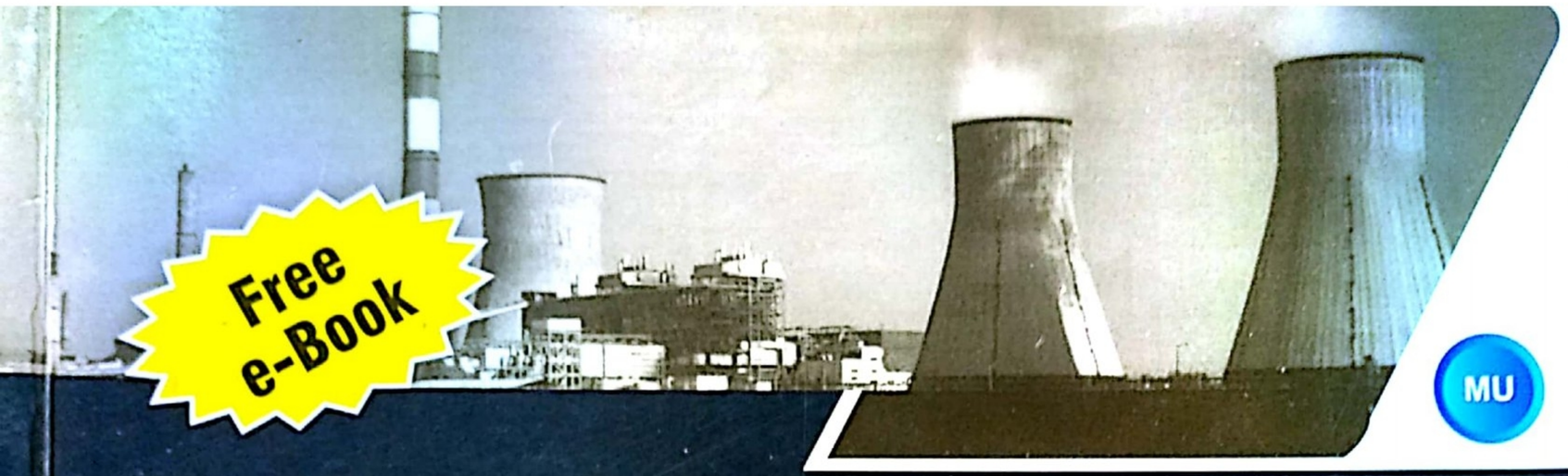

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Applied Chemistry - II

Semester II – Common to All Branches

Dr. Jayshree A. Parikh

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FEC103 : Applied Chemistry-II

Course Code	Course Name	Teaching scheme (Contact Hours)			Credits Assigned			
		Theory	Pract.	Tut.	Theory	TW/Pract	Tut.	Total
FEC203	Applied Chemistry-II	03	01	--	03	0.5	--	3.5

Course Code	Course Name	Examination Scheme							
		Theory				Term Work	Pract	Oral	Total
		Internal Assessment			End Sem Exam				
		Test 1	Test 2	Av of Test 1 & 2					
FEC203	Applied Chemistry-II	15	15	15	60	25	--	--	100

Objectives

1. To provide necessary background in applied chemistry relevant to chemical industries.
2. To provide exposure in conducting experiments and interpret and report the results in professional format

Outcomes : Learner will be able to...

1. Identify types of corrosion and factors affecting it related to problems affecting all industries.
2. Identify different types of corrosion control methods to study corrosion control in various industries.
3. Apply the knowledge of different types of fuels, including their production and refining methods and combustion mechanisms.
4. Illustrate composition and properties of different types of alloys and the process of powder metallurgy
5. Illustrate princpales of green chemistry.
6. Illustrate properties and applications of different types of composite materials.

Module	Detailed Contents	Hrs.
01	**Corrosion** Introduction: Types of Corrosion- (I) Dry or Chemical Corrosion-i) Due to oxygen ii) Due to other gases (II) Wet or Electrochemical corrosion- Mechanism i) Evolution of hydrogen type ii) Absorption of oxygen. Types of Electrochemical Corrosion- Galvanic cell corrosion, Concentration cell corrosion (differential aeration), Pitting corrosion, Intergranular corrosion, Stress corrosion. Factors affecting the rate of corrosion- Nature of metal, position of metal in galvanic series, potential difference, overvoltage, relative area of anodic and cathodic parts, purity of metal, nature of the corrosion product, temperature, moisture, influence of pH, concentration of the electrolytes. Methods to decrease the rate of corrosion- Material selection, Proper designing, Use of inhibitors, Cathodic protection- i) Sacrificial anodic protection ii) Impressed current method, Anodic protection method, Metallic coatings- hot dipping- galvanizing and tinning, metal cladding, metal spraying, Electroplating, Cementation. Organic coatings – Paints (only constituents and their functions). **(Refer chapter 1)**	11
02	**Alloys** Introduction, purpose of making alloys, Ferrous alloys, plain carbon steel, heat resisting steels, stainless steels (corrosion resistant steels), effect of the alloying element- Ni, Cr, Co, Mn, Mo,W and V; Non-Ferrous alloys- Composition, properties and uses of- Alloys of Aluminium- i) Duralumin ii) Magnalium. Alloys of Cu- (I) Brasses-i) Commercial brass ii) German silver, (II) Bronzes- i) Gun metal ii) High phosphorous bronze. Alloys of Pb- i) Wood's metal ii) Tinmann's solder. Powder Metallurgy- Introduction, (1)Methods of powder metal formation- i) Mechanical pulverization ii) Atomization iii) Chemical reduction iv) Electrolytic process v) Decomposition (2) Mixing and blending. (3) Sintering (4) Compacting- i) Cold pressing ii) Powder injection moulding (iii) Hot compaction. Applications of powder metallurgy. Shape Memory Alloys- Definition, properties and Uses. **(Refer chapte**	07
03	**Fuels** Definition, classification of fuels-solid, liquid and gaseous. Calorific value- Definition, Gross or Higher calorific value & Net or lower calorific value, units of heat (no conversions), Dulong's formula & numerical for calculations of Gross and Net calorific values. Characteristics of a good fuel.	

Module	Detailed Contents	Hrs.
	Solid fuels- Analysis of coal- Proximate and Ultimate Analysis with Significance and numericals. Liquid fuels- Crude petroleum oil, its composition and classification and mining (in brief). Refining of crude oil- i) Separation of water ii) Separation of 'S' & iii) Fractional Distillation with diagram and composition and uses table. Cracking- Definition, Types of cracking- I) Thermal cracking – (i) Liquid phase thermal cracking (ii) Vapour phase thermal cracking. II) Catalytic cracking- (i) Fixed-bed catalytic cracking (ii) Moving-bed catalytic cracking. Advantages of Catalytic cracking. Petrol- Refining of petrol, unleaded petrol (use of MTBE), Catalytic converter, Power alcohol, Knocking, Octane number, Cetane number, Antiknocking agents. Combustion- Calculations for requirement of only oxygen and air (by weight and by volume only) for given solid & gaseous fuels. Biodiesel- Method to obtain Biodiesel from vegetable oils (Trans-esterification), advantage and disadvantages of biodiesel. Fuel cell- Definition, types and applications. **(Refer chapter 3)**	
04	**Composite Materials** Introduction, Constitution- i) Matrix phase ii) Dispersed phase. Characteristic properties of composite materials. Classification- (A) Particle - reinforced composites- i) Large – particle reinforced composites ii) Dispersion – strengthened composites. (B) Fiber – reinforced composites- i) Continuous – aligned ii) Discontinuous – aligned (short)- (a) aligned (b) randomly oriented (C) Structural Composites- i) Laminates (ii) Sandwich Panels. **(Refer chapter 4)**	04
05	**Green Chemistry** Introduction, Twelve Principles of Green chemistry, numerical on atom economy, Conventional and green synthesis of Adipic acid, Indigo, Ibuprofen and Carbaryl. Green solvents (water,supercritical CO2) and products from natural materials. **(Refer chapter 5)**	06

Suggested Experiments : (Any Five)

1. Estimation of Zn- Complexometric titration.

2. Estimation of Ni- Complexometric titration.
3. Estimation of Al- Complexometic titration.
4. Flue gas analysis using Orsat's apparatus.
5. Estimation of Fe from plain carbon steel
6. Estimation of Ni by gravimetric method.
7. Estimation of Sniodometrically.
8. Preparation of Biodiesel from edible oil.
9. Estimation of Cu- Iodometrically.
10. Estimation of percentage moisture in coal.
11. Estimation of percentage ash in coal.
12. To estimate the emf of Cu-Zn system by potentiometry.
13. Demonstration of Electroplating.

Term work

Term Work shall consist of minimum five experiments. The distribution of marks for term work shall be as follows:

1. Attendance (Practical and Theory) : 05 marks
2. Laboratory Work (Experiments and journal) : 10 marks
3. Assignments and Viva on practicals : 10 marks

Assessment

Internal Assessment Test:

Assessment consists of two class tests of 15 marks each. The first class test is to be conducted when approx. 40% syllabus is completed and second class test when additional 35% syllabus is completed. Duration of each test shall be one hour.

End Semester Theory Examination

1. Question paper will comprise of total 06 questions, each carrying 15 marks.
2. Total 04 questions need to be solved.
3. Question No: 01 will be compulsory and based on entire syllabus wherein sub-questions of 3 marks will be asked.
4. Remaining questions will be mixed in nature.(e.g. Suppose Q.2 has part (a) from module 3 then part (b) will be from any module other than module 3)
5. In question paper weightage of each module will be proportional to number of respective lecture hrs as mentioned in the syllabus.

□□□

Module 1

Syllabus : Introduction. Types of Corrosion- (I) Dry or Chemical Corrosion-i) Due to oxygen ii) Due to other gases (II) Wet or Electrochemical corrosion. Mechanism i) Evolution of hydrogen type ii) Absorption of oxygen. Types of Electrochemical Corrosion. Galvanic cell corrosion, Concentration cell corrosion (differential aeration), Pitting corrosion, Intergranular corrosion, Stress corrosion. Factors affecting the rate of corrosion. Nature of metal, position of metal in galvanic series, potential difference, overvoltage, relative area of anodic and cathodic parts, purity of metal, nature of the corrosion product, temperature, moisture, influence of pH, concentration of the electrolytes. Methods to decrease the rate of corrosion. Material selection. Proper designing. Use of inhibitors, Cathodic protection- i) Sacrificial anodic protection ii) Impressed current method, Anodic protection method. Metallic coatings- hot dipping, galvanizing and tinning, metal cladding, metal spraying, Electroplating, Cementation. Organic coatings – Paints (only constituents and their functions).

Chapter 1 : Corrosion ..... **1-1 to 1-59**

✓ **Syllabus Topic** : Introduction 1-1

1.1 Introduction 1-1

1.1.1 Corrosion-Definition 1-2

✓ **Syllabus Topic** : Types of Corrosion 1-3

1.2 Types of Corrosion 1-3

1.2.1 Dry / Chemical Corrosion/Atmospheric Corrosion 1-3

1.2.2 Wet or Electrochemical Corrosion 1-8

1.2.3 Mechanism of Electrochemical Corrosion/ Wet Corrosion 1-9

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✓ **Syllabus Topic** : Types of Electrochemical Corrosion-Galvanic cell corrosion, Concentration cell corrosion (differential aeration), Pitting corrosion, Intergranular corrosion, Stress corrosion. 1-13

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1.3.3 Pitting Corrosion 1-16

1.3.4 Intergranular Corrosion 1-17

1.3.5 Stress Corrosion 1-18

✓ **Syllabus Topic** : Factors affecting the rate of corrosion-Nature of metal, position of metal in galvanic series, potential difference, overvoltage, relative area of anodic and cathodic parts, purity of metal, nature of the corrosion product, temperature, moisture, influence of pH, concentration of the electrolytes. 1-22

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1.4.9 Moisture 1-24

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1.5 Methods to Decrease the Rate of Corrosion 1-25

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1.5.4 Cathodic Protection Method 1-30

1.5.4.1 Comparison between Cathodic and Anodic Protection 1-32

1.5.5 Anodic Protection Method 1-33

✓ **Syllabus Topic** : Metallic coatings-hot dipping-galvanizing and tinning, metal cladding, metal spraying, Electroplating, Cementation. Organic coatings-Paints (only constituents and their functions) 1-34

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1.7.3 Metal Spraying 1-

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1.7.4.2 Process of Electroplating 1-

1.7.4.3 Disadvantages of Electroplating 1-

1.7.4.4 Advantages of Electroplating 1-

1.7.4.5 Applications of Electroplating 1-

1.7.5 Cementation / Diffusion 1-

1.8 University Questions and Answers 1-

Module 2

Syllabus : Introduction, purpose of making alloys, Ferrous alloys, plain carbon steel, heat resisting steels, stainless steels (corrosion resistant steels), effect of the alloying element- Ni, Cr, Co, Mn, Mo,W and V; Non-Ferrous alloys- Composition, properties and uses of- Alloys of Aluminium- i) Duralumin ii) Magnalium. Alloys of Cu- (I) Brasses-i) Commercial brass ii) German silver, (II) Bronzes- i) Gun metal ii) High phosphorous bronze. Alloys of Pb- i) Wood's metal ii) Tinmann's solder. Powder Metallurgy- Introduction, (1)Methods of powder metal formation- i) Mechanical pulverization ii) Atomization iii) Chemical reduction iv) Electrolytic process v) Decomposition (2) Mixing and blending. (3) Sintering (4) Compacting- i) Cold pressing ii) Powder injection moulding (iii) Hot compaction. Applications of powder metallurgy. Shape Memory Alloys- Definition, properties and Uses.

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Module 3

Syllabus : Definition, classification of fuels-solid, liquid and gaseous. Calorific value- Definition, Gross or Higher calorific value & Net or lower calorific value, units of heat (no conversions), Dulong's formula & numerical for calculations of Gross and Net calorific values. Characteristics of a good fuel.
Solid fuels- Analysis of coal- Proximate and Ultimate Analysis with Significance and numericals.
Liquid fuels- Crude petroleum oil, its composition and classification and mining (in brief). Refining of crude oil- i) Separation of water ii) Separation of 'S' & iii) Fractional Distillation with diagram and composition and uses table.
Cracking- Definition, Types of cracking-
I) Thermal cracking – (i) Liquid phase thermal cracking (ii) Vapour phase thermal cracking. II) Catalytic cracking- (i) Fixed-bed catalytic cracking (ii) Moving-bed catalytic cracking. Advantages of Catalytic cracking.
Petrol- Refining of petrol, unleaded petrol (use of MTBE), Catalytic converter, Power alcohol, Knocking, Octane number, Cetane number, Antiknocking agents.
Combustion- Calculations for requirement of only oxygen and air (by weight and by volume only) for given solid & gaseous fuels.
Biodiesel- Method to obtain Biodiesel from vegetable oils (Trans-esterification), advantage and disadvantages of biodiesel.
Fuel cell- Definition, types and applications

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Module 4

Syllabus : Introduction, Constitution- i) Matrix phase ii) Dispersed phase. Characteristic properties of composite materials. Classification- (A) Particle - reinforced composites- i) Large – particle reinforced composites ii) Dispersion - strengthened composites. (B) Fiber – reinforced composites- i) Continuous - aligned ii) Discontinuous - aligned (short)- (a) aligned (b) randomly oriented (C) Structural Composites- i) Laminates (ii) Sandwich Panels.

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✓ **Syllabus Topic :** Classification of Composites : Classification- (A) Particle - reinforced composites- i) Large – particle reinforced composites ii) Dispersion – strengthened composites. (B) Fiber – reinforced composites- i) Continuous – aligned ii) Discontinuous – aligned (short)- (a) aligned (b) randomly oriented (C) Structural Composites- i) Laminates (ii) Sandwich Panels 4
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4.4.3 Structural Composites or Layered Composites 4-
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4.4.3.2 Sandwich Panel 4-
4.5 Application of Composite Materials 4-
4.7 University Questions and Answers 4-

Module 5

Syllabus : Introduction, Twelve Principles of Green chemistry, numerical on atom economy, Conventional and green synthesis of Adipic acid, Indigo, Ibuprofen and Carbaryl. Green solvents (water, supercritical CO_2) and products from natural materials

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□□□

CHAPTER 1

MODULE 1

Corrosion

Syllabus

Introduction : Types of Corrosion - (I) Dry or Chemical Corrosion-i) Due to oxygen ii) Due to other gases (II) Wet or Electrochemical corrosion-Mechanism i) Evolution of hydrogen type ii) Absorption of oxygen. Types of Electrochemical Corrosion-Galvanic cell corrosion, Concentration cell corrosion (differential aeration), Pitting corrosion, Intergranular corrosion, Stress corrosion. Factors affecting the rate of corrosion- Nature of metal, position of metal in galvanic series, potential difference, overvoltage, relative area of anodic and cathodic parts, purity of metal, nature of the corrosion product, temperature, moisture, influence of pH, concentration of the electrolytes. Methods to decrease the rate of corrosion- Material selection, Proper designing, Use of inhibitors, Cathodic protection- i) Sacrificial anodic protection ii) Impressed current method, Anodic protection method, Metallic coatings-hot dipping- galvanizing and tinning, metal cladding, metal spraying, Electroplating, Cementation. Organic coatings – Paints (only constituents and their functions)

Syllabus Topic : Introduction

➢ Topics covered : What is corrosion ? Definition, Adverse effects of corrosion.

1.1 Introduction

What is corrosion ?

- Corrosion is nothing but the *deterioration* of a substance due to its reaction with its environment. Thus it is the *destruction* of the metal due to *unwanted reaction* between the metal (starting from surface) and the atmosphere. The *tendency* of the metals to undergo such reactions readily with atmospheric gases and other matters, *owes to their origin.*

- Metals occur in nature in the form of their *ores*. These ores are subjected to several metallurgical processes to extract the *metal in pure form*. Thus the extraction processes reduce ores to their *metallic states*. But as soon as the metals are extracted from ores, the metals become *highly reactive* and enter into reaction with the other elements present in the *surrounding/vicinity* of it. This natural reactivity/tendency of metals gives *rise to corrosion*, and thereby metals *again enter into combined states*.
- *Metals show great affinity to oxygen* present in the atmosphere, and form oxides. There are few other impurities of atmosphere which also affect metals, forming *carbonates, sulphides, sulphates* etc. Thus the corrosion can also be defined as,the process by which the metals have a tendency to go back to their combined state is known as *corrosion*.

The environment/atmosphere surrounding metals can be *air, water, sea water, acids, alkalies, steam, gases, other molten metals, soils*, etc. The metals come in contact with all these *corrosion influencing factors* at varying temperatures ranging from room temperature to working temperature of the various processes. This contact results in gradual transformation of metal into its compounds. This is also known as *weathering of metals or weeping of metals*. Such weathering is exhibited by *timber, wood, concrete etc. Even leading of glass or cracking of plastics are examples of 'corrosion'*.

1.1.1 Corrosion-Definition

MU – Dec.2012. May 2016

"Any process causing deterioration or destruction of any material is known as *corrosion*". *Metals* being *highly reactive*, are greatly affected by action of the factors responsible for corrosion.

Different metals possess affinity for different gases in atmosphere.

For example :

1. Iron reacts with oxygen to form oxide.
2. Copper forms *carbonate* by reacting with CO_2 *present in air*
3. *Silver reacts* with *chlorine* or H_2S from atmosphere forming corresponding compounds.

Adverse effects of corrosion

(i) Metal loses its efficiency and many of its useful properties get altered.

(ii) Maintenance cost and cost of material increases while production rate decreases.

(iii) The purity of the product gets affected.

Knowing these destructive effects of corrosion, it becomes essential to understand the mechanism of corrosion, which is discussed in this chapter.

Syllabus Topic : Types of Corrosion

➢ **Topics covered :**

Dry / Chemical Corrosion/Atmospheric Corrosion, Corrosion due to oxygen Mechanism of chemical corrosion due to oxidation Role of oxide film, Stable oxide films, Porous oxide layer, Non-porous oxide layer : Unstable oxide films, Volatile oxide films, Corrosion due to other gases, Wet or Electrochemical Corrosion-Basic principle : Theory : Mechanism of Electrochemical Corrosion/Wet Corrosion Evolution of Hydrogen type, Absorption of oxygen type, Comparison between Dry and Wet Corrosion

1.2 Types of Corrosion

There are two types of corrosion,

	Types of corrosion
(a)	Dry or Atmospheric corrosion / Chemical corrosion
(b)	Wet or Immersed corrosion / Electrochemical corrosion

1.2.1 Dry / Chemical Corrosion/Atmospheric Corrosion

MU - May 2013. Dec. 2013. May 2014. Dec. 2014. May 2015. Dec. 2015

- Chemical/Atmospheric or dry corrosion occurs mainly by, *direct attack* of atmospheric gases such as O_2, CO_2, H_2S, *halogens*, SO_2 etc. on the surface of metals. The metal forms corresponding compounds such as *oxides, carbonates, sulphides, halides or sulphates*. The action of some *organic* or *anhydrous inorganic liquids, or melt of metals* also cause this type of corrosion.
- **This type of corrosion is divided into following classes :**
  - (i) Corrosion due to oxygen – leading to formation of oxides.
  - (ii) Corrosion due to other gases – leading to formation of other compounds.
  - (iii) Corrosion due to other corrosive liquids – such as other molten metals.

(i) **Corrosion due to oxygen**

- This type of corrosion occurs due to attack of atmospheric oxygen on metal surface either at low or high temperatures, forming metal oxide as

$$\text{Metal} + O_2 \longrightarrow \text{Metal oxide}$$

Normally, more active metals get corroded faster than less active metals. For example, alkali metals and alkaline earth metals get oxidized even at low temperatures as compared to other metals which are less active.

Mechanism of chemical corrosion due to oxidation

$$\text{Metal} \xrightarrow{\text{Oxid}^n} M^{n+} + ne^- \quad \text{e.g. } Fe \xrightarrow{\text{Oxid}^n} Fe^{2+} + 2e^-$$

$$\frac{1}{2}O_2 + 2e^- \xrightarrow{\text{Red}^n} O^{2-} \quad \frac{1}{2}O_2 + 2e^- \xrightarrow{\text{Red}^n} O^{2-}$$

$$M^{n+} + O^{2-} \longrightarrow M_2O_n \quad Fe^{2+} + O^{2-} \longrightarrow FeO$$

- The extent of the corrosion, depends upon the type of the oxide film formed by metals. The oxide films formed are classified into three categories.

a) Stable oxide film i) Porous – e.g. Iron Oxide
ii) Non-porous – e.g. Oxides of A1, Ni, Cr etc.

b) Unstable oxide film – e.g. Oxides of noble metals

c) Volatile oxide film – e.g. Oxides of molybdenum

Table 1.2.1 : Role of oxide film

Sr. No.	Type of oxide film	Example	Role/ Effect
(a)	Stable oxide film (i) porous oxide film.	Iron oxide FeO / Fe_2O_3 / Fe_3O_4.	Being porous film, the corrosion of under lying metal continues. The rate of corrosion slows down.
	(ii) Non-porous	Al_2O_3 Al-oxide	Being non-porous film, the corrosion of underlying metal stops till the film is intact.

Sr. No.	Type of oxide film	Example	Role/ Effect
(b)	Unstable oxide film	Oxides of noble metals.	Being unstable film, the oxide decomposes and metal surface continues to be exposed. Hence, corrosion of underlying metal continues.
(c)	Volatile oxide film	Oxides of some metals like molybdenum.	Being Volatile oxide, it is lost to environment, leaving fresh metal exposed. Rate of corrosion very high, till entire metal lost.

a) **Stable oxide films** normally get adhered to the underlying metal surface and hence provide a protective layer on surface, thereby reducing rate of further corrosion. But, extent of further corrosion depends upon the type of stable film formed.

(i) **Porous oxide layer**

If oxide film formed on metal surface is *porous* in nature, the *rate of further corrosion is not reduced* much. This can be understood better by taking example of alkali metals such as Li, Na, K or alkaline earth metals such as Ca, Mg etc. These metals react with oxygen, forming oxide such as Na_2O, K_2O, CaO, MgO, etc. where *volume of oxide formed is less than the volume of reacted metal.* Thus, oxide layer is not able to cover the entire surface of metal block/piece. Hence, in oxide film, *pores are developed*. These *pores give free access* to oxygen, which attacks the underlying pure metal. Thus, *corrosion does not stop* till pure metal is available.

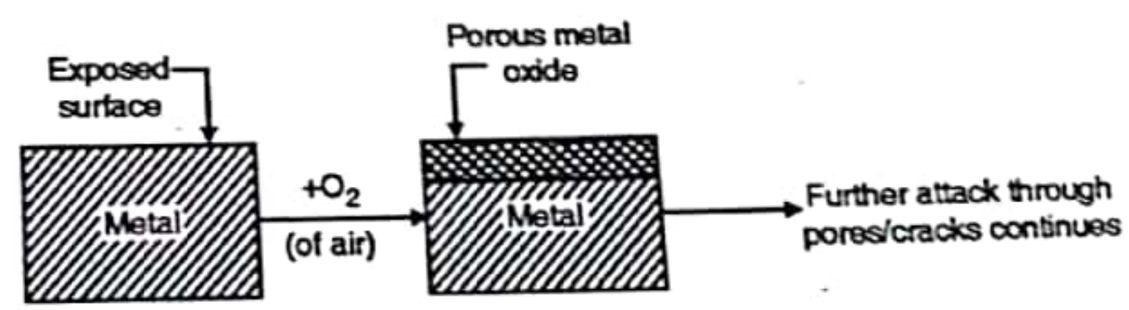


Fig. 1.2.1 : Porous oxide layer

(ii) **Non-porous oxide layer**

If the oxide film formed is *non-porous in nature*, the *rate of corrosion reduces* considerably and in most of the cases, corrosion of metal stops.

The metals like Al, Cr, etc. form their oxides such as Al_2O_3, Cr_2O_3, etc. whose volume is greater than the volume of metals. Hence, the oxide *film formed, covers the underlying metals completely, not leaving any access for further attack of oxygen*, thereby *stopping further corrosion*. Thus, metals develop a *protective oxide layer* and become *passive* till this layer is uninterrupted.

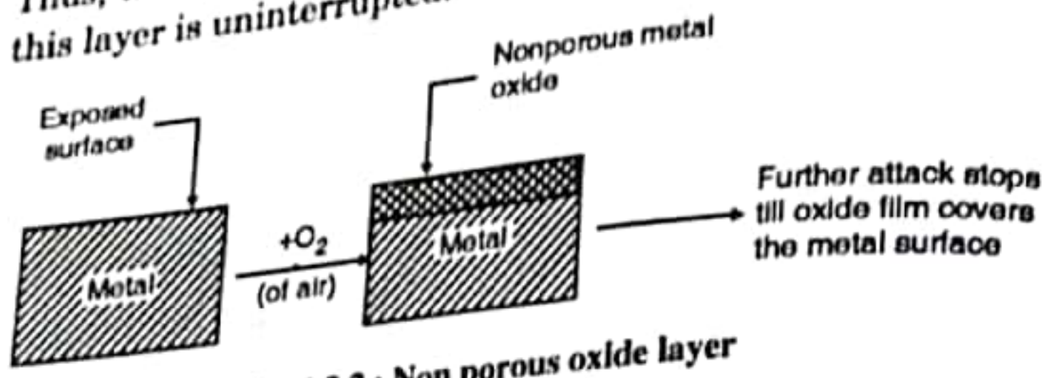


Fig. 1.2.2 : Non porous oxide layer

b) **Unstable oxide films** are those which get decomposed on the metal surfaces forming back the metal and oxygen.

Metal + Oxygen → Metal oxide → Metal + Oxygen

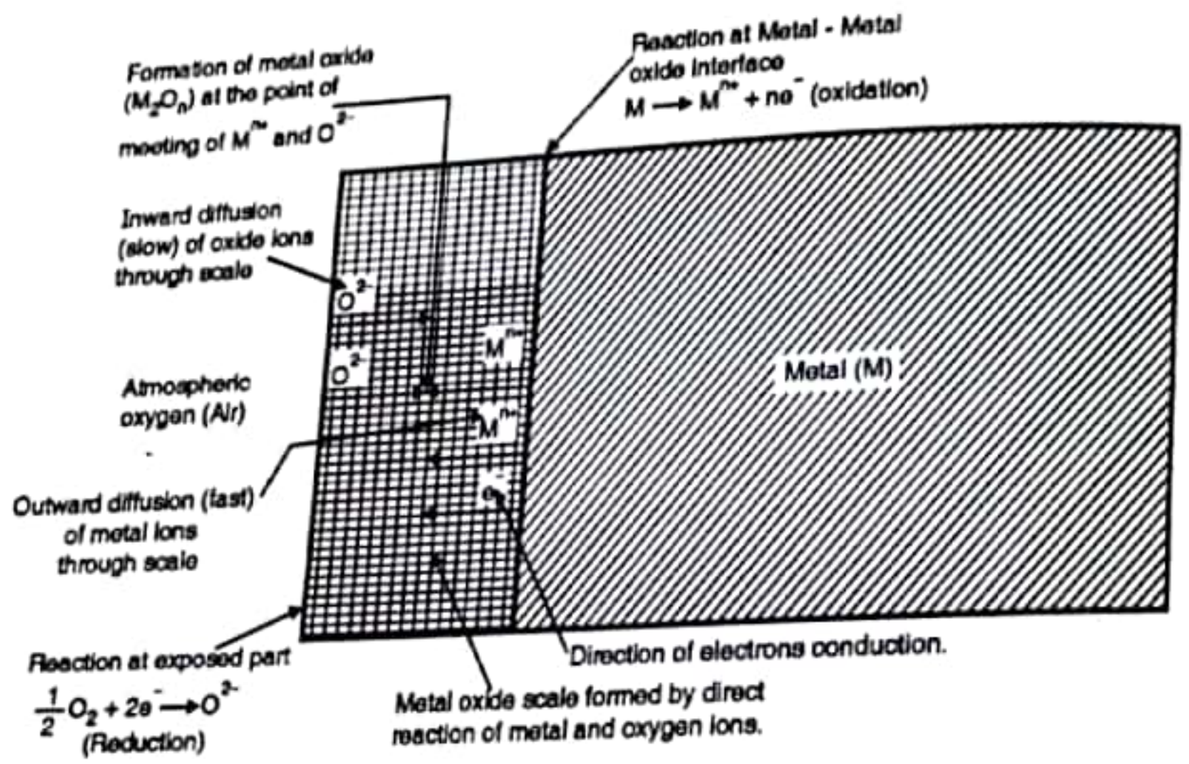


Fig. 1.2.3 : Schematic representation of oxidation mechanism of metals

Example : Oxides of metals like gold, platinum, silver, etc.

Hence, *such metals* forming unstable oxide film *do not get corroded,* but loss of metal continues, slowly.

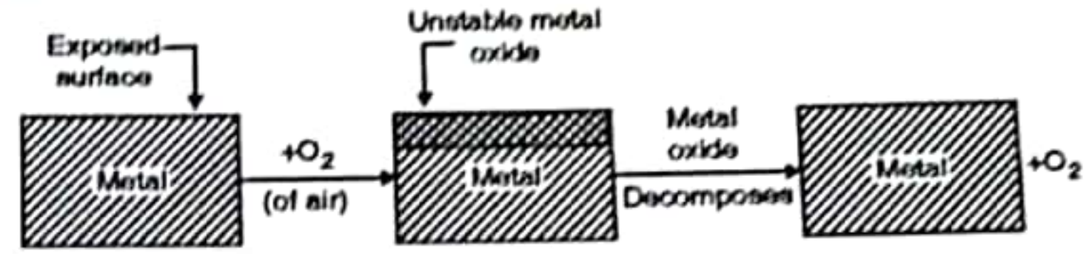


Fig. 1.2.4 : Unstable oxide layer

c) **Volatile oxide films** are those which get *vaporised* from metal surfaces as soon as they are formed, leaving behind the underlying metal surfaces for further attack of oxygen.

Metal + Oxygen → Metal oxide.

For example : *Molybdenum* metal forms its oxide, which is volatile. Thus, in such cases, *corrosion continues* till the metal is available.

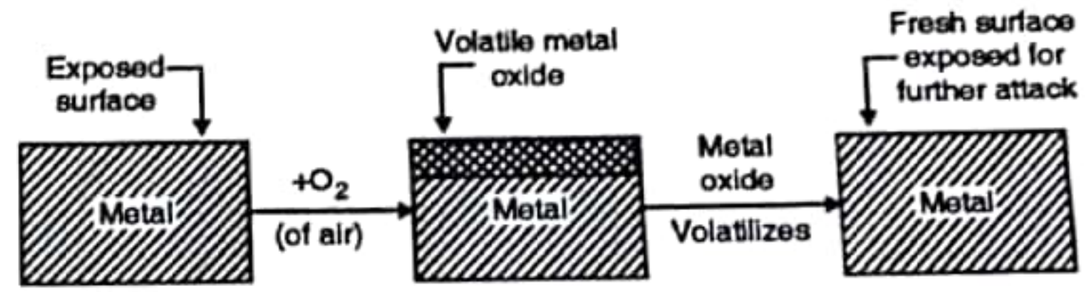


Fig. 1.2.5 : Volatile oxide layer

(II) Corrosion due to other gases

- Gases such as CO_2, H_2S, SO_2, Cl_2, F_2 etc. react on the metal surface resulting in formation of a film of corresponding compound.
- The extent of corrosion is mainly governed by the chemical affinity of metal and attacking gases. The rate of further corrosion depends upon the volume of the film of corrosion product and the volume of the metal.
- In case of the attack of other gases e.g. Cl_2, the nature of product differs from metal to metal e.g. Cl_2 reacts with *silver* to give highly *protective film* of silver chloride whereas same gas reacts with *tin* to form the corresponding chloride which is *volatile in nature*, as,

Example : $2\,Ag + Cl_2 \rightarrow 2\,AgCl$ (Protective)

$Sn + 2\,Cl_2 \rightarrow SnCl_4$ (Volatile)

- Here, the film of *silver chloride is protective* (non-porous), hence rate of further corrosion reduces, while that of *stannic chloride is volatile* in nature, hence rate of corrosion is enhanced.
- Thus it is obvious that the corrosion of silver due to the attack of chlorine stops on the surface of metal whereas that of tin continues till the tin metal gets completely vanished.
- Similarly, H_2S attacks the metals like Fe as,

$$Fe + H_2S_{(aq)} \rightarrow FeS + 2H \text{ (Atomic hydrogen)}$$

The atomic hydrogen thus formed, penetrates the voids in metal by diffusion, and gets accumulated there, and recombines to form molecular hydrogen,

$$H + H \rightarrow H_2$$

- As the concentration of molecular hydrogen in voids increases, it causes blisters and fissures in the metal. Thus, strength and ductility of metals reduces considerably. This is known as *hydrogen embrittlement.*
- At high temperature, molecular hydrogen decomposes thermally forming atomic hydrogen, which is highly active and hence reacts with other element present in metal.
- **Example :** Carbon present in steel is available for attack of atomic hydrogen, at high temperature forming methane gas (CH_4). This type of attack is nothing but *intergranular corrosion.* This *causes reduction in strength of metal / alloy, and metal becomes brittle.*

1.2.2 Wet or Electrochemical Corrosion

MU - May 2013, May 2014, Dec. 2014, Dec. 2015

Basic principle

An electrochemical reaction is one which results in the transfer of electrons.

