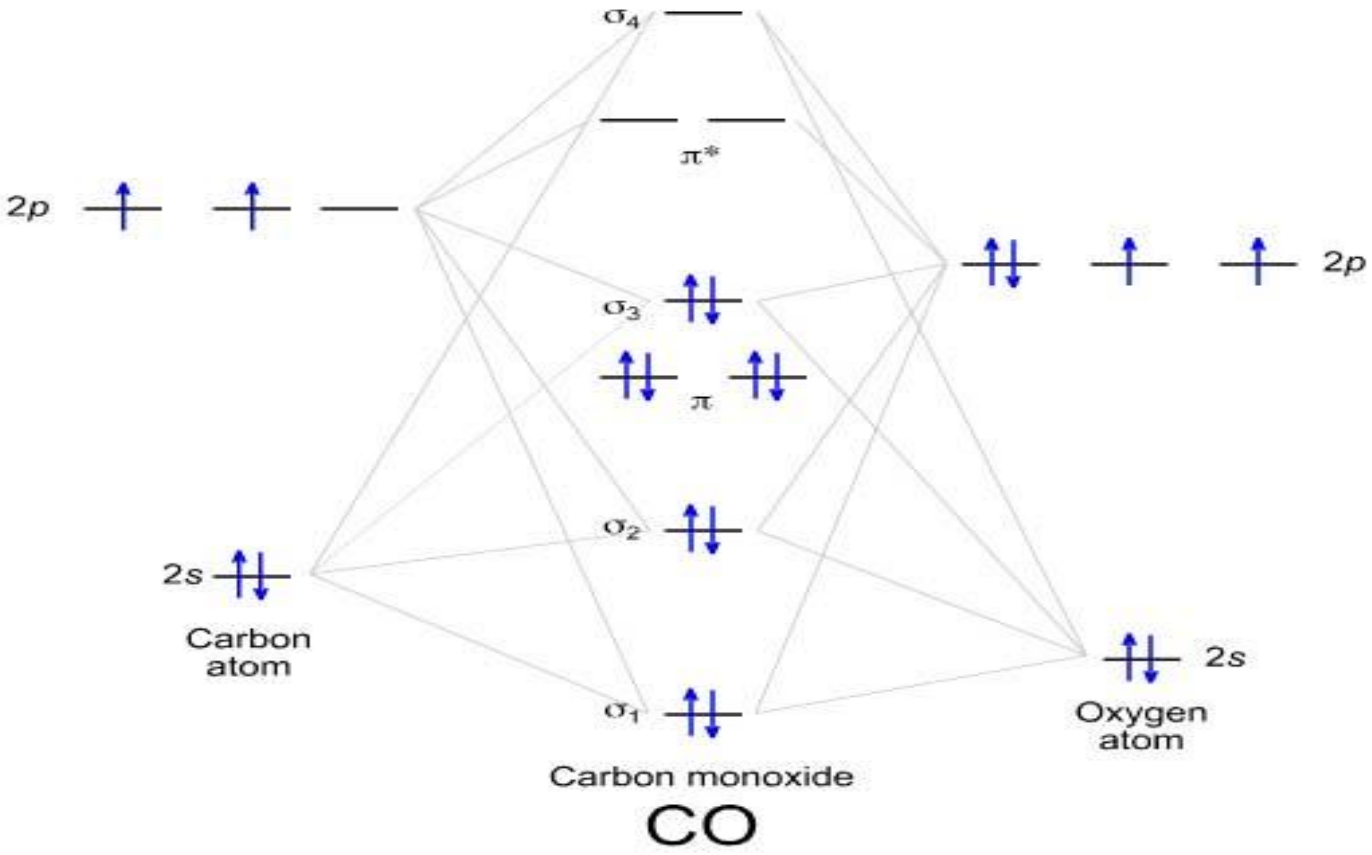
CO: $(1s^2)\ \sigma^*(1s^2)\ \sigma(2s^2)\ \sigma^*(2s^2)\ \pi(2p_x{}^2)\ \pi(2p_y{}^2)\sigma(2p_z{}^2)$

Bond order = 1/2 [10-4] = 3

The number of covalent bonds in Carbon Monoxide is three.

Presence of no unpaired electron indicates it to be diamagnetic.

Energy Level Diagram of CO



Energy Level Diagram of NO

NO :

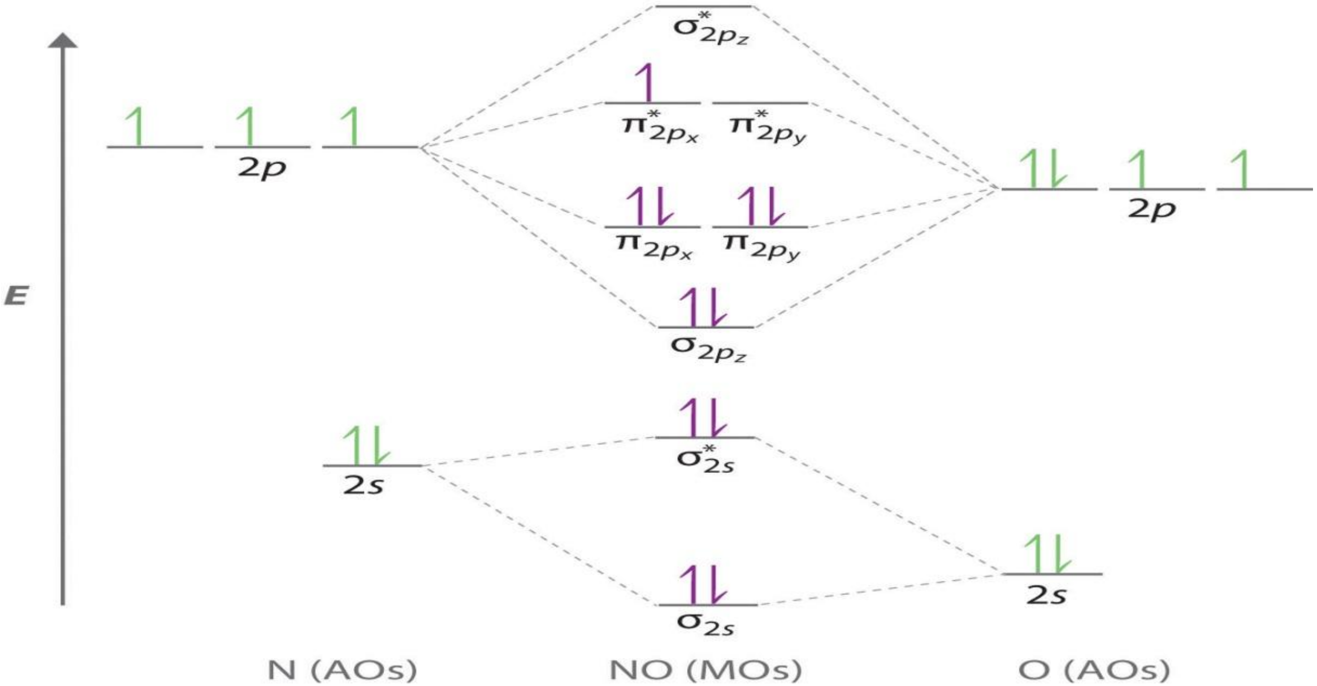
$\sigma\ (1s^2)\ \sigma^*(1s^2)\ \sigma(2s^2)\ \sigma^*(2s^2)\ \sigma(2p_Z{}^2)\ \pi\ (2p_x{}^2)\ \pi(2p_y{}^2)$
$\pi^*(2p_X{}^1)$

Bond Order = 1/2 [10-5] = 2.5

Number of covalent bond in Nitric Oxide is 2.5.

Presence of unpaired electron indicates it to be Paramagnetic.

Energy Level Diagram of NO



Theoretical Questions

1Q. Write the MO electronic configuration of a homo di atomic molecule having a bond order of three.

Ans. A diatomic molecule having the bond order of three is Nitrogen(N_2),

whose MO configuration is :$(1s^2)\ \sigma^*(1s^2)\ \sigma(2s^2)\ \sigma^*(2s^2)\ \pi(2p_x^{\,2})\ \pi(2p_y^{\,2})\sigma(2p_z^{\,2})$.

2Q. Calculate the bond order of O_2 molecule?

Ans. Electronic configuration of O_2 is:

$(1s^2)\ \sigma^*(1s^2)\ \sigma(2s^2)\ \sigma^*(2s^2)\ \sigma(2p_z^{\,2})\pi(2p_x^{\,2})\ \pi(2p_y^{\,2})\ \pi^*(2p_x^{\,1})\ \pi^*(2p_y^{\,1})$

Bond order $= 1/2\ [N_a - N_b\ ]$

$= 1/2\ [10-6] = 2$

Theoretical Questions

3Q. What is an antibonding molecular orbital?

Ans. A molecular orbital obtained by subtraction of wave functions of the atomic orbital's.

4Q. What is bond order?

5Q. What do understand by bonding molecular orbital?

Ans. The molecular orbital formed by the additive effect of the wave functions of atomic orbital's.

6Q. Write any two molecules with same bond order?

Ans.Two molecules with same bond order is CO, N_2 . And bond order is 3.

Theoretical Questions

7Q. Which hetero di atomic molecule paramagnetic in nature? Write its electronic configuration.

Ans. Nitrogen Oxide is paramagnetic in nature, electronic configuration is

$NO : \sigma(1s^2)\ \sigma^*(1s^2)\ \sigma(2s^2)\ \sigma^*(2s^2)\ \sigma(2p_Z^2)\ \pi(2p_x^2)\ \pi(2p_y^2)\ \pi^*(2p_X^1)$

8Q. Write the MO electronic configuration of a hetero di atomic molecule having a bond order of three.

Ans. : A hetero di atomic molecule having bond order of three is CO, its electronic configuration is :

$(1s^2)\ \sigma^*(1s^2)\ \sigma(2s^2)\ \sigma^*(2s^2)\ \pi(2p_x^2)\ \pi(2p_y^2)\sigma(2p_z^2)$

Bond order = 1/2 [10-4] = 3

Crystal field theory

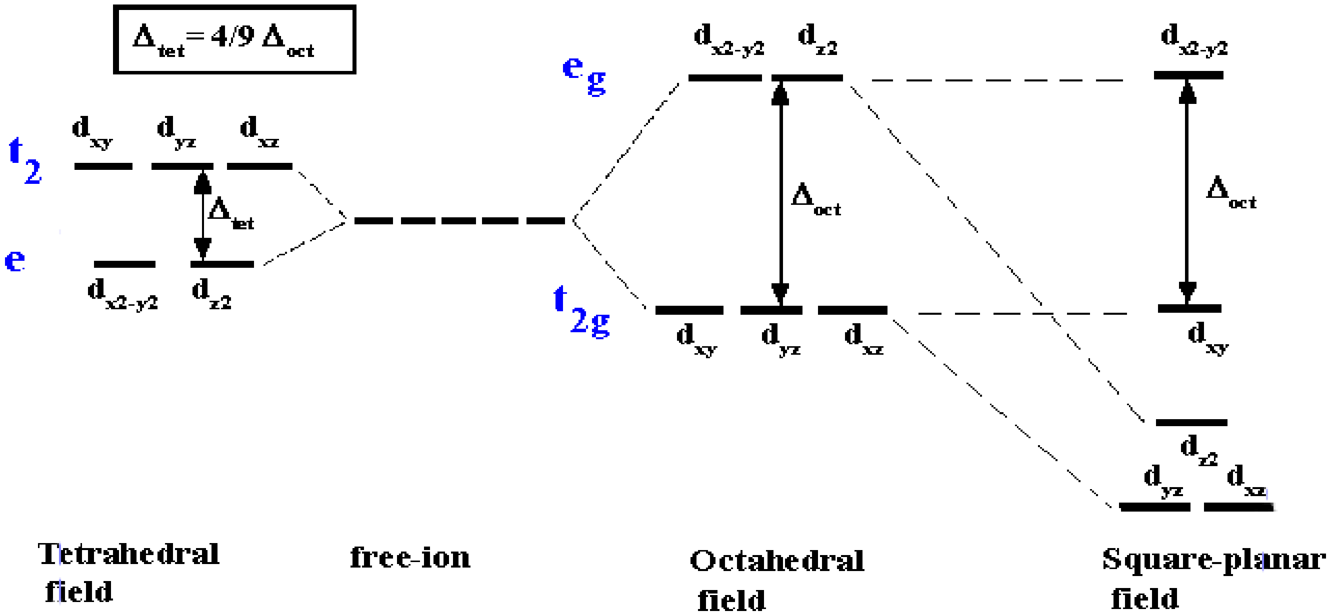
Crystal field theory was developed to describe important properties of complexes (magnetism, absorption spectra, oxidation states, co-ordination etc.). CFT explains splitting in d-orbital.

In free metal atom all d-orbital's have same energy, when a ligand coalescence with d-orbital splits into t_2g, eg orbital's having different energies.

- The important assumptions are
- i. Ligands are treated as point charges.
- ii. There is no interaction between metal orbital’s and ligand orbital’s.
- In free metal atom all d-orbital’s have same energy (degenerate) when a complex is formed d-orbital’s have different energies.

Crystal field theory

Energy levels of the d-orbitals in common stereochemistries



Applications of CFT

i. Crystal field theory explains magnetic properties of metal complexes.

ii. The spin-only formula (μs) applies reasonably well to metal ions from the first row of transition metals: (units = μB,, Bohr-magnetons).

The **spin-only** formula

$$\boxed{\mu s = \sqrt{n(n+2)}}$$

Crystal field theory

[CoCl6]4- Co2+, 3d 7 ,Cl- weak ligand, HS, 3 unpaired e’s ~ 3.9 BM [Co(CN)5(H2O)]3-. Co2+, CN- strong ligand, LS 1 unpaired e 1.73 BM [Co(R2NCS2)3], Co3+, 3d 6 , 0 BM means ligand is strong field and low spin complex.

iii. Crystal field theory explains bond order of metal complexes.
iv. Crystal field theory explains colour properties of metal complexes.

Crystal Field Stabilization Energy

Crystal Field Stabilization Energy(CFSE) and pairing (P) Energy

The CFSE is defined as net gain in energy achieved by preferential filling of electrons in lower lying d orbital's over the energy of complete random occupancy of electrons in all five d orbital's.

It is 2 to 10% of actual bond energy. The energy required to pair the electrons in the same orbital
known as mean pairing energy and it is constant for the same metal ion.

Crystal Field Stabilization Energy

Noticeable features

When magnitude of Δ0 is higher than P, electrons tend to pair in the lower lying orbital thus spin paired or low spin complexes are formed. On the other hand,if Δ0 is less than P, high
spin or spin free complexes are formed. If Δ0 is approximately equal to P,single temperature changes
may affect spin changes. Sum of CFSE and P gives Total Stabilization Energy(TSE).

For d^4 and d^7 low spin systems only one P is added in CFSE to get TSE because only one electron is to be paired in the same orbital, rest are paired in natural configuration while for d^5 and d^6 low spin systems twice of pairing energy is required to be added to get TSE.

Crystal Field Stabilization Energy

In the octahedral complexes, ligand approach along the axes.

As a result, the d-orbitals where electron density is oriented along the axes, dx^2-y^2 and dz^2 are repelled much more by the ligands while the orbitals dxy, dyz, dxz having electron density oriented in between the axes are repelled lesser by the ligands.

Thus two sets of orbital’s eg and t2g,doubly and triply degenerate respectively, are formed.

The magnitude of $\Delta0$ depends on mainly on field strength of ligand, oxidation state of metal and down the group from 3d to 4d or 5d metals.