- When metal surface is in immediate contact of *aqueous acidic/alkaline/neutral/electrolytic solutions,* the short circuited galvanic cells get set all along the surface of metal. This gives rise to corrosion which proceeds by electrochemical principles. In fact,
- Wet corrosion is more common than dry corrosion.

- The co-ordinating metal(s) behave like *galvanic cells* thereby the *part of metal acting as an anode* is consumed while *the other part* which is *acting as a cathode* remains unchanged.
- **Theory :** This type of corrosion occurs, under following conditions,
  - (i) Where a conducting liquid is in contact with metal, or
  - (ii) Where two dissimilar metals or alloys are either immersed or dipped partially in a solution.
- These type of conditions are always suitable for formation of *separate anodic and cathodic areas* between which the electric current can flow through the conducting solution.
- *At anode,* the liberation of electrons takes place, i.e. *oxidation reaction.* Consequently at anode, *the destruction of metal occurs,* either by dissolving it as metal ions or by converting it into a compound such as its oxide.
- *At cathode,* the absorption of electrons takes place, i.e. *reduction reaction.* These reactions do not affect the part of the metal acting as a cathode, since most of the metals cannot be further reduced.
- Thus, corrosion occurs always at anode.

Reactions : *At anode*

$$\underset{\text{(Metal)}}{M} \longrightarrow \underset{\text{(Metal ion)}}{M^{n+}} + \underset{\text{(Electrons)}}{ne^-}$$

- Formation of metal ions (M^{n+}) at anode causes dissolution of metal and free electrons are liberated. These free electrons are consumed in cathodic reactions with either.
  - (a) Evolution of H_2 gas. Or,
  - (b) Formation of a product [oxide of metal] due to absorption of O_2 gas. depending upon the nature of the corrosive environment.

1.2.3 Mechanism of Electrochemical Corrosion/ Wet Corrosion

a) Evolution of Hydrogen type

MU - May 2013, May 2014, Dec. 2014, May 2016

- Corrosion, by this mechanism occurs usually if environment, surrounding to the metal is acidic.
- **Example :** Pipe lines made from iron metal get corroded if industrial waste material, or solutions of non-oxidising acids, is transported through them.

The following reaction occurs

$$\text{Anode} \xrightarrow[\text{flow}]{\text{Electrons}} \text{cathode}$$

$$Fe \rightarrow Fe^{+2} + 2e^- \longrightarrow 2H^+ + 2e^- \rightarrow H_2$$

Acidic environment

Bulk of the metal

- From above reactions, we can say that the *flow of electrons takes place from the anode to the cathode.* These electrons are gained by cathodic reaction, and at cathode H^+ ions are eliminated as H_2 gas. The overall mechanism can be represented as

$$Fe + 2H^+ \rightarrow Fe^{2+} + H_2$$

- Thus displacement of H_2 ions from acidic solution by metal ions takes place.

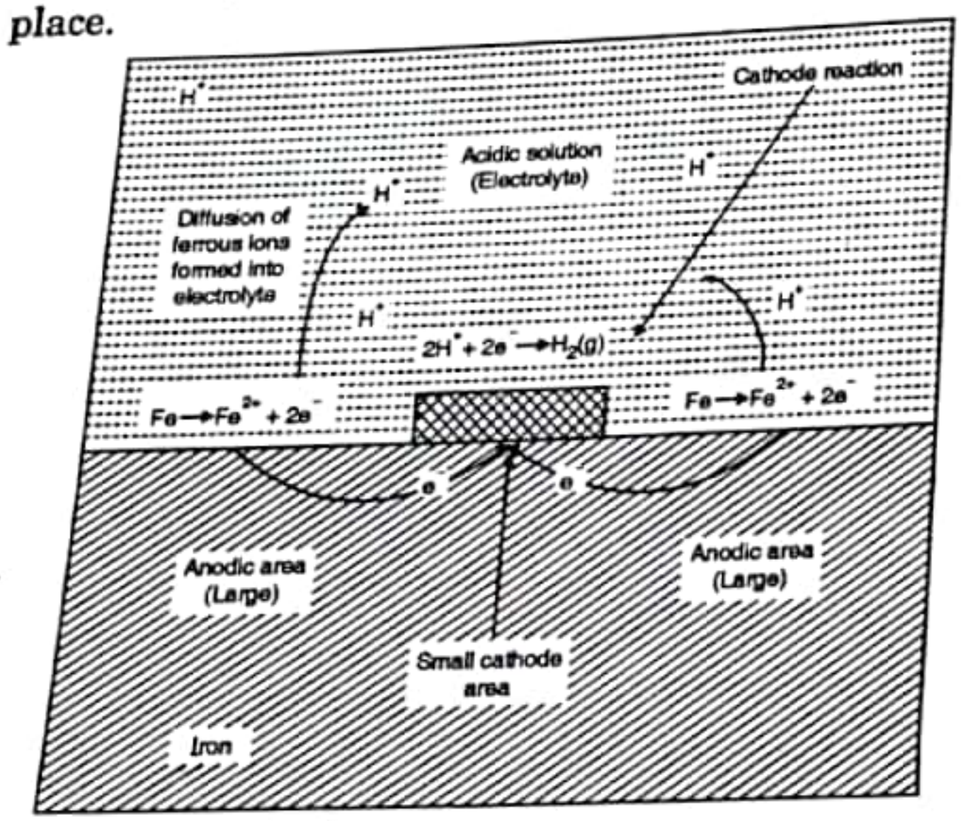


Fig. 1.2.6 : Schematic representation of Mechanism of wet corrosion by hydrogen evolution

Thus, all metals have tendency to get dissolved in the acidic solution with simultaneous evolution of H_2 gas.

b) *Absorption of oxygen type*

- ***Rusting of iron*** *in neutral aqueous solution of electrolytes in the presence of atmospheric oxygen is the most common example of this type of corrosion (mechanism).*

- Thus, iron metal in such cases is always with a coat of thin film of iron oxide (Fe_2O_3). Since, the film is porous in nature, the surface of iron exposed to atmosphere acts as an anode while rest of surface acts as a cathode.

Anodic reaction

$$Fe \rightarrow Fe^{2+} + 2e^- \text{ (Oxidation)}$$

Thus, at anode iron dissolves as ferrous ions with liberation of electrons.

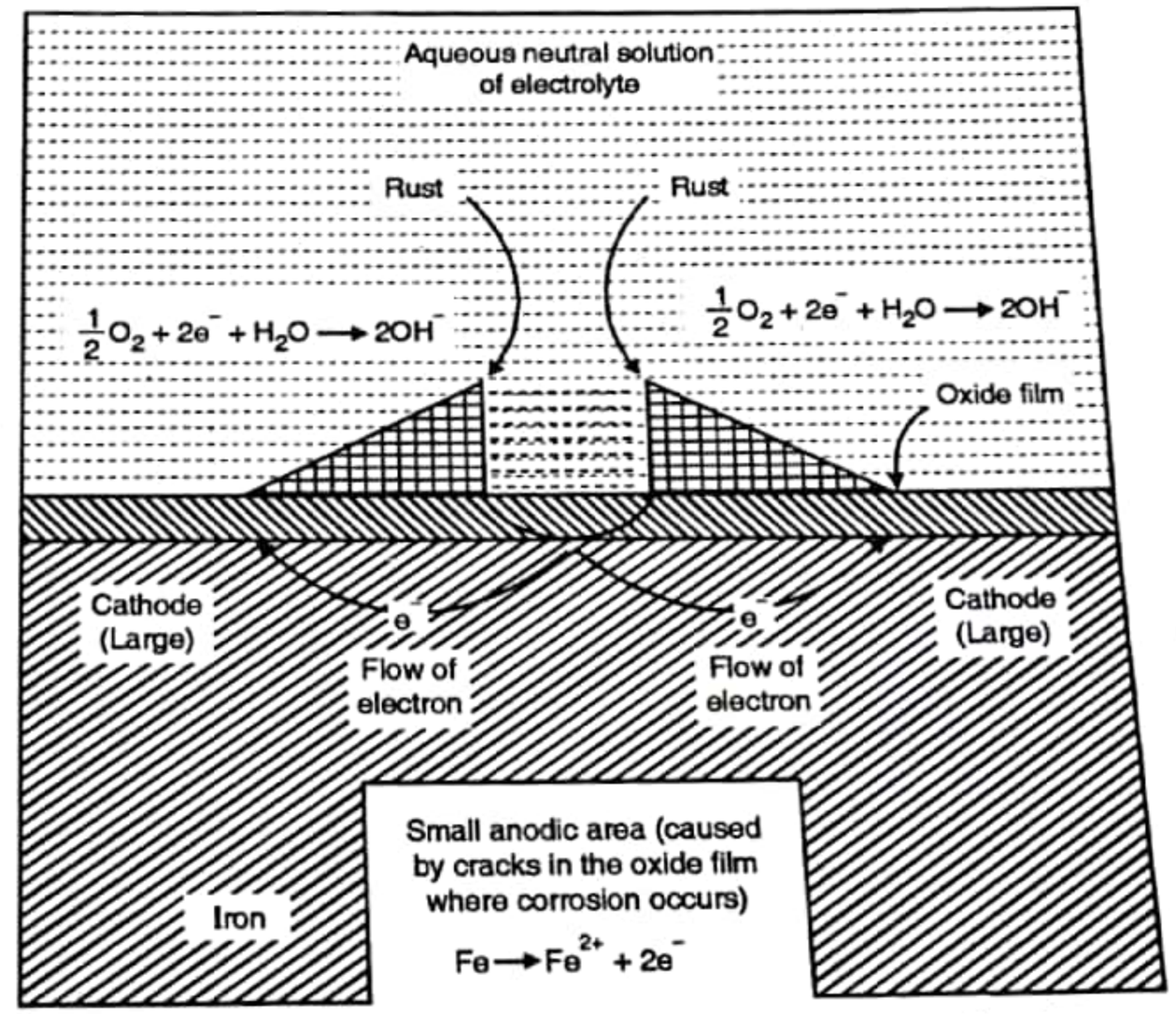


Fig. 1.2.7 : Schematic representation of Mechanism of wet corrosion by oxygen absorption

Cathodic reaction

The liberated electrons flow through iron metal from anode to the cathode, where electrons are intercepted by the dissolved oxygen as

$$\frac{1}{2}O_2 + H_2O + 2e^- \rightarrow 2OH^- \text{ (Reduction)}$$

The Fe^{+2} ions and OH^- ions diffuse and when they meet, $Fe(OH)_2$ is precipitated, as

$$Fe^{2+} + 2OH^- \rightarrow Fe(OH)_2 \downarrow$$

Effect of O_2 supply on corrosion product :

- If enough supply of O_2 is available, then $Fe(OH)_2$ readily get oxidized to $Fe(OH)_3$ as

$$4Fe(OH)_2 + O_2 + 2H_2O \rightarrow 4Fe(OH)_3 \downarrow \text{ (yellow Rust)}$$

This substance is commonly known as *yellow rust* and it actually corresponds to

$$Fe_2O_3H_2O \text{ or } FeO(OH) \text{ and not } Fe(OH)_3$$

- If the supply of oxygen is limited, the product formed may be Ferroso-ferric hydroxide.
- If oxygen supply is increased, cathodic reaction is influenced forming more number of OH^- ions, and subsequently anodic reaction is also influenced, eliminating more number of electrons, thereby increasing the rate of corrosion.

1.2.4 Comparison between Dry and Wet Corrosion

Sr. No.	Dry corrosion	Wet corrosion
1.	It mainly occurs by direct contact of at mospheric gases.	It occurs when metal surface is in immediate contact with aqueous solutions.
2.	The gases are O_2,CO_2, SO_2 H_2S, hydrogen etc.	The aqueous solutions are acids/ alkalis / neutral / electrolytic
3.	There is no formation of galvanic cells	Galvanic cells are formed all along the surface of metal being in contact with aqueous solution.
4.	Nature of corrosion product is governed by characteristics of metal	Nature of corrosion product depends upon medium either with O_2 dissolved or H^+ ions being present.
5.	Mechanism is not explained with electrochemical principles.	Mechanism is explained with electrochemical principle

Sr. No.	Dry corrosion	Wet corrosion
6.	Rate of corrosion is governed by nature of corrosion product	Rate of corrosion is governed by cathodic product
7.	Mechanism	Mechanism
	$\text{Metal} \xrightarrow{\text{oxid}^n} M^{n+} + ne^-$ e.g. $Fe \longrightarrow Fe^2 + 2e^-$ $\frac{1}{2}O_2 + 2e^- \xrightarrow{\text{Red}^n} O^{2-}$ $M^{n+} + O^{2-} \longrightarrow M_2O_n$ $Fe^{2+} + O^{2-} \longrightarrow FeO \downarrow$	At anode $\text{Metal} \xrightarrow{\text{oxid}^n} M^{n+} + ne^-$ e.g. $Fe \longrightarrow Fe^{2+} + 2e^-$ At cathode, $\frac{1}{2}O_2 + H_2O + 2e^- \xrightarrow{\text{Red}^n} 2\,OH^-$ $Fe^2 + 2\,OH^- \longrightarrow Fe(OH)_2 \downarrow$

Syllabus Topic : Types of Electrochemical Corrosion-Galvanic cell corrosion, Concentration cell corrosion (differential aeration), Pitting corrosion, Intergranular corrosion, Stress corrosion.

1.3 Types of (Examples) of Electrochemical Corrosion

1.3.1 Galvanic Cell Corrosion

MU - May 2012, Dec. 2012, Dec. 2015

The *name* of this type of corrosion is *indicative* that there must be formation of a *galvanic cell* on metal surface causing corrosion. Such cells get set up all along the surface of metal when it faces the electrolytic environment and two dissimilar metals in contact.

For example, in ships floating on the sea water, the portion of it in contact with marine water gets corroded, if there is a difference in the materials used in assembling the ship.

- If metal iron or brass alloy is used together to join various parts, due to difference in potential, a galvanic cell gets set, leading to corrosion.
- In such cases all along the surface of metal small galvanic cells are set up, where *area of high potential acts as an anode and the one with lower potential acts as a cathode.*

- The portion of metal acting as anode, deteriorates and at cathode the cathodic product gets evolved/deposited, depending upon the environment, and mechanism of the corrosion, i.e. by absorption of oxygen or evolution of hydrogen, as the case may be.
- The case where the former type of mechanism takes place is seen in *electrolytic/alkaline environment* while the latter type is seen in *acidic* environment.
- The rate of corrosion is obviously very high in latter type. In former one, for iron metal generally three types of iron oxides are formed in succession with the increasing valency of iron. **For example : FeO, Fe_2O_3 and Fe_3O_4.**
- In such type of environment, on metal surface small anodic and cathodic areas are formed. Here, cathodic area is slightly larger and hence rate of corrosion is comparatively higher. The mechanism of corrosion in slightly alkaline medium, proceeds as, At anode $M \rightarrow M^{2+} + 2e^-$

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

$$M^{2+} + 2OH^- \rightarrow M(OH)_2 \downarrow$$

- If the metals are surrounded by *aqueous alkaline/acidic/neutral solution*, the mechanism of cathodic reaction proceeds to form OH^- ions, and subsequently $Fe(OH)_2$ or $Fe(OH)_3$.
- If the metal is exposed to acidic medium the mechanism at cathode proceeds to form H_2 gas, while anodic reactions remain the same.

To avoid the formation of galvanic cells,

a) The metals should be pure.

b) The materials used to assemble the different parts should be of same potentials.

c) Moisture and other electrolytic/aqueous medium, if present, other corrosion controlling methods may be used.

1.3.2 Concentration Cell (Differential Aeration) Corrosion

MU - May 2012, Dec. 2013, Dec. 2014, May 2015

- This type of corrosion is due to the *electrochemical attack* on the metal surface, which is exposed to an electrolyte *of varying concentrations* or *of varying aeration*.
- The variation is caused due to local difference in metal ion concentration caused by,
  - (i) Local difference in temperature
  - (ii) Inadequate agitation
  - (iii) Slow diffusion of metal ions, produced by oxidation at anode.
- It is the most common type of corrosion, and it occurs when one part of the metal is exposed to a different air concentration from the other part.
- *This causes a difference in potential between differently aerated areas.* It has been found that *poor oxygenated parts are anodic and rest are cathodic.* Consequently, differential aeration of metal causes a flow of current, called *differential current.*
- **Example :** Metal (Iron) tank/drum storing water or a strip of zinc metal partially dipped in dilute solution of salt; like NaCl and if solution is not agitated properly then the parts of the strip above and closely adjacent to the water line are more strongly aerated; because they have more supply of oxygen while remaining parts of the same strip which are immersed to greater depth have less supply of oxygen and these are poorly aerated and show lower oxygen concentration or lesser access of oxygen, and thus they become anodic.
- Thus, difference of potential is created which causes a flow of current between the two differently aerated areas of the same metal. Zinc will dissolve at anodic areas as,

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

O_2 will take up electrons at the cathodic areas to form OH^- ions.

$$\frac{1}{2}O_2 + H_2O + 2e^- \rightarrow 2OH^- \text{ (Reduction)}$$

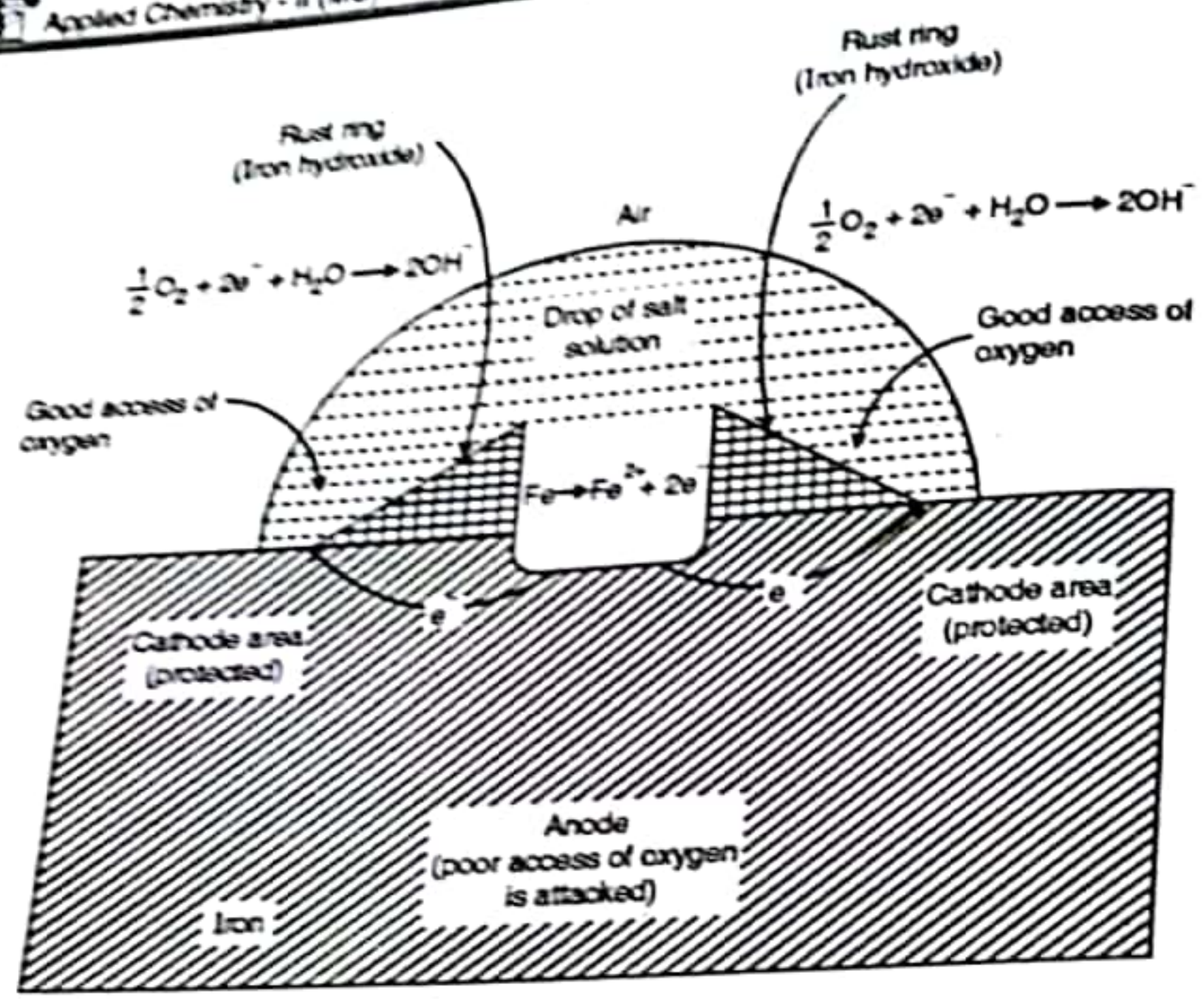


Fig. 1.3.1 : Concentration cell corrosion

1.3.3 Pitting Corrosion

When metal surface coats / protective film on a metal breaks down, pin holes / pits / cavities are formed.

Around such pits, small anodic and large cathodic areas are formed. Due to this corrosion is accelerated in localized area, known as "pitting corrosion".

Such pits are formed due to,

(a) Local strain, due to alternating or non-uniform stresses, on metal.

(b) Improper finish - surface roughness.

(c) Scratches due to friction or sliding under heavy load.

(d) Severe action of some chemicals or solutions.

When such metal encounters appropriate environment, corrosion current arises. Fig. 1.3.2 represents schematically, pitting corrosion due to differential aeration, around the area of "pit" on metal surface.

The small part under drop of water / impurity acts as an "anode" and surrounding large area acts as "cathode". This type of corrosion proceeds continueously with increasing rate [After formation of "pit"].

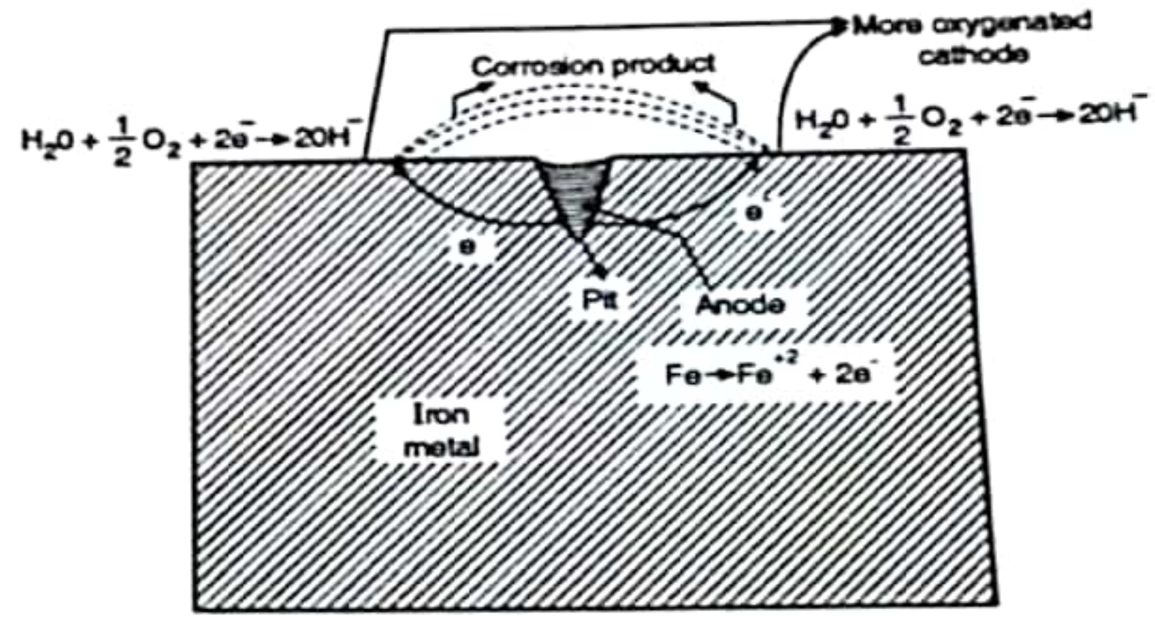


Fig. 1.3.2 : Pitting corrosion on Iron surface

Pitting corrosion can be controlled/minimized by,

(1) By finishing metal surfaces properly.

(2) By maintaining metal coating intact.

(3) By using lubricants to control friction.

(4) By avoiding unwanted contact with corroding solutions / dust / dirt / impurities.

1.3.4 Intergranular Corrosion

MU - May 2016

- This type of corrosion occurs along grain boundaries under following conditions
  - (i) The material, highly sensitive to corrosive attack and
  - (ii) Corrosive liquid possesses *a selective character of attacking only at the grain boundaries*, but leaving the grain centres (interiors) untouched or only slightly attacked.
- This type of corrosion is due to the fact that the grain boundaries contain material, which shows electrode potential more anodic than that of the grain centre in the particular corroding medium. This may be due to precipitation of certain compounds at the grain boundaries,
- Due to such disproportionated precipitation, a solid solution is aggregated at centre, adjacent to boundary.

- The solid solution thus formed is *anodic* with respect to the grain centres as well as to the precipitated compound. Hence it gets attacked preferentially in the corrosive environment (see Fig. 1.3.2(a)).

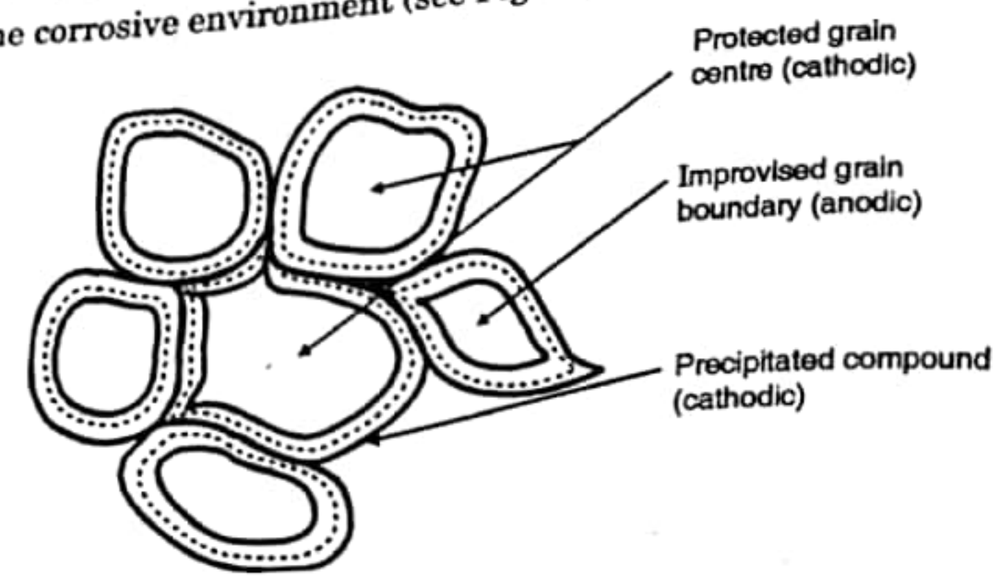


Fig. 1.3.2(a) : General intergranular attack

- This type of corrosion is, generally, observed in alloys. For example : During the welding of stainless steel (an alloy of Fe, C and Cr), chromium carbide is precipitated at the grain boundaries.
- Hence chromium composition adjacent to grain boundaries is increased and is more anodic with respect to the solid solution within the grain (which is richer in chromium) and it is also anodic to the particles of the chromium carbide so-precipitated.
- Intergranular corrosion is observed to occur near the grain boundaries and occurs on microscopic scale, without any apparent external signs of any intensive attack.
- On account of this, sudden failure of material occurs (without any pre-warning), due to loss of cohesion between grains.
- The remedy is *proper heat-treatment,* followed by rapid quenching to avoid the heterogeneous precipitation that, usually, occurs due to slow-cooling (annealing).

1.3.5 Stress Corrosion

MU - Dec. 2012

- It is similar to intergranular corrosion.
- Stress corrosion (or stress cracking) "is the combined effect of static tensile stresses and the corrosive environment on a metal."

- It is characterized by a highly localized attack which occurs even when overall corrosion is negligible.
- For stress corrosion to occur the essential conditions are : (i) presence of tensile stress, and (ii) a specific corrosive environment .
- The specific substances act as the corrosive agents and are selective for particular material in particular environment,
- **For example :**
  (a) Caustic alkalis and strong nitrate solution for mild steel;
  (b) Traces of ammonia for brass; (c) acid chloride solution for stainless steel.

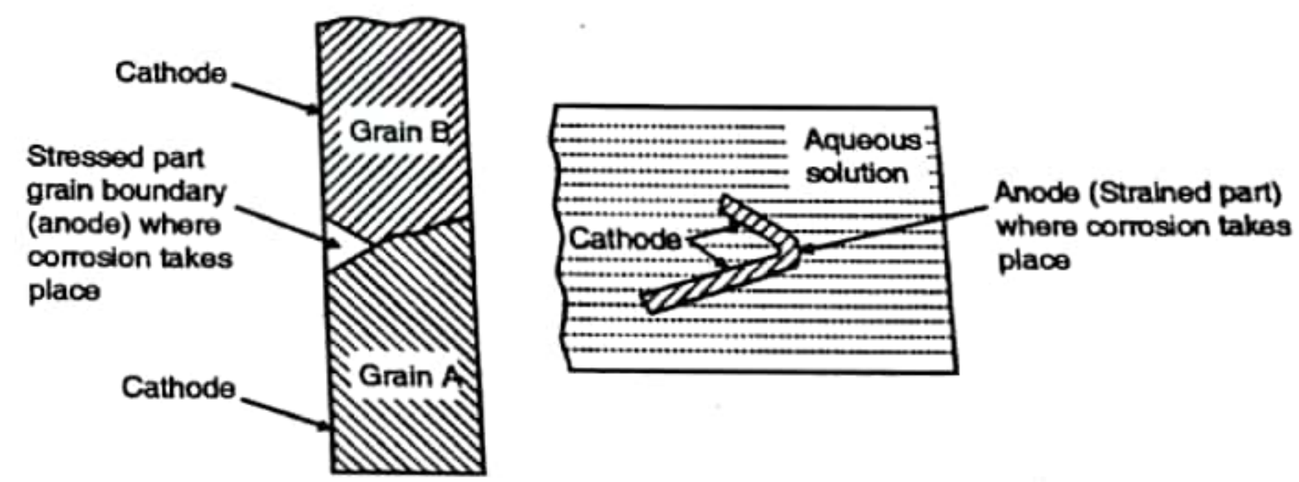


Fig. 1.3.3 : Stress corrosion

- This type of corrosion is seen in fabricated articles of certain alloys (like high-zinc brasses and nickel brasses) due to the presence of stresses caused by heavy working like rolling, drawing or insufficient annealing.
- The pure metals are relatively immune to stress corrosion.
- Stress corrosion involves in a localized electrochemical corrosion, forming anodic areas with respect to the more cathodic areas at the metal surface.
- Presence of stress produces strains, which result in localized zones of higher electrode potential.
- These chemically-active sites are attacked, even by a mild corrosive environment.
- This results in the formation of a crack, which grows and propagates in a plant.
- The attack of corrosion continues till failure of structure occurs.

Some typical examples of stress corrosion are given below :

1) **Seasonal cracking** is a term applied to stress corrosion of copper alloys, mainly brasses. Pure copper is immune to stress corrosion, but presence of small amounts of alloying element (like P, As, Sb, Zn, Al, Si) result in marked sensitivity. For examples, alpha brass (which when highly stressed) undergo intergranular cracking in an atmosphere, containing traces of ammonia or amines.

2) **Caustic embrittlement :** Caustic embrittlement is another example in this type of corrosion. Boiler-water, usually, contains a certain proportion of *sodium carbonate*, added for water hardening purposes. In *high-pressure boilers, this breaks up to give sodium hydroxide and carbon dioxide.*

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

- NaOH makes boiler-water *alkaline.* This very dilute alkaline boiler-water (in boiler) flows through the minute hair-cracks and crevices (by capillary action).
- The water evaporates and the caustic soda concentration builds up in the crevices.
- This concentrated alkali reacts with iron to form sodium ferroate (hypoferrite) which gets deposited in crevices, cracks. Hence, the metal is stressed.
- The sodium ferroate (Na_2FeO_2) then decomposes, according to either of the following reactions :

$$3Na_2FeO_2 + 4H_2O \longrightarrow 6\,NaOH + Fe_3O_4 + H_2$$

$$6Na_2FeO_2 + 6H_2O + O_2 \longrightarrow 12\,NaOH + 2\,Fe_2O_4$$

Sodium hydroxide is regenerated and magnetite (Fe_3O_4) is precipitated, thereby enhancing further dissolution of iron.

- *Caustic embrittlement* can be explained by considering the following electrochemical cell :

$$^{+}\text{Iron} \mid \text{Concentrated NaOH} \mid \text{Dilute NaOH} \mid \text{Iron}^{-}$$

The iron surrounded by the dilute NaOH (main body) is the *cathodic side*; while the iron in contact with more concentrated caustic soda (e.g., crevices, hair-cracks, rivets) is the *anodic portion*, undergoing corrosion and is thus dissolved.

Prevention of caustic embrittlement

It can be prevented by "Internal conditioning".

The best is addition of sodium sulphate to the boiler-water. Another is to use tannin or lignin as additive to the boiler-water. Both these methods prevent caustic cracking by blocking up the hair-cracks and crevices with inocuous harmless substances, thereby preventing the sodium hydroxide from infiltrating.

- The driving force of an electrochemical corrosion process is the potential difference between the anode and the cathode.
- The corrosion rate is controlled by the current flowing in the circuit.
- The addition of certain inorganic or organic substances (called inhibitors) to the corroding environment reduces the extent of corrosion.
- These inhibitors cause certain irreversible changes around the electrodes.
- Such changes tend to oppose the direction of the corrosion current flow.
- This phenomenon is called polarization of electrodes which alters makes the cathode to be less cathodic (or more anodic) and that of the anode to be less anodic (or more cathodic).
- As a result of this, the potential difference and current between the anodic and cathodic areas decreases, thereby the corrosion rate also decreases.
- **Polarization at the electrodes is due to :** (i) concentration changes in the electrode region, (ii) overvoltage or (iii) presence of surface films on the electrodes.
- Generally, the concentration of corrosive electrolyte species gets accumulated at the anode and depleted at the cathode. This in turn creates a concentration difference between the bulk of the corrosive electrolyte and the electrode surface.
- Now for corrosion reaction to progress, the electrolyte species must be supplied around the electrode depleted with respect to electrolyte species or removed around the electrode concentrated with respect to electrolyte continuously.
- Both these processes (of supplying or removing electrolyte species) occur by diffusion.
- The diffusion becomes sluggish in (i) stagnant situations, (ii) low concentration of the electrolyte species and (iii) low temperature.

- Such delayed diffusion has a tendency to *polarize electrodes*, thereby decreasing *corrosion current* and *corrosion rate*.
- As the corrosion reaction progresses, the potential difference between the anodic and cathodic areas alters and ultimately as steady state, called *corrosion potential* (E_{corr}) is reached, when the sum of the rates of all anodic (oxidation) reactions become equal to the sum of the rates of all cathodic (reduction) reactions.
- The corresponding values of current at this potential, is called corrosion current (I_{corr}), whose value depends on :

Syllabus Topics : Factors affecting the rate of corrosion-Nature of metal, position of metal in galvanic series, potential difference, overvoltage, relative area of anodic and cathodic parts, purity of metal, nature of the corrosion product, temperature, moisture, influence of pH, concentration of the electrolytes.

1.4 Factors Influencing Rate of Corrosion

1.4.1 Nature of Metal

MU - Dec. 2013

Nature of metal depends upon its position in galvanic series and potential difference.

1.4.2 Position of Metal in the Galvanic Series

MU - Dec. 2012, May 2014, Dec. 2014

This is a major factor for corrosion of metals. If two dissimilar metals are in corroding environment, the metal having higher electrode potential and position in the galvanic series undergoes corrosion, i.e. it acts as an anode.

1.4.3 Potential Difference

Amongst the two metals in contact, greater the difference in the electrode potential, higher is the rate of corrosion.

1.4.4 Overvoltage

MU - May 2012, May 2015, May 2016

- When a metal, which occupies a high position in galvanic series (say zinc), is placed in 1N-H_2SO_4, it undergoes corrosion forming a film and evolving hydrogen gas.

- The initial rate of reaction is quite slow, because of high overvoltage (= 0.70 V) of zinc metal, which reduces the effective electrode potential to a small value.
- If a few drops of copper sulphate ($CuSO_4$) are added, the corrosion rate of zinc is accelerated, because some copper gets deposited on the zinc metal, forming *minute cathodes*, where the hydrogen overvoltage is only 0.33 V. *Thus, reduction in overvoltage of the corroding metal/alloy accelerates the corrosion rate.*

"The difference between the potential of the electrode when the gas evolution was actually observed and the theoretical reversible value of the same solution is called the overvoltage or overpotential".

1.4.5 Areas Occupied by the Anode and Cathode

MU - May 2012, Dec. 2012, May 2013, Dec. 2013, May 2014, Dec. 2014, Dec. 2015

- If two *dissimilar* metals are in contact, one forming anode while another forming cathode, then the corrosion of the anodic metal (part) is directly proportional to the ratio of the areas occupied by the cathode and anode.

$$\text{Thus, corrosion at anode } \alpha = \frac{\text{Area of cathodic part}}{\text{Area of anodic part}}$$

- Hence, if cathode is large and anode is small, then corrosion at anode is higher and vice-versa.

1.4.6 Purity of the Metal

MU - Dec. 2015, May 2016

- If the metals are impure, then the impurities present in them cause heterogeneity, which *gives rise to small electro-chemical cells* at the sites where metal and impurities are exposed, to the corrosive environment and thus, the corrosion starts, which then affects the entire metal.
- **Example** : Zinc metal, if with the impurities of Fe or Pb, undergoes corrosion at the sites where the impurities are exposed because of the formation of local small electrochemical cell. *Thus more the percentage of impurity, higher is the corrosion of zinc metal.*

1.4.7 Nature of Corrosion Product

MU – May 2016

Note : All students to, Entire description under chemical corrosion should be referred and included for this point (Refer to Sec. 1.2.1.).

MU - Dec. 2012

1.4.8 Temperature

The rate of corrosion is greater at higher temperature, because diffusion of gases increases with the rise in temperature. Another example of increase of corrosion with rising temperature is *caustic embrittlement* as observed in boiler.

1.4.9 Moisture

The corrosion also is found to enhance in humid air as compared to in dry air. This is because, humid air/moist air has tendency to dissolve gases such as O_2, CO_2 etc. and also the acidic vapours from industries. Due to this, it becomes easy to set up an electrochemical cell on the surface of metal. Some metals like Mn, Cr, Fe, Mg etc. get corroded in moist air, even in the absence of oxygen, forming few other compounds.

1.4.10 Influence of pH

MU - May 2012, May 2013, Dec. 2013, May 2014, May 2015, Dec. 2015

In acidic, pH, the rate of corrosion is higher, because the mechanism of electrochemical corrosion proceeds by evolution of hydrogen gas at cathode. On the contrary, in alkaline or neutral electrolytic medium the electrochemical corrosion occurs by following the mechanism of absorption of oxygen; thereby forming an oxide film as a cathodic product. Such a film gets adhered to the surface of the metal and further rate of corrosion is governed by *nature of the corrosion product* which is discussed earlier.

1.4.11 Influence of Concentration of Electrolyte

- *Presence of other ions* also influences the rate of corrosion. For example : if in vicinity of metal, Cl^- ions are present, the effect is so severe that even a passive surface film of metal gets destroyed by Cl^- and corrosion starts, on the exposed metal surface.
- *Another example is of metal copper present in mine water.* When such mine water is transported in iron pipes, presence of copper which is less electropositive than iron, influences the formation of galvanic cell and thereby the iron pipes get corroded at a very high rate.
- In fact each and every metal shows its own characteristic behaviour. The amazing behaviour of magnesium metal is worth noting. The presence of N/10 NaCl makes magnesium to corrode while strong KOH solution does not affect the metal.

Syllabus Topics : Methods to decrease the rate of corrosion- Material selection, Proper designing, Use of inhibitors, Cathodic protection- (I) Sacrificial anodic protection (ii) Impressed current method, Anodic protection method,

1.5 Methods to Decrease the Rate of Corrosion

- '*Corrosion*' is one of the major causes of increasing maintenance cost in all the industries, therefore either prevention or subsequent control of corrosion becomes all the more important.
- The methods for corrosion control vary from condition to condition, because as we have discussed, the types of corrosion are many and conditions under which corrosion occurs also differ to wider extent. *This makes it difficult to apply any single method to solve the problem.*

The methods to prevent the corrosion are as follows :

1) Material selection
2) Proper designing.
3) Use of inhibitors
4) Cathodic protection.
   i) Sacrificial anodic protection.
   ii) Impressed current method.
5) Anodic protection method.
6) Application of protective coatings.
   a) Metallic coating.
   b) Nonmetallic coating.

1.5.1 Material selection

The selection of material for making machine part plays a very vital role in controlling the corrosion. The choice is between an absolutely pure metal or the alloys.

Using Pure Metal

If the metal used to manufacture machine parts is 100% pure, the corrosion resistance is more as compared to the impure metal. This is because, impurities cause heterogeneity. Thus, use of pure metal or purifying the metals prevents corrosion. This method is useful only if corrosion proceeds by electrochemical mechanism.

Using Metal Alloys

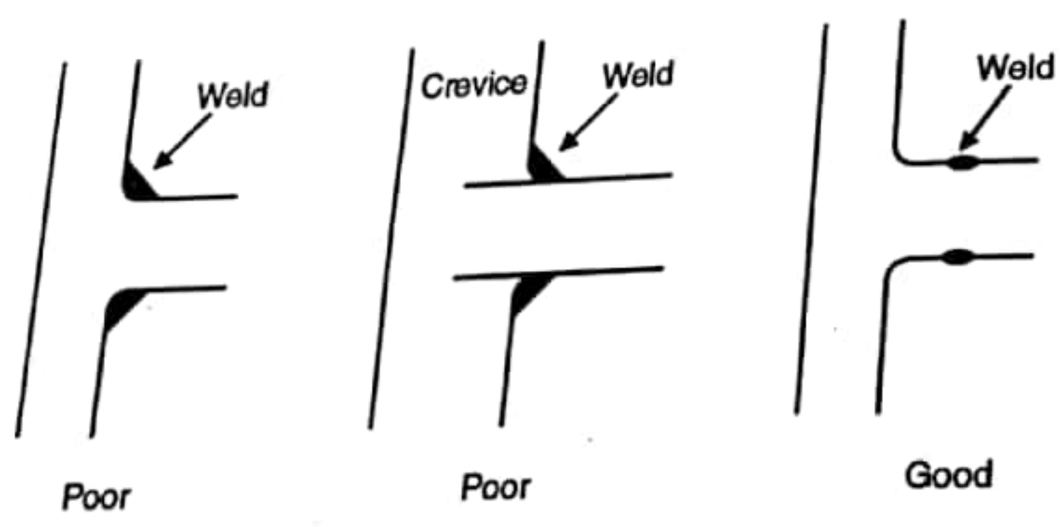
Corrosion resistance of metals can be improved by alloying the metals. Alloying can help to greater extent, if it gives homogeneous product.

Example : Iron can be alloyed with chromium and carbon to give steel, which has better corrosion resistance. Here, chromium metal has a tendency to form an oxide which gets adhered to the surface. Also, this oxide film, if broken gets healed immediately. Thus, steels containing 13% chromium are normally used to make cutlery, surgical instruments, springs, etc. while higher percentage of chromium such as upto 25% are used to prepare turbine brackets, heat resisting parts etc.

Brass is another example. Individually, copper or zinc are less resistant to corrosion, but alloy of these two metals possesses better resistance to the corrosion.

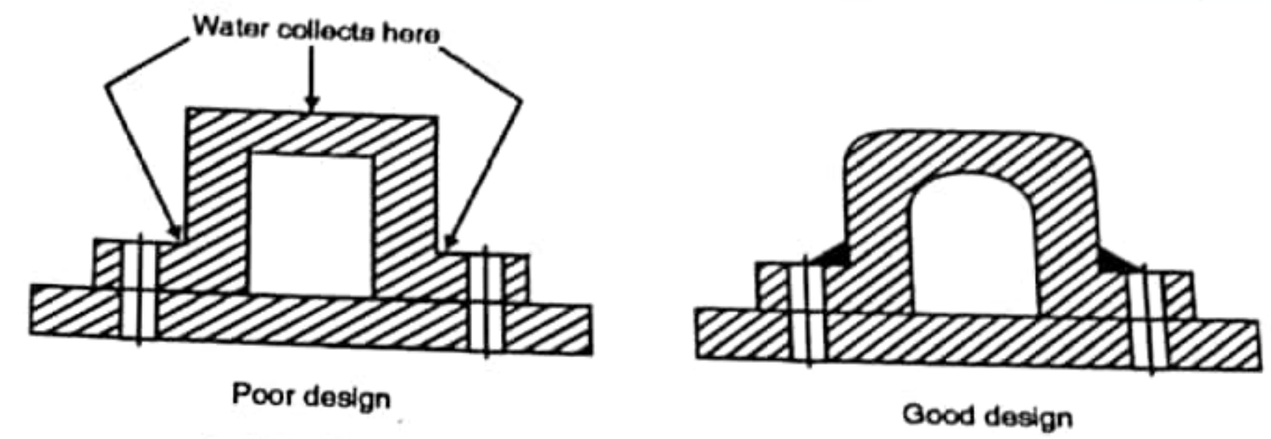
1.5.2 Proper Designing

- Designing of the parts should be such that it avoids sharp bends, stresses, etc. or as far as possible the use of screws, nuts, bolts should be avoided, rather welding should be preferred; or the material selections should be in such a way that potential difference does not exist to greater extent.
- The surfaces of two joining parts should be as smooth as possible, so that crevices are as thin as possible, which avoids accumulation of the corrosive liquids, suspended particles, dust. dirt, grit stagnation of water, free circulation of air, etc.

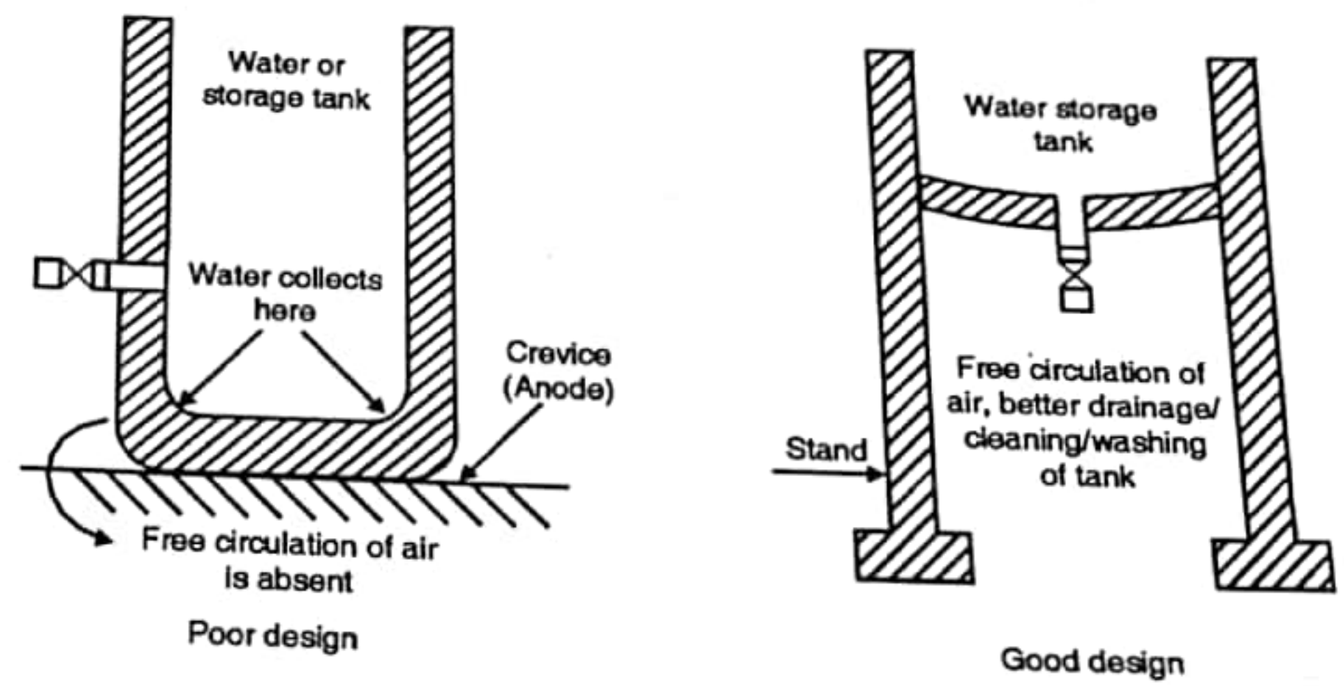


(a) Sharp corners and recesses to be avoided

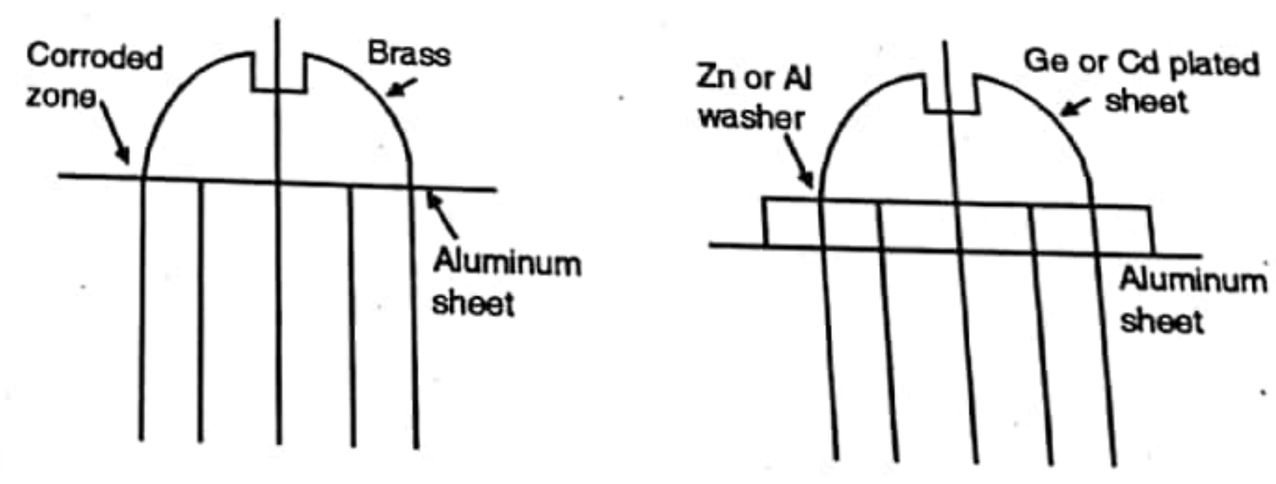
Fig. 1.5.1 Contd....



(b) Avoidance of water stagnation and crevice corrosion



(c) Storage containers



(d) Materials for joining parts

Fig. 1.5.1 Contd....

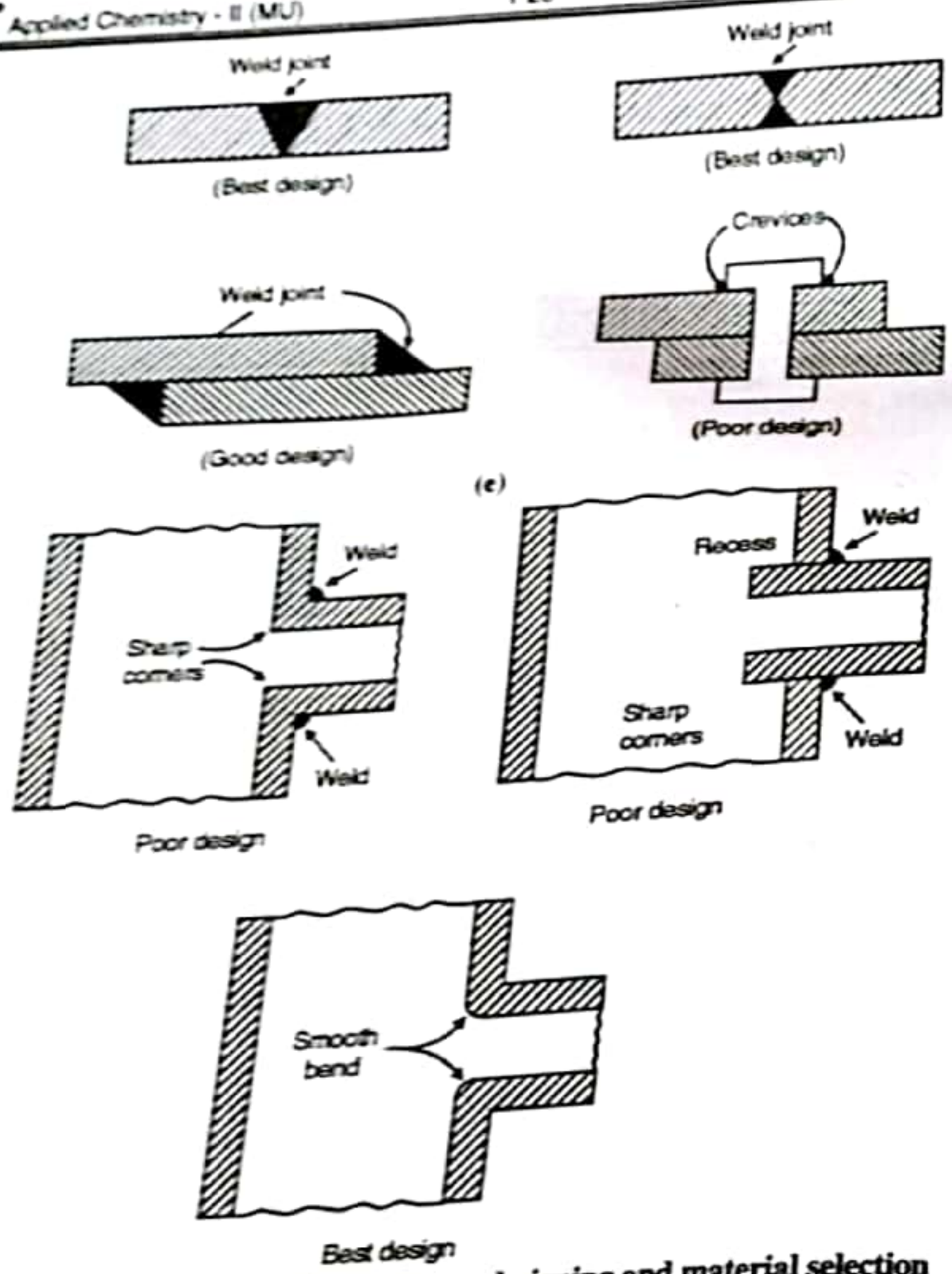


Fig. 1.5.1(f) : Control of corrosion by proper designing and material selection

1.5.3 Use of Inhibitors

- *A corrosion inhibitor may be defined as any substance which inhibits the corrosion, when added in the corrosive environment.*
- *Inhibitors are generally organic or inorganic substances, soluble in the corrosive environment, but capable to form a protective layer on either anodic or cathodic areas. Inhibitors are of two types.*

a)	*Anodic Inhibitors*
b)	*Cathodic Inhibitors*

a) Anodic Inhibitors

- The substances like chromates, phosphates, tungstates or other ions of transition elements generally with high oxygen content are capable of suppressing the anodic reaction and thereby preventing the dissolution of metal acting as an anode.
- These inhibitors normally form a sparingly soluble compound with metal ion formed at anode due to anodic reaction (i.e. loss of electrons). This compound gets adsorbed on the surface of metal and forms a protective film; thereby reducing corrosion rate.
- This method is highly effective, but for only one drawback, that sometimes if entire surface does not get covered by the protective film formed, the unprotected area forms a small anode, which invites severe local attacks. Hence the method is *rarely used.*

b) Cathodic Inhibitors

- This type of inhibitors are used in both, acidic as well as neutral solution.
- In acidic solutions the cathodic reaction is evolution of hydrogen.

$$2H^{\oplus} + 2e^- \rightarrow H_2 \uparrow$$

- In such working environment, corrosion can be reduced if diffusion of hydrated $H^{\oplus}$ ions is slowed down. This is achieved by using organic substances such as *amines, heterocyclic nitrogen compounds, mercaptans, substituted urea or thiourea, heavy metal soaps*, because these compounds are having a tendency to get adsorbed on metal surface, forming a protective film.
- In neutral solution, the cathodic reaction is due to the absorption of oxygen gas and formation of OH^- ions as

$$H_2O + \frac{1}{2}O_2 + 2e^- \rightarrow 2\,OH^-$$

Under such condition, the rate of corrosion can be reduced either by eliminating oxygen from the corroding medium by de-aeration methods or by retarding the diffusion of O_2 to the cathodic areas.

- For de-aeration purpose, some reducing agents such as *sodium sulphite, hydrazine hydrate, ferrous hydroxide* etc. are used.
- Some inorganic inhibitors, such as Zn, Mn or Cr salts also are useful. These compounds react with OH^- ions formed at the cathode, thereby forming insoluble hydroxides, which get adhered to the cathodic area serving as a barrier. This reduces the formation of corrosion product due to the reaction between the metal ions and OH^- ions. This also helps to slow down the anodic reaction, and ultimately, dissolution of anodic metal gets controlled.

1.5.4 Cathodic Protection Method

MU - May 2012, May 2013, Dec. 2013, May 2014, Dec. 2014, May 2015

- Cathodic protection is nothing but a method used to reverse the flow of current between the two dissimilar metals, under corroding environment thereby reversing the action of the metals in contact. This is achieved by applying the external circuit and forcing the anodic metal to behave as a cathode.
- Anodic protection involves suppression of anodic reaction by adjusting the potential of the more reactive metal, i.e. making metal passive in the working environment.

Methods of cathodic protections

Cathodic protection can be achieved by two different method as :

i) By using sacrificial anode method/Auxiliary anode method

ii) By using impressed current method.

Both the methods are discussed here in detail.

(I) Use of sacrificial anode

MU - May 2012, Dec. 2013

- To achieve protection by *sacrificial anode* method, the metal to be protected from corrosion is *connected by a wire* to another piece of metal which is *more reactive* than the *base metal* itself.
- This results in the corrosion of the piece of metal connected, thereby saving base metal.
- Since the more active metal sacrifices itself, by undergoing corrosion and saving the base metal, *the method is named as sacrificial anode or auxiliary anode method.*
- When the piece of more active metal gets corroded completely, it is simply replaced by new piece.
- The metals normally used are Mg, Zn or Al.
- This method is used normally to protect pipelines carrying water or industrial wastes, and which are normally embedded under the soil, thereby facing the conditions of soil corrosion as well as microbiological corrosion.
- Applications of this method are seen to protect *cables or iron pipelines*, by connecting them to *Mg-blocks;* and in case of *marine structures, ships* are *protected by using Zn-plates* as sacrificial anode. Even *water tanks, boilers* are protected by using *Zn metal.*

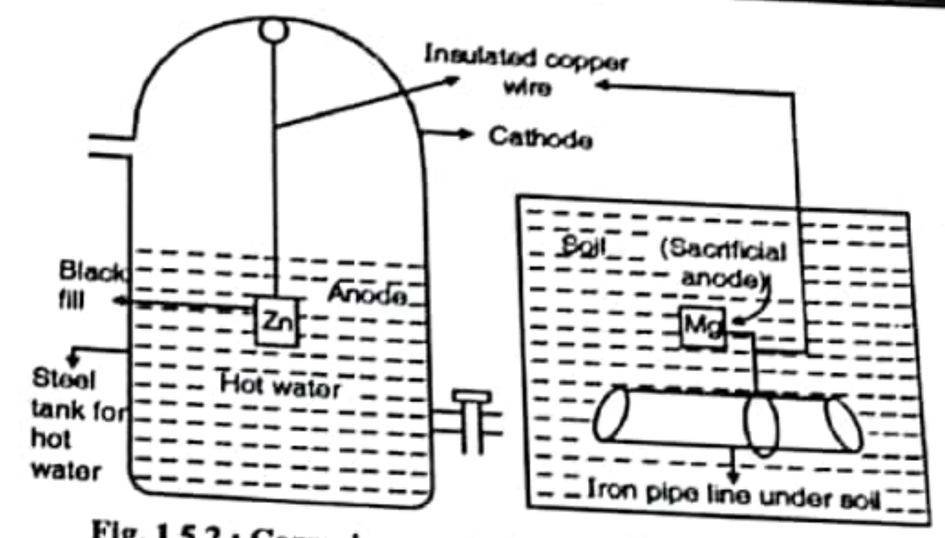


Fig. 1.5.2 : Corrosion control by sacrificial anode method

(II) Use of impressed current

MU - May 2013, Dec. 2013, May 2015

- In impressed current method, a current is applied in the opposite direction to that of corrosion current, thereby nullifying the effect of the latter one on the base metal, i.e. converting the base metal, to cathode from an anode.

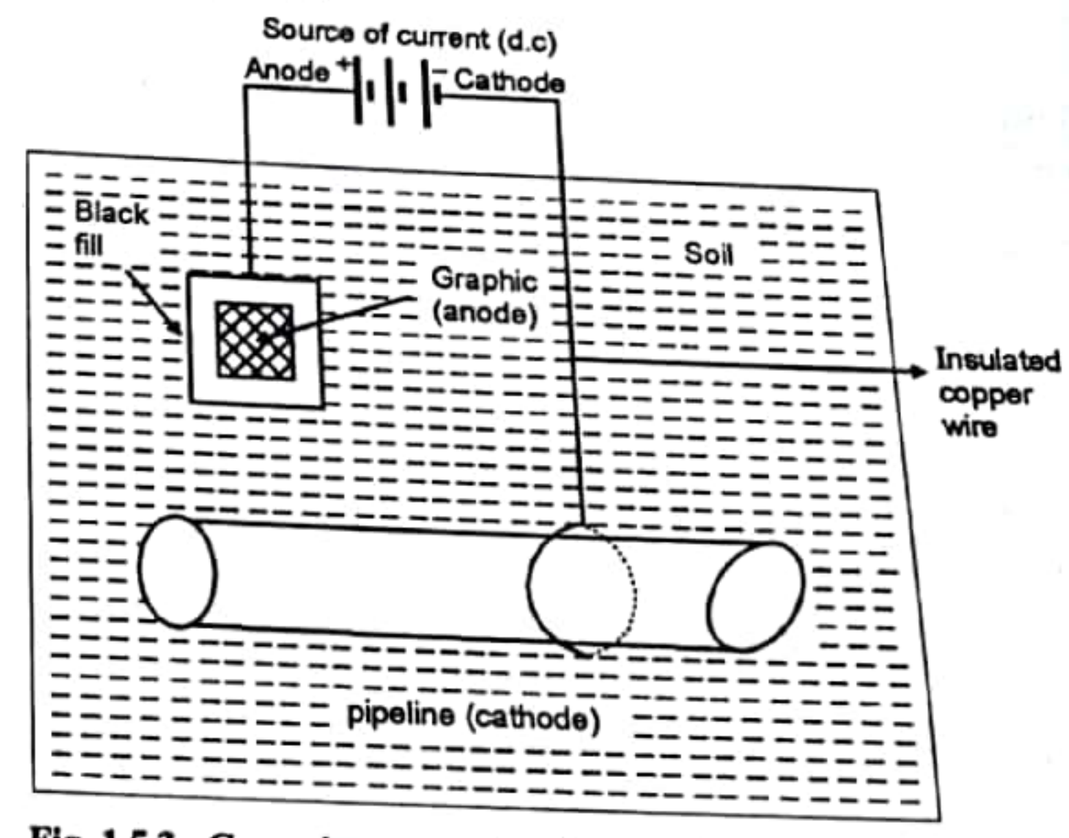


Fig. 1.5.3 : Corrosion control by impressed current method

- Such an impressed current can be obtained by using *d.c. source such as battery or dry cell* along with an insoluble anode such as *platinum, stainless-steel, graphite etc.*

- In this method, as shown in Fig. 1.5.3, the insoluble anodic metal used (i.e. platinum, steel, scrap iron etc.) is normally *embedded underground*. To this, with the help of d.c. current source, the impressed current is applied, and whole of this assembly is connected to the metallic structure to be protected.
- The connections are done by using wires.
- The insoluble anode is kept inside back-fill made up of *gypsum or any such material*, which can help in increasing the electrical contact with the soil.
- Such an anode can be single, if the area of the metallic structure to be protected is small.
- There can be many such anodes, *connected in series* if the area of the metallic structure to be protected is wider, i.e. long pipeline etc.

Advantages

i) This method is highly useful, because it can protect the long length structures for a long term, thereby reducing frequency of monitoring as well as maintenance cost.

ii) These both methods are most widely used, because the protection provided to the base metal is long term and maintenance is easy.

Disadvantage

Due to the application of the impressed current, the anode deteriorates and hence, it has to be replaced from time to time.

Application

This method are seen in the case of water tanks, buried pipe lines carrying water or oil, condensers, transmission line towers, laid-up ships, etc.

1.5.4.1 Comparison between Cathodic and Anodic Protection

Sr. No.	Cathodic protection	Anodic protection
1.	The basic principle " is to force the metal to be protected to behave like a cathode."	The basic principle is, "to increase the passivity of the base metal by applying current in the direction in which the metal would become more anodic."

Sr. No.	Cathodic protection	Anodic protection
2.	The cathodic protection involves reverse the flow of current between two dissimilar metals.	The Anodic protection involves suppression of anodic reaction by adjusting the potential of the more reactive metal i.e. making metal passive.
3.	The cathodic protection can be achieved by two different techniques (a) Sacrificial anode (b) Impressed current	There are no different techniques for anodic protection.
4.	In this method, either Mg, Zn or Al is used as sacrificial anode. It can be applied to most of metals to protect form corrosion.	No such sacrificial anode used, but passivity of metal is increased at low current density. It is neccessary to have passive base metal.
5.	It can protect long length structures for long term.	It can protect complicated structures over wide range of corroding environment.
6.	It is not very costly.	The initial cost is high, though operating cost is low.
7.	It can provide steady, consistent protection for long term.	It may not provide steady protection; If system goes out of control, the rate of corrosion may increase suddenly.

1.5.5 Anodic Protection Method

MU - Dec. 2014

This method to protect base metal is used under certain conditions, such as, where metal to be protected possesses active passivity. e.g. stainless steel.

The principle involved is to increase the passivity of the base metal by applying current in the direction in which the metal would become more anodic.

The important factors which *influence* this method can be summarized as below :

i) The metal to be protected should possess high passivity, over wider range of potential.

ii) The passivity should be increased at low current density, thereby reducing the cost.

iii) The cathodic metal used should possess adequate resistance to corrosion under working conditions. Generally, platinum clad metals or other corrosion resistant alloys are used.

By using *anodic protection* technique, the complicated metal structures can be protected, because *the method is highly effective*, if proper selection is done in choosing cathodic metal for a given set of working conditions.