Crystal Field Theory in octahedral complex

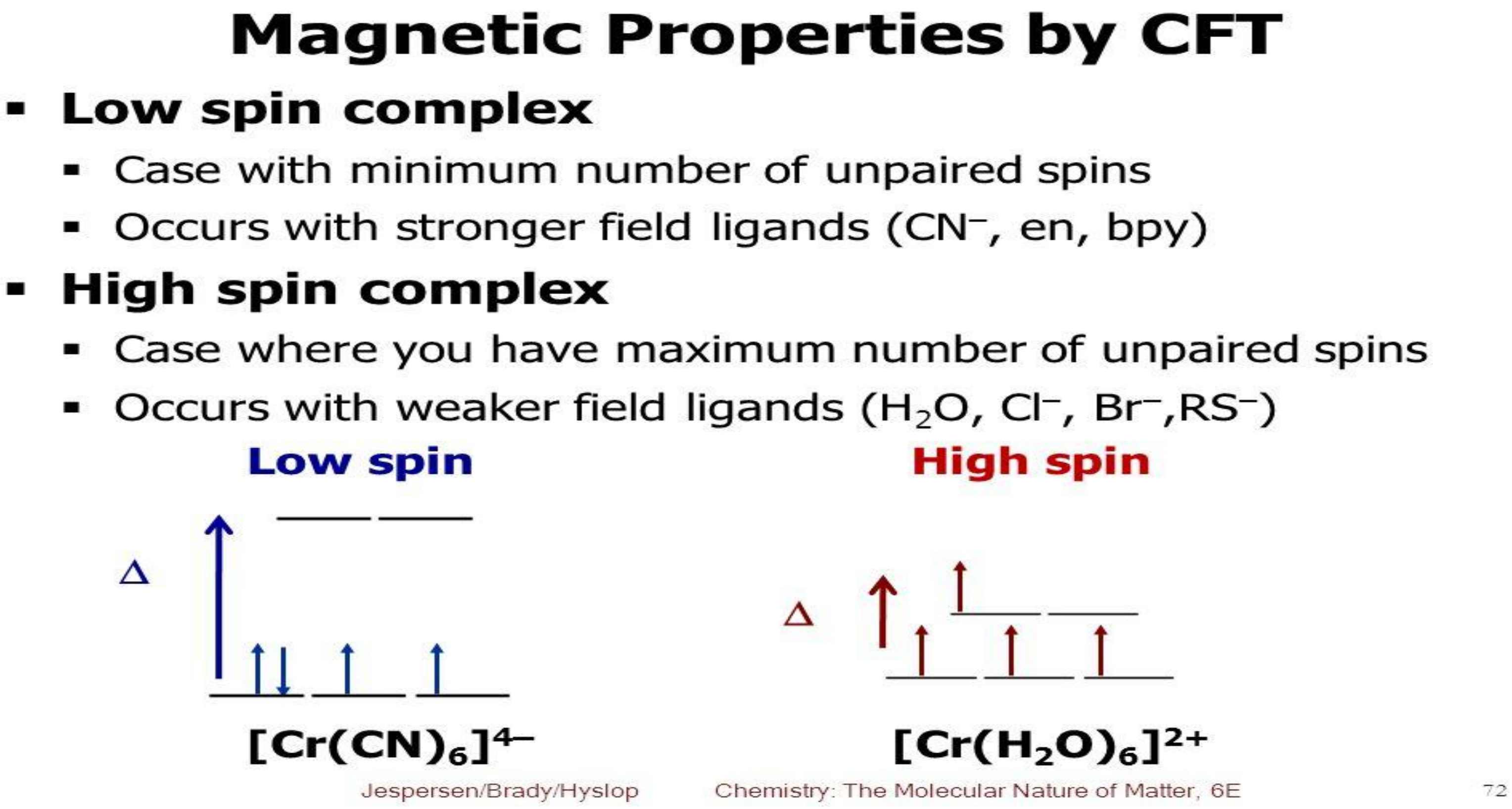
Δ_o Depends upon:

1. Nature of ligand
2. Charge on metal ion.
3. Principal Quantam No. of d-orbital (3d,4d,5d)

   $\Delta_o(5d) > \Delta_o(4d) > \Delta_o(3d)$

Spectrochemical series:

$I^- < Br^- < S^{2-} < SCN^- < Cl^- < N_3^-, F^- <$ urea, $OH^- <$ ox, $O^{2-} < H_2O < NCS^- <$ py, $NH_3 <$ en $<$ bpy, phen $< NO_2^- < CH_3^-, C_6H_5^- < CN^- < CO$.



Magnetic Properties by CFT

- **Low spin complex**
  - Case with minimum number of unpaired spins
  - Occurs with stronger field ligands (CN^-, en, bpy)
- **High spin complex**
  - Case where you have maximum number of unpaired spins
  - Occurs with weaker field ligands (H_2O, Cl^-, Br^-, RS^-)

Low spin

Δ

$[Cr(CN)_6]^{4-}$

High spin

Δ

$[Cr(H_2O)_6]^{2+}$

Jespersen/Brady/Hyslop Chemistry: The Molecular Nature of Matter, 6E 72

Crystal Field Theory in Tetrahedral complex

In tetrahedral geometry, the ligand approach is in between the axes. The eg orbitals lie exactly between L- M-L bond.

In tetrahedral complex, the four ligands occupy alternate corners of a cube and the metal ion is placed in the center.

Hence the d-orbitals are not pointed directly towards ligands.

The dxy, dyz, dxz (non-axia) orbitals are closer to ligands then dx^2-y^2 and dz^2 (axial orbitals).

Therefore the energy of t_2g orbital raised and eg orbital's are lowered from the center.

Crystal Field Theory in Tetrahedral complex

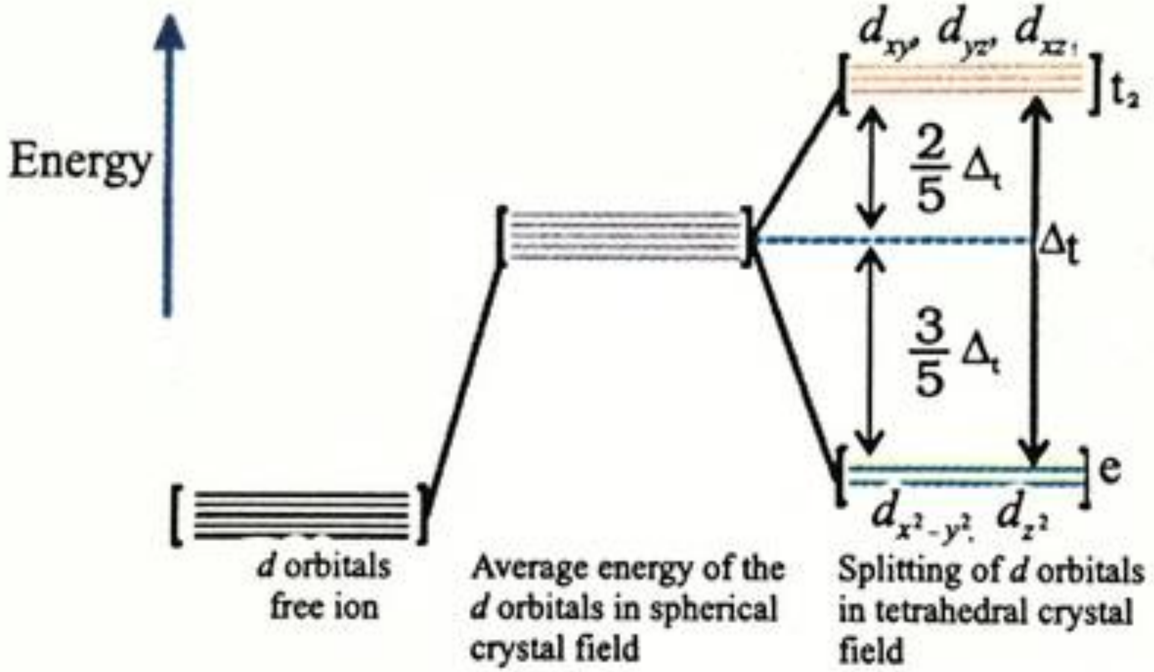
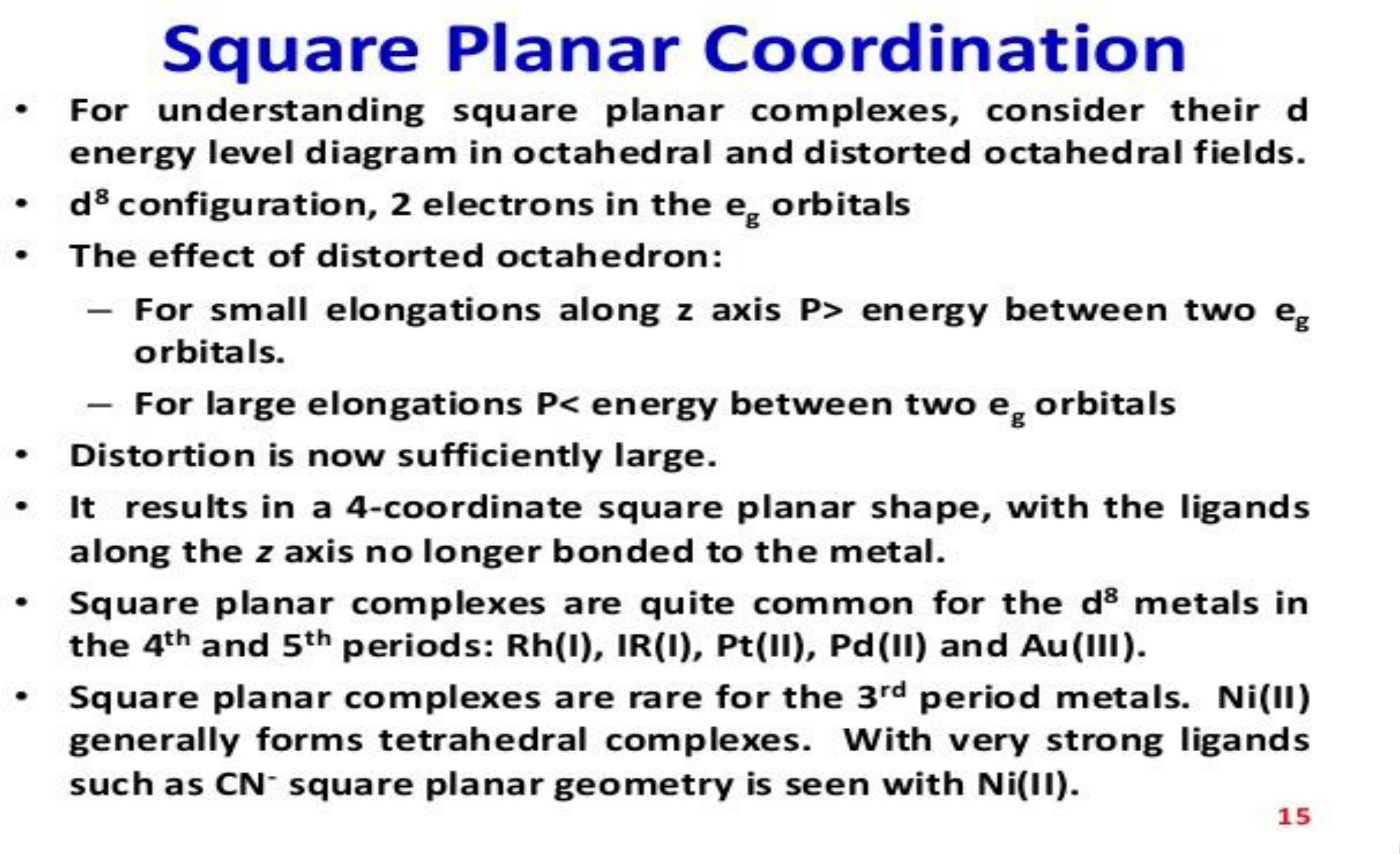


Fig.9.9: *d orbital splitting in a tetrahedral crystal field.*

Square Planar Complex

The electrons present singly in dx2-y2 and dz2 are paired up in dz2 and dx2-y2 becomes vacant, therefore four ligands can now approach along x, y directions but experience too much repulsion along z direction. Consequently, square planar complex is formed instead of octahedral complex.

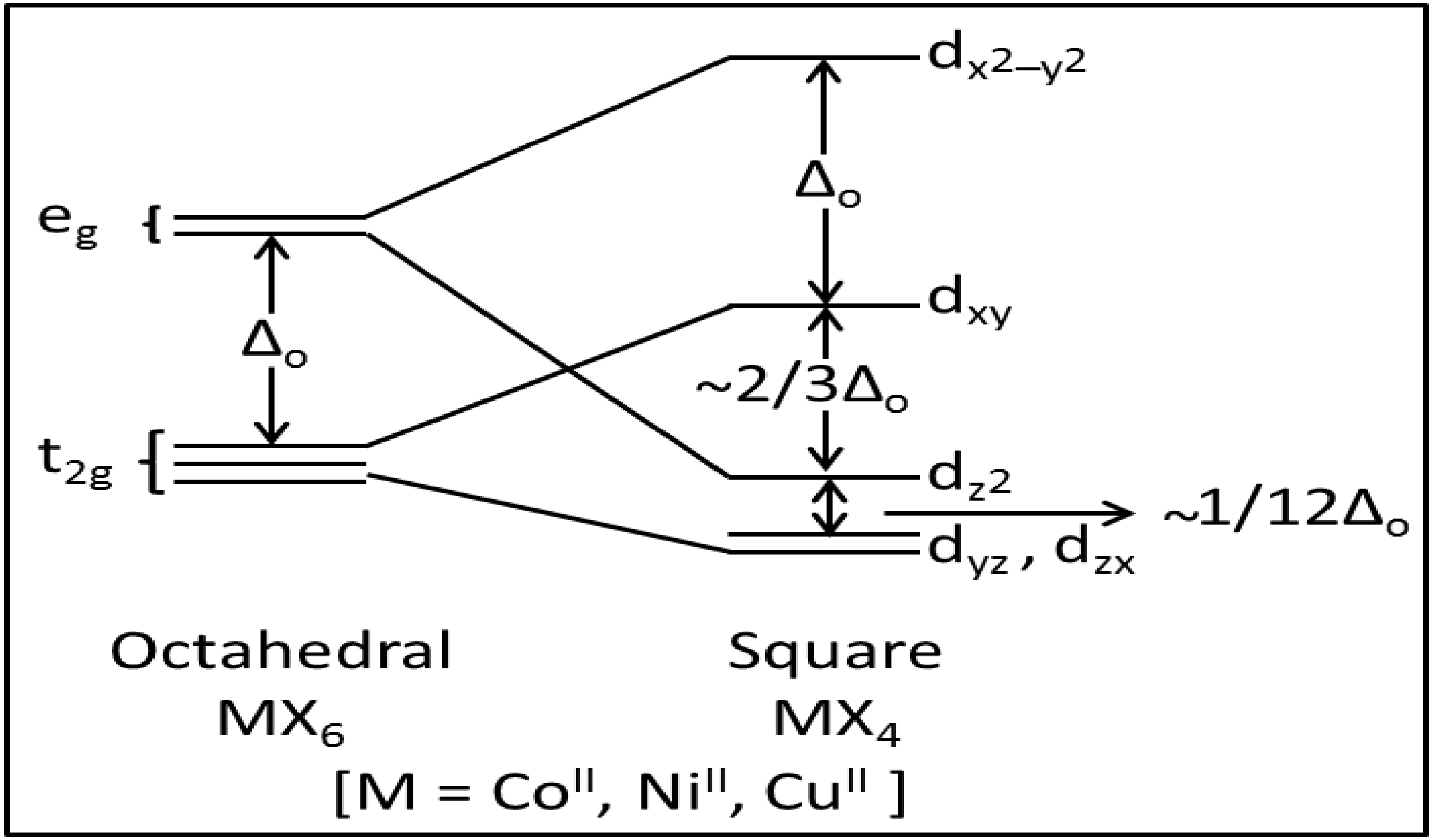
Square Planar Complex



Square Planar Coordination

- For understanding square planar complexes, consider their d energy level diagram in octahedral and distorted octahedral fields.
- d^8 configuration, 2 electrons in the e_g orbitals
- The effect of distorted octahedron:
  - For small elongations along z axis P> energy between two e_g orbitals.
  - For large elongations P< energy between two e_g orbitals
- Distortion is now sufficiently large.
- It results in a 4-coordinate square planar shape, with the ligands along the *z* axis no longer bonded to the metal.
- Square planar complexes are quite common for the d^8 metals in the 4th and 5th periods: Rh(I), IR(I), Pt(II), Pd(II) and Au(III).
- Square planar complexes are rare for the 3rd period metals. Ni(II) generally forms tetrahedral complexes. With very strong ligands such as CN^- square planar geometry is seen with Ni(II).

Crystal Field Theory in Square planar complex



Band structure of solids

Ionic bond

i. It forms a metal and non-metal.

ii. There is electron transfer from less electronegative atom to more electronegative atom.

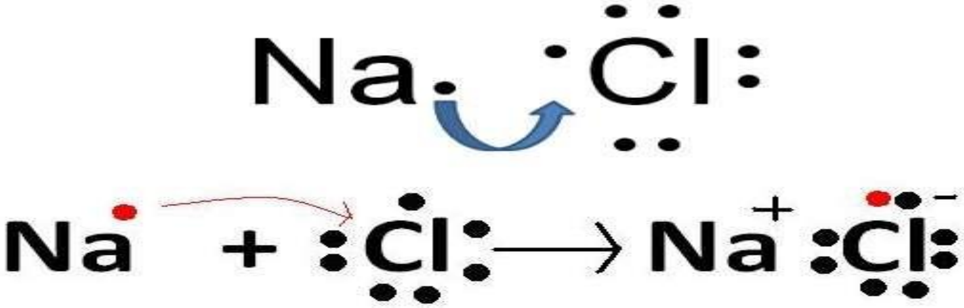
iii. Electrostatic attractions take place between opposite charged ions.

It is a non directional bond formed by strong electrostatic interactions.

Band structure of solids

Due to strong electrostatic attractions ionic compounds has high melting and evaporation points, hard and brittle solids at room temperature.

vi. They do not conduct electricity (except in molten state). Example:NaCl



Covalent bond:

i. It forms between non-metallic elements of the periodic table.

ii. This bond involves the sharing of electrons between atoms.

iii. Covalent bonds are directional in nature.

iv. These compounds have low melting and boiling points.

v. These are soft, brittle solids has poor electrical, thermal conductivity.

Example: H_2

$$H\bullet + \bullet H \longrightarrow H\bullet\bullet H \text{ (or) } H \quad H$$

Metallic Bond:

i. In metal the outer energy levels tend to overlap. The valence electrons then moves about a group of metal atoms, making the metals positively charged.

ii. The positively charged ion then attracts electrons from other metal atoms. The attraction of a positive metallic ion for delocalised electrons is called metallic bond.

iii. Metals owe their physical properties to their delocalised electrons for example metals are malleable, ductile, conductors, shiny etc.Example: Metals

The role of doping on bond structures:

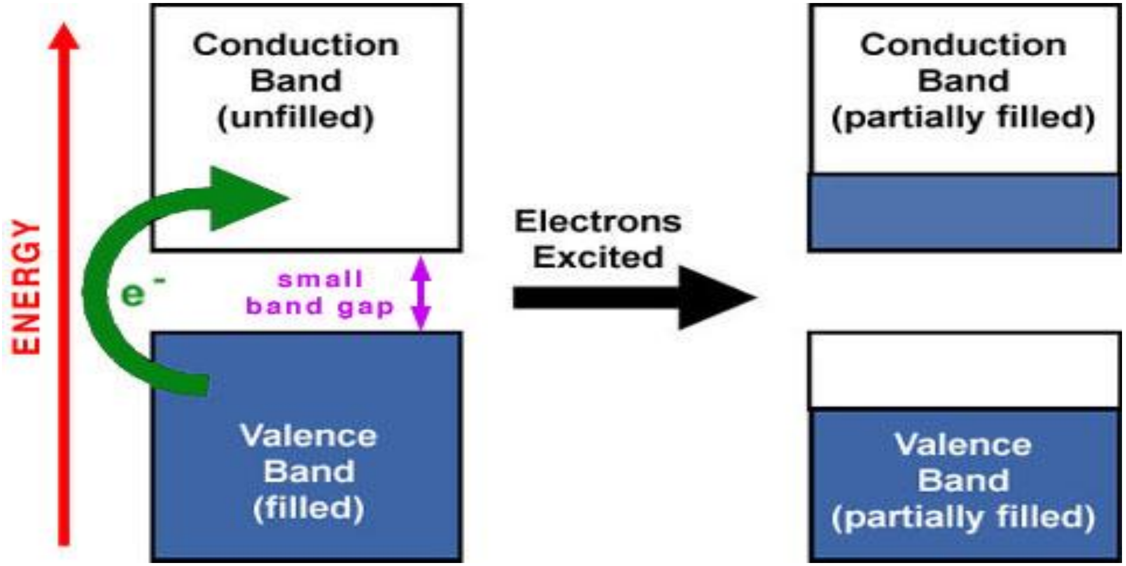
As isolated atoms brought together to form a solid, various interactions occurs between neighboring atoms. In the process, important changes occur in the electron energy configuration. When the solid is formed the energy levels are so closely spaced that they form bands. The electrons can move freely through the material from conduction band (empty shell) to valence band (valence shell) and vise versa.

Based on gap between conduction band and valence band solids are divided into three types

i. Insulators

ii. Semi conductors

iii. Conductors



Insulators And Semiconductors

i. Insulators:

The gap between valence band and conduction band is quite high, electrons are fail to jump from valence band to conduction band. Such solids show less conductivity or no conductivity is called insulators.

Example: Glass.

ii. Semiconductors:

The gap between valence band and conduction band is small, some electrons jump from valence band to conduction band and thus show some conductivity. Such solids show less or no conductivity is called semiconductors.

Examples: Germanium, Silicon.

Conductors

iii. Conductors:

There is no band gap between valence band and band, electrons can move through valence band to conduction band and shows conductivity. Such solids called as conductors.

Examples: Copper, Silver, Gold

Doping:

Doping is the process of adding impurities to increase conductivity nature of semiconductors. Two of the most important materials silicon can be doped with, are boron and phosphorus. Other materials are aluminium, and arsenic, antimony.

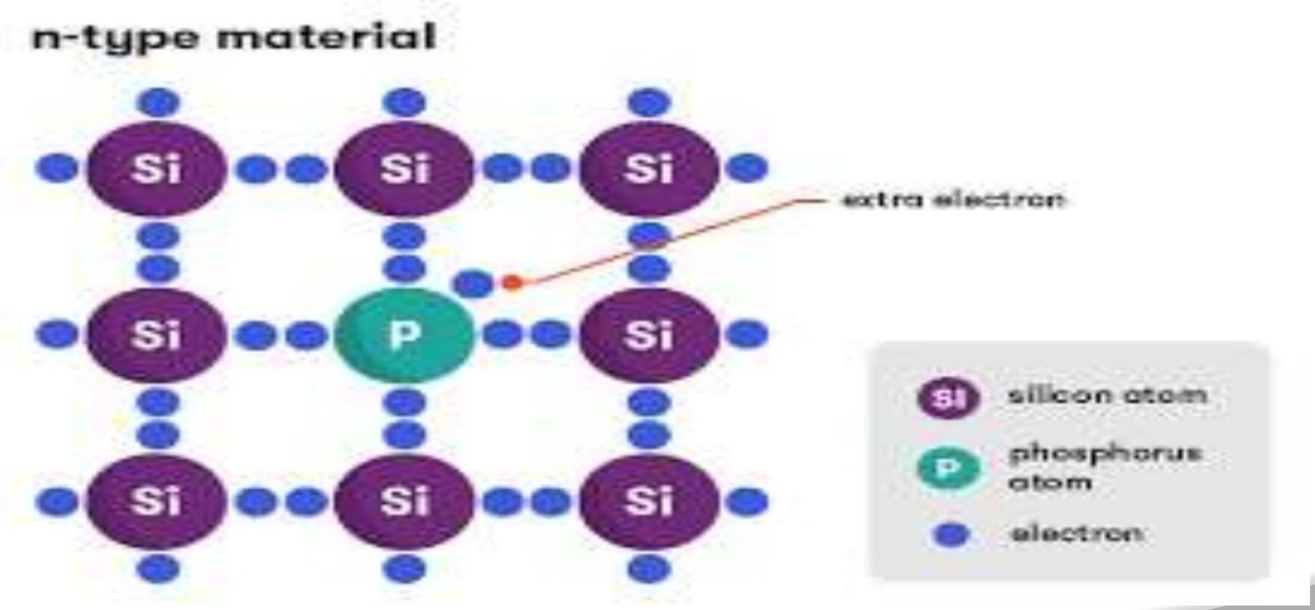
n-type semiconductor:

- n-type semiconductor is an excess negatively charged electrons containing semiconductor and obtained by adding extremely small quantity of a pentavalent element impurity (like phosphorous, arsenic or antimony) to pure semiconductor (like silicon, germanium, tellurium etc.) crystal lattice.

Based on adding impurities doping process is two types

i. n-type

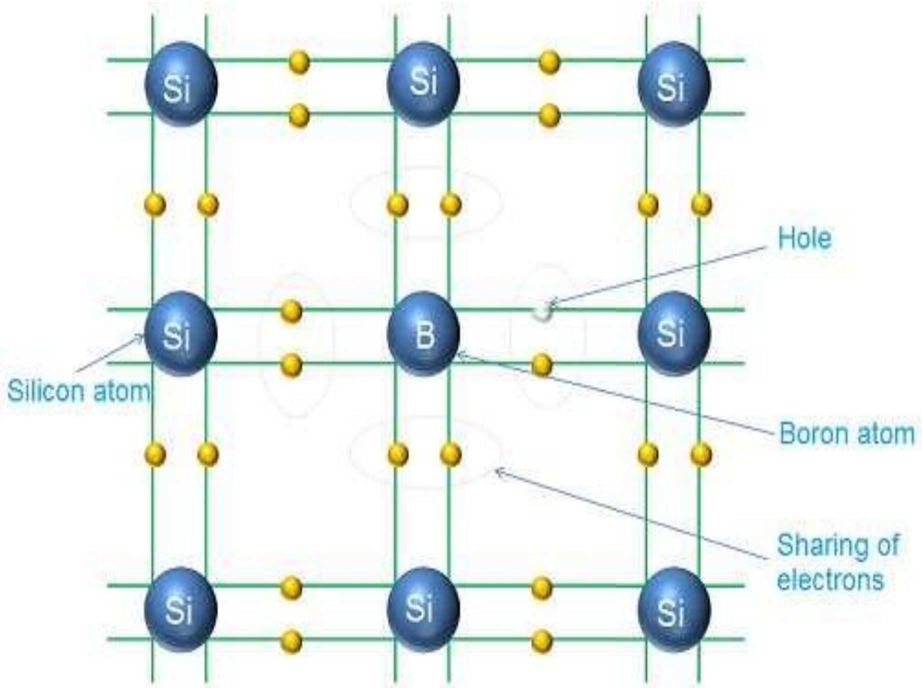
ii. p-type



ii. P-type semiconductor

P-Type semiconductor is an excess positivity charged holes-containing semiconductor and is obtained by adding an extremely small quantity of trivalent element (like boron, aluminium) to the pure semiconductor (like silicon, germanium, etc.) crystal lattice

P-Type semiconductors



Copyright © 2013-2014, Physics and Radio-Electronics, All rights reserved

MODULE - IV

STEREOCHEMISTRY,REACTION MECHANISM AND SYNTHESIS OF DRUG MOLECULES

Introduction

Stereochemistry is the study of the relative arrangement of atoms or groups in a molecule in three dimensional space. Stereochemical isomers are molecules, which have the same chemical formula and bond connectivity but different relative arrangement in three- dimensional space. In contrast, constitutional isomers have same molecular formula but different bond connectivity. Thus, n-butane and isobutene are structural isomers while the isomers of limonene, the compound which gives different taste to lemon and orange are examples of Stereochemical isomers (Figure 1).

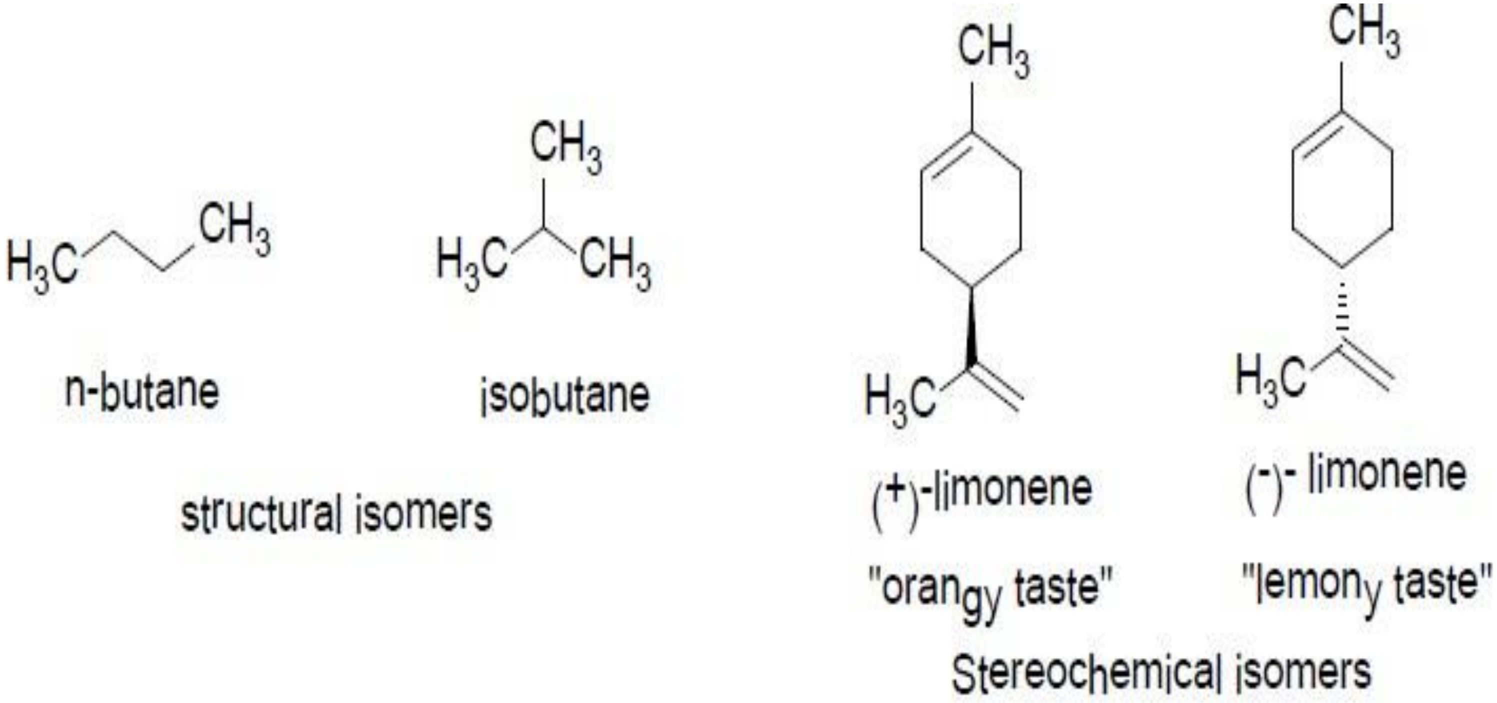
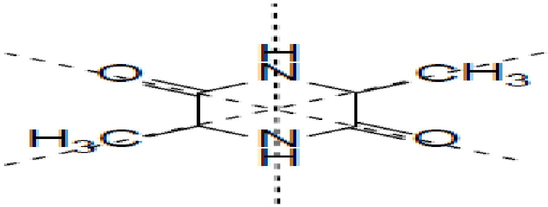

H3C
CH3
n-butane
CH3
H3C
CH3
isobutane
structural isomers
CH3
H3C
(+)-limonene
"orangy taste"
CH3
H3C
(-)- limonene
"lemony taste"
Stereochemical isomers

Figure 1

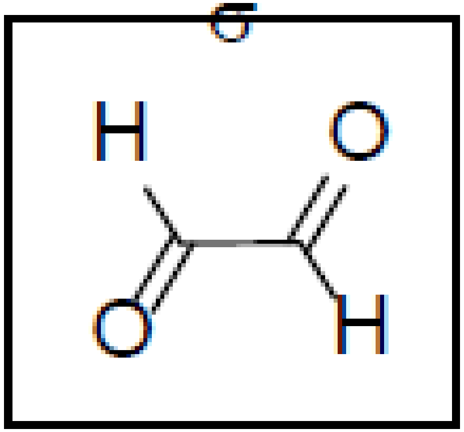
Center of symmetry

The center of symmetry is a point in space such that if a line is drawn from any part (atom) of the molecule to that point and extended an equal distance beyond it, an analogous part (atom) will be encountered. Thus the molecule 3,6-dimethylpiperazine-2,5-dione has centre of symmetry (sometimes referred to as centre of inversion) running through the centre of the molecule.



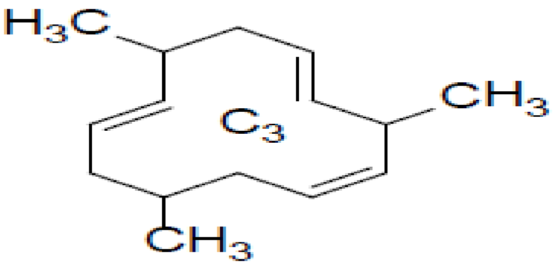
Plane of symmetry (σ):

A plane of symmetry is a reflection plane which brings into coincidence one point of the molecule with another one through the mirror reflection. Thus, glyoxal has a plane of symmetry running through the molecular plane.