Advantages of Anodic Protection Method

i) Operating cost is low.

ii) Wide range of corroding environments can be tackled.

iii) Complicated metallic structures can be protected.

iv) The applicability of method can be checked in laboratory on small scale and use of cathodic metal can be fixed by trial and error techniques, before going on large scale.

v) During operation, from protection current density, rate of corrosion can be known.

Disadvantages Anodic Protection Method

i) Method is useful only for metals showing *passivity*.

ii) Initial cost of installation is high, due to use of high-starting current, reference electrode, auxiliary electrode and a potentiostat.

iii) If system goes out of control, the rate of corrosion increases suddenly.

Syllabus Topic : Metallic coatings-hot dipping-galvanizing and tinning, metal cladding, metal spraying, Electroplating, Cementation. Organic coatings-Paints (only constituents and their functions)

➢ **Topics covered :** Protective coatings-Application of protective coatings, Types of protective coatings : Metallic coatings (1) Anodic coatings (2) Cathodic coatings : Comparison between Anodic and Cathodic Coatings, Non-metallic coatings, Metallic coatings : Methods of Application of Metallic Coatings- Hot Dipping - Galvanising and Tinning; Comparison between Galvanizing and Tinning, Metal Cladding [Alclad], Metal spraying, Electroplating, Cementation, Organic Coatings , Characteristic of Good Paint Paints- constituents and their functions

1.6 Application of Protective Coatings

This method is most easy and effective of all the methods discussed earlier, for the simple reasons, that it can provide a continuous barrier between the metal surface and the corrosive environment. The problem of localized corrosion starts

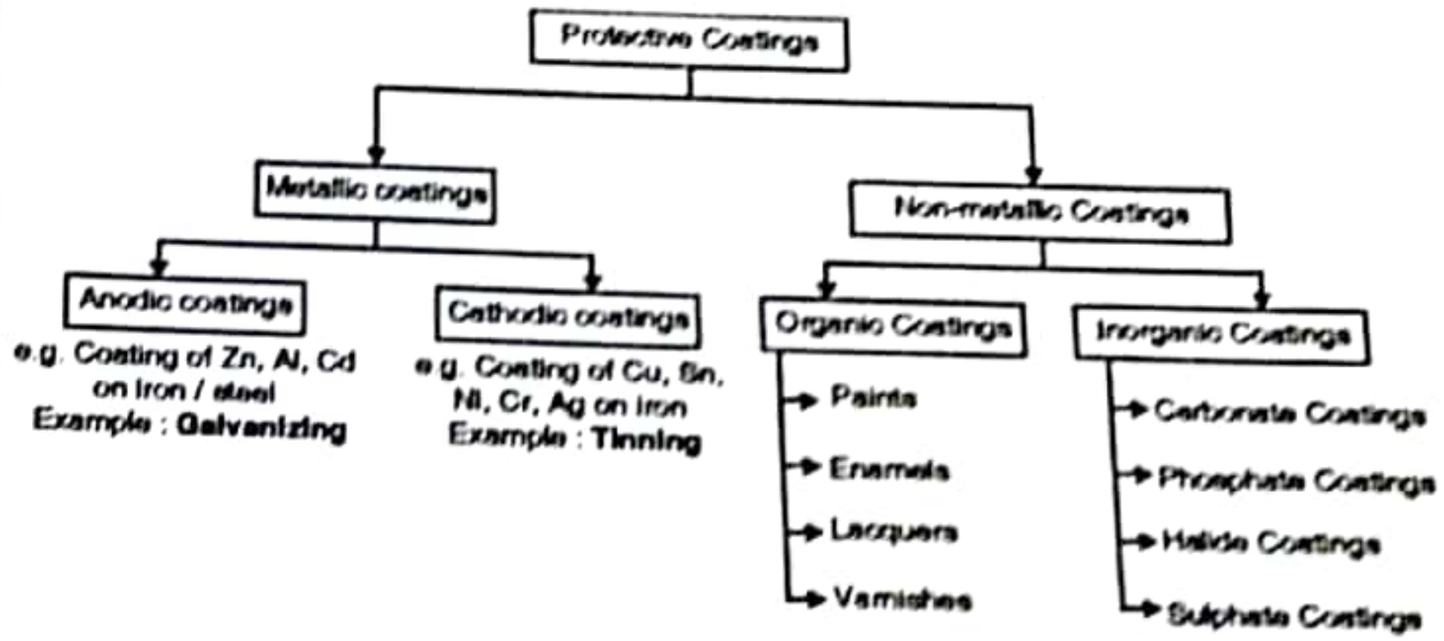
only when the protective coat gets broken, due to friction or by any other wear and tear of metal surface.

Types of protective coatings :

There are mainly two types of protective coatings.

(a) Metallic coatings

(b) Non-metallic coatings



1.6.1 Metallic Coatings

MU - May 2013, May 2014

- Methods of cleaning and preparation of metal surfaces :

(1)	Solvent cleaning	(2)	Acid cleaning
(3)	Chemical cleaning	(4)	Alkali cleaning
(5)	Mechanical cleaning	(6)	Flame cleaning
(7)	Sand blasting	(8)	Acid pickling and etching

This type of coatings are either anodic or cathodic depending upon the electrode potential of base metal and coating metal.

(1) Anodic coatings

- Metals like *Zn, Al or Cd*, if coated on iron or steel, serve as *anodic coatings*, because their electrode potentials are higher than the base metal.
- Here, as long as coat layer is intact, the corrosion of base metal is totally under control, but in case any *pores, cuts or breaks* occur, there is a formation of galvanic cell, between the coated metal portion and the exposed base metal portion.

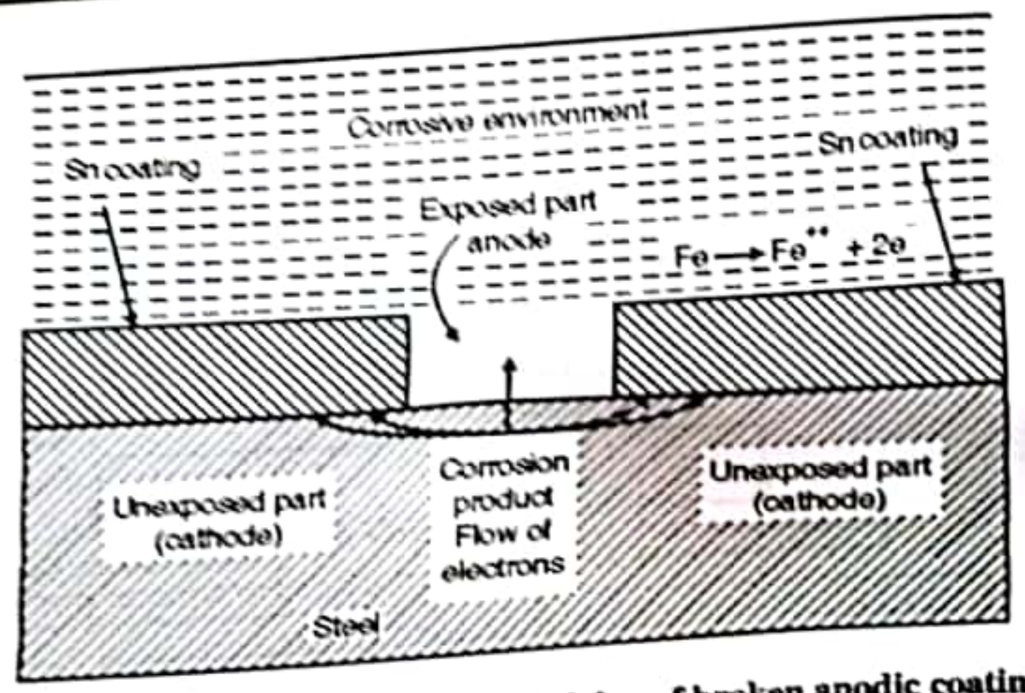


Fig. 1.6.1 : Corrosion of base metal due of broken anodic coatings (Schematic representation)

- In the case of galvanized steel, where Zn is coated on iron (steel), if coating of zinc is broken due to stress or friction, galvanic cell originates.
- As Zn is anodic to iron, it dissolves and hence iron is protected even though cell is set up and *iron remains protected* till entire amount of zinc gets dissolved.

(2) Cathodic coatings

- In case of *cathodic coatings*, a coat of more noble metal is applied on the base metal surface. As the electrode potential of the noble metal is lower, they protect the base metal.
  e.g. Application of Cu, Sn, Ni, Cr, Ag coating on iron surface.
- Cathodic coating can provide complete protection to the base metal till the coat layer is intact. But the moment this layer is broken, the base metal get exposed.
- Since the electrode potential of base metal is higher than that of the coated metal, a galvanic cell is set up where anode is small (exposed base metal) and cathode is larger (coated metal). This gives rise to severe corrosion of base metal.

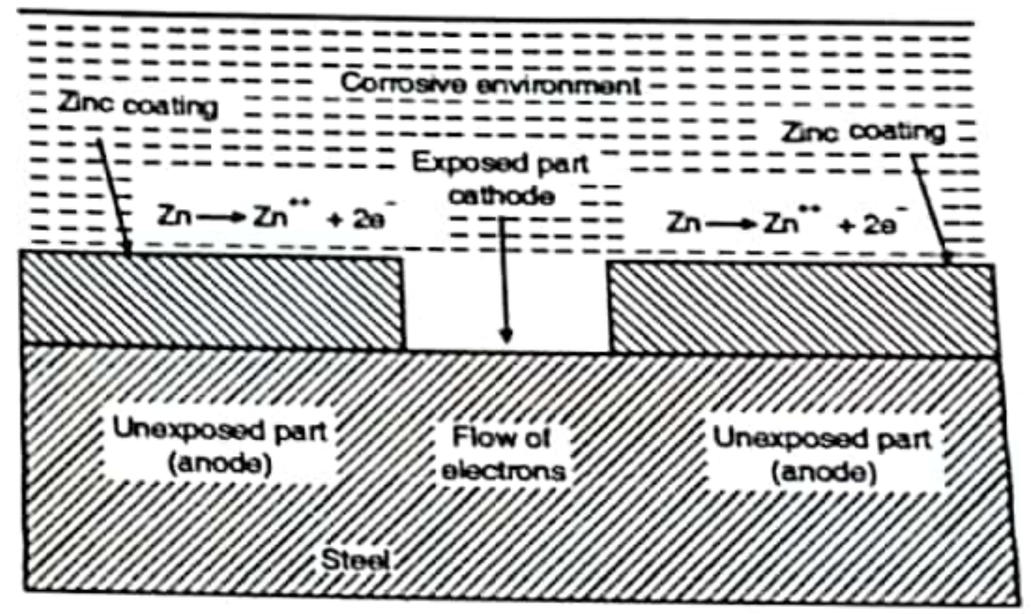


Fig. 1.6.2 : Poor protection of base metal due to cathodic coating (Schematic representation)

- **Example :** *Tin coating on iron surface.* In this case, tin coating can provide protection to iron surface *only till the coated layer is without any breaks.* If, due to any external factors, the coated layer is punctured, immediately there is formation of galvanic cell where *base metal (iron) acts as an anode* and the coated metal (tin) acts as a cathode. Since, cuts are normally minute, *the anode is small and cathode is large.* Thus, in corroding environment, the rate of corrosion is very high. This continues, till coated layer is repaired to be intact again.

1.6.1.1 Comparison between Anodic and Cathodic Coatings

MU - May 2014

Sr. No.	Anodic coating	Cathodic coating
1.	This type of coatings protect base metal "sacrificially".	This type of coatings protect the base metal because of **high corrosion resistance and noble behaviour.**
2.	The coating metal is at lower electrode potential than base metal.	The coating metal is at higher electrode potential than base metal.
3.	Corrosion of base metal does not enhance even on breaking "anodic coating", as it heals its film.	Corrosion of base metal enhances, if there is small cut / break in coating.

Sr. No.	Anodic coating	Cathodic coating
4.	e.g. Galvanizing, i.e. Zn coating on iron / steel.	e.g. Tinning, i.e. Tin coating on iron / steel / copper / brass.

1.6.2 Non-metallic Coatings

This type of coatings can be either inorganic coatings or organic coatings. In this chapter we shall discuss only organic coatings.

1.6.2.1 Organic Coatings

- Organic coatings are normally liquid formulations of different ingredients mixed in appropriate proportions. Any organic coating can give high protection from corrosion depending upon its chemical inertness in the corroding medium, adhesion with the underlying surface non-porous nature, etc. These qualities are influenced by the method used for these coatings to be applied.
- Generally, the thickness of coating should be adequate, particularly at bends, crevices or edges, which helps to sustain the wear and tear due to abrasion or friction.
- The adhesion of the coating with underlying surface can be enhanced by using properly cleaned surfaces for application of coatings. If the surface is covered with certain impurities, contact with the coating is interrupted; and thus leads to poor adhesion. Subsequently, such a coating undergoes cracks at an early stage.
- Organic coatings such as paints, varnished, enamels, lacquers etc. provide good corrosion resistance against temperature.

1.6.2.2 Types of Organic Coating

The organic coatings are of following four types :

1) Paints 2) Varnishes
3) Enamels 4) Lacquers

1.6.2.3 Characteristic of Good Paint

MU - Dec. 201

Ideally a paint should possess the following characteristics :

1) Its power to cover the surface should be as high as possible.
2) Its consistency should be adequate so that it can be spread easily.

3) On drying it should be able to give strong, uniform, highly adherent and impervious film.
4) The layer should not be cracked, peeled or blistered on drying.
5) The layer should be washable and durable.
6) Its colour should not be changed on prolonged exposure to air.
7) Its corrosion resistance should be high.
8) The texture of the dried coat should be smooth, uniform and glossy.

1.6.2.4 Paints

MU - Dec. 2012, May 2013, May 2014, Dec. 2015, May 2016

Paints are formed by using various ingredients which are listed below. Each ingredient is mixed for a particular function..

(i) Drying oils/medium/vehicle. (ii) Pigments
(iii) Thinners (iv) Driers

We shall list these constituents with the examples and functions in tabular form as given here.

Organic coating	Constituent	Examples	Functions
1) Paint	Drying oils or vehicle	Linseed oil, soyabean oil, dehydrated castor oil, neem oil, fish oil, etc.	They help pigments to be held on surface. They provide dried film by oxidation or polymerisation. They provide durable water resistant film of paint.
ii) Pigments	White pigments : White lead, ZnO, Titanium oxide, *Coloured pigments* Red lead, Fe_2O_3, chrome red, etc.		Provide opacity, colour strength, and protection. Provide resistance against abrasion. Minimise shrinkage and cracking caused on drying.
iii) Thinners	Turpentine, spirits, benzene, naphtha, xylol, kerosene, methylated naphthalene etc.		Adjust viscosity of formulation. Help in drying of the paint. Suspend the pigments and dissolve film forming material.

Organic coating	Constituent	Examples	Functions
	iv) Driers	Oxygen carrying catalysts, Linoleates of Co, Mn, Zn, etc.	Improve drying process. Act as catalyst in drying process.

1.7 Methods of Application of Metallic Coatings

MU - Dec. 2012, May 20

The following methods are generally used for applying the metallic coating on the base metals :

(1) Hot dipping.
  (a) Coating zinc on iron, i.e. galvanizing. (Anodic coating)
  (b) Coating tin on iron, i.e. tinning. (Cathodic coating)

(2) Metal spraying.

(3) Diffusion or cementation.
  (a) Coating of zinc by diffusion, i.e. sherardising.
  (b) Coating of Al by diffusion, i.e. calorising.
  (c) Coating of Cr by diffusion, i.e. chromising.
  (d) Coating of Si by diffusion, i.e. siliconising.

(4) Metal cladding.

(5) Electroplating.

Each of these methods are further discussed, to know the details of process, equipment, application, advantages and disadvantages.

1.7.1 Hot Dipping

In this method, generally the coating metal is of low melting point compared to the base metal. E.g. Zn (m.p. 410° C) and Sn (m.p. 232° C) coating on iron surface.

a) Galvanising : (Anodic coating) - Coating Zn on Fe MU - Dec. 20

- The process involves simply dipping of base metal articles in the molten mass of zinc, i.e. the coating metal.

- To avoid irregular coating, normally the base metal surface is cleaned to wash away the presence of any unwanted oxides or any other compounds, present on its surfaces.
- This is done by passing the base metal through the flux before dipping into the molten mass of coating metal. This is shown in Fig. 1.7.1.
- Cleaning of the base metal surface, if severely covered by unwanted impurities is done by treating it with H_2SO_4, by picking method, or by using dil. H_2SO_4, for removing any scales, rust (oxide) and any other impurities.

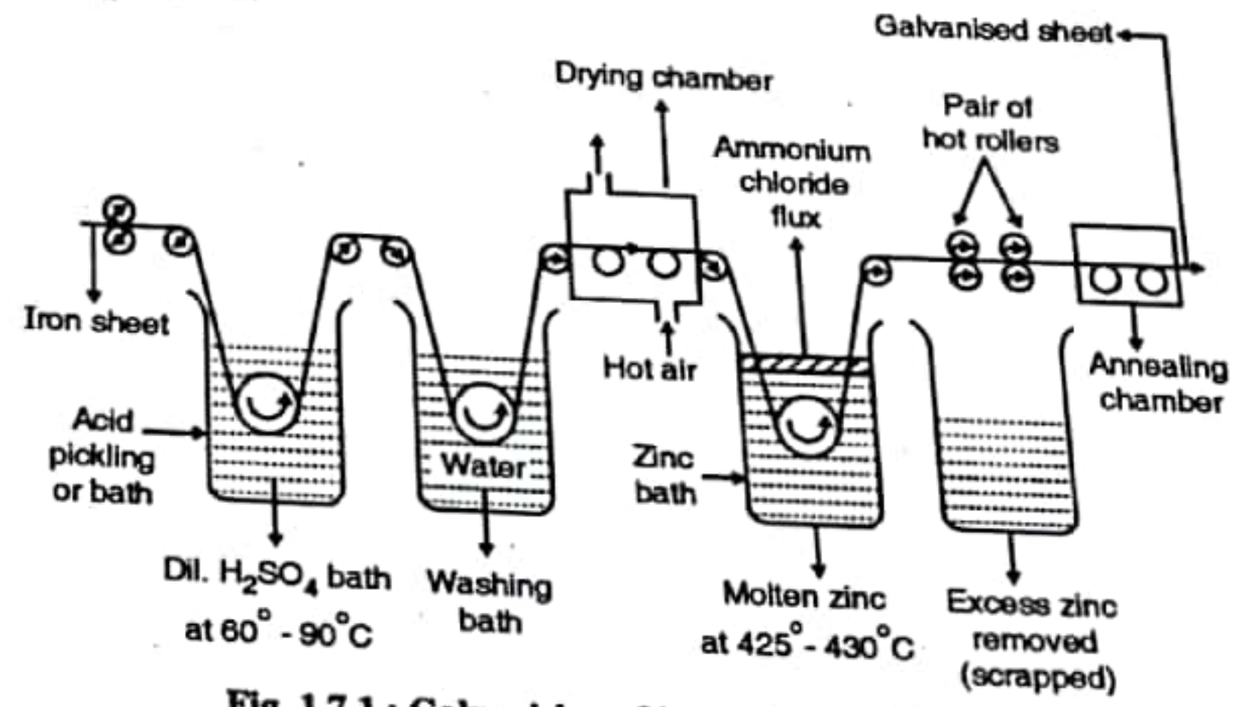


Fig. 1.7.1 : Galvanising of iron sheet by hot dipping

- Such surfaces are washed with water and dried properly, followed by dipping into a molten mass of metal, which is covered with flux solution generally NH_4Cl which prevents oxide formation (because clean metal surface immediately tends to form oxide by reacting with atmospheric oxygen).
- After dipping, when article is removed from bath of molten coating metal (425° C – 430° C), the article is found to be coated with thin uneven layer of zinc metal. The coated layer is levelled to *desired thickness* by passing article (pipe, sheet or wire) through the pairs of hot rollers, fixed at desired thickness apart, thereby removing excess of zinc coated unevenly.
- The coated metal is then subjected *to annealing* at lower temperatures and finally cooled slowly.

Applications

Galvanised iron is used for making water pipelines, roofing sheets, wires, nails, screws, bolts, nuts, tubes, etc. Being anodic coating, if coating is broken, even then corrosion rate does not increase, as iron (base metal) acts as cathode and Zn as anode. Hence, galvanizing gives better protection for iron than tin.

Disadvantage

Galvanised iron sheets cannot be used to make containers to store food stuffs (especially acidic food items) because coated metal (zinc) gets dissolved in acidic medium forming zinc compounds which are highly poisonous, if consumed.

b) Tinning : Cathodic coating -Coating Sn on Fe

- It is similar to the previous process, i.e. galvanizing except for the molten coating metal, i.e. tin.
- The process is also same, i.e. the base metal say iron is cleaned by dil. H_2SO_4, then washed clean with water and dried properly. Then the article is passed through $ZnCl_2$ flux and dipped in the molten mass of tin (m.p. 232° C).

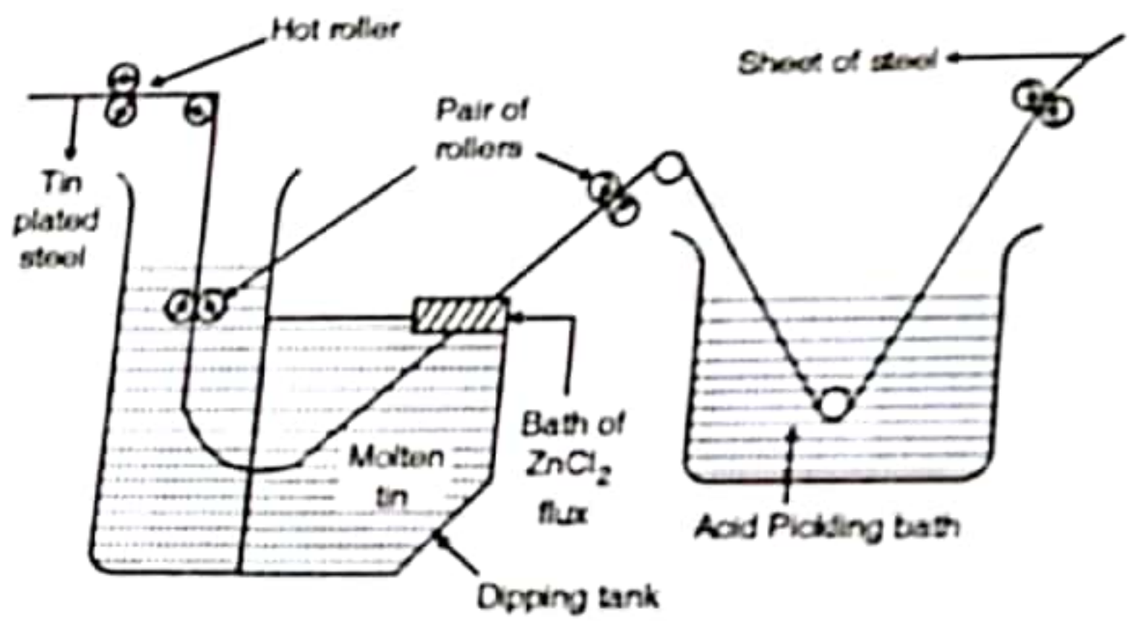


Fig. 1.7.2 : Tinning of iron steel by hot dipping

- After the dipping process, the article is taken out and then layer of coated tin is levelled by passing the article through a pair of hot rollers set at particular thickness. Hereby, excess of tin coated on base metal is scraped off. Later the coated article is annealed slowly to bring down to the room temperature.

- The rollers are normally kept under the layer of palm oil. T protects the freshly applied layer of tin from oxidation.

Applications

- Tinning is advantageous, because it is resistant to atmospheric corrosion and action of organic acids.
- Hence, tinned sheets are used to manufacture containers to store food – stuffs, oils, ghee, pickles, pharmaceuticals, because there is no danger of poisonous product formation as in case of galvanized articles.
- Tin is also used to cover copper wire which is to be subsequently insulated by coating rubber. Here, the intermittent coat of tin avoids contact between copper and rubber and subsequently protects copper, getting affected by sulphur present in rubber.
- For soldering, tinned copper wire is used, because this facilitates the soldering process.

Disadvantage

It being a cathodic coating, if the coat is broken, the corrosion is initiated due to formation of small anode of Fe.

1.7.1.1 Comparison between Galvanizing and Tinning

MU - May 2013, Dec. 2014, May 2015

Sr. No.	Galvanizing	Tinning
1.	It is a process of coating iron/steel with a thin coat of zinc to protect them from rusting. Not used for coating copper or brass sheets.	It is process of coating iron/steel with a thin coat of tin to protect them from corrosion. Also used to coat brass or copper sheets.
2.	The iron / steel sheets are cleaned with dilute H_2SO_4 i.e. "pickling" to remove scales / oxides / impurities.	The steel articles are cleaned with dilute H_2SO_4, "pickling". Which removes oxides / scales / impurities.
3.	In this process, NH_4cl flux is used.	In this process, $Zncl_2$ flux is used.
4.	Molten zinc is maintained at 425-430°C.	Molten Tin is maintained at about 230-235°C.

Sr. No.	Galvanizing	Tinning
5.	Galvanized sheets are used in making roof tops, nails, wires, buckets, tubes, pipes etc.	Tinned sheets are used in making containers.
6.	Galvanized sheets can not be used to store food stuffs as Zinc gets dissolved in dilute acids and produces poisonous compounds.	Tinned containers are used to store food stuffs, oils, ghee etc. as it is safe and does not react with dilute acids and does not produce any poisonous compounds.

MU - Dec. 2012, Dec. 2015, May 2016

1.7.2 Metal Cladding

- It is a process by which a dense, homogeneous layer of coating metal and base metal sheet in the form of a sandwich is passed through the roller under pressure and at elevated temperature, which results in close adherence known as metal cladding.
- Choice of cladding material depends upon the extent of corrosion resistance desired and the given conditions of a corroding environment in which the base metal is placed / to be used.

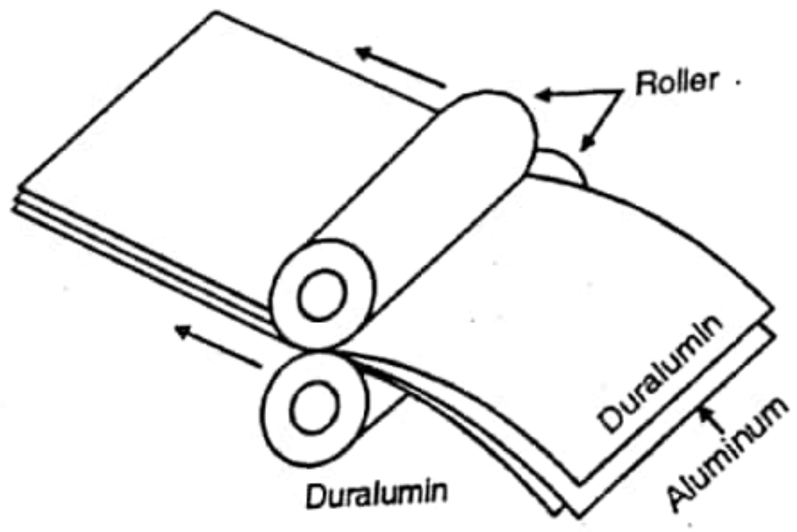


Fig. 1.7.3 : Metal cladding[Alclad]

Generally, passive metals like Ni, Cu, Pb, or alloys such as stainless steel, alloys of Ni, Cu, Pb are used as cladding material.

The method is highly useful especially to produce long sheets, cladded with thin metals like aluminium. The cladded sheets known as alcad are widely used in aircraft industry in which a plate of duralumin is sandwiched between two layers of 99.5% pure aluminium.

1.7.3 Metal Spraying

MU - May 2016

In this method, the coating metal is filled in spraying gun or piston and it is sprayed on roughened surface of the base metal.

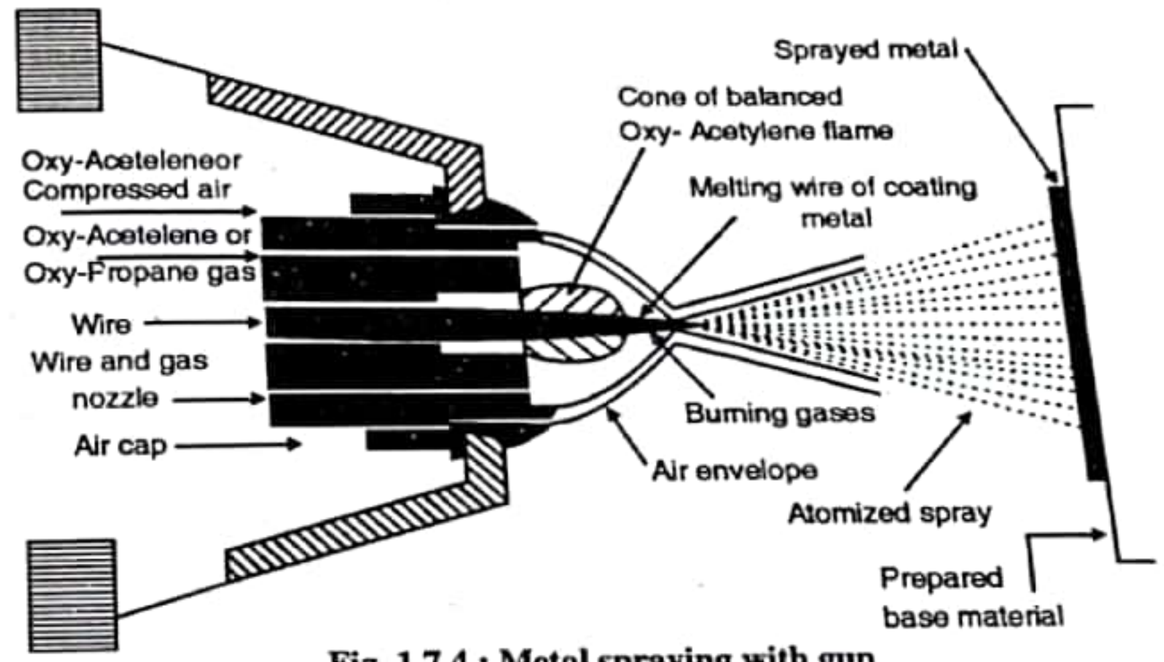


Fig. 1.7.4 : Metal spraying with gun

- The metal used for coating is taken in the form of a wire, and this wire is fed into the gun. When base metal is to be coated with this metal (normally low melting like Zn, Pb, Sn, etc.) the gun is operated. As the gun is equipped with oxyacetylene flame and supply of compressed air as shown in Fig. 1.7.4, melting of metal wire and spraying the molten mass occurs simultaneously and an uniform coating is developed on the surface of base metal.
- Protective coat produced by this method is normally uniform, but if the surface of base metal is not clean, then peeling occurs, or some pores are left in the coat and thus coat does not get adhered to the base metal surface.

Advantages

i) High speed.

ii) Capable to cover larger area in short time.

iii) Able to provide desired thickness of coats, especially in the irregular restricted area, such as crevices in window grills, etc.

iv) Coating on non-metallic surfaces can also be done such as on glass wood, plastic etc.

v) Such coats can get adhered to the surfaces of fabricated structures without undergoing any damage, even when such parts are assembled.

vi) It can provide reclaimation of worn out machine parts also.

Disadvantages

i) Coating is less adhered to the surface, hence the underlying base metal surface is normally required to be slightly rough.

ii) Two or three coats are to be applied to get the final coating of desired thickness. Hence, there is wastage of coating metal and cost is more.

MU - May 2012

1.7.4 Electroplating

- In this method, freshly cleaned base metal is *made cathodic.*
- A galvanic cell is set up in suitable bath (electrolytic solution) containing solution of the compound of the metal to be coated on base metal. Anode is the coating metal.
- The method is highly useful to produce coatings of metals such as *Cu, Zn, Sn, Ni, Cr, Cd, Pb, Ag, Au, Pt* and various alloys.

1.7.4.1 Theory of Electroplating

- A metal salt in aqueous solution undergoes ionisation to form ions.
- When a potential difference is applied to this salt solution by dipping two electrodes in the solution, the metal ions migrate to the cathode and get deposited there.
- If anode is of the same metal of which the salt is in the solution, the salt is reformed by the anode metal passing into the solution in the form of ions.

1.7.4.2 Process of Electroplating

- Electroplating is carried out in an electrolytic cell. As shown in Fig. 1.7.5.
- The article to be electroplated is first cleaned with organic solvents to remove oils, greases etc and then treated with dilute HCl (e.g. for copper and nickel plating) and dilute H_2SO_4 (e.g. for chrome plating) to remove oxide scales etc. The cleaned article is then made cathode of the electrolytic cell and is hung on racks placed on the cathode bar.
- The anode is either the coating material or an electrode of inert material like graphite.

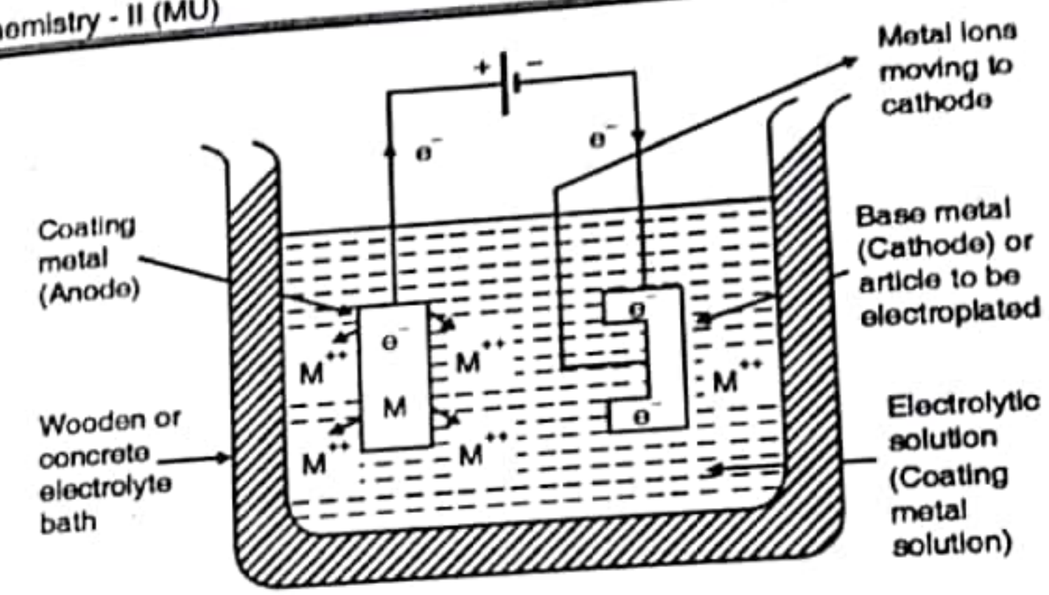


Fig. 1.7.5 : Electroplating

- The electrolyte, which is a soluble salt solution of coating metal is taken in the cell.
- The anode and cathode are dipped in the electrolytic solution and a direct current of electricity is passed.
- Under the influence of electric current, coating metal ions migrate to the cathode and get deposited there. Thus a thin coating of metal is produced on the article made as cathode.
- In order to have brighter and smooth deposits, low temperature, high current density and low metal ion concentration etc are the favourable conditions. Small articles like bolts, nuts, screws, washers etc are packed in barrel and the latter is slowly rotated during electroplating.