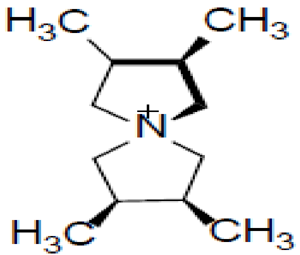
Axis of symmetry (C_n)

Symmetry axis C_n, also called n-fold axis, is an axis which rotates the object (molecule) around by 360°/n, such that the new position of an object is superimposable with the original one. For example, (1Z,4E,8E)- 3,7,11-trimethylcyclo-dodeca-1,4,8-triene has 3-fold rotation axis.



Rotary reflection axis (S_n)

Rotary reflection axis is an axis which rotates the object (molecule) around by 360°/n, followed by rotation in a plane perpendicular to the axis, such that the new position of an object is superimposable with the original one. All odd values of S_n are identical with C_n.



(1)

Enantiomers

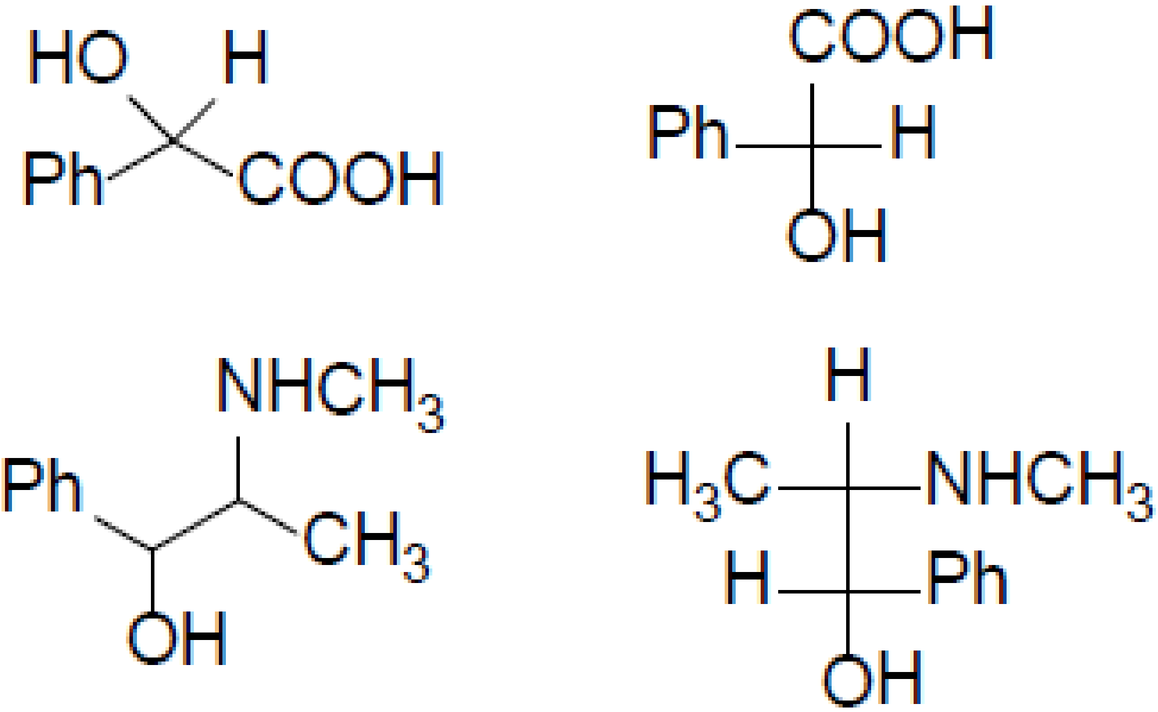
If a molecule is non-superimposable on its mirror image, then the molecule is said to have enantiomeric relationship with its mirror image molecule. For example, in 2- chloropropane, the molecule is superimposable with its mirror image, so they are identical molecules, but in 2-chlobutane, the molecule is not superimposable with its mirror image and the two molecules are called enantiomers (Figure 3). Thus, enantiomers are stereoisomers since they differ only in the relative arrangement of the different groups in space but not in bond connectivity.

Fischer projection formula

It is a representation of a 3D molecule as a flat structure where a tetrahedral carbon is represented as two crossed lines. The two vertical bonds about the stereocentre are above the plane of paper (towards the viewer) while the horizontal bonds are below the plane of the paper (away from the viewer) (Figure8).

A few examples of depiction of molecules in Fischer projection formula is given below. It must be noted that when bonds are rotated by 180°, they result in the same identical molecule

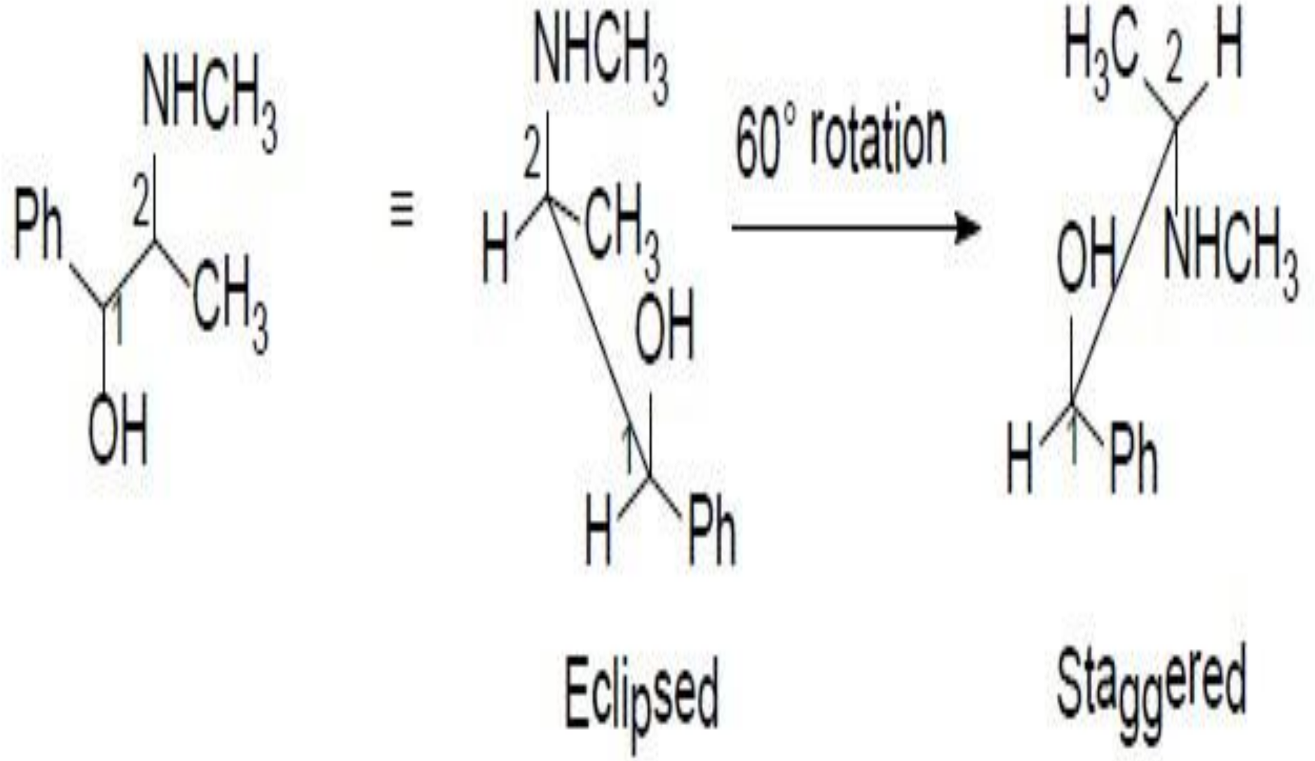
Fischer projection formula



Sawhorse projection formula

Sawhorse projection formulas are used to denote two principal stereocentres. It is a view of a molecule down a particular carbon-carbon bond, with the groups connected to both the front and back carbons are drawn using sticks at 120° angles. Sawhorse Projections can also be drawn so that the groups on the front carbon are staggered (60 ° apart) or eclipsed (directly overlapping) with the groups on the back carbon.

Sawhorse projection formula



Newman projection formula

In this notion, the molecule is again viewed by looking down a particular carbon-carbon bond. The front carbon of this bond is represented by a dot, and the back carbon is represented by a large circle. The three remaining bonds are drawn as sticks coming off the dot (or circle), separated by one another by 120°. Just like Sawhorse projection formula, Newman Projection can be drawn such that the groups on the front carbon are staggered (60 ° apart) or eclipsed (directly overlapping) with the groups on the back carbon

Newman projection formula

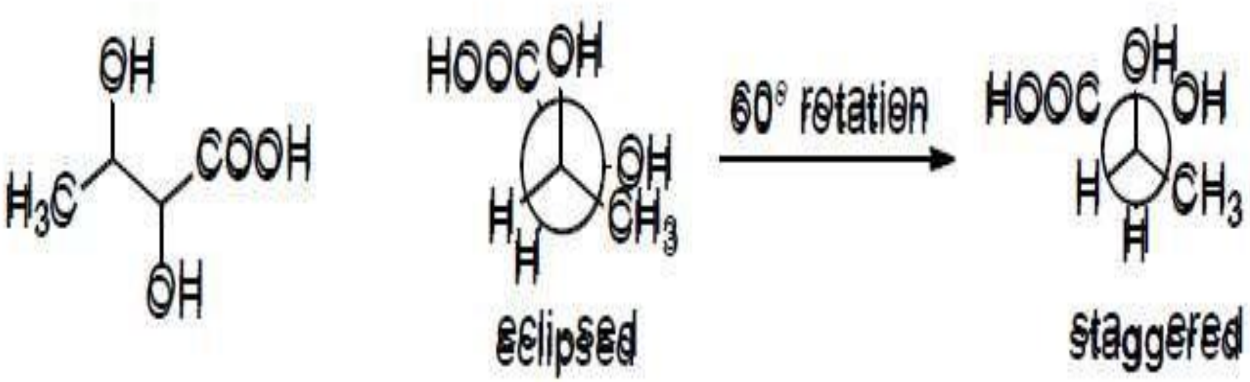


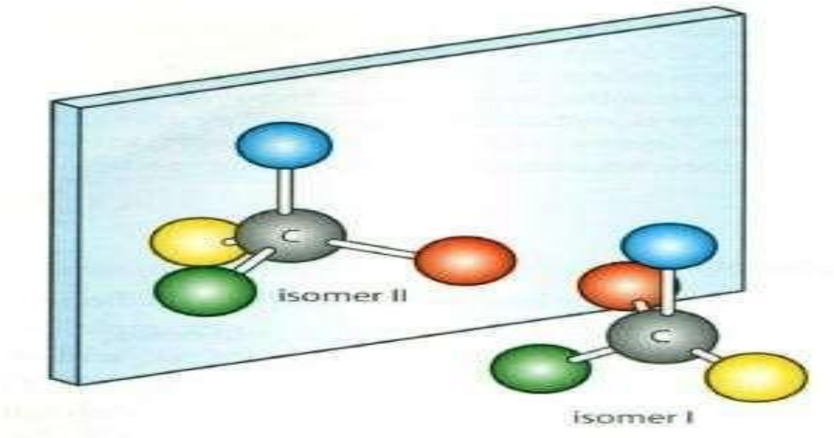
Figure 11

Optical isomers

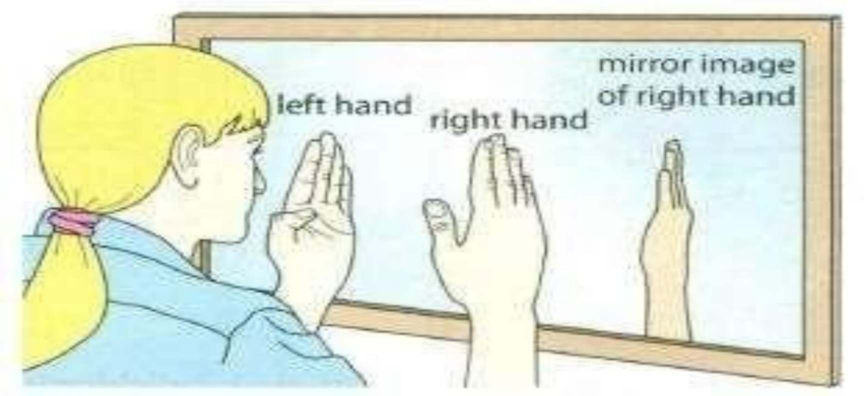
A carbon atom attached to four different atoms or groups is known as **asymmetric** or **chiral.** The four groups, arranged tetrahedrally around the carbon atom with bond angles of 109.5°, can be arranged in two different three-dimensional configurations which are mirror images of each other. This is known as **optical isomerism.** The term refers to the ways in which the isomers interact with plane-polarized light, discussed below. They are said to be **chiral molecules** and have no plane of symmetry.

Optical isomers

In the following figure, an asymmetric, or chiral, carbon atom, shown in black, is bonded to four different atoms or groups shown here in different colors. This gives rise to two configurations which are mirror images of each other.



The word chiral is derived from the Greek word for “hand”. Lord Kelvin first introduced the term into science in 1904 with the now celebrated definition: “I call any geometrical figure, or group of points, chiral, and say it has chirality if its image in a plane mirror, ideally realized, cannot be brought to coincide with itself.” His definition can therefore be applied much more generally to structures outside Chemistry, such as knots.



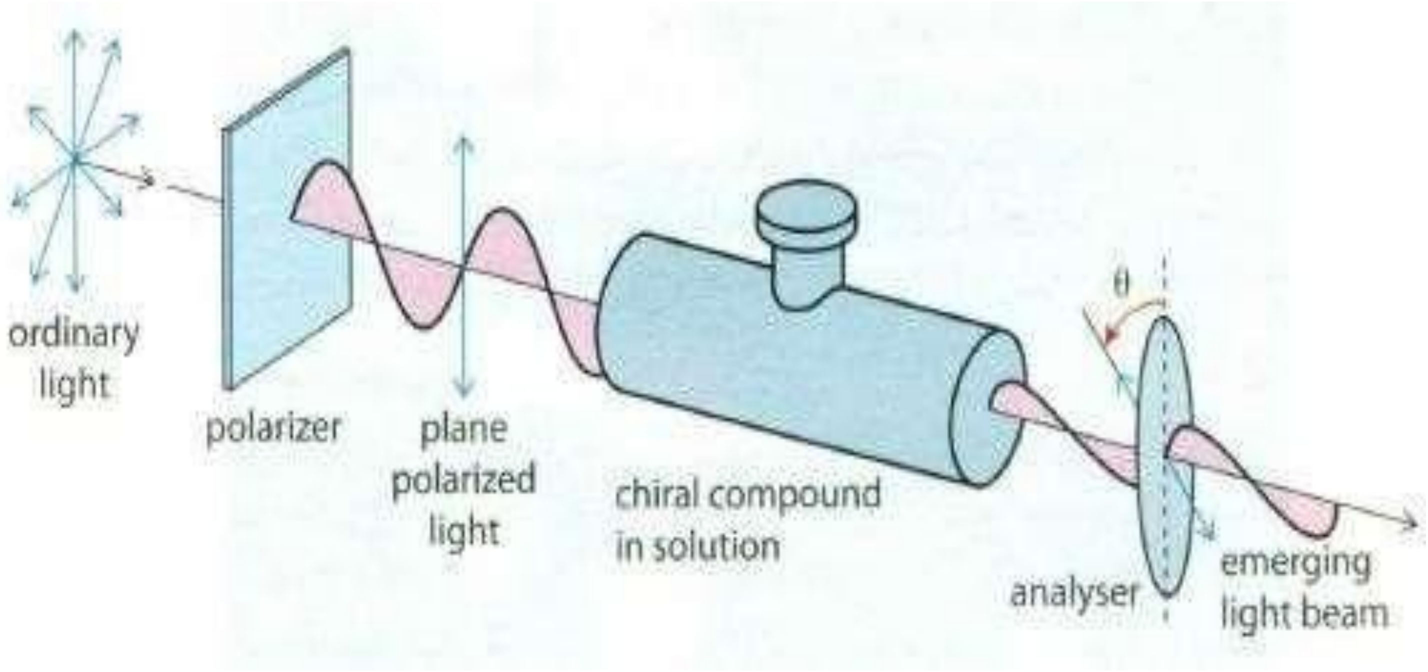
The same is true for optical isomers, and the two non-superimposable forms are known as enantiomers. A mixture containing equal amounts of the two enantiomers is known as a racemic mixture or a racemate. As we will see, such a mixture is said to be optically inactive.