1.7.4.3 Disadvantages of Electroplating

To achieve highly uniform coating, certain precautions are to be taken :

i) Current density should not fluctuate.

ii) Composition of electrolytic solution should be consistent.

iii) Temperature should not fluctuate.

iv) Rates of anodic and cathodic reactions should be same.

- It is experienced that during electroplating, maintaining consistency in above parameters is very tedious and it requires skilled supervision.
- Hence, electroplating method is used for the articles where it is unavoidable, such as anodizing a particular metal or plating of noble metals where layer has to be as thin as possible without wastage etc.

1.7.4.4 Advantages of Electroplating

i) It improves the appearance of the base metal. The electroplated metal thus becomes resistant to corrosion, chemical attack and wear.

ii) It increases the hardness of base metal and also improves frictional and non-galling behaviour.

1.7.4.5 Applications of Electroplating

(a) Electroplating is used for decoration or better appearance

(b) Plating for protection

(c) Plating for special surfaces

(d) Electroplating for engineering effect

(e) Electroplating on non-metallics

(f) Electroforming

1.7.5 Cementation / Diffusion

MU - May 2016

a) Sherardising

- This is a process in which by diffusion method zinc is coated on iron. The method is normally employed for small structures like screws, nails, nuts and bolts etc. where the process of galvan zing by hot dipping cannot be useful.
- The surfaces of base metal articles are cleaned by acid pickling or any other suitable method and after washing and drying, these articles are packed with Zn dust in a drum, which is sealed so as to avoid the contact of oxygen from atmosphere.
- The drum is then slowly rotated at the temperature of about 350°C - 400°C. (Temperature raised by gas heating or by electricity) for about 3 to 12 hours in an inert atmosphere.
- Due to high temperature, zinc gets diffused and due to uniform rotation gets coated on to the surfaces of small articles in contact there by forming an iron – alloy on the surface of base metal.
- As the heating and rotation is continued, finally, on outer part of base metal surface, an uniform layer of zinc gets adhered providing a very high level protection to the base metal.

- Method is highly advantageous, because the operation is simple, cost is low and it can provide a very thin layer of zinc on small articles with intrinsic designs without changing the shapes or dimensions. Such zinc coated steel is used in making furnitures, hinges, window casements etc.

b) Calorizing

- When base metal is coated with a layer of a compound of aluminium and iron (Al_3Fe) on the surface of iron, it is known as calorizing.
- Similar to previous process, here in this method too, the surface of base metal is cleaned by pickling and sand blasting and then it is packed with a mixture of powdered aluminium, oxide and ammonium chloride (flux). This mixture is subjected to heating in a reducing atmosphere of hydrogen. At the end of uniform heating for about 12 hours, a layer of compound Al_3Fe is been formed on the surface of the base metal articles.
- Valves, condensers in oil refineries are calorized to provide corrosion resistance.

c) Chromizing

- The base metal, such as low carbon steel is normally chromized. Such a steel contains 0.1 to 0.2% carbon.
- The steel articles are heated together with chromium powder and alumina powder. The purpose of using alumina powder is to prevent the coalescence of the chromium particles. The temperature of the process is at about 1300°C to 1400°C and heating is continued for about 3-4 hours. During this time, base metal interacts with chromium powder and it is believed that solid solution of iron and chromium is formed.
- Chromized steel parts are used in appliances where resistance to corrosion by salt spray, steam or dil. HNO_3 is desirable For example : Gas–turbine blades.

d) Siliconizing

- In this method, base metal and silicon chloride are heated together thereby reducing silicon chloride to silicon which gets adhered to base metal.

- Generally, these coatings are more useful for metals forming volatile oxides.
- For example, Molybdenum metal is coated by silicon to get protected at high temperature; because, it forms an oxide which is volatile in nature.

Important Terms and Definitions

- Corrosion is nothing but the *deterioration* of a substance due to its reaction with its environment
- Corrosion is also known as weathering of metals or weeping of metals.
- Such weathering is exhibited by timber, wood, concrete etc. Even leading of glass or cracking of plastics are examples of 'corrosion'
- Thus corrosion can also be defined as "any process causing deterioration or destruction of any material is known as *corrosion*."
- The potential difference between the electrode and its ionic solution at equilibrium at a given temperature is called as *single electrode potential (E)*.
- *Oxidation potential* can be defined as, "the potential developed between an electrode and its ions in the solution due to *oxidation reactions* at equilibrium at given temperature (E_{Oxd})".
  a) *Reduction potential* can be defined as, "the potential developed between an electrode and its ions in the solution due to reduction reactions at equilibrium at given temperature (E_{Red})".
  b) *Standard electrode potential* can be defined as, "the potential difference between an electrode (element) and its ions in solution at 25°C (298 K) when concentration of all ions are unit molar (E°)".

  There are two types of standard electrode potentials,

  (i) Standard oxidation potential

  (ii) Standard reduction potential.
- Chemical/Atmospheric or dry corrosion occurs mainly by, *direct attack of atmospheric gases* such as O_2, CO_2, H_2S, *halogens*, SO_2 etc. on the surface of metals, thereby forming corresponding compounds such as *oxides, carbonates, sulphides, halides or sulphates*. The action of some *organic or*

anhydrous inorganic liquids, or melt of metals also cause this type of corrosion.
- **Electrochemical or Wet corrosion :** When metal surface is in immediate contact of *aqueous acidic/alkaline/ neutral/electrolytic solutions*, the short circuited galvanic cells get set all along the surface of metal. This gives rise to corrosion which proceeds by electrochemical principles.
- Differential aeration corrosion is due to the *electrochemical attack* on the metal surface, exposed to an electrolyte *of varying concentrations* or *of varying aeration*. This may be the result of local difference in metal ion concentration caused by,

  (i) Local difference in temperature

  (ii) Inadequate agitation
- Slow diffusion of metal ions, produced by corrosion.
- **Polarization :** The phenomenon which alters/ makes the cathode to be less cathodic (or more anodic) and that of the anode to be less anodic (or more cathodic) is called polarization of electrodes.

  Note : Polarization at the electrodes is due to : (i) concentration changes in the electrode region, (ii) overvoltage or (iii) presence of surface films on the electrodes.
- "The difference between the potential of the electrode when the gas evolution was actually observed and the theoretical reversible value of the same solution was called the *overvoltage or overpotential*".
- **Note :** Overvoltage may occur at the anode as well as the cathode.
- Cathodic protection involves reversal of the flow of current between the two dissimilar metals, under corroding environment thereby reversing the action of the metals in contact.

  Note : This is achieved by applying the external circuit and forcing the anodic metal to behave as a cathode.
- Anodic protection involves suppression of anodic reaction by adjusting the potential of the more reactive metal, i.e. making metal passive in the working environment.

Review Questions

Q. 1 Describe the various factors which influence the rate of corrosion.

Q. 2 Give an account of the different methods used for the application of metallic coatings for prevention of corrosion.

Q. 3 Discuss the corrosion caused due to the formation of concentration cells.

Q. 4 Explain following methods for corrosion control.

i) Design and protection ii) Cathodic protection.

Q. 5 Write a short note on the following :

i) Concentration cell corrosion ii) Galvanic corrosion

Q. 6 What is corrosion ? Discuss the corrosion caused due to the combination of metals of different electrode potentials.

Q. 7 Mention the various methods of metallic coatings and explain any two of them.

Q. 8 What is corrosion ? Discuss the corrosion caused due to the formation of galvanic cells.

Q. 9 Mention the important methods of controlling corrosion and explain the method of cathodic protection.

Q. 10 What is corrosion ? Explain the mechanism of electrochemical corrosion.

Q. 11 What are the methods adopted for protection against corrosion ?

Q. 12 Explain, why zinc gives better protection for iron than tin.

Q. 13 Write informative notes on :

(i) Electroplating. (ii) Integranular corrosion

(iii) Ingredients of paint and their function (iv) Cathodic protection

Q. 14 How do the metals undergo corrosion ?

Q. 15 Explain, how corrosion can be prevented by the following methods :

(i) Proper design (ii) By using alloys

Q. 16 How do the following factors influence the corrosion rate :

(i) Position of metal in galvanic series (ii) Oxygen (iii) Temperature

Q. 17 How can you prevent the corrosion of buried pipelines ?

Q. 18 Write a note on electroplating.

Q. 19 Describe any two methods of metallic coating for corrosion control.

Q. 20 What are the factors responsible for influencing corrosion.

Q. 21 Define paint. What are the constituents present in it ? Give examples.

Q. 22 Discuss the principle of electro-plating.

Q. 23 What is corrosion ? Explain the dry/chemical corrosion ?

Q. 24 How is the rate of corrosion influenced by the following factors :

(i) Temperature (ii) Nature of corrosion products

Q. 25 What is corrosion ? Discuss the corrosion due to differential aeration.

Q. 26 Discuss electro-chemical theory of corrosion taking suitable examples with neat sketch.

Q. 27 Distinguish between anodic and cathodic coatings.

Q. 28 Galvanized containers are not used for storage of food stuff, but tinned containers are used. Comment on the statement.

Q. 20 Define corrosion, name the different theories of corrosion. Discuss galvanic corrosion.

Q. 21 State the characteristics of a good paint.

1.8 University Questions and Answers

May 2012

Q. 1 Give the anode and cathode reactions involved in the corrosion of steel pipe connected to copper plumbing. (3 Marks)

(Ans. : Refer section 1.3.1)

Q. 2 Discuss the effect of the following factors on the rate of corrosion :

(a) Relative area of anode and cathode (6 Marks)

(Ans. : Refer section 1.4.5)

(b) pH

(Ans. : Refer section 1.4.10)

(c) Over voltage

(Ans. : Refer section 1.4.4)

Q. 3 What is cathodic protection ? Discuss the sacrificial anode method of corrosion control. (5 Marks)

(Ans. : Refer sections 1.5.4 and 1.5.4(i))

Q. 4 Explain concentration cell corrosion with the help of suitable example. (6 Marks)

(Ans. : Refer section 1.3.2)

Q. 5 Discuss the electroplating method of applying metallic coating in detail. (5 Marks)

(Ans. : Refer section 1.7.4)

Dec. 2012

Q. 1 Explain Galvanic corrosion. (3 Marks)

(Ans. : Refer section 1.3.1)

Q. 2 Define corrosion. Explain stress corrosion with appropriate diagram and examples. (5 Marks)

(Ans. : Refer section 1.1.1 and 1.3.5)

Q. 3 Explain the following factors affecting the rate of corrosion :

(i) position of metal in galvanic series.

(Ans. : Refer section 1.4.2)

(ii) temperature

(Ans. : Refer section 1.4.8)

(iii) Relative area of cathodic and anodic parts. (6 Marks)

(Ans. : Refer section 1.4.5)

Q. 4 Define paints. Explain the different constituents of paints with their functions. (5 Marks)

(Ans. : Refer section 1.6.2.4)

Q. 5 What are the methods of metallic coatings? Describe metal cladding with appropriate diagram. (4 Marks)

(Ans. : Refer section 1.7 and 1.7.2)

May 2013

Q. 1 Why silver, gold and platinum do not undergo oxidation corrosion ? (3 Marks)

(Ans. : Refer section 1.2.1(b))

Q. 2 State the characteristics of a good paints. (3 Marks)

(Ans. : Refer section 1.6.2.4)

CHAPTER 2

MODULE 2

Alloys

Syllabus

Introduction, purpose of making alloys, Ferrous alloys, plain carbon steel, heat resisting steels, stainless steels (corrosion resistant steels), effect of the alloying element- Ni, Cr, Co, Mn, Mo,W and V; Non-Ferrous alloys- Composition, properties and uses of- Alloys of Aluminium- i) Duralumin ii) Magnalium. Alloys of Cu- (I) Brasses-i) Commercial brass ii) German silver, (II) Bronzes- i) Gun metal ii) High phosphorous bronze. Alloys of Pb- i) Wood's metal ii) Tinmann's solder.

Powder Metallurgy : Introduction, (1)Methods of powder metal formation- i) Mechanical pulverization ii) Atomization iii) Chemical reduction iv) Electrolytic process v) Decomposition

(2) Mixing and blending. (3) Sintering

(4) Compacting- i) Cold pressing ii) Powder injection moulding (iii) Hot compaction. Applications of powder metallurgy. Shape Memory Alloys- Definition, properties and Uses.

Syllabus Topic : Introduction

> **Topics covered :** Alloy-Definitions

2.1 Introduction

- Metals possess many useful properties, such as high malleability, ductility, lustre, good electrical conductivity being a few to mention. But, in nature metals are not available in pure state.

- When metals are extracted from their natural sources. i.e. minerals or ores, some impurities are carried along with the pure metals. Hence, to get pure metal, further purification has to be done, by various different methods. But after all this processing, the pure metal obtained from its ore, *loses some vital characteristics* and becomes practically less useful for engineering purposes.
- Some of such characteristics are, its *tensile strength, corrosion resistance and toughness*. The pure metals are very soft, highly chemically reactive, highly malleable and ductile. Thus changes in these vital properties, *reduce shock and wear resistance* of metals. The high chemical reactivity makes pure metal susceptible to corrosion.
- The properties of pure metals can be improved by alloying the pure metal with another suitable metal/non-metal, For example, Pure iron can be alloyed to get steel, which shows the desired properties such as, toughness, *high corrosion resistance etc.* Here, steel is an alloy of iron with carbon (non-metal), chromium/manganese (metals) etc.

2.1.1 Alloy-Definitions

MU - Dec. 2013, May 2014, May 2015

- *An alloy is a solid mixture of two or more metals or non-metals.* Alloy must have necessarily,
  - (i) at least one metal (base metal)
  - (ii) at least one additional metal or non-metal.
- The properties of given metal (base metal) can be improved by alloying it with other metals or elements like *carbon, phosphorus* etc.
- When two or more metals are mixed in their molten state and when this mixture is cooled, the two metals remain in intimate mixture without separation, thus forming a solid mixture. This solid homogeneous mixture of two metals is called as alloy. Thus, an *alloy is a substance/material formed by solidification of metallic solution of two or more metals/elements.*
- **Alloy** can also be defined *as a solid solution where the solutes are the alloying elements whereas the solvent is the element in excess proportion (base or main metal).*
- The *homogeneous mixture* of two or more metals must retain metallic characteristics and it also must improve the properties of individual elements.

Syllabus Topic : Purpose of Making Alloys

- **Topics covered :** Main Purpose of Making Alloys, Improvements in properties of metals on alloying, Classification of Alloys (Types of Alloys)

2.2 Purpose of Making Alloys

MU - Dec. 2013, May 2014, May 2015, May 2016

- Metals are used as a basic material in making various machines, used in industries or household articles or in other areas like making ships, railways, bridges, buildings etc.
- During metallurgical processes involved in extraction of pure metal from its ores, the most important characteristics of metal are been lost/reduced, as discussed above. This affects the performance of metals during operation under given service conditions in engineering uses.
- The undesirable changes in the malleability, ductility, tensile strength, elastic limits, hardness have to be improved to make the metal suitable for its uses, which are affected by mixing the metals with other suitable elements.
- Thus alloy formation, basically helps in getting the desired performance in the given service conditions economically.
- The following properties of metals are generally modified/improved by alloying the metal, i.e. the purpose of alloying the metal is to improve,

(i) Hardness
(ii) Tensile strength
(iii) Corrosion resistance
(iv) Castability
(v) Colours While to decrease,
(vi) Melting point
(vii) Malleability and ductility
(viii) Chemical reactivity.

The Table 2.2.1 shows different examples indicating the improvements in the characteristics of main element on alloying with others.

Table 2.2.1 : Improvements in characteristics

Sr. No	Characteristic	Main Metal	Alloying Elements	Modification in Properties of Main Metal
1)	Hardness	Pure Lead	Arsenic (0.5%)	*Hardness* of lead *improves* and it is used to make bullets.
		Pure Gold	Copper	Ornaments of gold are prepared as *hardness of gold improves.*
		Pure Iron	Carbon (upto 1.5%)	To make steels with greater hardness.
		Pure Copper Pure Copper	Tin Zinc	Alloy is harder than pure copper.
2)	Tensile strength	Pure Iron	Carbon (1%)	Ten times increase in tensile strength of iron
3)	Corrosion resistance	Pure Iron	Chromium, Nickel	The alloy (stainless steel) *does not get corroded,* not only by moisture but even in acids, whereas pure iron gets corroded easily by the attack of atmospheric gases, moisture etc.
4)	Castability	Pure Lead	Tin, antimony	Castability of this alloy improves and hence it is used in making *'printing type'.*
5)	Colours	Silver *(White)*	Gold *(yellow)*	The alloy is *purple* coloured.
		Silver *(White)*	Tin *(white)*	The alloy is *pink* coloured
		Copper *(Red)*	Zinc *(silvery white)*	The alloy is *yellow* coloured.

Sr. No	Characteristic	Main Metal	Alloying Elements	Modification in Properties of Main Metal
		Aluminium *(Silvery white)*	Zinc *(silvery white)*	The alloy is *golden yellow* in colour.
6)	Melting point	Pure Iron M.P. = 1539°C (Bi) Bismuth M.P.= 271°C	Carbon (2%) Cd (321°C) Pb (327°C) Sn (232°C)	M.P. of alloy *is decreased* to *1130 °C* The alloy (wood's metal) has M.P. of only 71°C, which is very low as compared to alloying elements.
7)	*Malleability and ductility*	Copper Gold	Zinc Copper	The alloy (brass) is less ductile as compared to copper. The malleability of gold is reduced.
8)	Chemical activity	Iron	Chromium Nickel	The alloy (stainless steel) has very low reactivity as compared to pure iron.

Thus, from above table, the purpose of making alloys in understood clearly, as each example indicates the modification/improvements in specific property (drawback) of pure metal. *The alloying helps in enhancing the utility of metals for engineering purposes.*

2.2.1 Classification of Alloys (Types of Alloys)

Alloys are classified on the basis of following criteria :

(i) *Based on metallurgical structure*
- Single phase alloys For example; Brass, Monel metal
- Two phase alloys For example; Muntz metal

(ii) Based on the presence or absence of iron

For example; Ferrous alloys

Non–ferrous alloys

(iii) Based on principal metals (constituents) in alloy

For example;
- Alloys of copper with zinc – Brasses
- Alloys of copper with tin – Bronzes
- Alloys of aluminium – Duralumin
- Alloys of Mg
- Alloys of Lead
- Alloys of Tin
- Alloys of Nickel

(iv) Based on method of fabrication

For example; Wrought alloys

Casting alloys

Syllabus Topic : Ferrous Alloys

2.3 Ferrous Alloys

- The alloys of iron as a major constituent, with other metal(s) or/and non-metal are known as *ferrous alloys*. These are commonly known as *alloy steels*. The metal iron generally forms alloys by mixing with carbon, and any other element (metal) such as either nickel alone or nickel and chromium both.
- Based on this, the alloy of iron and carbon (i.e. steels – *Widely known as plain carbon steels)* are either,

  (a) Three components i.e. (Fe, C, Ni)

  or (b) Four components i.e. (Fe, C, Ni, Cr)
- *Since these steels essentially contain iron and carbon, are known as plain carbon steels.* The percentage of carbon in steels ranges from 0.008% to 2%. The plain carbon steels are named on the basis of its carbon content.

Syllabus Topic : Plain Carbon Steels

> **Topics covered :** Plain Carbon steels, Classification of Plain Carbon Steels Drawbacks of Plain Carbon Steels

2.4 Plain Carbon Steels

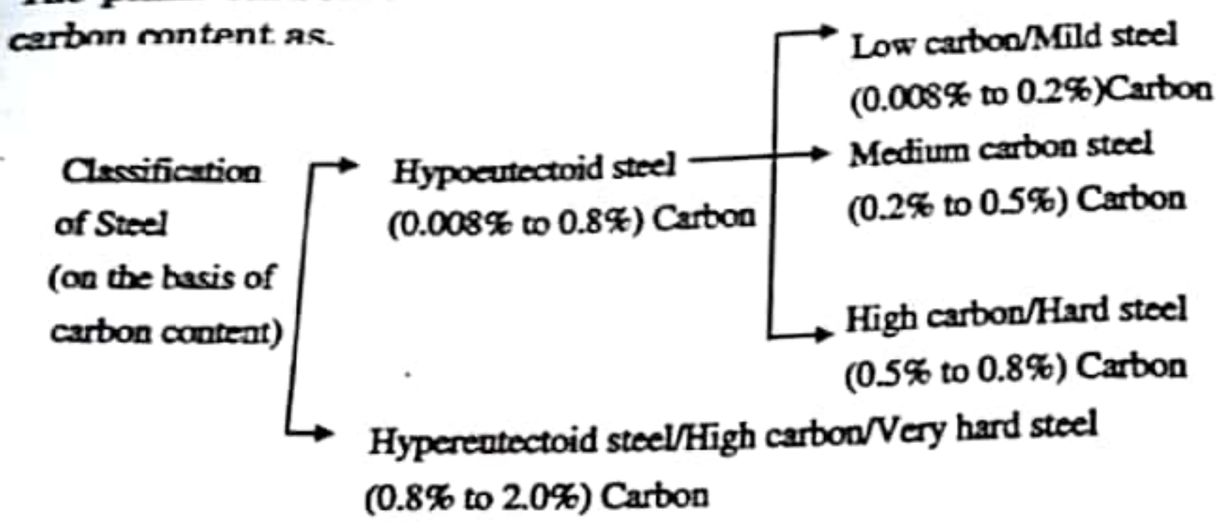
MU - Dec. 2014, May 2016

- The alloys of iron with other metal (s) or/and non-metal are known as *ferrous alloys*. The metal iron generally forms alloys by mixing with carbon, known as "Plain Carbon Steels".
- Since these steels essentially contain iron and carbon, are known as plain carbon steels. The percentage of carbon in steels ranges from 0.008% to 2%.

2.4.1 Classification of Plain Carbon Steels

MU - Dec. 2014, Dec.2015

- **The plain carbon steels** are further classified/named on the basis of its carbon content as.



2.4.2 Drawbacks of Plain Carbon Steels

MU - May 2014, Dec. 2014, Dec.2015, May 2016

(i) With increasing percentage of carbon, the *ductility decreases* and *brittleness increases.*

(ii) Plain carbon steels cannot be deep hardened on heat treatment, because due to effect of heat, only *surface of steel gets hardened* while the *inner layers* of steel *remains soft.*

(iii) During the use, the *mechanical properties* of plain carbon steels get deteriorated at higher temperature. Thus the *uses of plain carbon steels* to make/manufacture various machine parts has limitation of temperature.

(iv) The *corrosion resistance* of plain carbon *steels is very low*. As a result, this steel has *limited use* in manufacturing various machine parts, though strength and welding characteristics may be suitable.

- The above drawbacks make the plain carbon steel unfit for engineering purposes under the working atmosphere where temperature is high, corroding environment persists etc. Hence, it becomes necessary to make further modifications, so as to make the plain carbon steels more useful.

Syllabus Topic : Heat Resisting Alloy Steels

2.5 Heat Resisting Alloy Steels

MU - Dec. 2013

These are steels which are exposed to high temperatures during preparation of equipments.

Heat resistance / sustainance is improved by adding specific metals in appropriate proportion.

Following metals are used / added in stainless steel to make them "heat resting".

(1) Molybdenum : 3.5 % addition of this metal improves heat resistance of steel.

(2) Chromium : Through this is a constituent in steels, but if added more than 12%, it imparts high grade heat resistance to steel. Such a steel is called as "Nichromes".

Nichrome	Ni = 60 % Cr = 12 %	Can be used upto 1000 to 1100° C temperature.
	If Cr = 16 to 20% and [C = 0.06 to 0.15 %]	Upto 900° C, steel is oxidation resistance.
	If Ni = 18% with low of columbium	Can be used upto 900° C.

Uses of Heat Resisting Steels

For making equipments Facing high temperatures. i.e. Gas turbines, retorting, parts of boilers, stills, steam-linings, aero-engine valves, annealing boxes etc.

Syllabus Topic : Stainless steel (corrosion resistanting steel)

2.6 Stainless Steel [Corrosion Resisting Steel]

These steels do not get corroded when exposed to atmosphere, or to chemicals.

Their composition is,

Chromium [Ideally ≥ 16%]

Nickel

Molybdenum

Chromium deposits thick film of its oxide, on the metal surface. Chromium being a metal from passivity series, its oxide film, if gets broken, heals up automatically by reacting with atmospheric oxygen.

There are two types of corrosion resisting steels based on content of carbon and chromium.

(a) Heat treatable stainless steel

Contains C = 1.2 %

Cr = < 18 % [12 to 16%]

Properties

(1) These are magnetic and tough.

(2) These can be moulded easily.

Uses

In surgical instruments, scissors, blades, cutlery etc. (Temperature upto 900° C)

(b) Non heat treatable stainless steel

These steels generally lose their strength as temperature increases, but their corrosion resistance increases with temperature.

Depending upon content of chromium and carbon, these steels are categorised as,

(i) Magnetic

Cr = 12 to 22 %

C = < 0.35%

Properties

(1) These can be machined, cold drawn or forged.

(2) They have good corrosion resistance.

Uses

These are used in making parts for automobiles, chemical equipments etc.

(ii) Non-magnetic

Cr = 18 to 26 %

C = upto 0.15 %

Ni = 8 to 21 %

Properties

(1) Total % of Cr and Ni is = 23%

(2) High corrosion resistance.

(3) Steels with 18% Cr + 8 % Ni are very common, known as "18/8 stainless steels"

(4) Addition of little molybdenum, increases their corrosion resistance further.

Uses

To make dental instruments, surgical instruments, decorative articles, water sinks etc.

Syllabus Topic : Special Effects of Alloying Elements on Alloy Steels

2.7 Special Effects of Alloying Elements on Alloy Steels

MU - Dec. 2012, May 2013

- The addition of various different elements has been taken up with plain carbon steels. It is found that, *every element has some special effect on the properties of plain carbon steels.*
- The commonly added elements are aluminium, boron, chromium, cobalt copper, lead, manganese, molybdenum, nickel, niobium, phosphorus, silicon sulphur, titanium, tungsten, vanadium, etc. The special effects of these elements on alloy steels is given in Table 2.7.1.

Special Effect of elements on alloy

MU – Dec. 2012, May 2013, Dec. 2013, May 2014, Dec. 2014, May 20

Table 2.7.1

Sr. No.	Element	Special Effects
i)	Nickel	Enhances ductility, toughness, resistance to heat and corrosion elasticity, tensile strength etc.
ii)	Chromium	Added upto 18 % Enhances hardenability, corrosion and oxidation resistance, increases high-temperature strength. In high carbon steels, it increases abrasion resistance and toughness.
iii)	Cobalt	Contributes to hardness of steel.
iv)	Manganese	Improves certain properties with respective range of proportions : e.g. 1.0 to 1.5 % = Steel gains toughness plus brittleness, also improves strength. If high % i.e. 11 to 14 % = Steel gains high degree of hardness.
v)	Molybdenum	Enhances, (i) Resistance to softening in tempering. (ii) Tensile and creep strengths at high temperatures. (iii) Hardenability (iv) Corrosion resistance of stainless steels especially in chloride environment. (v) In austenite the grain coarsening temperature. (vi) Resistance to susceptibility to embrittlement during tempering
vi)	Tungsten	It helps to form hard and abrasion resisting carbide film in tool steels. Increases shock resistance ; Imparts high temperature hardness in tempered steels. It enhances creep strength in some high temperature steels.
vii)	Vanadium	Increases hardenability, tensile strength, shock resistance, ductility.

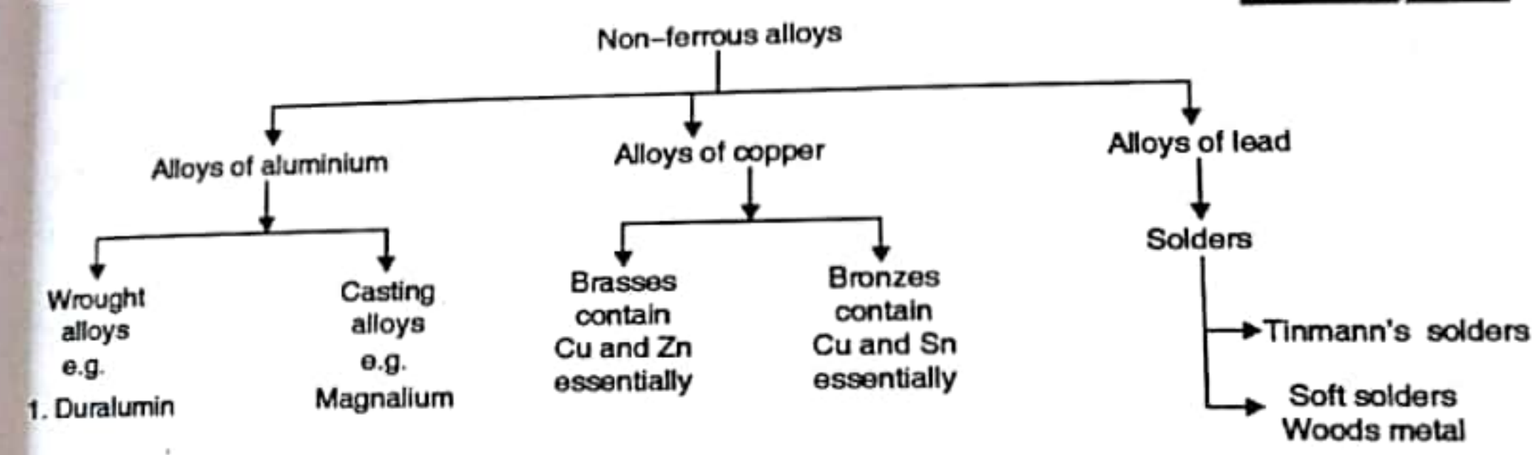
The *improvements in properties* of *alloy steels* due to special effect of certain metals *makes the steels more useful for engineering purposes.*

Syllabus topic : Non-Ferrous Alloys

➤ **Topics covered :** Alloys of Aluminium (a) Duralumin (b) Magnalumin Alloys of Copper Brasses and Bronzes ; Comparison of Brasses and Bronzes Commercial Brass/French Gold/Guilding metal, German silver, Gun metal High phosphor bronze **Alloys of Lead :** Woods metal, Tinmann's solder

2.8 Non-Ferrous Alloys

MU - May 2016



Ferrous alloys are used in exceedingly large quantities, because they have a wide range of mechanical properties. However, they possess some limitations which are :

1. They possess relatively *high density* hence are *heavier in weight*.
2. Their electrical conductivity is *low*.
3. They show tendency of corrosion in some common environments.

Thus for many applications, it is advantageous or even necessary to utilize other alloys having combinations of properties which are, more suitable to working condition. Most of such alloys do not contain iron. Hence, they are called as *'non-ferrous alloys'*. These alloys have been proved suitable for many purposes. Hence, they can be very easily used in place of ferrous alloys. Since these alloys do not contain iron as one of their components, the main components of non-ferrous alloys are other metals such as, copper, lead, zinc, aluminium etc. *Usually, their melting points are lower than ferrous alloys.* They find wide applications because of their following properties :

2.8.1 Alloys of Aluminium

MU - May 2012, Dec. 2014, May 2016

- These alloy materials have higher percentage of aluminium, with other elements such as *Cu, Mn, Mg etc.*
- Two of its alloys are widely used (i) Duralumin (ii) Magnalium

The composition, properties and uses of these two examples of aluminium alloys is given in the Table 2.8.1.

Table 2.8.1 : Non ferrous alloys – Alloys of aluminium

Element Composition	Properties	Uses
(a) Duralumin Al = 95% Cu = 4% Mn = 0.5% Mg = 0.5%	It is light weighted, tough, highly ductile, easily castable, good conductor of heat and electricity and corrosion resistant. It can easily be worked as it possesses high machinability. Its tensile strength can be raised by heat treatment, upto about 2000 kg-cm² without affecting its ductility. It approaches steel in strength and yet its density is one third that of steel.	Due to high strength with low density, it finds extensive use in aircraft industry in the form of a 'clad'. It is also used in making surgical instruments, cables, fluorescent tube caps etc. It is also used in making automobile and locomotive parts because of its high ductility and good electrical conductivity.
(b) Magnalumin Al = 70 – 90% Mg = 30 – 10%	It is strong and tough and lighter than aluminium. It possesses mechanical properties similar to brass.	It is used for making scientific instruments, balances aeroplane parts etc.