Optical isomers

Optical isomers, the enantiorners, have identical physical andchemical properties – with two important exceptions:

opticalactivity

reactivity with other chiralmolecules


ordinary light
polarizer
plane polarized light
chiral compound in solution
θ
analyser
emerging light beam

Optical Activity

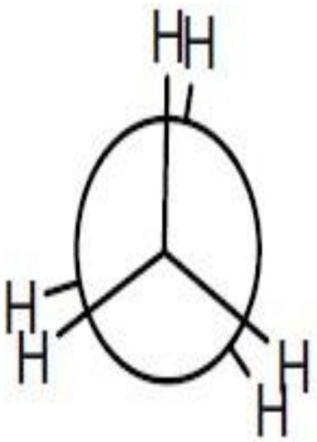
As we know from their name, optical isomers show a difference in a specific interaction with light. A beam of ordinary light consists of electromagnetic waves that oscillate in an infinite number of planes at right angles to the direction of travel. If, however, this light is passed through a device called a **polarizer,** only the light waves oscillating in a single plane pass through, while light waves in all other planes are blocked out. This is known as **plane-polarized light.**

Conformations

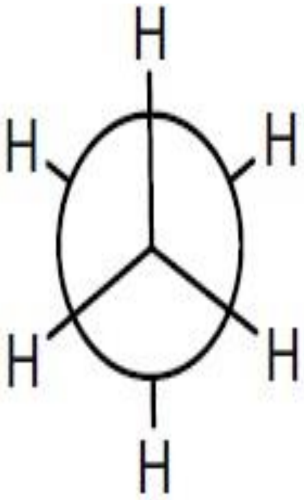
Electron distribution of carbon-carbon bond is cylindrically symmetrical about the line joining the two carbon nuclei. Rotation is possible about a single bond and this rotation means that, while localized arrangement of atoms stays the same, the molecule as a whole can adopt a number of different shapes.

Conformations

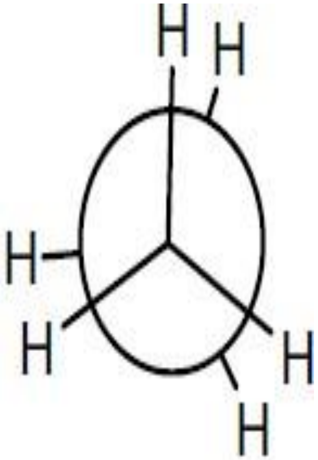
ethane the simplest C-C bond possible molecule, could have an arrangement like **1** in which the hydrogen's exactly oppose each other, an arrangement like **2** in which the hydrogen's are perfectly staggered and an infinite number of intermediate arrangements **3** which is neither **1** nor**2**.



1



2



3

Nucleophiles

A nucleophile is a compound that has a relatively high energy pair of electrons that is available to react with an electrophile. In other words, any Brønsted base is also a nucleophile.

In this Unit we will be talking about substitutions at C(sp^3) electrophiles, and in these cases the nucleophile is generally either a metal salt (KOH, $NaNH_2$, EtSK, $CH_3CH_2CH_2CH_2ONa$, NaBr) or a neutral compound with a lone pair (R_3N, H_2O, ROH, RCO_2H, R_2S, R_3P).

Substitution

Let's look at the mechanism of nucleophilic substitution reactions. Substitution can in principle occur in three ways. The nucleophile comes in at the same time as the leaving group leaves.

The leaving group leaves, then the nucleophile comes in. The nucleophile comes in, then the leaving group leaves

SN2 Mechanism

In the first mechanism for substitution, the nucleophile attacks the electrophilic C atom directly. As the nucleophile comes in, the C atom begins to acquire more than eight electrons, so the bond to the leaving group breaks simultaneously. In the TS, the C atom is partially bound to both the nucleophile and the leaving group. The nucleophile continues to come in and the leaving group continues to leave, until finally the product has been obtained

SN1 Mechanism

In the second possible mechanism for substitution, the leaving group might leave first to generate an electron-deficient intermediate called a carbocation. This intermediate then combines with a nucleophile to give the product. This mechanism for substitution is

calledS_N1

Addition Reactions

The nucleophilic and electrophilic substitution and abstraction reactions can be viewed as ways of activation of substrates to allow an external reagent to directly attack the metal activated ligand without requiring prior binding of the external reagent to the metal. The attacking reagent may be a nucleophile or an electrophile. The nucleophilic attack of the external reagent is favored if the LnM fragment is a poor π−base and a good σ−acid *i.e.*, when the complex is cationic and/or when the other metal bound ligands are electron withdrawing such that the ligand getting activated gets depleted of electron density and can undergo an external attack by a nucleophile Nu−, like LiMe or OH−.

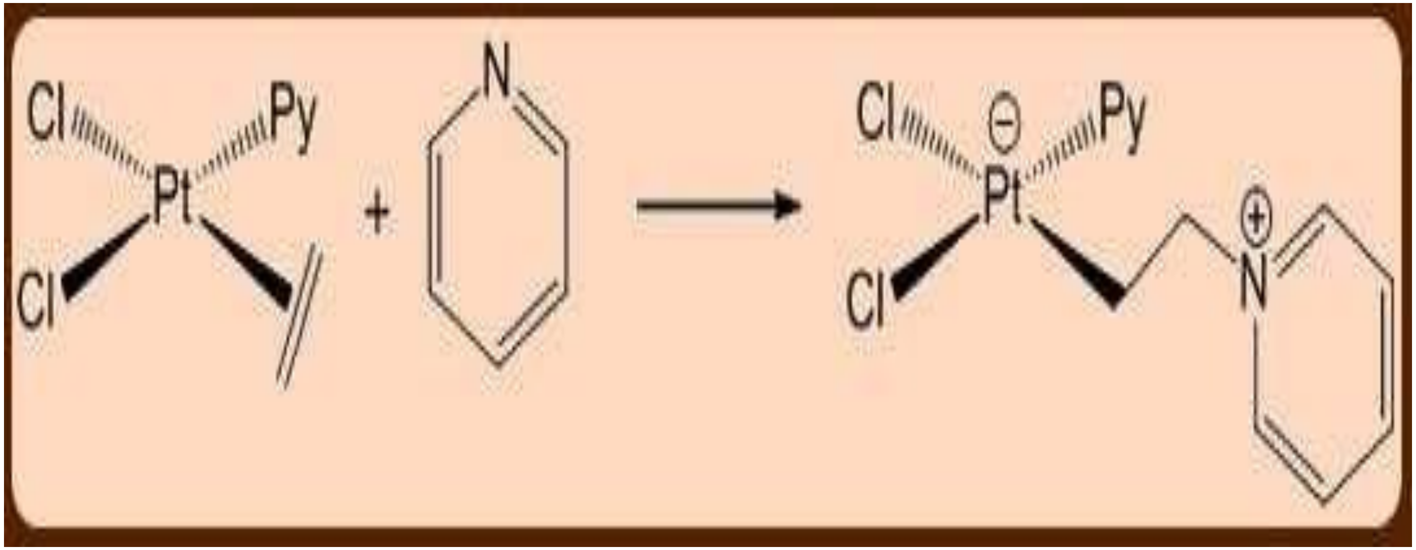
Addition Reactions

The attack of the nucleophiles may result in the formation of a bond between the nucleophiles and the activated unsaturated substrate, in which case it is called nucleophilic addition, or may result in an abstraction of a part or the whole of the activated ligand, in which case it is called the nucleophilic abstraction. The nucleophilic addition and the abstraction reactions are discussed below,

Addition Reactions

Nucleophilic Addition Reactions:

An example of a nucleophilic addition reaction is shown below



Addition Reactions

Carbon monoxide (CO) as a ligand can undergo nucleophilic attack when bound to a metal center of poor π−basicity, as the carbon center of the CO ligand is electron deficient owing to the ligand to metal σ−donation not being fully compensated by the metal to ligand π−back donation. Thus, activated CO ligand undergoes nucleophilic attack by the lithium reagent to give an anionic acyl ligand, which upon alkylation generates the famous Fischer carbenecomplex

Electrophilic Addition Reactions

Similar to the nucleophilic addition and abstraction reactions, the electrophilic counterparts of these reactions also exist. An electrophilic attack is favored if the LnM fragment is a good π−base and a poor σ−acid *i.e.,* when the complex is anionic with the metal center at low−oxidation state and/or when the other metal bound ligands are electron donating such that the ligand getting activated becomes electron rich from the π−back donation of the metal center and thus can undergo an external attack by an electrophile E^+ like H^+ and CH_3I.

Electrophilic Addition Reactions

The attack of the electrophiles may result in the formation of a bond between the electrophile and the activated unsaturated substrate, in which case it is called electrophilic addition, or may result in an abstraction of a part or the whole of the activated ligand, in which case it is called the electrophilic abstraction.

Addition of Hydrogen Halide

The reaction with hydrogen halides, the reaction with hydrogen, called catalytic hydrogenation and the reaction with water, called hydration. These reactions will be used to establish some important principles of chemical reactivity that are very useful in organic chemistry.

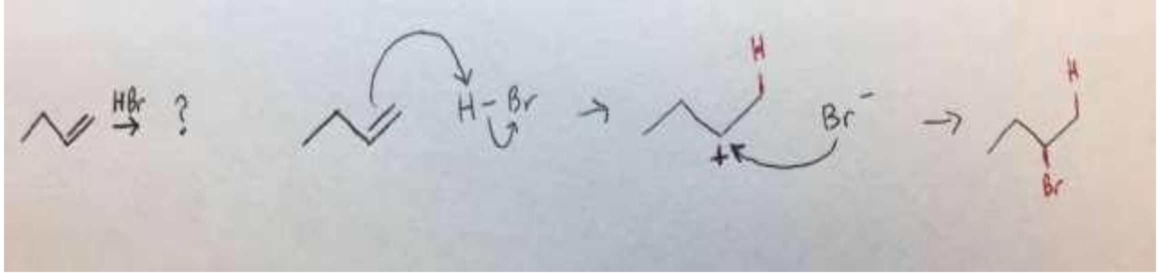
The most characteristic type of alkene reaction is addition at the carbon– carbon double bond. The addition reaction can be represented generally as follows

Markonikov's Rule

Markovnikov's Rule:

In an addition reaction of a protic acid HX (hydrogen chloride, hydrogen bromide, or hydrogen iodide) to an alkene or alkyne, the hydrogen atom of HX becomes bonded to the carbon atom that had the greatest number of hydrogen atoms in the starting alkene or alkyne.

We will use Butene and H-Br as an example



Anti-Markonikov’s Rule

Anti-markovnikov’s Rule:

In an addition reaction of a generic electrophile HX to an alkene or alkyne, the hydrogen atom of HX becomes bonded to the carbon atom that had the least number of hydrogen atoms in the starting alkene or alkyne.

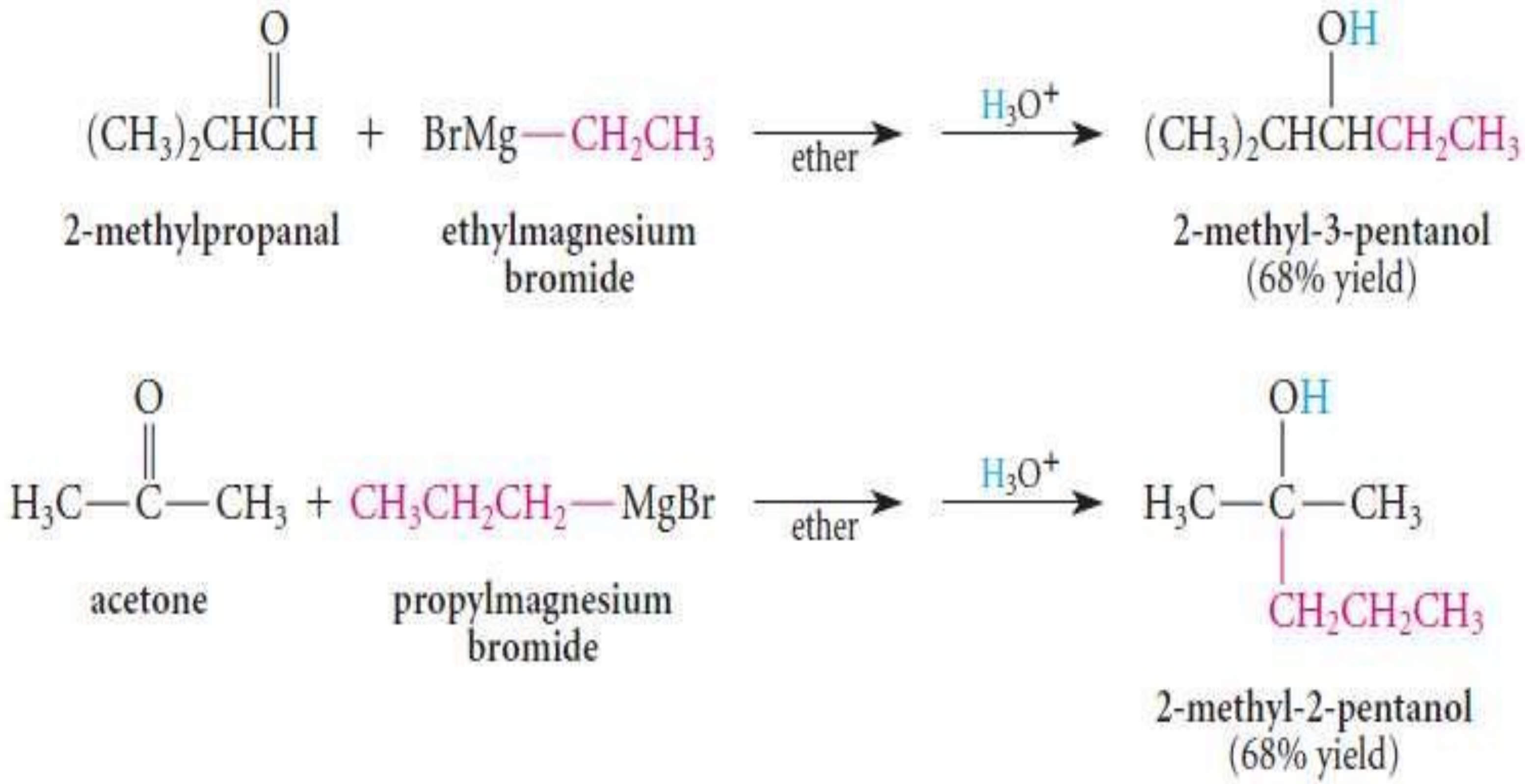
Notice that the Hydrogen from the H-Br is now attached at the carbon of the alkene that had only 1 hydrogen thus does not follow Markovnikov’s rule and is the minor product.

Grignard Additions

Grignard Additions On Carbonyl Compounds:

The reaction of Grignard reagents with carbonyl groups is the most important application of the Grignard reagent in organic chemistry. Addition of Grignard reagents to aldehydes and ketones in an ether solvent, followed by protonolysis, gives alcohols.

Grignard Additions



$$(CH_3)_2CH\overset{O}{\overset{\|}{C}}H + BrMg{-}CH_2CH_3 \xrightarrow[\text{ether}]{} \xrightarrow{H_3O^+} (CH_3)_2CH\overset{OH}{\overset{|}{C}}HCH_2CH_3$$

$$H_3C{-}\overset{O}{\overset{\|}{C}}{-}CH_3 + CH_3CH_2CH_2{-}MgBr \xrightarrow[\text{ether}]{} \xrightarrow{H_3O^+} H_3C{-}\underset{CH_2CH_2CH_3}{\underset{|}{\overset{OH}{\overset{|}{C}}}}{-}CH_3$$

Saytzeff’s Rule

Saytzeff's Rule:

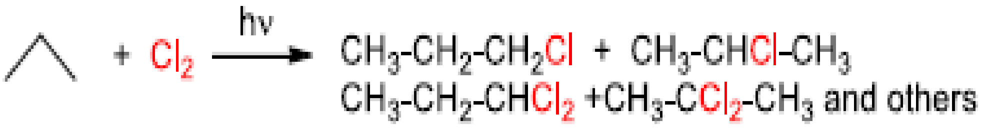
A double bond is formed due to loss of water molecule. It is an elimination reaction. According to Saytzeff's rule (also Zaitsev's rule), during dehydration, more substituted alkene (olefin) is formed as a major product, since greater the substitution of double bond greater is the stability of alkene.