2.8.2 Alloys of Copper Brasses and Bronzes

MU - Dec. 2012, May 2013, Dec. 2015, May 2016

- *These are the alloys of copper and other metals in which percentage of copper is higher.*
- **There are two types :** (i) Brasses and (ii) Bronzes
- *Brasses are alloys of copper and zinc in varying percentages.*
- *Bronzes are the alloys of copper and tin in varying percentages.*

Table 2.8.2 : Comparison of Brasses and Bronzes

	Brasses	Bronzes
1.	These are non-ferrous alloys of copper, with zinc, known as "Common Brasses"	These are non-ferrous alloys of copper with tin common bronzes.
2.	They may contain trace amount of tin, apart from Cu and Zn, known as "Special Brasses"	They may contain trace amount of Phosphorus / Aluminium / Iron – special bronzes.
(3)	**Main brasses are :** (a) Commercial brass (b) Dutch metal (c) Cartridge brass	**Main Bronzes are :** (a) Coinage/common bronze (b) Gun metal (c) High phosphorus bronze
(4)	**Special brasses are :** (a) German silver (b) Admirality brass	**Special bronzes are :** (a) Nickel bronze (b) Aluminium bronze
(5)	Copper % ranges between 25 to 90 % in different brasses.	Copper % ranges between 80 to 95% in different bronzes.

Table 2.8.3 : Non-ferrous alloys – Alloys of copper – brasses

Sr. No.	Name of alloy	Composition	Properties	Uses
i)	Commercial Brass/French Gold/Guilding metal	Cu = 90% Zn = 10%	Golden in colour, harder and stronger than copper	Architectural metal works, imitation jewellery, hardwares, screws, forgings, rivets etc.
ii)	German silver	Cu = 25-50 % Zn = 10-35 % Sn = 5-35 %	Posseses good strength, high corrosion resistance to electrolyte ; High ductility, malleability. Appears like silver.	Decorative articles, utensils, table wares, ornaments, cutlery, etc.

Table 2.8.4 : Non-ferrous alloys-alloys of copper-bronzes

Sr. No.	Name of alloy	Composition	Properties	Uses
i)	Gun metal	Cu = 85% Zn = 4% Sn = 8% Pb = 3%	Highly strong, can resist explosion, hard, tough.	For hydraulic fittings, high pressure steam plants marine pumps, water fillings etc.
ii)	High phosphor bronze	Sn = 10 – 13% P = 0.4 – 1% Cu = Rest %	Good strength and resistance to corrosion under sea water, castable, can be rolled or drawn into wires. Abrasion resistant hard, brittle, low coefficient of friction.	For springs, turbine blades, pumps, boiler fittings, bearing plates, spindle, for valves. For gear wheels, side, valves, bearings, taps, bushes springs, turbine blades etc.

2.8.3 Alloys of Lead

MU - Dec. 2013, May 2014

These alloys are commonly known as solders. The most widely used examples of this category are given in Table 2.8.5 with their compositions, properties and uses.

Table 2.8.5 : Alloys of lead

Sr. No.	Name of alloy	Composition	Properties	Uses
i)	Woods metal	Bi = 50 % Pb = 25 % Sn = 12.5 % Cd = 12.5 %	Melting point 65.5°C Density 9.7 gms/cu.cm Stable. Incompatible with acids, oxidizing agents, halogens, interhalogen compounds.	Wood's metal is useful as a low-melting solder, low-temperature casting metal, as a filler when bending thin-walled metal tubes. Wood's

Sr. No.	Name of alloy	Composition	Properties	Uses
			Harmful by inhalation or if swallowed. May be harmful in contact with the skin. Skin and eye irritant. Non-hazardous for air, sea and road freight.	metal is also useful for repairing antiques.
ii)	Tinmann's solder	Pb = 34 % Sn = 66 %	Low melting alloys	Used for joining articles (soldering) and tinning.

Syllabus Topic : Powder Metallurgy

➤ **Topics covered :** Definition and Explanation , Advantages of Powder Metallurgy (PM) **Disadvantages of Powder Metallurgy**

- Processes or Steps Involved in Powder Metallurgy , Metal Powder Formation
- Mechanical Communition / Pulvurisation, Atomisation Process
- Reduction of Metal Oxides / Chemical Reduction
- Electrodeposition / Electrolytic Process, Decomposition,
- Manufacture of Oxide and Non-oxide Ceramic Powders : Silicon Carbide [SiC]
- Alumina Powder (Al_2O_3) [Oxide Ceramic Powder]
- Mixing and Blending Sintering, Compacting, Cold Pressing Technique, Powder Injection Moulding (PIM) ,Hot Compaction.

2.9 Powder Metallurgy

MU - May 2012

2.9.1 Definition and Explanation

MU - Dec. 2013, Dec. 2014, May 2015,Dec.2015

Powder metallurgy is a process which deals with the product of useful components from fine metal powders, from individual, mixed or alloyed with or without the inclusion of non-metallic constituents. In this process,

- Metal is obtained in powder form.

- Powdered metal is mixed with other element(s), in powder form.
- It is then subjected to high pressure so as to get compressed into desired shape.
- The shaped form is then finished into final form.
- Various combinations with metals and/or non metals are possible.

Thus powder metallurgy can be summarised in following steps/stages.

(a) Converting metal/s into powders.

(b) Blending and mixing of powders.

(c) Pressing or compressing or compacting in appropriate shapes.

(d) Sintering the pressed powder compacts.

(e) Sizing or coining the product.

Solder ; an alloy of tin and lead.

Tungsten carbide cutting tool tips

Powder metallurgy is used in manufacturing alloys such as *Wood's metal*, where hot intimate mixture of powders of respective constituents is compressed under high pressure in a mould.

2.9.2 Advantages of Powder Metallurgy (PM)

MU - May 2014

Powder metallurgy has been proved to be advantageous over other usual techniques in multiple ways, such as,

- By PM, materials can be made using, *metal-metal* or *metal-non-metal* in any desirable compositions.
- *Dimensional accuracy* and *finish of the materials are excellent.*
- *Porosity* of material can be controlled; along with control over *size, shape* and *distribution of pores*, to achieve desired properties.
- *By PM it is possible to produce materials with properties similar to the parent metals unlike in typical alloying.*

For example : *Electrical contact material. Cu and Ag have high conductivity while W or Mo have high hardness.* If these metals are mixed by PM, *we can prepare material with high conductivity as well as high hardness.* Thus *the component would be superior for use.*

- *By PM, refractory metals such as W, Ti, Th etc. can be produced.*

For example : *Manufacture of ductile tungsten* in wire form for *incandescent lamp filament.*

From above examples, **the advantages of PM can be summarised as :**

1. Process is cleaner, quieter and gives long lasting materials.
2. Production rates are high.
3. Components formed are defect-free, have uniform structures and grain size.
4. Wastage of material as scrap is almost nil. Thus 100% material is utilised unlike in casting, press forming etc.
5. Components with different shapes can be formed.
6. Materials with wide variations in compositions and materials can be produced.
7. Process does not require highly skilled or qualified labour.
8. Super hard cutting tools can be produced by PM.
9. Process is helpful in increasing use of diamond in the industry.

2.9.3 Disadvantages of Powder Metallurgy

Powder metallurgy has some disadvantages which limit its applications in some of the situations.

The disadvantages or drawbacks of P.M. can be summarised as :

1. The process is not suitable for manufacture of small number of components, because of, high initial investment on tooling and die cast and other equipment.
2. The process does not suit for forming components from metals like *Mg, Al, Zr, Ti* etc. This is because, such metals in powder form may explode and cause *fire hazards* when they come in *contact with air.*
3. Storage of metal powders requires precautions, because powder metals get oxidised in air if exposed. This causes wastage.
4. Process is not suitable to produce large size components because presses available for compaction are of limited capacity.
5. Process is not suitable to take care of density variation in components, as parts pressed from top tend to be less dense at the bottom.

   Thus components with theoretical density can not be manufactured.
6. Process has limitation so as to manufacture the parts with complex shapes. This is because powdered metal can not flow as freely as molten metals.
7. Process forms components, which have poor resistance to corrosion because *they are porous.*

Due to porosity, exposure of large internal surface to corrosive environment enhances rate of corrosion.

Due to porosity, the component formed is poor in the following properties,

(a) Mechanical properties such as malleability and ductility.

(b) Tensile strength

(c) Toughness

(d) Surface finish.

As compared to components manufactured by conventional methods.

Processes or Steps Involved in Powder Metallurgy **MU - May 2014, Dec. 2015**

The following processes are involved in manufacturing :

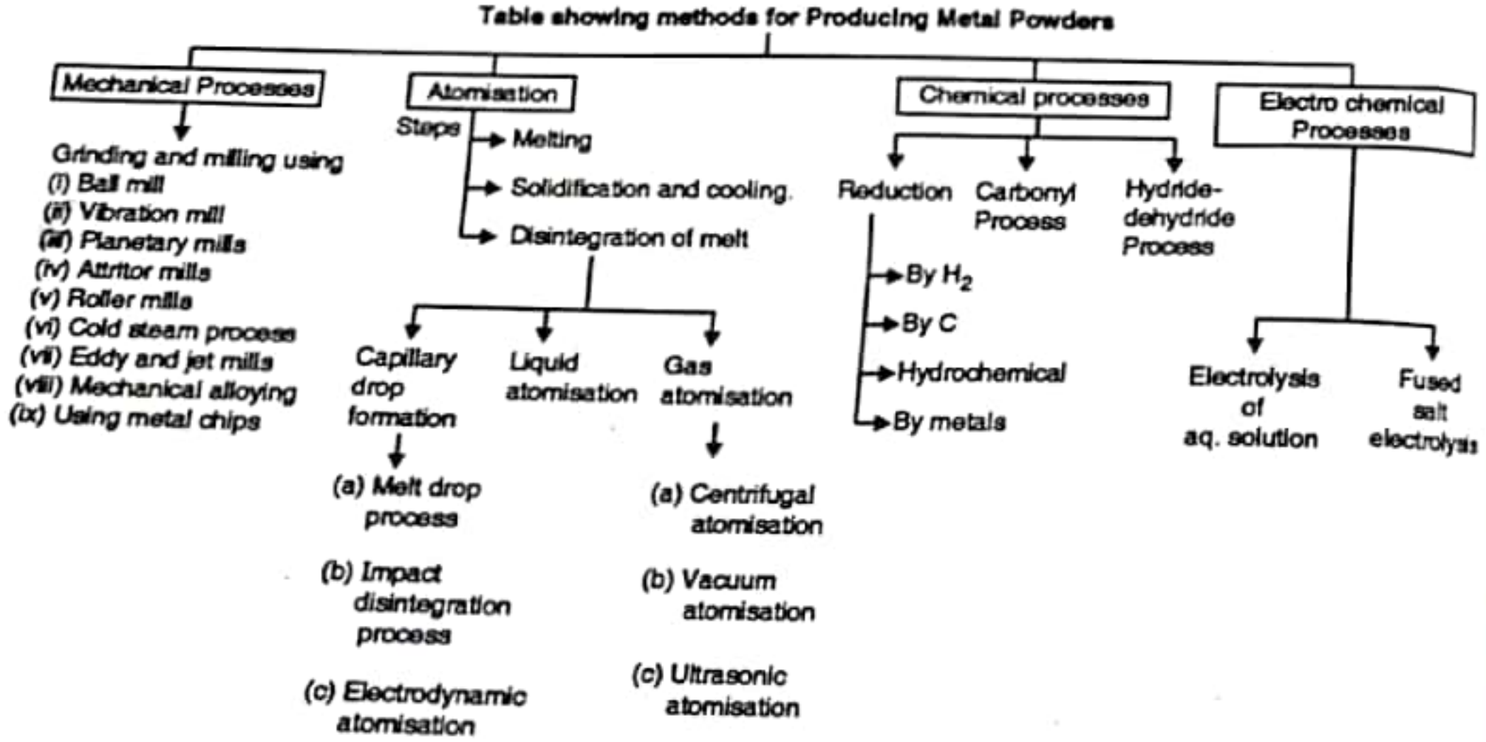
(i) **Metal powder formation :** Metals are powdered in required granular sizes.

(ii) **Mixing and blending of powders :** Constituents are mixed and blended properly.

(iii) **Compacting the metal powder :** Mixture is made into desired shape.

(iv) **Sintering :** Shaped mould is heated slowly and then cooled which is helpful for increasing strength.

Table showing methods for Producing Metal Powders



2.9.4 Metal Powder Formation

MU - Dec. 2013

Metal powders are generally pure products. Their degree of purity, particle size and shape depends on the method by which the metal powder is manufactured.

The following methods have been used in powder production.

1. Mechanical communition
2. Atomisation
3. Reduction of metal oxides.
4. Electrodeposition
5. Decomposition.

Each of these methods are discussed here in brief.

2.9.4.1 Mechanical Communition / Pulvurisation

- This method is generally applied to metals like antimony which is comparatively brittle in nature. Such brittle metal can be (crushed to a size of 1×10^{-4} mm., their shape being angular particles, which are most suitable in powder metallurgy.
- Ductile metals can give powder form on crushing and milling, but the resulting product is *flaky* which is *not suited in powder metallurgy*.

2.9.4.2 Atomisation Process

MU – May 2015

In this method, liquid metal is forced through a small orifice and jet of liquid is broken down by blast of compressed gas. Now a days in advanced/modified atomisation process, the metal is atomised by striking a rapidly rotating disc.

2.9.4.3 Reduction of Metal Oxides / Chemical Reduction

MU – May 2015

- In this process oxides of metals are reduced by using appropriate reduction technique.
- **For example :** Iron powders, are obtained by reducing iron oxides. Such oxides are obtained in the form of iron ore concentrates, mill scales or steel scraps.
- Reduction of metal oxide to metal powder is achieved using solid or gaseous reducing medium.

  For example : Ferrochrome, which is an alloy of chromium and iron is prepared in powder form by reducing chromium iron ore, with carbon.

$$FeO \cdot Cr_2O_3 + 4\,C \rightarrow \underset{\text{Ferrochrome}}{Fe + 2\,Cr} + 4\,CO$$

2.9.4.4 Electrodeposition / Electrolytic Process

This method involves all principles of electroplating techniques. To obtain metal powders, in electroplating technique, all conditions are adjusted in such a

manner that a spongy or brittle deposits are obtained at cathodes. These deposits are subsequently ground to powder having particular size.

Brittle deposits give angular particles whereas spongy deposits give flattened particles.

2.9.4.5 Decomposition

In this method decomposition of corresponding compounds of metals give metal powders :

e.g. Iron or Nickel carbonyls.

$Fe(CO)_5$ or $Ni(CO)_4$

When these carbonyls are decomposed, pure iron and nickel powders are obtained. These powders are usually spherical.

2.9.5 Mixing and Blending

- The metal powders formed by any of the above mentioned methods are thoroughly checked for their particle size.
- Then the mixing is done by choosing the desired metal powders required for the jobs, in appropriate proportions. For *effective blending*, agents such as *lubricants, volatilising agents or non-metallic particles* are also included, which are made to get distributed homogeneously, with the metal powder.
- Particles with same size, shape and density get mixed very effectively giving perfect homogeneous mixture. Whereas, if size or shape or density is different amongst the particles, then uneven mixing results.

2.9.6 Sintering

MU - May 2012. May 2013

The sintering operation consists of following steps :

(i) Heating the compacted components in furnaces provided with controlled atmosphere.

(ii) Soaking

(iii) Cooling

The heating is done keeping temperature below the melting point of all principal constituents of compact, or in certain cases at least any one constituent of compact.

The different types of furnaces used for sintering operation are :

(a) Belt type (b) Walking beam type

(c) Sealed high temperature batch type (d) Pusher type

(e) Roller hearth type (f) Vaccume type.

In most commonly employed commercial sintering operations, controlled atmosphere applied/maintained, is with respect to *endothermic gas, nitrogen-hydrogen mixture, exothermic gas, cracked ammonia etc.*

2.9.7 Compacting

MU - May 2013. May 2016

- The blended and mixed metal powders are then fed into suitable dies to give them desired shape. This process requires specific pressure. This is an important step in powder metallurgy, because proper shape of finished product (alloy/mixture) governs many properties.
- Compacting is important because,

(i) It reduces void space between metal particles

(ii) It increases density of compact.

(iii) It produces adhesion and cold welding of powders.

(iv) It facilitates the sintering operation,

(a) By deforming the powder plastically so as to allow re-crystallisation during sintering, and

(b) By increasing the contact areas between the powder particles i.e. increasing green strength and facilitating subsequent sintering.

The compacting is carried out in either hydraulically or mechanically operated press.

(i) Cold Pressing (ii) Powder Injection Moulding (PIM)

(iii) Hot Compaction.

2.9.7.1 Cold Pressing Technique

MU - May 2012

The ceramic powder alone or with a binder are fed to die made out of rigid material.

There are two modes for cold pressing :

(a) Axial (b) Isostatic

Axial Process

In this powders are compacted between two punches as shown in Fig. 2.9.1 The steps are as shown,

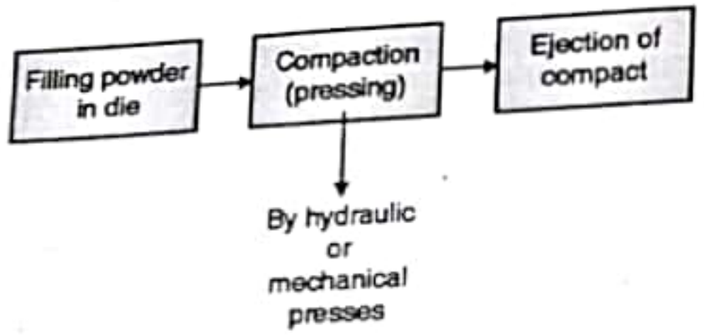
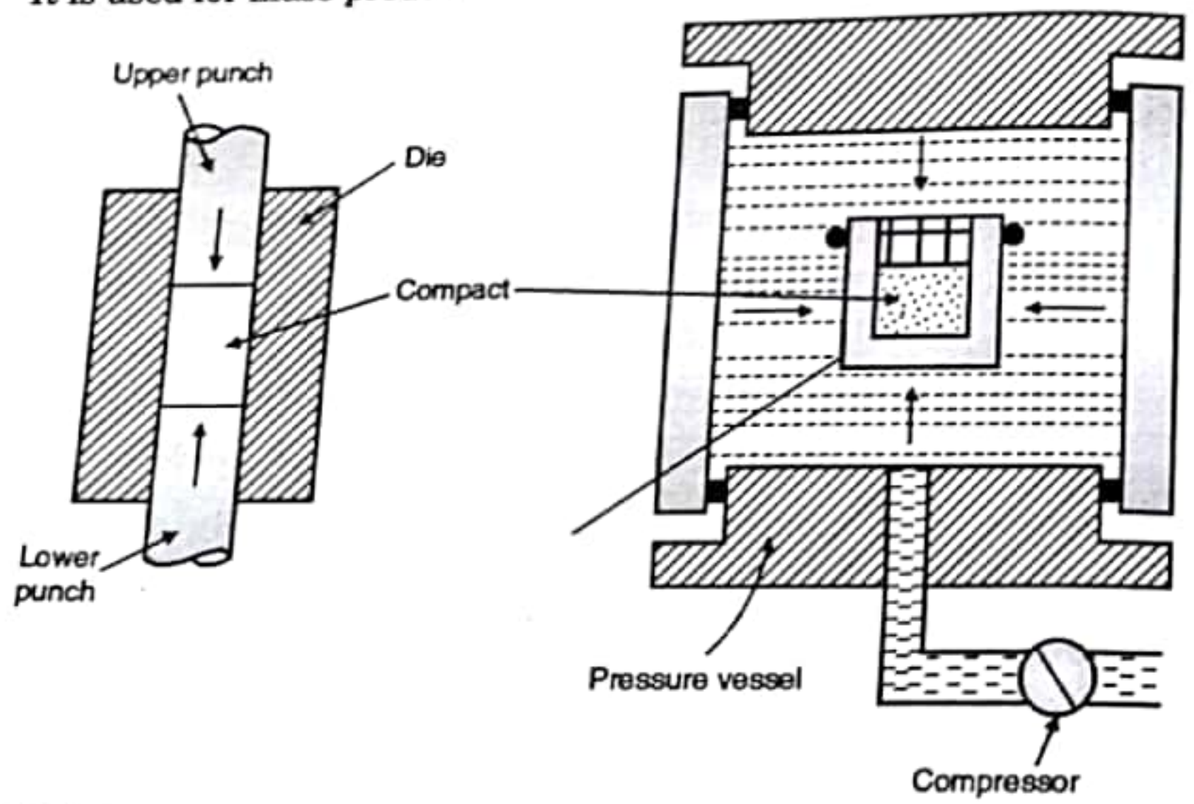


Fig. 2.9.1

Advantages

(1) The process is simple, economical

(2) It is used for mass production.



(a) Axial pressing (b) Isostatic pressing

Fig. 2.9.2 : Schematic representation of cold pressing principles

Isostatic Pressing

In this the powder is compacted by taking in die, applying high pressure.

2.9.7.2 Powder Injection Moulding (PIM)

MU - Dec. 2012, Dec. 2014, May 2016

The metal / ceramic powder is converted into suitable feed stock. Then it is mixed with a chemical compound which acts as "binder". The role of binder is to impact flow properly to feed stock, which enable it to be mouldable under conditions of temperature. The Fig. 2.9.2 shows PIM equipment.

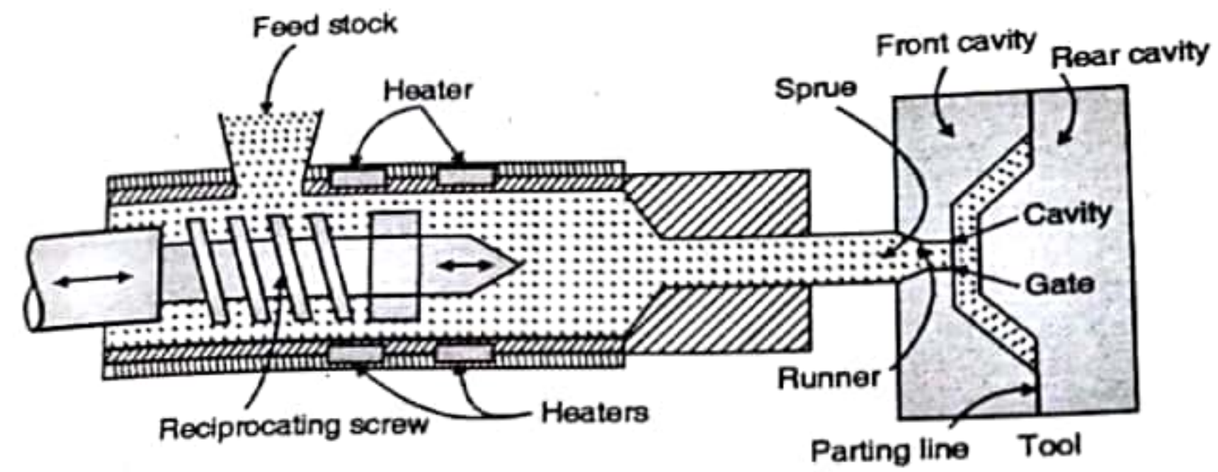


Fig. 2.9.3 : Schematic representation of powder injection moulding equipment

The feed stock is heated, to melt and then is forced through sprue and runner channel as shown in Fig. 2.9.3.

Uses : PIM is used to mould complicated shapes.

Flow sheet of PIM

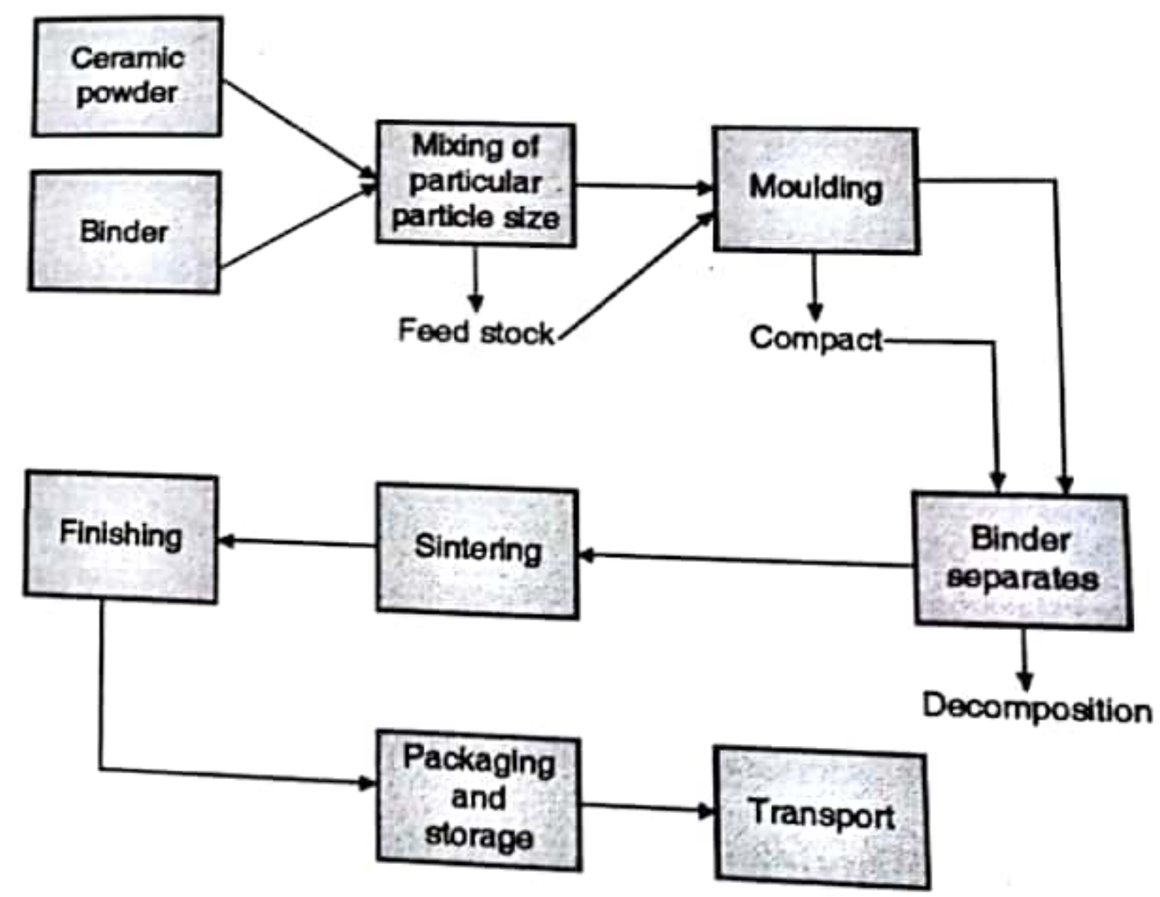
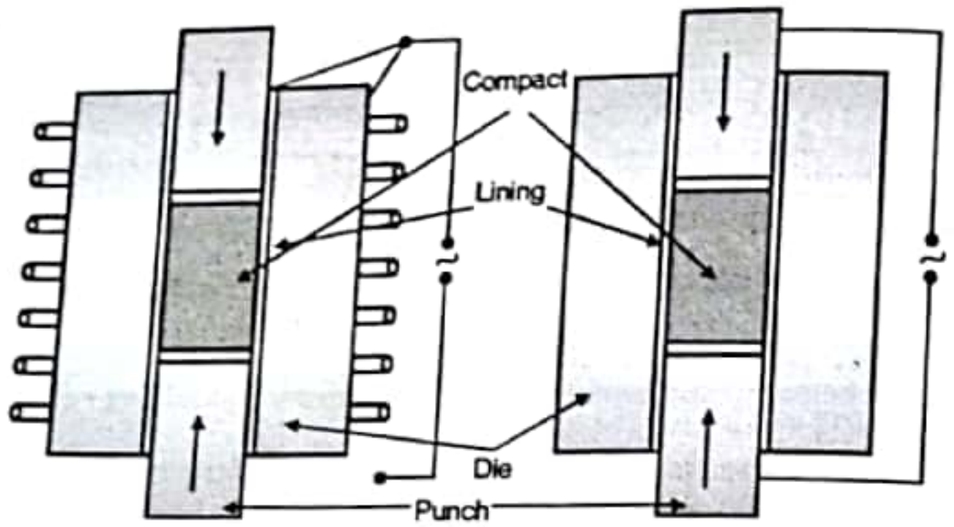


Fig. 2.9.4

2.9.7.3 Hot Compaction

The equipment used is similar to that used in "Cold Pressing", shown in Fig. 2.9.5.



(A) By induction heating (B) by direct current heating

Fig. 2.9.5 : Tooling for axial hot

But the process is operated at higher temperature, and pressure. The ceramic powder with binder are fed into die and pressed at high temperature and pressure, into article, followed by sintering and finishing. The temperature can be raised by direct current of induction current.

Uses :

Process is used for making tools such as metal bonded diamond tools, or carbide compacts.

2.9.8 Manufacture of Oxide and Non-oxide Ceramic Powders

MU - May 2012, Dec. 2012

The oxides / Non oxides ceramics are made into powders, with different particle size and varying properties, such as,

(a) Composition of phase (b) Chemical composition

(c) Appropriate sinterability (d) Compatibility

(e) Purity etc.

The following methods are used to manufacture ceramic powders :

(1) Solid state reactions

It is suitable method for preparing powders of oxide ceramics. The powder is made from hydroxides / carbonates / other suitable compound which is subjected to thermal decomposition. e.g. Alumina can be made from aluminium hydroxide.

(2) Gas phase reactions

It is suitable for producing powders of oxide ceramics. The method involves vapour phase decomposition or hydrolysis in flame. The process can be made continuous.

e.g. SiO_2 / TiO_2 powders

$$SiCl_4 / TiCl_4 + 2\,H_2O \rightarrow SiO_2 / TiO_2 + 4\,HCl$$

(3) Solid-Gas reactions

It is suitable for both-oxides and Non-oxide ceramic powders. The method involves reaction of metal with oxygen / hydrocarbon / N_2 / NH_3 etc. producing corresponding oxide or non-oxide ceramic powder.

(4) Melting

The method involves arc melting followed by milling, produces oxide ceramic powder of desired particle size.

(5) Reaction in solutions

In this method, precursor of ceramic powder is made into aqueous / non-aqueous solution. The precursor is chosen, which can give oxide ceramic powder (it is starting material). Such solutions are subjected to any of following techniques to form ceramic powders of fine particles. The technique is selected considering nature of ceramic powder to be prepared.

e.g.

(i) For advanced ceramics : Sol-gel process

(ii) For oxide ceramics from organometallic precursor : Solution combustion technique.

(iii) For ZrO_2 powder from $ZrOCl_2$ solution : Hydro thermal decomposition at high temperature and pressure.

(iv) For single compound ceramic like alumina silica etc. : Simple precipitation followed by filtration drying.

(v) **For simple ceramics** : Direct evaporation of freeze drying of solution, if non aqueous solution, it can be by solvent vaporisation.

2.9.8.1 Alumina Powder (Al_2O_3) [Oxide Ceramic Powder]

MU - May 2012, May 2016

Alumina is most widely used ceramic.

There are two types of alumina on the basis of purity :

(a) High purity (b) Low purity

(1) Manufacture

(a) High purity alumina : Purity > 99.99 % it is prepared by using highly pure precursor salts of aluminium such as sulphates / nitrides / chlorides, which are decomposed to give alumina ceramic powder.

(b) Low purity alumina : This is produced from aluminium ore-bauxite by Bayer process – yielding two oxides, i.e. Al_2O_3 and Fe_2O_3 with trace quantity of other oxides. Alumina is separated from other oxides by converting into sodium aluminate which is inturn converted into $Al(OH)_3$ by hydrolysis and then calcined to get Al_2O_3.

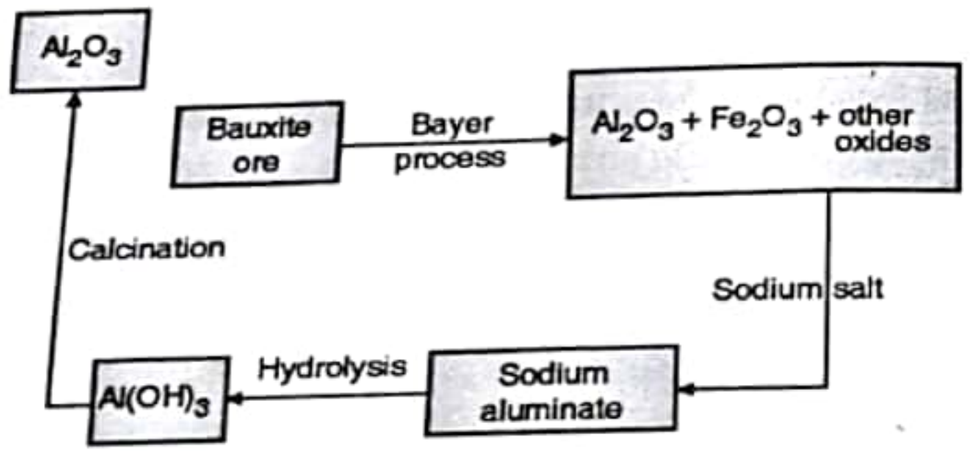


Fig. 2.9.6

(2) Uses of alumina

- High purity alumina is used
  - (1) To make high transluscent tubes used in sodium vapour lamps
  - (2) In various high tech electronic applications,

(3) In other applications which require easy sinterability.

- Low purity alumina powders are used
  - (1) In cutting tools,
  - (2) As bioceramics,
  - (3) In chinaware,
  - (4) For making spark plugs, electronic and machine parts.
  - (5) Special glasses

2.9.8.2 Silicon Carbide [SiC]

MU - Dec. 2012

This is one of the important non-oxide ceramic which is widely used.

Types of SiC

There are α - SiC and β - SiC. Initially [α · SiC] this ceramic was produced as,

$$\underset{\text{(sand)}}{SiO_2} + 3C \xrightarrow[2000 - 3000°C]{4} \underset{\text{crystalline product}}{SiC} + 2\,CO$$

Continuously heated (with graphite electrode) for several hours (≈ 30 hours) to get good crystalline product.

β-Sic can be prepared from $SiCl_4$ by gas phase reaction with hydrocarbons, and carrier gases such as hydrogen or argon. The temperature is generally moderately high as 800 to 1500° C. β-SiC is cubic, where as α-SiC is hexagonal. α-SiC is more stable.

Uses of SiC

This non-oxide ceramic powder is used in manufacture of

(a) Abrasives or wear-resistant materials.

(b) Other sintered materials with certain additives like Boron or carbon.