Preparation of Alkyl Halides:

Free Radical Halogenation

Usually this method gives mixtures of mono-,di-, tri- etc halogenated compounds, which is considered an inefficient method for the synthesis of a desired compound.

Consider propane:



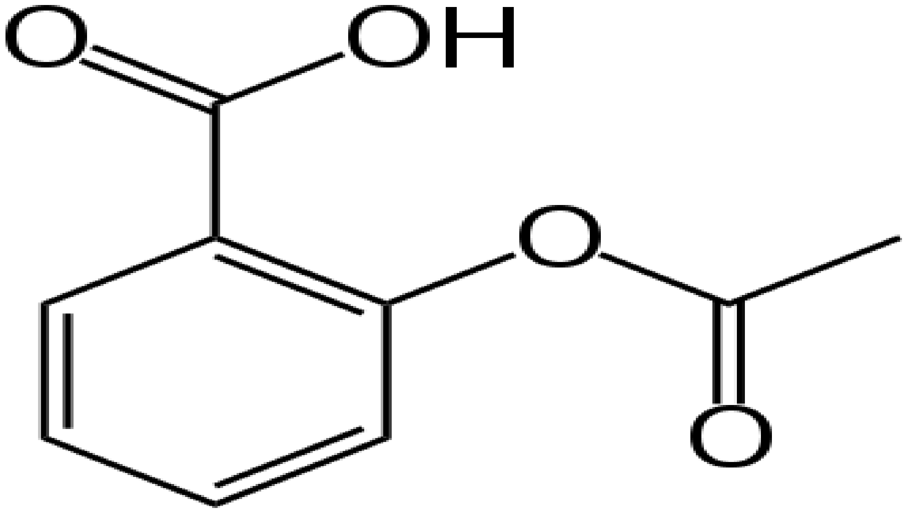
Pharmaceutical Applications Of Paracetomol:

1.It is a medicine used to treat pain and fever

2.It is typically used for mild to moderate pain relief.

ASPIRIN

Structure of Aspirin



Pharmaceutical applications of Aspirin:

Aspirin is used in the treatment of a number of conditions, including fever, pain, fever , and inflammatory diseases, such as arthritis

Lower doses of aspirin have also been shown to reduce the risk of death from a heart attack, or the risk of stroke in some circumstances

MODULE - V

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.

Introduction

- 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 twofactors:

- (i) based on occurrence (natural or primary and artificial or secondary)
- (ii) physical state of the fuel (solid, liquid, gas) or state of aggregation.

Classification of fuels

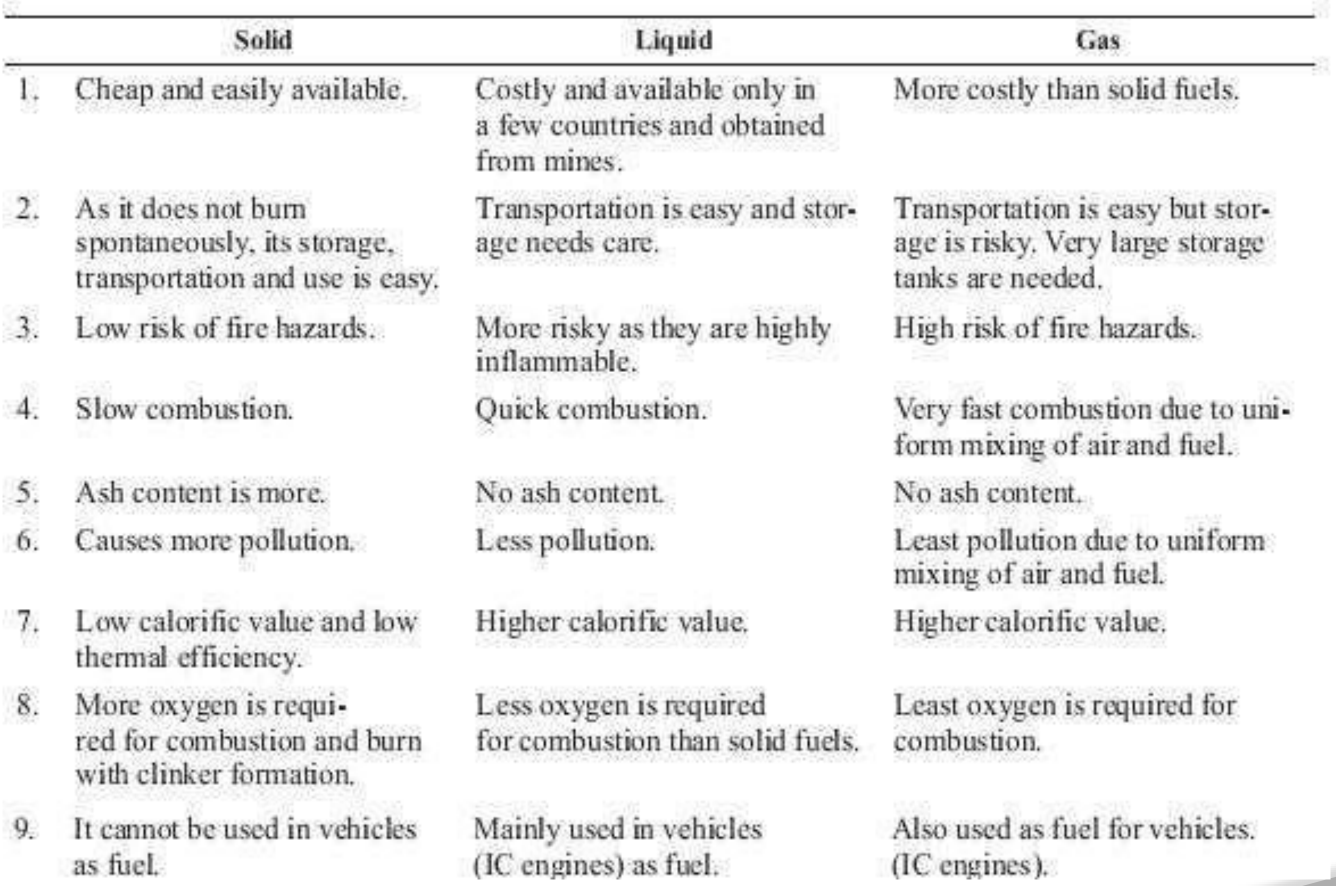
- **Natural Fuels (Primary Fuels)**

  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).

Characteristics of a Good fuel

A good fuel has the followingfeatures:

- 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 calorificvalue.
- 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.

Characteristics of a Good fuel

- 7. It must have moderate ignition temperature. Low (burning)/ignition temperature can cause fireaccident.
- 8. It should not burn spontaneously to avoid fire hazards.
- 9. It should not give harmful gases after combustion.
- 10. Its handling should beeasy.
- 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 fuel

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”.
- The calorific value is measured in several units of heat; they are calorie, kilocalorie, British thermal unit and Centigrade thermal unit (Centigrade heat unit).

Calorific Value

- **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

Types of Calorific value

- **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.

Types of Calorific value

- **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

LCV = HCV – latent heat of watervapour

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

= 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.
- Depending upon the percentage of carbon, hydrogen, moisture and calorific value, four different types of coals exist. It is called the ranking of coal.

Introduction of 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.

Introduction of Coal

- **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) ultimateanalysis.

  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 andcarbon.

Analysis of Coal

- **Moisture**: A known mass of finely powdered air-dried coal is taken in a crucible. It is heated up to 110C 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 x 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 thendetermined.

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

- **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 Proximate 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.

Significance of Proximate analysis

- **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:**
- 1. Ash reduces heating value ofcoal.
- 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.

Liquid fuels

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.

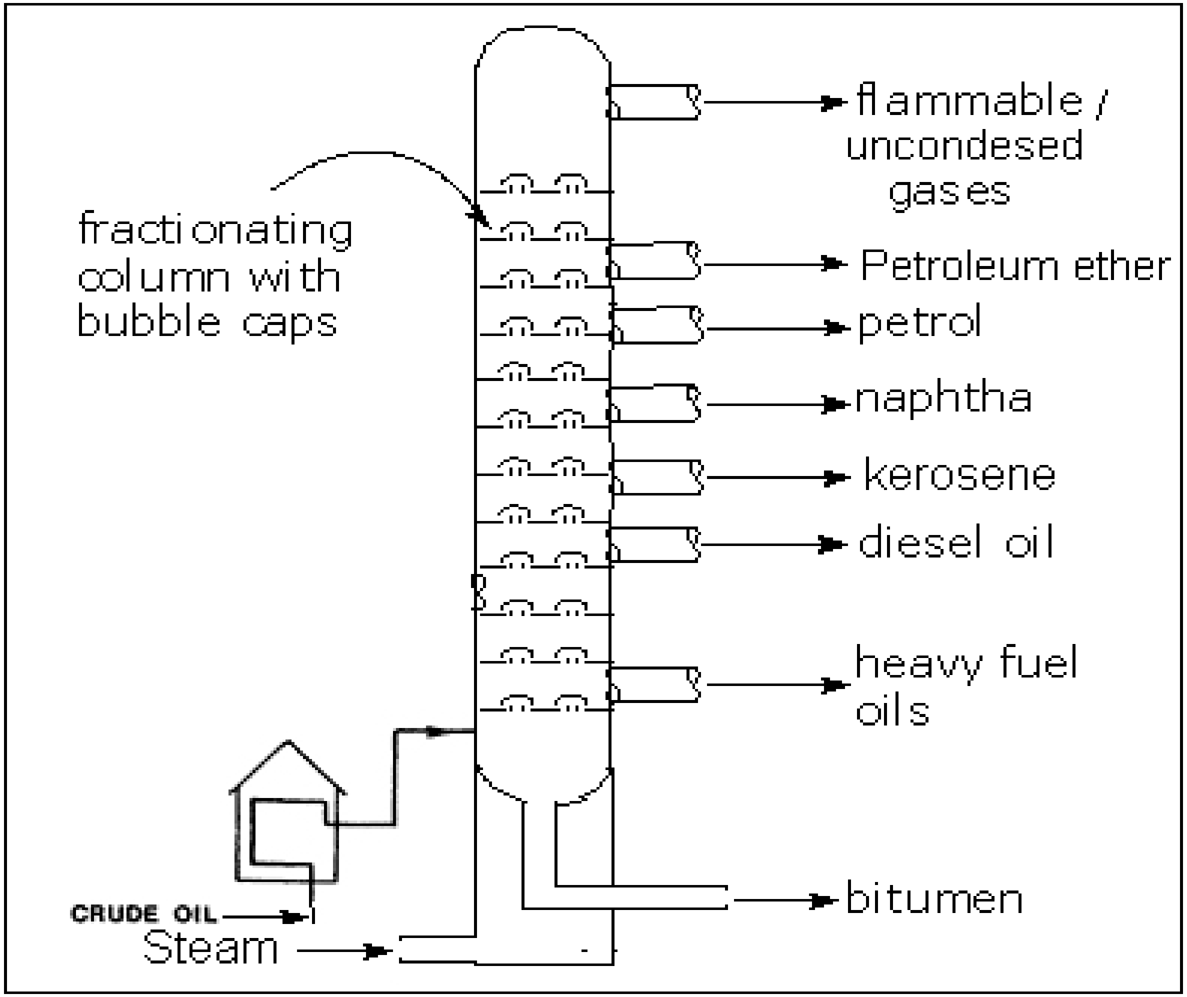
The word meaning of petroleum is ‘rock oil’ (petra = rock, oleum= oil).

Refining

- **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.

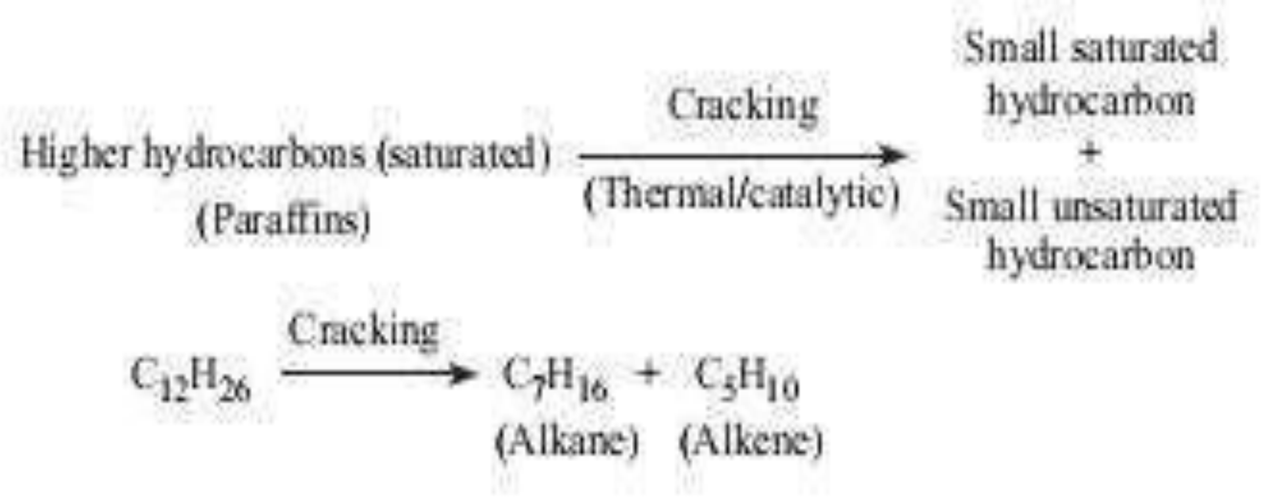
Refining

. **Fractional distillation:** Heating of crude oil around 400^0C 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 laterthe lower boiling fractions


fractionating column with bubble caps
flammable / uncondesed gases
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 molecularweights.



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

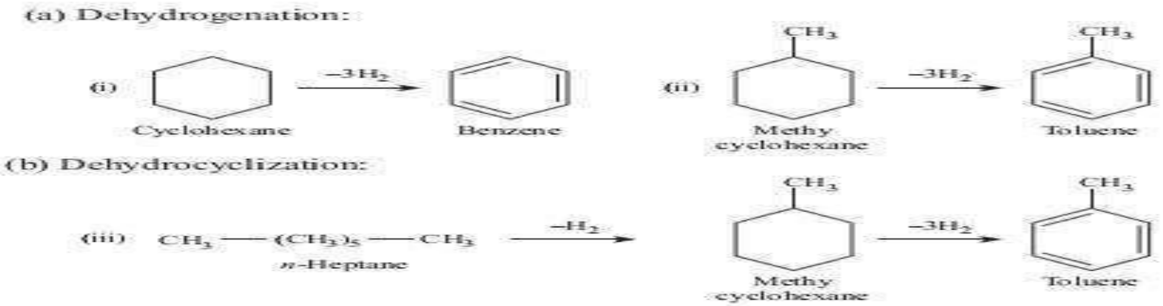
$$C_{12}H_{26} \xrightarrow{\text{Cracking}} \underset{\text{(Alkane)}}{C_7H_{16}} + \underset{\text{(Alkene)}}{C_5H_{10}}$$

Types of Cracking

Catalytic cracking

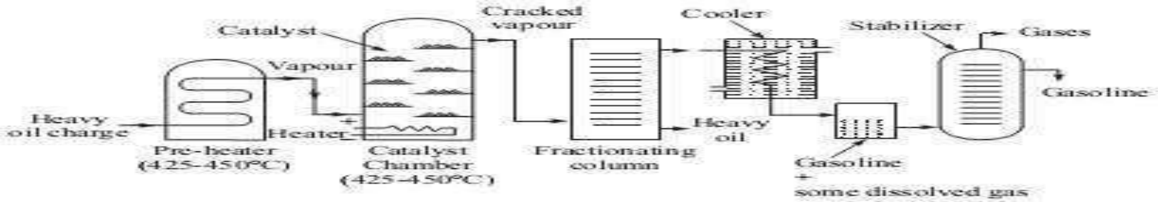
In this type of cracking catalysts are used. The best one is aluminosilicate with some metal oxides (oxides of Ca, Mg, Fe, Cr, Na). This process completes at lower temperature and lower pressure compared to the thermal process (300–450°C temperature; 1–5 kg/cm^2 pressure). Catalytic cracking is also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

Following chemical reactions take place in catalytic cracking.



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

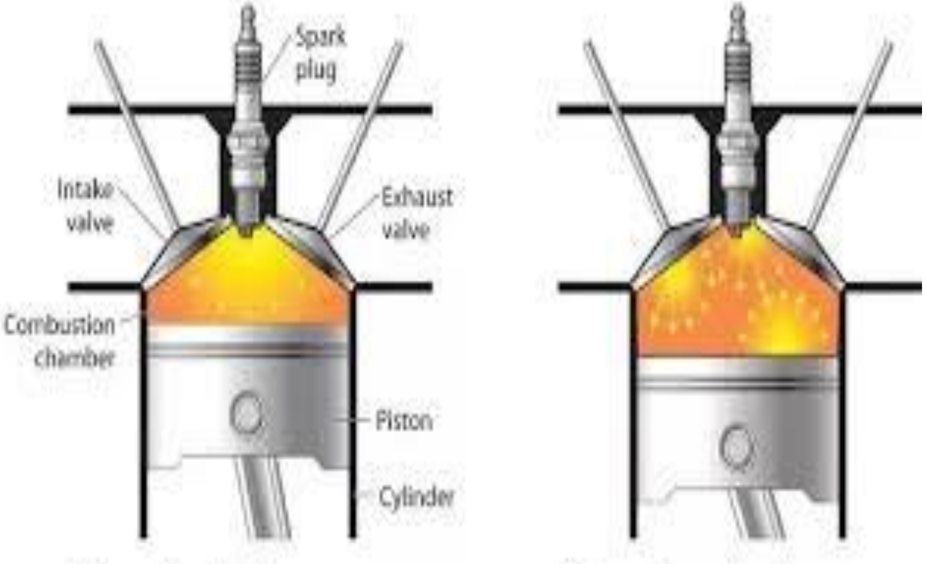
Catalytic cracking can be brought about by (i) fixed bed catalytic cracking and (ii) moving bed and fluid bed catalytic cracking.



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.

Knocking



(a) Normal combustion

(b) Premature combustion

Suction stroke: Here the fuel–air mixture is drawn into the cylinder during induction.

Compression stroke: Fuel–air mixture is compressed in the cylinder.

etly

Power stroke: Fuel–air mixture is ignited by electric spark. The hot gases producd due to combustion increase the pressure and push the piston down the cylinder.

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 enginecalled 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., C4H10) burn easily than higher alkenes, e.g. C7H16. 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

- **Octane number or Octanerating:**
- The anti-knocking value of fuel can be increased by adding combustion products 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. Theyare not eco-friendly.

Octane number

- 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 byusing:

(i) Good quality fuel with higher octanenumber.

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

(iii) By retarding spark plug ignition.

Prevention of knocking

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. ml) + TEL (2 ml).

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)

Cetane number

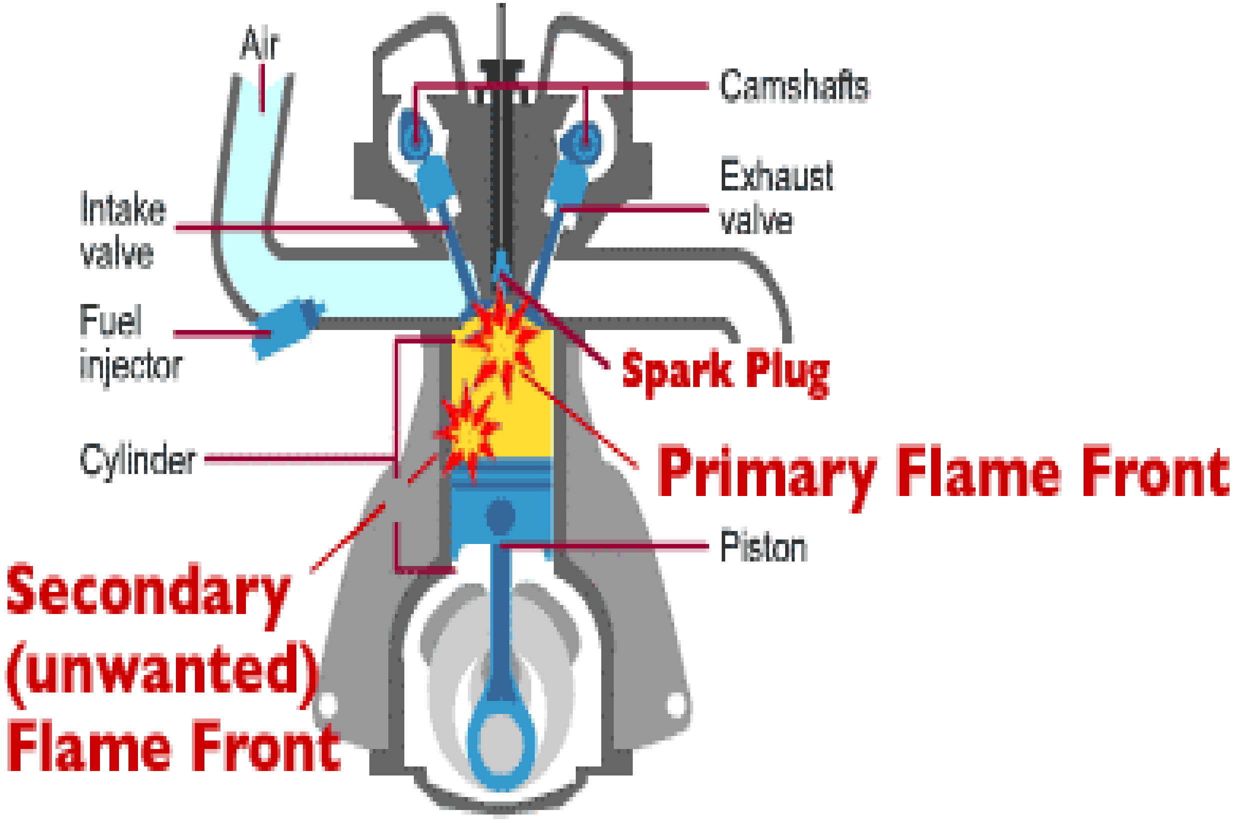
Cetane Number or CetaneRating:

- 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.

Cetane number

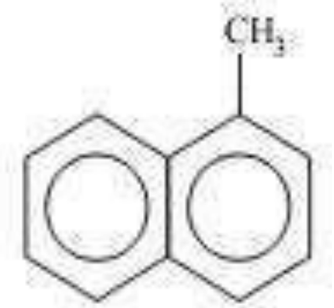
($C_{16}H_{34}$) n-hexadecane is a saturated hydrocarbon having a short ignition lag as compared to any commercial diesel fuel. Its cetane number is 100. It ignites below compression temperature. α-Methylnaphthalene has a very long ignition lag as compared to any commercial diesel oil. Its cetane number is taken as zero .

Cetane number



$CH_3—(CH_2)_{14}—CH_3$

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

Introduction to Gaseous Fuels:

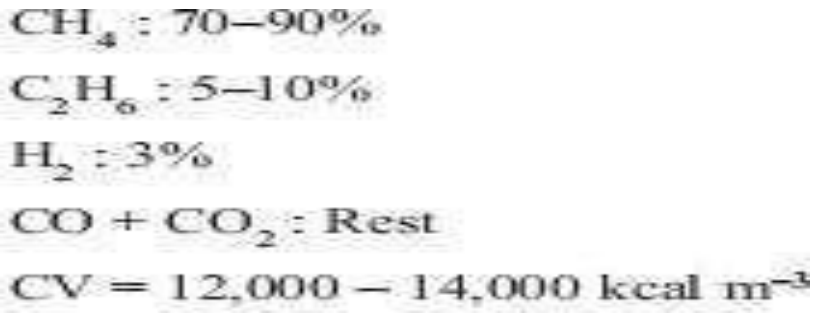
- Natural gas is the primary gaseous fuel. A variety of secondary fuels are obtained from coal or petroleum. They include coal gas, producer gas, water gas derived from coal, and LPG, CNG derived from natural gas and oil gas formed by cracking of kerosene oil.

Gaseous fuels

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

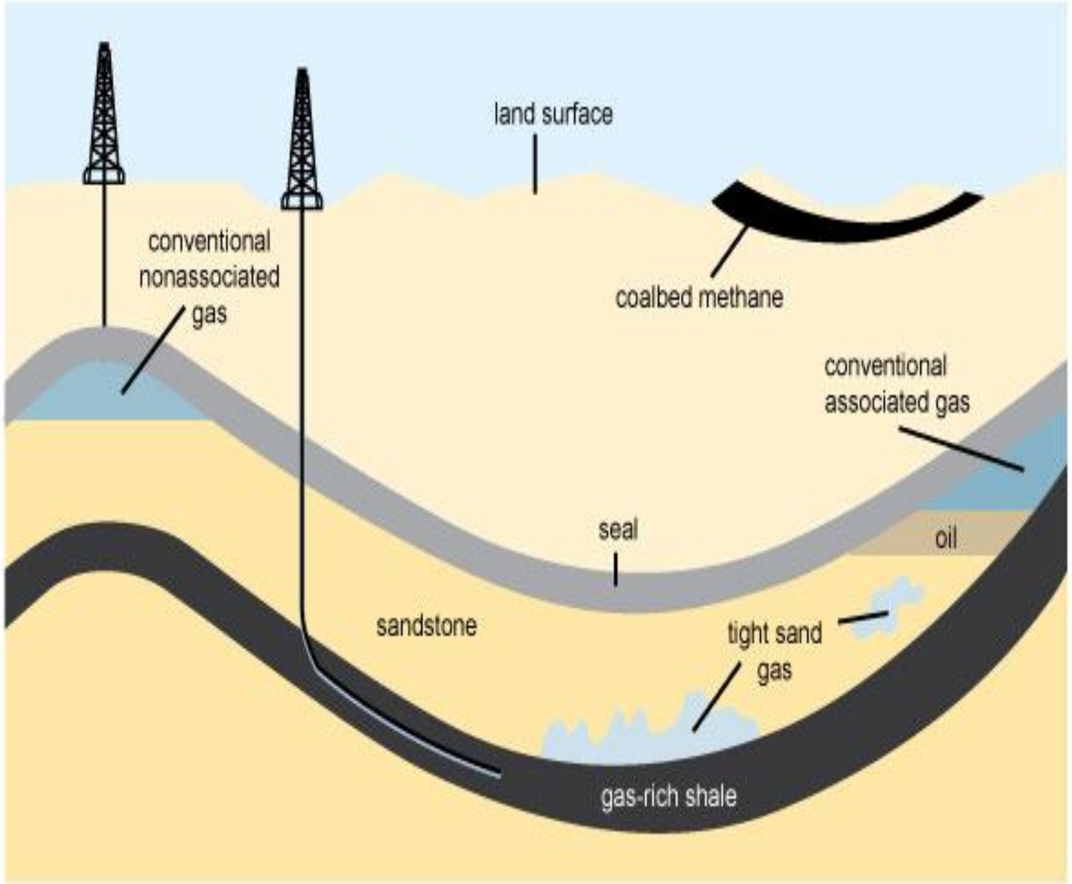
$CV = 12{,}000 - 14{,}000$ kcal m^{-3}

Natural Gas

- Naturalgas contains ethane,propane,butane and pentane along with main component methane Before the use of natural gas, other heavier hydrocarbon, CO_2, N_2, He and H_2 O 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.

Natural Gas

Schematic geology of natural gas resources



Source: Adapted from *United States Geological Survey factsheet 0113-01* (public domain)

- 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-aminoethanol

Applications of Natural Gas

- 1. It is used as a very good domestic fuel.
- 2. It is used in thepreparation of ammonia (used for urea manufacturing).
- 3. It is used to prepare carbon-black which is used as filler for rubberindustry.
- 4. It is used to prepare synthetic proteins for animal feed. (Methane on fermentation gives synthetic proteins used as animal feed.)

LPG

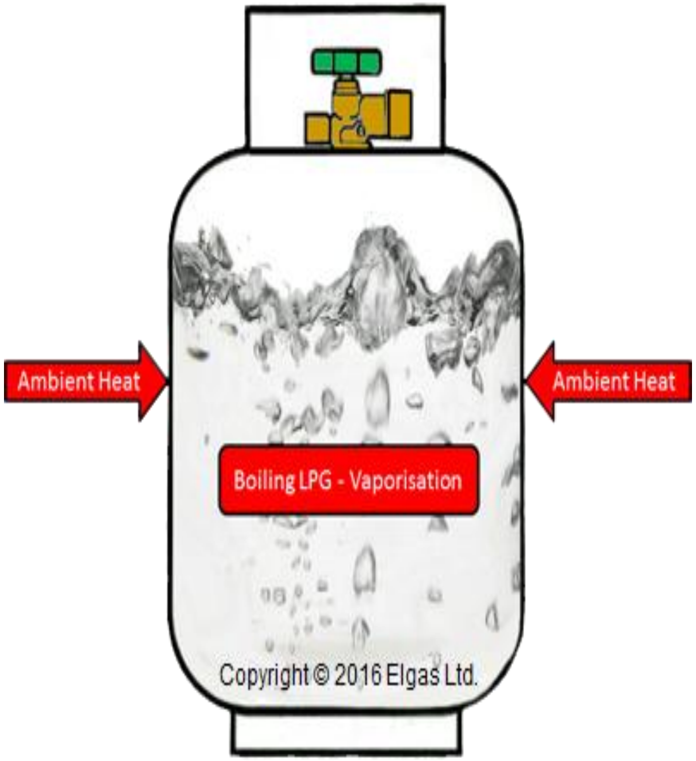
- Nowadays LPG has been a common fuel for domestic work and also in most of the industries. The main components of LPG or cooking gas are n-butane, isobutane, butylene and propane (traces of propene and ethane).
- The hydrocarbon are in gaseous state at room temperature and at atmospheric pressure but can be liquified under higher pressures.

LPG

- 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.

LPG


Indane
HP
Bharatgas


Ambient Heat
Ambient Heat
Boiling LPG - Vaporisation
Copyright © 2016 Elgas Ltd.

Characteristics of LPG

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 petroleumproducts.

- 1. It has high calorific value: 27800 kcal/m^3.
- 2. It gives less CO and least unburnt hydrocarbons. So it causes least pollution.

Characteristics of LPG

- 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.

Disadvantages of LPG:

- 1. It is difficult to handle as fuel.
- 2. Engines working at low compression ratio cannot use LPG as fuel.


CNG
100% RENEWABLE BIOMETHANE FUEL

CNG

Compressed Natural Gas:

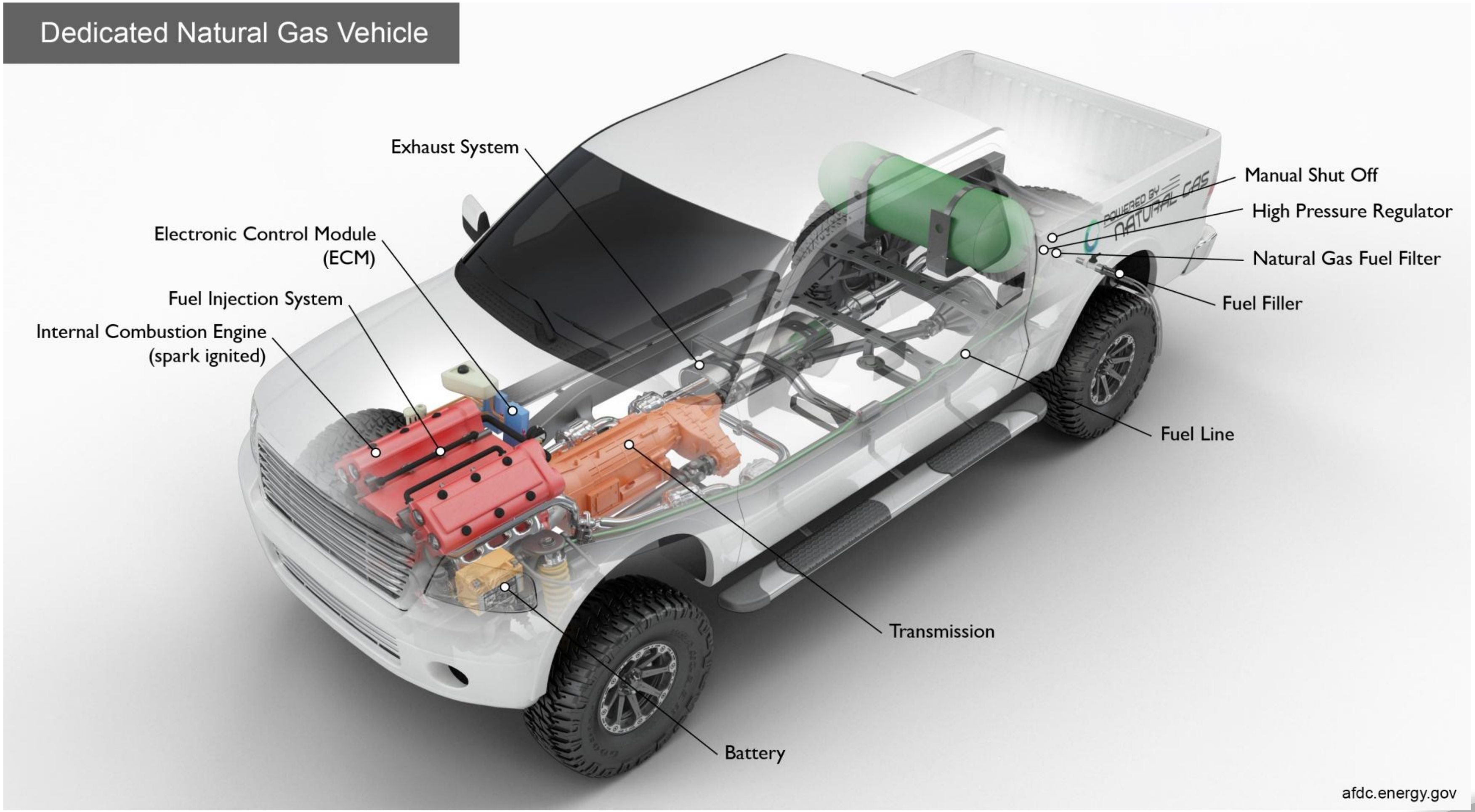
- Natural gas contains mainly CH_4. When natural gas is compressed at high pressure (1000 atm) or cooled to –160°C, it is converted into CNG. It is stored in cylinder made of steel. It is now replacing gasoline as it releases less pollutants during its combustion. It is environmentally clean alternative 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.