(c) **Some porous / clay / bonded materials which are recrystallised at high temperatures.**

Syllabus Topic : Applications of Powder Metallurgy

2.10 Applications of Powder Metallurgy

The powder metallurgy, which is widely used as the technology is advantageous. The method is used to manufacture products such as :

(a) Refractory materials

(b) Oil pump gears

(c) Babbit bearings for automobiles

(d) Ferrous products

(e) Electrical contact materials

(f) Diamond impregnated tools

(g) Sintered metal friction material.

(h) Alloys like ferro chromes, solders, wood's metal etc.

Examples

Tungsten wires for lamps can be prepared by using powder metallurgy technique. For this tungsten oxide is reduced using H_2 keeping temperature much lower than melting temperature of metal; i.e. below 3300°C. The tungsten powder obtained is blended with little quantity of ThO_2 (Thorium dioxide), which is followed by stages of compacting, sintering and then finally drawing into wires.

Bearings are manufactured by using powder metallurgy. In this, graphite is mixed with respective metal power *[i.e. of which bearing is desirable for use]*. The blend is compacted in shape, sintered to make bearing. Powder metallurgy method is found to be most suitable for making bearings because it is very difficult to make such bearings using fusion method. The most important aspect is, *there is no need of any lubrication for the bearing made by using powder metallurgy*. This is because the finish of the bearing is such that it minimises the friction to almost nil.

Cutting tools are made using this technique in which an abrasive is blended with metal powder. The *abrasive* used generally are *tungsten carbide*, which is very hard material having high melting point. The blending is then followed by *compacting*, and *sintering* to make cutting tool of desirable shape.

Syllabus Topic : Shape Memory Alloys - Definition, Properties and uses

2.11 Shape Memory Alloys- Definition, properties and Uses

Shape memory alloys

SMAs are the alloys that as if appears to have a memory.

Definition :

The shape-memory alloys (SMA, smart metal, memory metal, memory alloy, muscle wire, smart alloy) are metal alloys undergo deformed at one temperature, but on rising or falling temperature, they return to / regain their "original" shape.

Explaination

SMAs possess two stable forms /phases of material

1. *The martensite forms :* The low-temperature phase, called Martensite.
2. *The austenite forms :* The high-temperature phase, called Austenite

The change in shape involves a phase change in solid state phase with a molecular rearrangement between Martensite and Austenite

Examples

1) Nickel-titanium alloys
2) Copper-base alloys such as CuZnAl and CuAlNi
3) Ag-Cd 44/49 at.% C
4) Au-Cd 46.5/50 at.% Cd
5) Cu-Al-Ni 14/14.5 wt.% Al and 3/4.5 wt.% Ni
6) Cu-Sn approx. 15 at.% Sn
7) Cu-Zn 38.5/41.5 wt.% Z
8) Cu-Zn-X (X = Si,Sn,Al) a few wt.% of
9) In-Ti 18/23 at.% Ti
10) Ni-Al 36/38 at.% Al
11) Ni-Ti 49/51 at.% Ni
12) Fe-Pt approx. 25 at.% Pt
13) Mn-Cu 5/35 at.% Cu
14) Fe-Mn-Si
15) Pt alloys

Properties of SMA

SMA possess :

1. High fatigue strength
2. Excellent corrosion resistance
3. Hysteretic energy dissipation
4. Strain hardening at large strain levels
5. Controlled level of force at moderate strain levels
6. Excellent recentering capability

Uses / Applications

1. Orthopedic applications :
   - Microstents Simon filter Micro wrapper
2. Cardiovascular applications are
   - Microsurgery
   - Reinforce weak blood vessels
   - Promote flow in tubular passages
   - Microstents

- Eliminate vibrations of read/write heads in hard disk drives

3. Intravascular Therapy
   - Micro assembly for MEMS devices
   - Facilitates access to intricate regions of the body
   - Grab tiny foreign objects for removal from the body

Important Terms and Definitions

- An alloy is a solid mixture of two or more metals or non-metals an alloy is a substance/material formed by solidification of metallic solution of two or more metals/elements.
- Alloy can also be defined as a solid solution where the solutes are the alloying elements whereas the solvent is the element in excess proportion (base or main metal).
- The eutectic point or temperature is a physical constant of the homogenous mixture of two different elements. It signifies that the percentages of two different elements making homogeneous mixture composition gets disturbed.
- The *fix percentages* of two elements *at eutectic point* is known as *eutectic composition,* For example, Pb/Ag system, at 303°C while composition is Pb : Ag = 97.5 : 2.5 which is eutectic composition.
- The alloys of iron as a major constituent, with other metal(s) or/and non-metal are known as *ferrous alloys.* These are commonly known as *alloy steels.*

  Plain carbon steels : The alloy of iron and carbon are *Widely* known as plain carbon steels)
- Brasses are alloys of copper and zinc in varying percentages
- Bronzes are the alloys of copper and tin in varying percentages
- Solders are the alloys of Lead with other metals except Iron.

Powder metallurgy is a process which deals with the product of useful components from fine metal powders, from individual, mixed or alloyed with or without the inclusion of non-metallic constituents.

Review Questions

A) Ferrous Alloy

Q. 1 What are alloys ? What are the purposes of making alloy ?

Q. 2 Discuss briefly the principle of alloying.

Q. 3 What are alloy steels ? What is the purpose of making alloy steels ?

Q. 4 What are the specific effects of the following elements on the properties of steel ?
(1) Chromium (2) Cobalt
(3) Molybdenum (4) Vanadium (5) Tungsten

Q. 5 What are special steels ?

B) Non-Ferrous Alloy

Q. 1 Write short note on : (a) Alloys of copper (b) Alloys of aluminium (c) Alloys of lead

Q. 2 What are brasses ? List the varieties of brasses giving their composition, properties and uses.

Q. 3 Discuss important types of bronzes stating their composition, properties and uses.

Q. 4 Distinguish between brasses and bronzes.

C) Powder Metallurgy

Q. 1 What is powder metallurgy ? What are its salient features ?

Q. 2 What are advantages of powder metallurgy ?

Q. 3 What are disadvantages of powder metallurgy ?

Q. 4 How are metal powders prepared ?

Q. 5 Explain
a) Atomisation
b) Mechanical communition / Pulvurisation
c) Reduction of metal oxides / Chemical reduction
d) Electrodeposion / Electrolytic process

Q. 6 Explain the following :
a) Mixing and blending of metal powders
b) Compacting the material
c) Sintering process

Q. 7 List the important applications of powder metallurgy.

Q. 8 Explain how powder metallurgy is an useful technique.

Q. 9 Write notes on :
(a) Cold pressing (b) PIM(c) Hot compaction

Q. 10 How would you prepare oxide or non-oxide ceramic powders.

Q. 11 Write notes on :
(a) Alumina (b) Silicon carbide

Q. 5 Write a note on Compacting and Sintering.
(Ans. : Refer sections 2.9.7 and 2.9.6) **(May 2013)**

Q. 6 How are metal powders prepared ? *(Ans. : Refer section 2.9.4)* **(Dec. 2013)**

Q. 7 List various steps involved in powder metallurgy. Mention the aim of each step. Give any two advantages of powder metallurgy.
(Ans. : Refer sections 2.9.1 and 2.9.2) **(May 2014)**

Q. 8 How are metal powders prepared using.
(i) Atomization *(Ans. : Refer section 2.9.4.2)*
(ii) Chemical reduction *(Ans. : Refer section 2.9.4.3)* **(May 2015)**

Q. 10 Explain manufacture of high purity alumina ceramic powder.
(Ans. : Refer section 2.9.8.1) **(May 2016)**

□□□

CHAPTER 3

MODULE 3

Fuels

Syllabus

Fuels :

Definition, classification of fuels-solid, liquid and gaseous. Calorific value-Definition, Gross or Higher calorific value & Net or lower calorific value, units of heat (no conversions), Dulong's formula & numerical for calculations of Gross and Net calorific values. Characteristics of a good fuel. Solid fuels-Analysis of coal- Proximate and Ultimate Analysis with Significance and numericals. Liquid fuels- Crude petroleum oil, its composition and classification and mining (in brief). Refining of crude oil- i) Separation of water ii) Separation of 'S' & iii) Fractional Distillation with diagram and composition and uses table. Cracking- Definition, Types of crackingI) Thermal cracking – (i) Liquid phase thermal cracking (ii) Vapour phase thermal cracking. II) Catalytic cracking- (i) Fixed-bed catalytic cracking (ii) Moving-bed catalytic cracking. Advantages of Catalytic cracking. Petrol- Refining of petrol, unleaded petrol (use of MTBE), Catalytic converter, Power alcohol, Knocking, Octane number, Cetane number, Antiknocking agents.

Combustion- Calculations for requirement of only oxygen and air (by weight and by volume only) for given solid & gaseous fuels.

Biodiesel- Method to obtain Biodiesel from vegetable oils (Trans-esterification), advantage and disadvantages of biodiesel.

Fuel cell- Definition, types and applications.

Introduction

- Fuels are all those substances which on combustion give large amount of heat energy.
- During combustion they combine with oxygen to form various combustion products, and side by side produce a huge amount of heat energy.

- Thus fuel is an essential requirement of industries as well as of domestic operations, to get heat energy required to conduct various processes.

Syllabus topics : Fuels Definition

3.1 Definition

- Fuels can be defined as, "substances which undergo combustion in the presence of air to produce a large amount of heat that can be used economically for domestic and industrial purpose".
- This definition does not include nuclear fuel because it cannot be used easily by a common man.
- The various fuels used economically are wood, coal, kerosene, petrol, diesel gasoline, coal gas, producer gas, water gas, natural gas (LPG) etc.
- The fossil fuels such as wood, vegetable oils etc., which burn to produce heat are called as chemical fuels.

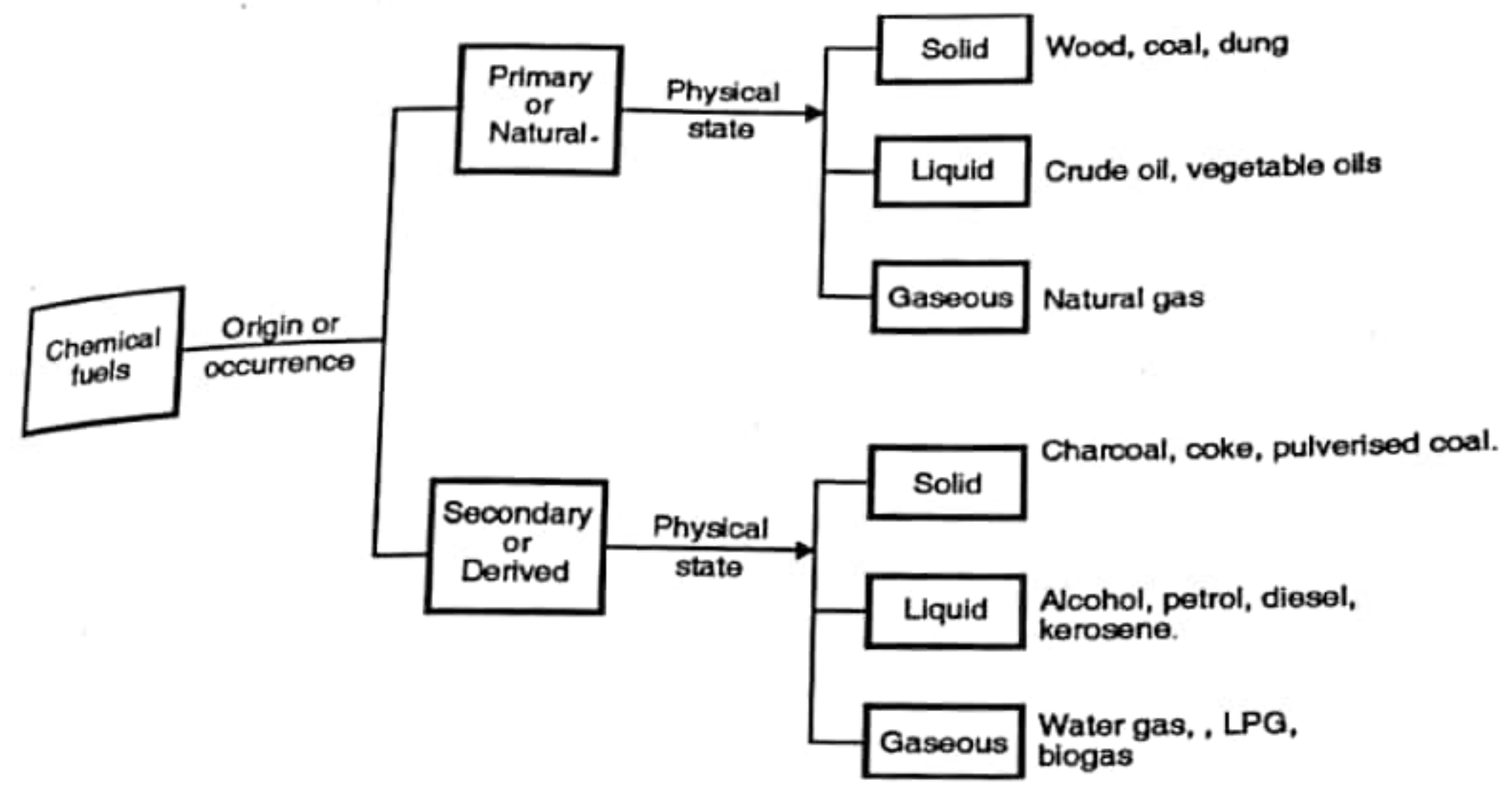
Syllabus topic : Classification of Chemical Fuels - solid, liquid and gaseous

3.2 Classification of Chemical Fuels

- Chemical fuels can be broadly classified on the basis of origin as,
  - (i) Primary or natural fuels
  - (ii) Secondary or artificial or derived fuels.
- On the basis of physical state both the fuels are further classified into :
  - (i) Solid fuels
  - (ii) Liquid fuels
  - (iii) Gaseous fuels
- Primary and secondary fuels can be in any physical state. The following table summarises the fuels in different classes on the basis of their origin and physical state.

Thus, the Table 3.2.1 shows the various fuels categorized on the basis of their origin and/or physical state.

Table 3.2.1 : Classification of fuels



Syllabus topic - Calorific Value – GCV and NCV

➢ **Topic covered :** Definition, Ignition temperature, Units, Dulong formula, numerical

3.3 Calorific Value – GCV and NCV

- Amongst all the above properties, the most important for fuels is calorific value; which can be defined as *"the number of units of heat evolved during complete combustion of unit weight of the fuel"*.
- Calorific value can also be defined as, "the number of parts of water which gets heated through 1°C by the heat evolved by the complete combustion of one unit weight of fuel (unit volume for gaseous fuels) under the conditions such as, (i) whole of heat evolved is absorbed by water (ii) the products formed leave the system at atmospheric temperature and pressure".
- From both the above definitions, it is clear that a fuel, to be most useful, must possess high calorific value because the heat evolved by combustion of definite weight of fuel is directly related/proportional to the calorific value of the fuel.

Ignition temperature

- Ignition Temperature is " Minimum temperature to which a substance must be heated before it burns spontaneously independently of the source of heat; e.g. ethanol has an ignition temperature of 425°C/798°F and a flash point of 12°C/54°F.
- Each fuel should be brought above its Ignition Temperature for starting the combustion process. An appropriate air-fuel ratio is also necessary. The minimum ignition temperature at atmospheric pressure for some substances are:
  - carbon 400° C
  - gasoline 260° C
  - hydrogen 580° C
  - carbon monoxide 610° C
  - methane 630° C

3.3.1 Units of Calorific Value

- The calorific value of solid fuels is expressed as British Thermal Units per Pound (B.T.U. per 1b) or Kilogram Centigrade Unit per kilogram (K.C.U. per kg.)
- A British Thermal Unit may be defined as, the heat required to raise the temperature of one pound of water from 60° F to 61° F.
- The Calorie, a unit of heat may be defined as, the heat required to raise the temperature of one kg of water from 15°C to 16°C.
- Taking both above definitions of these units, a correlation between them be writes as,

$$1 \text{ B.T.U.} = 2.252 \text{ k.cals} = 252 \text{ cals}$$
$$1 \text{ k.cal} = 1000 \text{ cals}$$
$$1 \text{ k.cal} = 3.968 \text{ B.T.U.}$$

- The calorific value can also be expressed as centigrade heat unit (C.H.U) which is the amount of heat required to raise temperature of 1 pound water through one degree centigrade.

$$\text{Thus } 1 \text{ k.cal} = 2.2 \text{ C.H.U} = 3.968 \text{ B.T.U.}$$

$$\text{Also } 1 \text{ k.cal/kg} = 1.8 \text{ BTU/1b}$$
$$1 \text{ k.cal/m}^3 = 0.1077 \text{ BTU/ft}^3$$
$$1 \text{ BTU/ft}^3 = 9.3 \text{ k.cals/m}^3$$

3.3.2 High and Low Calorific Values

- Calorific values are of two types as,
  (i) High or Gross Calorific Value (H.C.V. or G.C.V.)
  (ii) Low or Net Calorific Value (L.C.V. or N.C.V.)
- High calorific value may be defined as, "the total amount of heat products when one unit of the fuel has been burnt completely and the products combustion have been cooled to 16°C or 60°F".
- Low calorific value may be defined as, "the net heat produced when unit mass or volume of fuel is completely burnt and products are allowed to escape".

Thus,

Net or low C.V. = Gross C.V. – Latent heat of water formed

Or = Gross C.V – Mass of hydrogen × 9 × Latent heat of steam

(Because 1 part by weight of hydrogen produces 9 parts (1 + 8) by mass of water)

3.3.3 Dulong Formula

- The calorific value of fuels (e.g. Coal) is determined theoretically by Dulong formula, or I.A. Davies formula.
- Dulong formula can be expressed as,

$$Q = \frac{1}{100}\left[8080\,C + 34500\left(H - \frac{O}{8}\right) + 2240\,S\right]$$

Where,
Q = Calorific value in K.C.U/kg
C = % Carbon
H = % Hydrogen
O = % Oxygen
S = % Sulphur

In this formula, it is assumed that calorific value of fuel is nothing but the sum total of calorific values of each element and oxygen in fuel (coal) is in combined state as water and hence it does not contribute to heating value of fuel.

The same formula in terms of H.C.V and L.C.V can be expressed as,

$$H.C.V = \frac{1}{100}\left[8080\,C + 34500\left(H - \frac{O}{8}\right) + 2240\,S\right]$$

and $$L.C.V = \left[H.C.V - \frac{9}{100}H \times 587\right]$$

Experimentally the calorific value of solid and liquid fuels is determined by using Bomb calorimeter.

Example 3.3.1 : *A sample of coal contains, C = 60%; O = 33%; H = 6%; S = 0.5%; N = 0.3%; Ash = 0.2%. Calculate the gross calorific value of the coal.*

Solution :

$$\text{Gross calorific value} = \frac{1}{100}\left[8080C + 34500\left(H - \frac{O}{8}\right) + 2240\,S\right]$$

(or H.C.V)

$$= \frac{1}{100}\left[8080 \times 60 + 34500\left(6 - \frac{33}{8}\right) + 2240 \times 0.5\right]$$

$$= 5506 \text{ kcal/kg.}$$

$$\text{Net calorific value} = [H.C.V. - (0.09 \times \%H \times 587)]$$

(or L.C.V)

$$= 5506 - (0.09 \times 6 \times 587) = 5506 - 316.98$$

$$= 5189.02 \text{ kcal/kg}$$

Ans. :	*H.C.V = 5506 kcal/kg*
	L.C.V = 5189.02 kcal/kg

Example 3.3.2 : *A sample of coal has the following composition by mass : C = 70%, H = 9%, and O = 4%, S = 2%, N = 1%, and Ash = 14%. Calculate gross calorific value of the fuel using Dulong's formula.* **MU - May 2016, 3 Marks**

Solution :

Given data

C = 70%	S = 2%
H = 9%	N = 1%

O = 4%	Ash = 14%

To calculate GCV and NCV of coal sample

$$GCV = \frac{1}{100}\left[8080\,C + 34500\left(H - \frac{O}{8}\right) + 22405\right]$$

$$= \frac{1}{100}\,[8080 * 70 + 34500\,(9 - 4/8) + 2240 * 2]$$

$$= \frac{1}{100}\,[565600 + 293250 + 4480] = \frac{1}{100}\,[863330]$$

$$= 8633.30 \text{ kcal/kg}$$

$$\therefore \quad \mathbf{GCV = 8633.30\ kcal/kg}$$ **...Ans.**

$$\text{Now} \quad NCV = GCV - (0.09 \times \%\,H \times 587)$$

$$= 8633.30 - (0.09 \times 9 \times 587)$$

$$= 8633.30 - 475.47$$

$$= \mathbf{8157.83\ kcal/kg}$$ **...Ans.**

Syllabus Topic : Characteristic Properties of Good Fuels

> **Topics covered :** Characteristic Properties of Good Fuels, comparison between solid, liquid and gaseous fuels

3.4 Characteristic Properties of Good Fuels

MU – Dec. 2012

- Fuels are characterized by testing certain physical and chemical properties.
- The physical properties for which fuels are tested and their ideal requirements are listed below. This help in selection of a fuel for given purpose :
  - (i) Calorific value should be as high as possible.
  - (ii) Ignition temperature - Moderate
  - (iii) Flame temperature should be as high as possible.
  - (iv) Flash and Fire point should be as high as possible.
  - (v) Aniline point should be low.
  - (vi) Cloud and Pour point should be as low as possible.
  - (vii) Viscosity should be adequate.
  - (viii) Coke number should be as high as possible.
  - (ix) Moisture content – As low as possible.

(x) Volatile matter – As low as possible

(xi) Ash matter should be absent

(xii) Easy risk free transportation should be possible.

(xiii) Storage space – Ideally fuel should occupy small space.

(xiv) Air requirements – Adequate

(xv) Harmless products should be produced on combustion.

- The chemical properties include the compositional analysis of fuel. This includes :

For solid and liquids fuels

(i) Percentage of various elements such as C, H, O, N, S, etc.

(ii) Percentage of moisture

(iii) Percentage of volatile matter

For gaseous fuels

(i) Percentage of combustible gases e.g. – CO, H_2, CH_4, C_2H_4, C_2H_6, C_4H_{10}, H_2S etc.

(ii) Percentage of non-combustible gases e.g. N_2, CO_2 etc.

3.4.1 Comparison of Solid, Liquid and Gaseous Fuels

Fuels are classified into three types viz. solids, liquids and gases. Their utility depends upon various factors which are discussed in Table 3.5.1. All fuels have some disadvantages which can be overcome by individual industry.

Table 3.4.1 : Comparison of solid, liquid and gaseous fuels

Sr. No.	Property	Solid Fuels	Liquid Fuels	Gaseous Fuels
1.	Calorific value	Low	Higher	Highest
2.	Specific gravity	Highest	Medium	Lowest
3.	Ignition point	High	Low	Lowest
4.	Efficiency	Poor	Good	Best
5.	Air required for combustion	Large and excess of air	Less excess of air	Slight excess of air
6.	Use in I.C. engine	Cannot be used	Already in use	Can be used
7.	Mode of supply	Cannot be piped	Can be piped	Can be piped

Sr. No.	Property	Solid Fuels	Liquid Fuels	Gaseous Fuels
8.	Space for storage	Large	50% less than solid fuel	Very high space
9.	Relative cost	Cheaper	Costly	More costly than other two
10.	Care in storage and transport	Less care required	Care is necessary	Great care required

Syllabus Topic : Solid Fuels

➤ **Topic covered :** Analysis of coal-Proximate and Ultimate Analysis with Significance and numericals

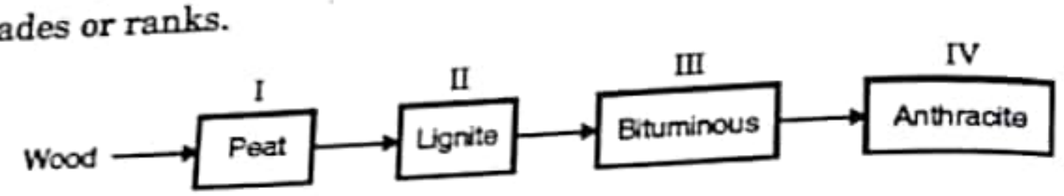
3.5 Solid Fuels

- The solid fuels are available in nature (primary fuels) and also prepared artificially known (secondary fuels).
- The common natural solid fuels are wood, peat, lignite and coal.
- The artificial solid fuels are charcoal, coke, briquettes.
- Other industrial fuels are fossil coals, oil shales, furnace slags, peat, boiler slags, anthracite etc.
- Coal is a combustible solid fuel. By and large, all the solid fuels are formed in nature from cellulose, lignin, proteins, resins, fats and waxes.
- All these raw materials, which are formed under the earth by the burials of partially decomposed vegetation, undergo fermentation liberating CH_4, CO_2 and H_2 gas and form peat, which is slowly converted into lignite and then by further pressure and heat, anthracite is formed.
- Transformation of coal in *lignite to anthracite* is known as *metamorphism or progressive alteration* in natural series.

3.5.1 Coal

- A mined sample of coal contains the coal substance, intermixed with mineral constituents such as kaolin, shale, chloride, sulphides etc. The major constituents of coal are carbon, hydrogen and oxygen. The properties of coal depend upon these constituents.

- There are hundreds of varieties of coal, depending upon its origin and chemical constituents of coal. The important types of coal are peat, lignite, bituminous and anthracite coal. The composition of these major types of coal is given in Table 3.6.2.
- The conversion wood (plant matter) into coal takes place progressively. Depending upon the extent of transformation, coals are divided into 4 types, or grades or ranks.



- During the progressive conversion from peat to anthracite there is;

Increase in carbon percentage, calorific value, density, lusture, hardness, black colour intensity.

Decrease in moisture, volatile matter, % of N, H, O, S, ash

I) Peat

i) Peat is brown and fibrous in texture.

ii) Freshly mined out peat contains large quantity of water as it is found in water logged areas.

iii) Air dried peat contains 15-25% moisture and it crumbles into powder during air drying.

iv) Calorific value of peat is about 5400 cal/gm

v) It has low density.

vi) It contains 57% C, 6% H, 35% O, 3-6% ash.

Uses

i) Peat type of coal gets powdered during combustion, therefore it is used after briquetting, as domestic and industrial fuel.

ii) It is used for soil conditioning.

iii) On carbonization (heating in absence of air) at 500° C, it produces charcoal light spirits.

iv) It can be used for steam raising, thermal insulation, packing, gas purification and some times for power generation.

II) Lignite

i) It is the intermediate stage between peat and black coal.

ii) It is brownish black and more compact than peat.

iii) It contains 45-50% volatile matter and burns with long flame.

iv) Its C.V. is 6000-6700 cal/gm and C% = 65-70%.

v) It contains 5% H, 20% O, 10-15% ash.

Uses

i) After briquetting it is used as domestic and industrial fuel.

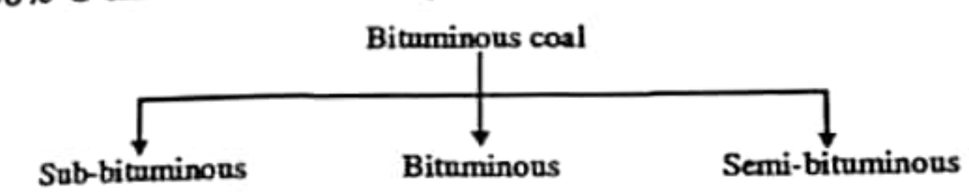
ii) Lignite is used for making 'producer gas'.

iii) It can be used for power generation.

iv) On carbonisation, it gives tar, which is used for making road and recovering various aromatic chemicals.

III) Bituminous Coals

These coals burn with smoky yellow flame and are dark-grey to black. They contain 70-90% C and therefore they are further classified as;



a) Sub-bituminous coal

- This coal has characters between lignite and bituminous coal.
- It is harder and denser than lignite. It is grey black and has dull waxy lusture.
- Its C.V. is about 7000 cal/gm and 70-75% C. It contains large volatile matter 35-40%.
- It crumbles into pieces on air drying and during transportation.
- It is non-caking coal.

Uses :

This coal is used for domestic and industrial purposes.

b) Bituminous coal

- This coal has *banded or laminated* structure with alternate bright and dull layers.
- It has cubical fracture.
- It is black, dense and hard.

- It contains 75-85% C and has C.V. 8000-8500 cal/gm.
- It is a caking coal and forms *coke* and *coal gas* on carbonisation, as it contains 20-30% of volatile matter.

Uses

i) For making metallurgical coke and coal gas as source of various aromatic chemicals.

ii) It is used most widely for domestic and industrial purposes.

iii) It is used for steam generation and power generation.

c) Semibituminous coal

- It has characters between bituminous and anthracite coals.
- It has low volatile matter and caking property. (caking = coal decomposing at about 400° C, melting, forming a plastic mass through which V.M. blows out forming highly swollen open structured coal called as coke.)
- Its C.V. is about 8400 cal/gm, C% = 85-90%.

Uses

Making of coke, high temperature heatings, coal gas for tar and chemicals.

IV) Anthracite Coal

This is the highest rank or grade coal.

i) It has C.V. about 8700 cal/gm and 92-98% C.

ii) It contains very low V.M., ash, moisture.

iii) It is highly lustrous black and hard coal.

iv) It shows chonchoidal fracture.

v) It burns with non-smoky short blue flame of high temperature.

Uses

i) Being costly coal, it is used for specific industrial purposes.

ii) It is used as metallurgical fuel.

iii) It is used for making electrodes.

iv) It is used for high temperature heatings.

Table 3.5.1 : Types of coals and their chemical composition

Sr. No.	Types of Coal	Moisture of Air Dried At 40°C	C%	H%	O%	Ash%	Calorific Value (kcal/kg)	Uses	Volatile matter %
1.	Peat	15-25%	57	≈ 6	35	3-6	5400	Power generation and domestic purpose.	
2.	Lignite	20	65 to 70	≈ 5	20	10-15	6000 to 6700	Manufacture of producer gas, thermal power plants.	45 to 50
3.	a) Sub-Bituminous	Low	70 to 75%	5	15	7	≈ 7000	For metallurgical	35-40%
	b) Bituminous	Low	75 to 85%	5	15	7	8000-8500	coke, coal gas, boiler,	20-30%
	c) Semi-Bituminous	Low	85 to 90%				≈ 8400	domestic purpose	Low
4.	Anthracite	Low	92 to 98%	≈ 3-4	≈ 2-3	Low	8700	Boilers, metallurgical fuel, domestic	Low

The selection of the coal is made by knowing these properties of different types of it given in Table 3.5.1. Thus it becomes easy to select the coal for a particular process. The Table 3.5.1 shows that, as carbon increases from peat to anthracite, the calorific value also increases. The moisture content decreases from peat to lignite. The selection of coal depends on its calorific value, moisture content, ash content and impurities present in it.

3.5.2 Analysis of Coal

The purposes for coal analysis are :

i) To decide price of coal.

ii) To determine quality.

iii) To specify use of coal for a particular purpose.

iv) To calculate theoretical calorific value of coal.

v) To calculate air requirement for complete combustion of coal and design the furnace fire box suitably.

A sample of coal taken out from coal mine is analyzed in two ways :

I) Proximate analysis

II) Ultimate analysis.

Analysis of coal

- Proximate Analysis
  - (1) Moisture %
  - (2) Volatile matter %
  - (3) Ash %
  - (4) Fixed Carbon %
- Ultimate Analysis
  - (1) Carbon and hydrogen %
  - (2) Nitrogen %
  - (3) Sulphur %
  - (4) Ash %

The proximate analysis is easy and quicker and it gives a fair idea of the quality of coal. The ultimate analysis is essential for calculating heat balances in any process for which coal is employed as a fuel.

3.5.2.1 Proximate Analysis of Coal

Proximate analysis is the study or analysis of coal sample in which the following constituents are estimated.

a) moisture %
b) volatile matter %
c) ash %
d) fixed carbon %

Procedure for proximate Analysis of coal

a) Moisture %

- A known weight of powdered and air dried coal sample is taken in a crucible (weighed) and it is placed in preheated oven for 1 hour at 110° C. Then the coal is cooled in a dessicator and weighed out.
- If the initial weight of the coal is m gms and final weight is m_1 gms.
- Then the loss in weight $(m - m_1)$ corresponds to moisture in coal.

$$\text{Moisture \%} = \frac{\text{loss in weight}}{\text{weight of coal sample}} \times 100 = \frac{(m - m_1)}{m} \times 100$$

b) Volatile matter (V.M.) %

- Moisture free coal left in the crucible in first experiment (m_1) is covered with a lid loosely. Then it is heated at 925° ± 20°C in a muffle furnace for 7 minutes.

- The crucible is taken out and cooled in a dessicator. Then it is weighed again, $(m_2$ gms).
- The loss in weight $(m_1 - m_2)$ is due to loss of volatile matter in the m gms of the coal sample. (Volatile matter is the lower molecular weight organic compounds in coal and they decompose coal during burning of coal and escape without combustion, in the form of smoke).

$$\text{volatile matter \%} = \frac{\text{Weight of volatile matter}}{\text{Weight of air dried coal}} \times 100$$

$$= \frac{(m_1 - m_2)}{m} \times 100$$

- The volatile matter % can also be determined by taking the fresh weight of the air dried coal but the loss in weight at 925° C, will be due to loss of moisture and volatile matter both.
- If w is the weight of air dried coal and w_1 is the mass of coal left at 925° C heating, then

$$\text{Volatile matter \%} = \frac{\text{loss in weight due to moisture and V.M.} \times 100}{\text{Weigth of coal sample}} - \text{moisture \%}$$

$$= \frac{(w - w_1) \times 100}{w} - \text{moisture \%}$$

c) Ash %

- The residual coal in the above experiments is heated and burnt in a open crucible at above 750° C for half an hour.
- The coal gets burnt. The ash left in crucible is cooled in a dessicator and weighed (m_3g).

$$\text{Ash \%} = \frac{\text{weight of ash}}{\text{weight of coal}} \times 100 = \frac{m_3}{m} \times 100$$

d) Fixed carbon %

It is found by calculation, as follows,

$$\text{F.C. \%} = 100 - (\text{moisture \%} + \text{V.M. \%} + \text{ash \%})$$

3.5.2.2 Significance/ Importantance of Proximate Analysis

a) Moisture

i) It decreases calorific value of coal largely as it does not burn and takes away heat in the form of latent heat.

ii) It increases ignition point of coal.