CNG

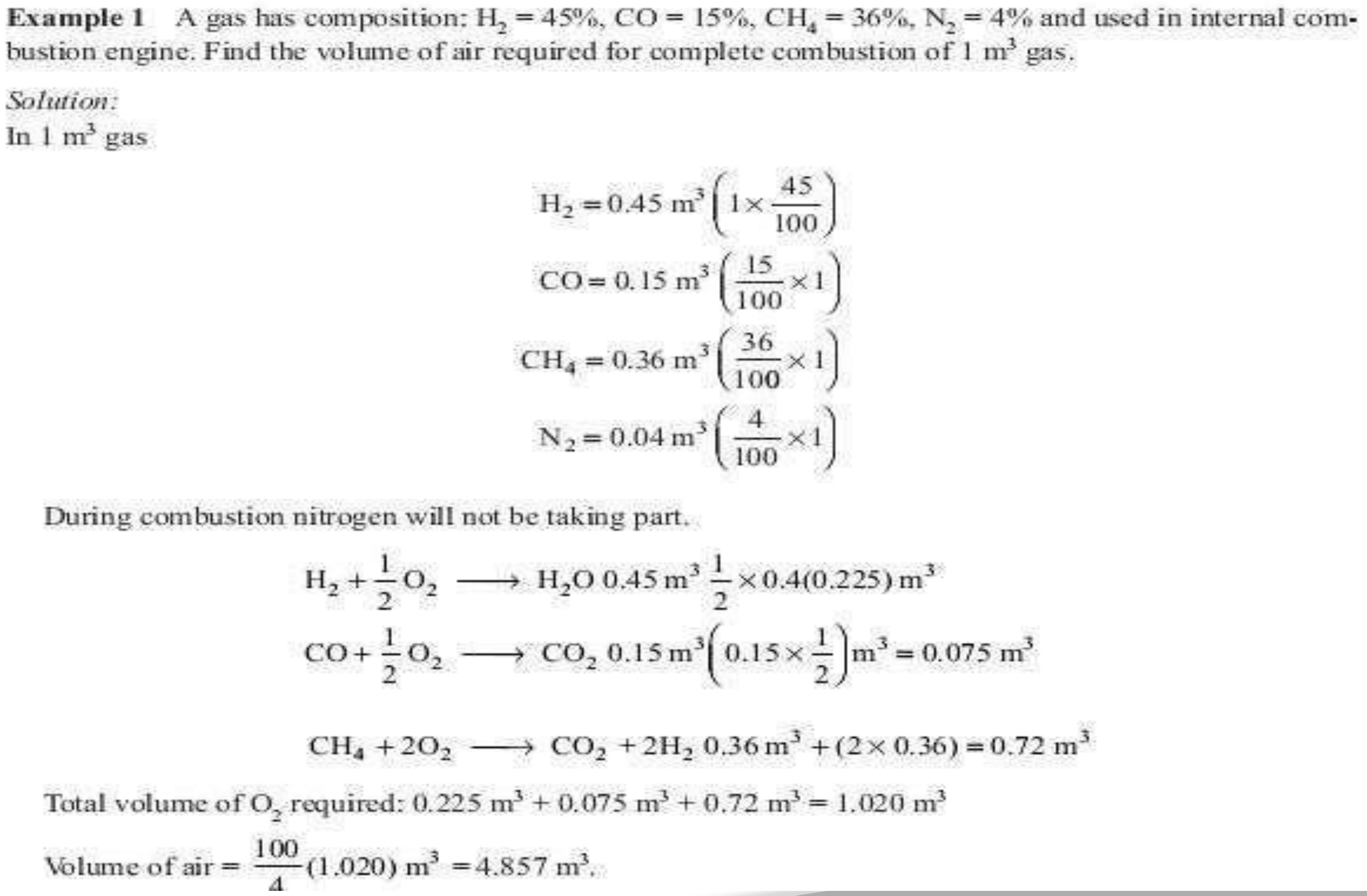
Advantages of CNG:

- 1. Due to higher temperatureof 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.

Dedicated Natural Gas Vehicle



afdc.energy.gov



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.

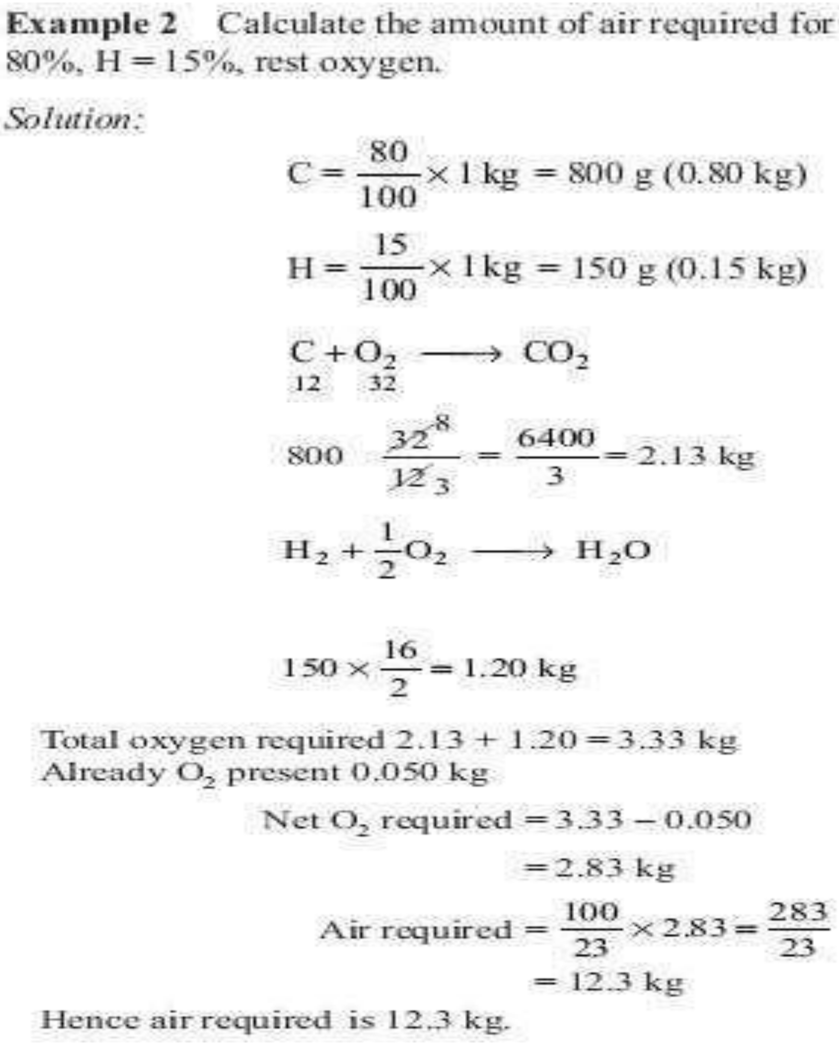
$$H_2 + \frac{1}{2}O_2 \longrightarrow H_2O\ 0.45\ m^3\ \frac{1}{2} \times 0.4(0.225)\ m^3$$

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

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

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:

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

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

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

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

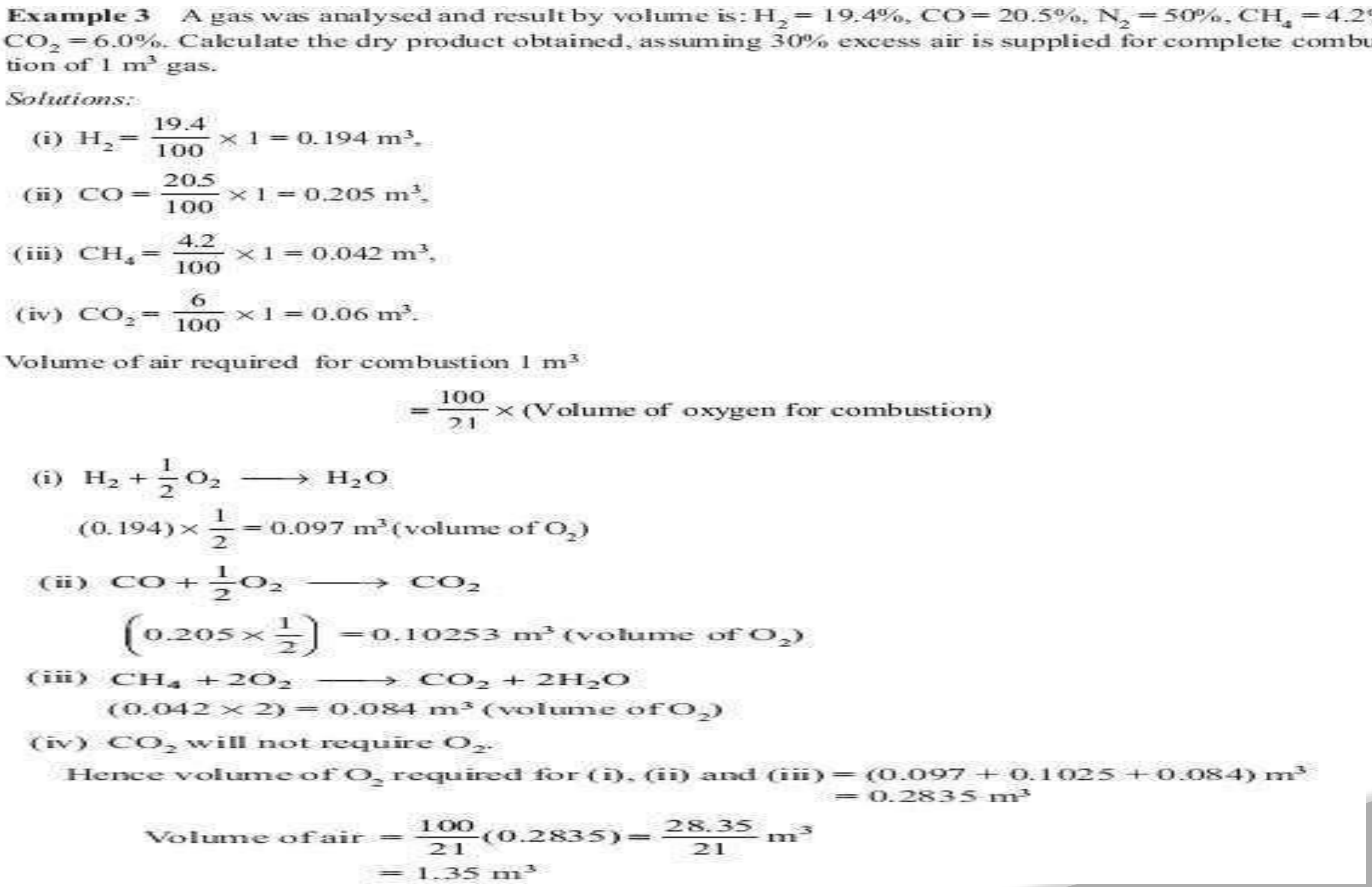
$$H_2 + \frac{1}{2}O_2 \longrightarrow H_2O$$

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

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)

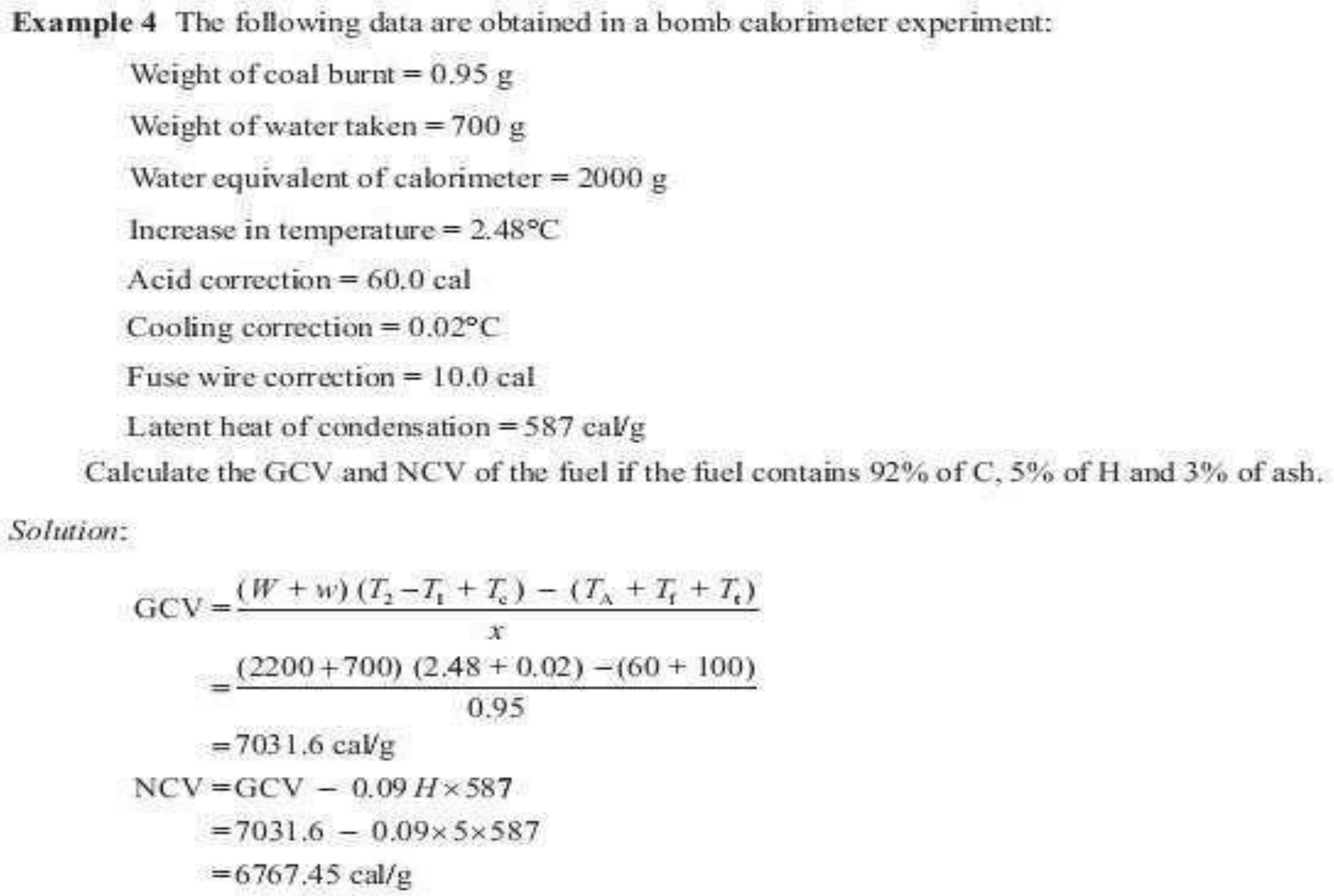
(iii) $CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O$

$(0.042 \times 2) = 0.084\ m^3$ (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:

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

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

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

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

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

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


Thank you