Hence, a coal with lower moisture % is better quality.

b) Volatile matter

i) It decreases calorific value of coal.

ii) It elongates flame and decreases flame temperature.

iii) It forms smoke and pollutes air.

- The coals containing 15-25% of V.M. on carbonisation gives coke oven gas which is the source of various organic aromatic chemicals.
- Such coals have good caking property and coke can be obtained from the coals.

iv) The coal with lesser V.M. is better quality coal.

c) Ash

i) Ash reduces calorific value of coal as ash is non-burning part in coal.

ii) Ash disposal is a problem.

iii) Ash fuses to form clinker at high temperature, obstructing the air supply to coal burning in furnace.

Hence, lesser the ash %, better is the quality of coal.

d) Fixed carbon

- Carbon is the burning part in coal and higher the FC% higher is calorific value.
- Hence a good quality coal should have high FC%.

Example 3.5.1 : *A sample of coal was analysed for content of moisture, volatile matter ash and fixed carbon From following data, calculate the percentage of the above quantities.*

(i) Weight of coal taken = 2.5 gms.

(ii) Weight of coal after heating at 100 °C = 2.365 gms.

(iii) Weight of coal after heating covered crucible at 950 ± 20° C = 1.165 gms.

(iv) Constant weight obtained at the end of experiment = 0.460 gms.

Solution :

Given data : Wight of coal = 2.5 gm = m

Weight of coal after heating at 100°C = 2.365 gm = m_1,

Weight of coal after heating at 950° ± 20°C = 1.165 g = m_3

(a) $$\text{Moisture \%} = \frac{\text{Loss in weight}}{\text{Weight of coal sample}} \times 100$$

$$= \frac{m - m_1}{m} \times 100 = \frac{(2.5 - 2.365)}{2.5} \times 100$$

$$= 0.185 = \frac{0.185}{2.5} \times 100$$

$$= \boxed{7.4\ \%}$$

(b) $$\text{Volatile matter (\%)} = \frac{\text{Loss in weight due to volatile matter}}{\text{Weight of coal taken}} \times 100$$

$$= \frac{m_1 - m_3}{m} \times 100 = \frac{2.365 - 1.165}{2.5} \times 100$$

$$= \frac{1.200}{2.5} \times \frac{100}{1}$$

$$= \boxed{48\ \%}$$

(c) $$\text{Ash\%} = \frac{\text{Weight of ash}}{\text{Weight of coal}} \times 100 = \frac{0.460}{2.5} \times 100$$

$$= \boxed{18.4\%}$$

(d) $$\text{Fixed carbon \%} = 100 - [\text{\% moisture} + \text{\% V. M} + \text{\% Ash}]$$

$$= 100 - [7.4 + 48.0 + 18.4] = 100 - [73.8]$$

$$= \boxed{26.2\%}$$

Ans. :

Moisture content = 7.4%,
Volatile matter content = 48%,
Ash content = 18.4%.
Fixed carbon content = 26.2%

3.5.2.3 Ultimate Analysis of Coal

The analysis of coal in which percentages of C, H, N, S and O (elements) are found out, is known as ultimate analysis.

a) % of C and H in coal

- A known weight of powdered and air dried coal sample is burnt in the presence of pure oxygen, in a combustion apparatus. C and H are converted to CO_2 and H_2O vapours respectively.
- The gaseous products are passed first through the preweighed U-tube containing anhydrous $CaCl_2$ (absorbs H_2O vapours) and then through the KOH solution in a preweighed U-tube (absorbs of CO_2).
- The increase in weight of U-tube containing anhydrous $CaCl_2$ corresponds to weight of water formed and increase in weight ofU-tube containing KOH solution corresponds to CO_2 formed, by combusting the coal sample.

$C + O_2 \rightarrow CO_2$; $2\,KOH + CO_2 \rightarrow K_2CO_3 + H_2O$

12 44

$H_2 + \frac{1}{2}\,O_2 \rightarrow H_2O$; $CaCl_2 + 7\,H_2O \rightarrow CaCl_2 \cdot 7\,H_2O$

2 18

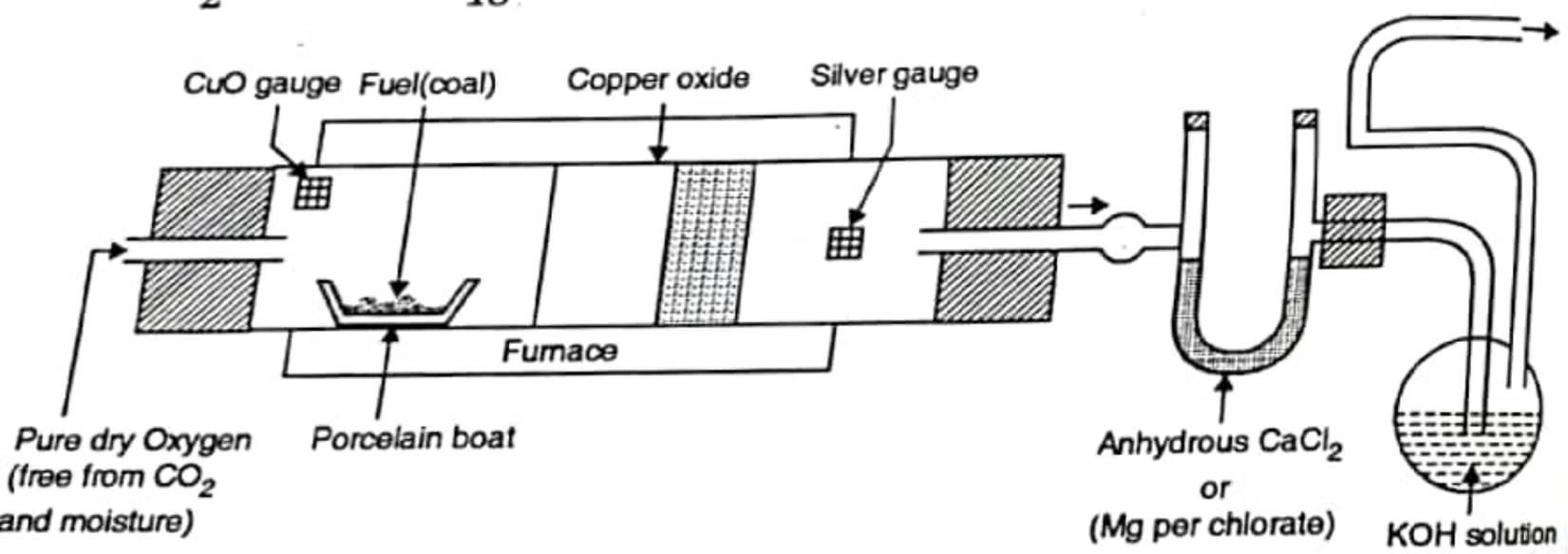


Fig. 3.5.1 : Combustion apparatus

The %C and %H are calculated as follows,

$$C\,\% = \frac{\text{Weight of } CO_2 \text{ formed}}{\text{Weight of coal sample}} \times \frac{12}{44} \times 100$$

$$H\,\% = \frac{\text{Weight of } H_2O \text{ formed}}{\text{Weight of coal sample}} \times \frac{2}{18} \times 100$$

Example 3.5.2 : *0.2 gm of coal sample is accurately weighed and is burnt in a combustion apparatus. The gaseous products of combustion are absorbed in potash bulb and calcium chloride tubes of known weight. The increase in weight of potash bulb and $CaCl_2$ tubes are 0.66 gm and 0.08 gm respectively. Calculate the percentage of carbon and hydrogen in the coal sample.*

Solution :

Weight of sample : 0.2 gms

Weight of CO_2 formed : = increase in wt of potash bulb = 0.66 gms

Weight of H_2O formed : = increase in $CaCl_2$ bulb = 0.08 gms

Reactions

$C + O_2 \rightarrow CO_2$ $\qquad$ $2\,KOH + CO_2 \rightarrow K_2CO_3 + H_2O$

12 32 44

$H_2 + \frac{1}{2}O_2 \rightarrow H_2O$ $\qquad$ $CaCl_2 + 7\,H_2O \rightarrow CaCl_2 \cdot 7\,H_2O$

2 16 18

$$\%\ \text{Carbon} = \frac{\text{Weight of } CO_2 \text{ formed}}{\text{Weight of coal sample}} \times \frac{12}{44} \times 100$$

$$= \frac{0.66}{0.2} \times \frac{12}{44} \times 100 = \boxed{90\ \%}$$

$$\%\ \text{Hydrogen} = \frac{\text{Weight of } H_2O \text{ formed}}{\text{Weight of coal}} \times \frac{2}{18} \times 100$$

$$= \frac{0.08}{0.2} \times \frac{2}{18} \times 100 = \boxed{4.4\ \%}$$

Ans. :

% Carbon	*= 90 %*
% Hydrogen	*= 4.4 %*

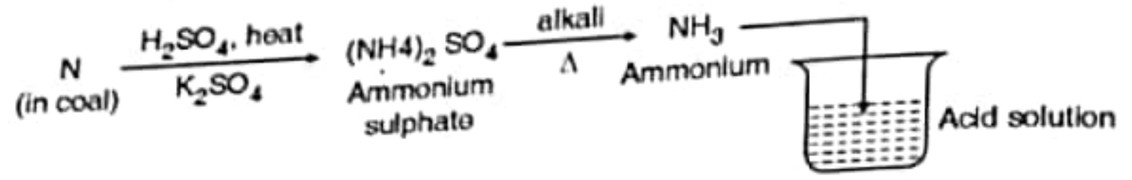
b) Nitrogen in coal

- A known weight of powdered and air dried coal is heated with concentrated H_2SO_4 alongwith K_2SO_4 catalyst in a long necked *Kjeldahl* flask.
- After the contents become clear, it is treated with alkali solution in a round bottom flask. The ammonia (basic gas) liberated is passed in known volume of standard acid solution.
- The unused acid is determined by back titration with NaOH solution.
  - i) Mass of coal = m gm.
  - ii) Volume of x N acid in which NH_3 is passed = V_1 m*l*.

iii) Volume of acid unused = V_2 m*l*

iv) Volume of the acid consumed by $NH_3 = (V_1 - V_2)$ m*l*.

$$N\ \% = \frac{\text{Volume of acid consumed} \times \text{normality of acid} \times 1.4}{\text{Weight of coal sample}}$$



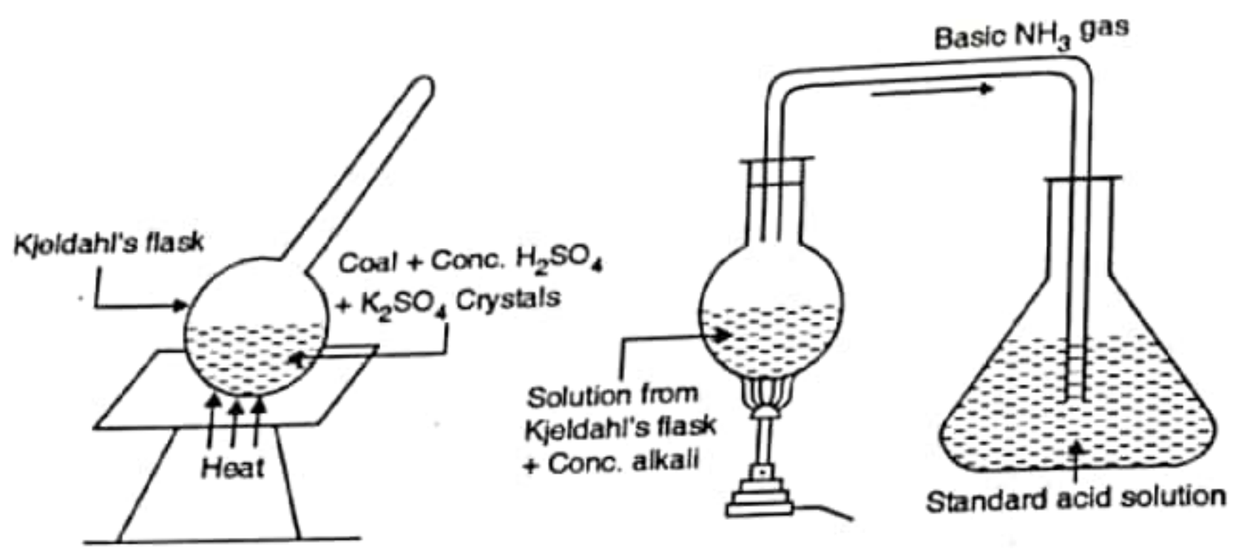


Fig. 3.5.2 : Estimation of nitrogen in coal

c) **Sulphur in coal**

- Take about 10 m*l* of distilled water in the Bomb pot. Burn the known weight of powdered and air dried coal sample in the Bomb calorimeter experiment.
- Then collect the washings of the Bomb pot in a beaker. Add $BaCl_2$ solution in it.
- Filter the precipitate of $BaSO_4$, dry it and weigh the precipitate of $BaSO_4$. From weight of $BaSO_4$ precipitate, calculate sulphur % as below;

$$S\ \% = \frac{\text{Weight of } BaSO_4 \text{ ppt}}{\text{Weight of coal sample}} \times \frac{32}{233} \times 100$$

$$S \xrightarrow{O_2} SO_2 \xrightarrow{O_2} SO_3 \xrightarrow{H_2O} H_2SO_4 \xrightarrow{BaCl_2} 2\,HCl + BaSO_4 \downarrow$$

(in coal)

d) **Ash % :** As carried out as under proximate analysis. Refer [3.6.3.1(c)]

e) **O % :** It is obtained by difference,

$$O\ \% = 100 - (C\% + H\% + N\% + S\% + \text{ash}\%)$$

Example 3.5.3 : *3 g of coal was heated in Kjeldahl's flask and NH_3 gas evolved was absorbed in 40 ml of 0.5 N H_2SO_4. After absorption, the excess acid required 18.5 ml of 0.5 N KOH for exact neutralization. 2.3 g of coal sample in quantitative analysis gave 0.35 g $BaSO_4$. Calculate percentage of N and S in coal sample.*

Solution

Calculation of % nitrogen

Given : Weight of sample = 3.0 gms

KOH consumed = 18.5 ml

Normality of H_2SO_4 and KOH = 0.5 N

Quantity of H_2SO_4 = 40 ml.

Amount of H_2SO_4 used = (40 – 18.5) ml.

= 21.5 ml.

Equivalents of H_2SO_4 = $21.5 \times 0.5 = 10.75$

= 10.75×10^{-3} milli equivalents

∴ Weight of Nitrogen = $10.75 \times 10^{-3} \times 14 = 0.1505$ gms

$$\therefore\ \%\ \text{Nitrogen} = \frac{\text{Weight of Nitrogen}}{\text{Weight of Coal sample}} \times 100$$

$$= \frac{0.1505}{3} \times 100$$

$$= \boxed{5.01\ \%}$$

Ans. : Percentage of nitrogen in coal sample = 5.01%.

Calculation of % sulphur

Given data :

Weight of sample = 2.3 gm

Weight of $BaSO_4$ = 0.35 gms

$$\%\ \text{Sulphur} = \frac{\text{Weight of } BaSO_4 \text{ ppt}}{\text{Weight of coal sample}} \times \frac{32}{233} \times 100$$

$$= \frac{0.35}{2.3} \times \frac{32}{233} \times 100$$

$$= \frac{1120}{535.9} = \boxed{2.09\ \%}$$

Ans. : Percentage of sulphur = 0.2 %

Example 3.5.4 : *A coal sample was subjected to ultimate analysis : 1.6 gm of coal on combustion in a Bomb calorimeter gave 0.47 gm of $BaSO_4$ Calculate % of sulphur in the coal sample.*

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Ans. :

Given data :

Weight of $BaSO_4$ ppt : 0.47 gms

Weight of coal sample : 1.6 gms

$$\%\ S = \frac{\text{Weight of } BaSO_4}{\text{Weight of Coal}} \times \frac{32}{233} \times 100$$

$$= [0.47 / 1.6] \times [32 / 233] \times 100$$

$$= 4.04\ \%$$

3.5.2.4 Significance of Ultimate Analysis

Carbon % : *Greater the % of carbon in coal, better is the coal quality and higher calorific value.*

Hydrogen% : *Most of the hydrogen in coal is in the form of moisture and volatile matter. Only a small percentage of hydrogen is combustible. Thus it decreases C.V. of coal. Smaller the H % better is the coal quality.*

Nitrogen% : *Nitrogen does not burn during coal combustion and therefore it has no calorific value. Hence a good quality coal should have negligible N%.*

Sulphur% : *Although sulphur can burn and increase calorific value of coal but it causes SO_x pollution and causes acid rain, corrosion of metallic equipment. Hence, lower the % of S in coal, better is coal quality.*

Oxygen% : *Most of the oxygen in coal is in the form of moisture. It decreases calorific value of coal (1 % oxygen in coal decreases calorific value by 1.7 %). Hence, lower the O %, better is coal quality.*

Syllabus Topic

Liquid fuels- Crude petroleum oil, its composition and classification and mining (in brief). Refining of crude oil- i) Separation of water ii) Separation of 'S' & iii) Fractional Distillation with diagram and composition and uses table

3.6 Liquid Fuels

- The liquid fuels are generally the products obtained from petroleum refining.
- The main constituents of crude or raw petroleum are paraffin, naphthalene and aromatic hydrocarbons. The concentrations of all these vary.
- The characteristic features of the liquid fuels are,
  - (i) Liquid fuels possess low flash and fire point.
  - (ii) The calorific value of liquid fuels is generally very high.
  - (iii) The viscosity of liquid fuels is low at ordinary temperature.
  - (iv) The moisture and sulphur content of liquid fuels is low.

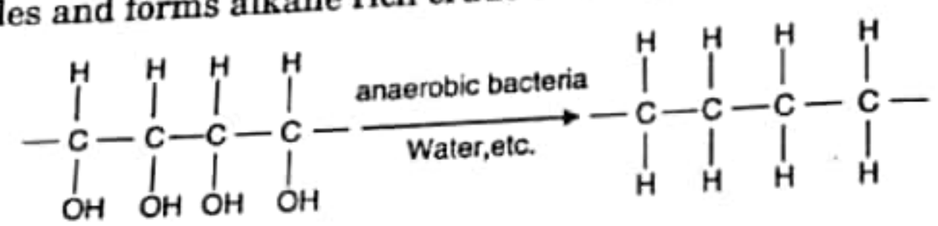
3.6.1 Crude Petroleum Oils

- Petroleum or crude oil is the main source of almost all liquid fuels used now and a large number of petrochemicals such as plastics, rubbers, fibres, organic chemicals, hydrogen etc. can be manufactured from crude oil fraction.
- It has negligible percentage of ash and moisture and has minute quantity of sulphur. It has very high calorific value such as 40,000 kJ/kg.
- Starting from crude petroleum, the various products such as motor spirit, petrol, diesel, kerosene oil etc. are obtained by fractional distillation.
- The residue left is known as fuel oil, which is normally used as an industrial fuel.
- Its calorific value is nearly same as that of crude petroleum.

3.6.2 Origin of Petroleum

- As per modern theory, petroleum is formed from buried debris of plants and animals (organic matter), under favourable conditions.

- The burial of the organic matter during volcano, upheavals in earth surface should take place alongwith large quantity of water and *under a dome* of hard, impervious rock.
- The anaerobic bacteria, higher temperature, radioactive substances enables degradation of organic matter, in the presence of water, under the dome, to form highly alkane rich matter as crude oil.
- The anaerobic bacteria take out oxygen atoms from cellulose, protein, oil molecules and forms alkane rich crude oil. For example,



a part of cellulose molecule

- Prolonged action of higher temperature and action of radioactive substances cause the breaking of very long hydrocarbon molecules to smaller.
- During the ages of time, the hydrocarbon molecules undergo structural changes, isomerisation, dehydrogenation, cyclisation, aromatisation etc. to produce the crude oil.

3.6.3 Composition of Petroleum

- Petroleum, commonly known as rock oil or mineral oil, is obtained from nature, under the earth, in the form of deep coloured highly viscous liquid.
- It contains a large number of different individual chemicals ranging from methane to asphalt.
- The composition of naturally occurring crude petroleum changes from place to place. But most of the constituents are straight chain paraffins and aromatic hydrocarbons.
- Nitrogen, sulphur and oxygen are also present.
- The common compounds of these elements are pyridine, quinoline derivatives, pyrrole (nitrogen compounds); alkyl sulphides, hydrosulphides, H_2S, thiophene (sulphur compounds); carboxylic acids, ketones, phenols (oxygen compounds).
- Average elemental composition of crude petroleum is,

  $C = 80$ to 87% $H = 11$ to 15%

  $S = 0.1$ to 3% $O = 0.1$ to 0.9%,

  $N = 0.4$ to 0.9%

- Petroleum contains following types of compounds :

1) Open chain alkanes
2) Cycloalkanes
3) Aromatics
4) Asphaltenes
5) Resins

1) **Open chain alkanes :** Both straight chain and branched chain alkanes are present in crude oil. In some crude oils, such alkanes make major part.
2) **Cycloalkanes :** Crude oil contains cycloalkanes like cyclopentane, cyclohexane and their alkyl substituted products. Some crude oils contain dominating amount of cycloalkanes.
3) **Aromatics :** In all the crude oils benzene and alkyl substituted benzenes are upto 2%.
4) **Asphaltenes :** All the crude oils contain the small amount of polycondensed aromatic solids as colloidal dispersion in crude oil. The asphaltenes also contain N, S, O atoms.
5) **Resins :** These are the polymeric substances. They are gummy and are lower molecular weight polymers. They also contain N, S, O atoms.

All the crude oils contain little amount of *emulsified water* and the water is rich with dissolved salts. The number of carbon atoms in the hydrocarbon molecules range from C_1 to C_{70}, in the crude oil.

3.6.4 Mining of Petroleum

- Petroleum gets formed and collected under the earth. The depth of such a storage of petroleum varies from few hundreds to few thousands of feet below the surface of the earth.
- It is accompanied/surrounded by layers of natural gas, under the earth. In short, the crude petroleum (oil) thus formed floats upon a layer of salt water and is embedded/surrounded by layer of natural gas, deep below the impervious rock. Mining of the oil is done by drilling holes in earth's crust and sinking pipe upto the oil bearing rocks.

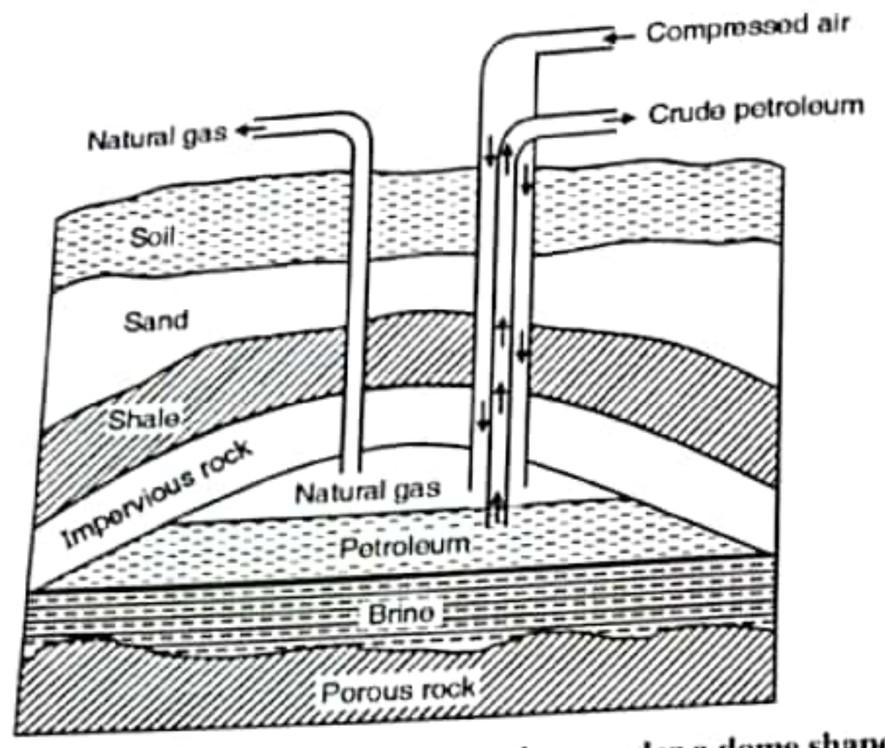


Fig. 3.6.1 : Mining of petroleum and natural gas under a dome shaped rock

- Due to the hydrostatic pressure exerted by natural gas, surrounding to the stock of petroleum helps to get petroleum piped out with pressure. This crude petroleum is then pumped out and transported through pipes.

3.6.5 Refining of Petroleum

- Crude oil cannot be directly used for any purpose. Refining or fractionation is the process of separation of various fractions from crude oil.
- The crude oil contains a large number of hydrocarbons, but by the process of refining, they are divided into few groups of molecular weights or boiling point ranges.
- They are as follows :
  1) Separation of water
  2) Separation of sulphur
  3) Fractionation / Fractional Distillation.

1) **Separation of water :** First the emulsified water alongwith salts dissolved, is removed by passing the crude oil between highly charged electrodes. The colloidal water droplets unite to form large drops which separate from oil.

2) **Separation of sulphur :** Then the crude oil is treated with hot CuO to remove sulphur from the sulphur compounds in crude oil.

3) **Fractional Distillation :** The principle of fractional distillation is that the vapours of higher boiling point compounds get condensed into liquid, during the stepwise cooling.

Construction [Fractional Distillation Column]

- The refining is carried out in a tall cylindrical tower called as fractionating column. The fractionating column is a stainless steel tower about 30 m in height and 3 m in diameter.
- There are 50-60 horizontal stainless steel trays at about half metre distances in the tower. Each tray is provided with 4-5 bubble cups with loose caps so that the rising vapours through the cups bubble in the liquid deposited on tray.
- Fractions are taken out from some bubble trays only and not from all.
- Temperature of the tower is 400° C near bottom and it decreases gradually to 40° C at top. The tower is cooled by open air.

Working / Refining process :

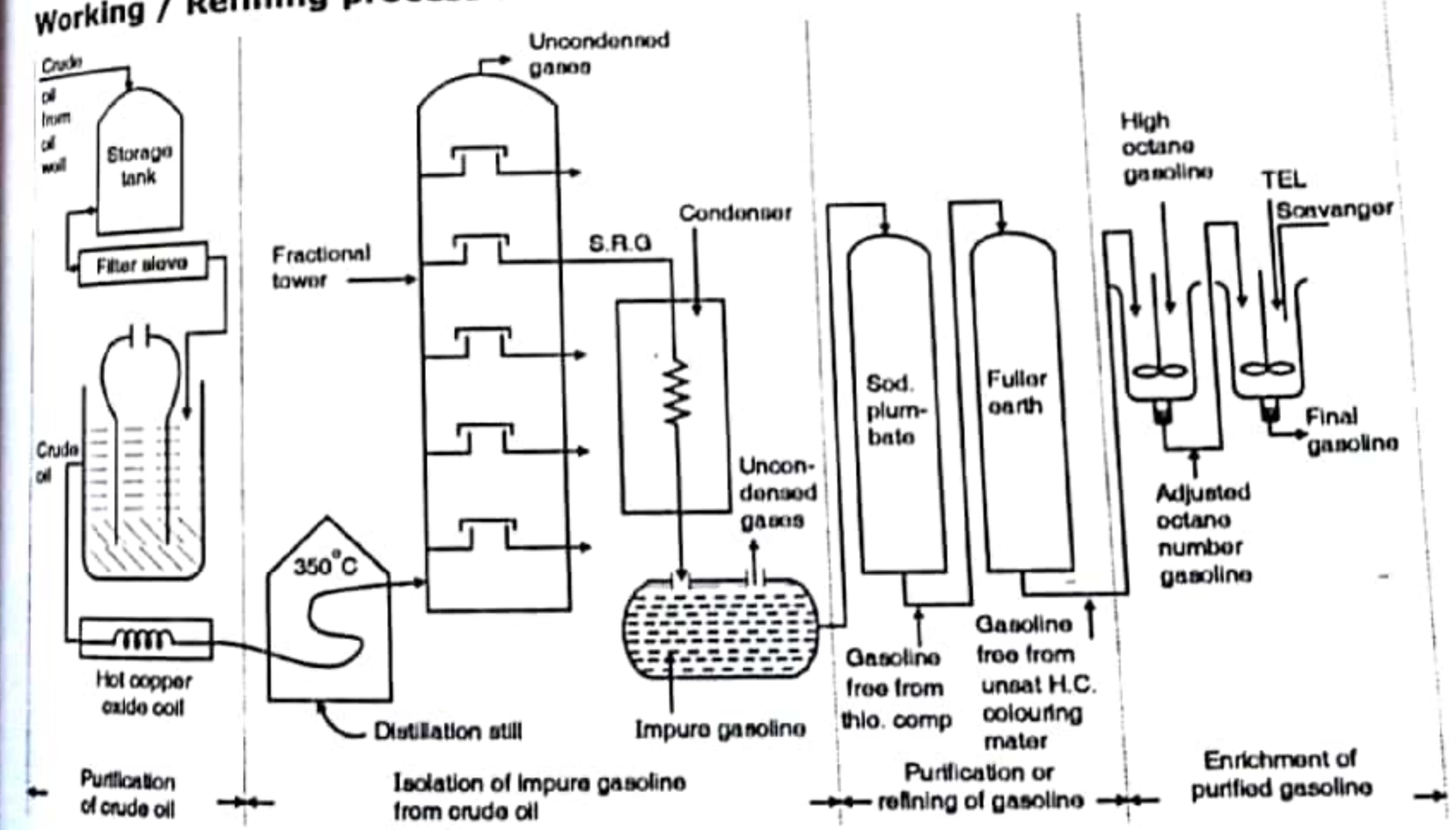


Fig. 3.6.2 : Petrol/Gasoline from crude oil by fractional distillation

- The crude oil is heated at about 400° C in a furnace or pipe still to convert it into vapours. The vapours enter into the fractionating column at the bottom.
- The vapours travel upwards through the bubble cups and gradually get cooled. The vapours of organic compounds with higher b.p. get condensed in lower level bubble cups and the liquid deposits on the trays.
- The uncondensed vapours rise up and get condensed turn by turn on upper bubble trays. There is vigorous bubbling action on each tray. In case, large part of the vapours get condensed on a tray, then the extra liquid flow down to lower trays of higher temperature and gets evaporated.
- From some bubble trays, the fractions like petrol, diesel, kerosene, naphtha, heavy oil etc. are taken out. Finally a small part of vapours comes out as uncondensed gases from the top where temperature is about 40° C.
- Heavy oil fraction can be further fractionated to get lubricating oils, vaseline, wax. The petrol obtained from refinery is called as straight run petrol but is not a good quality petrol.
- It is possible to convert any higher boiling fraction to convert into petrol or LPG by the process known as cracking.

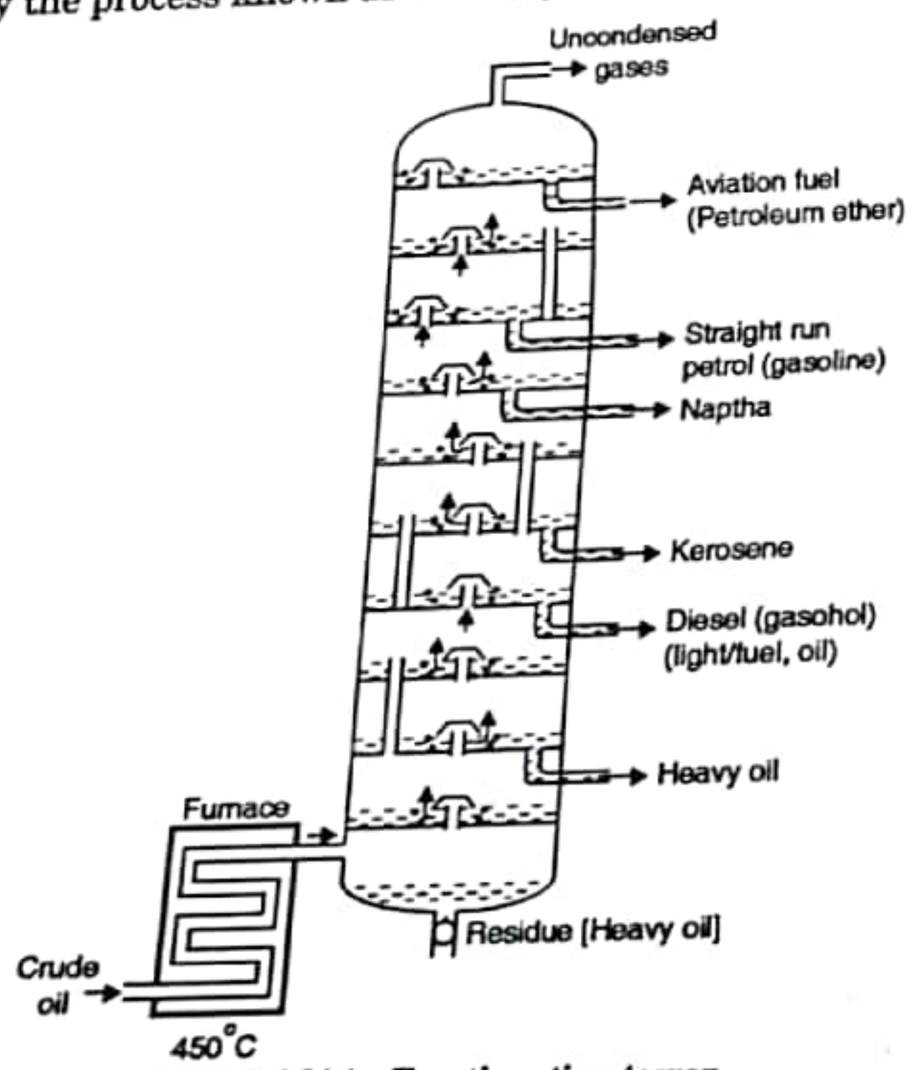


Fig. 3.6.3(a) : Fractionating tower

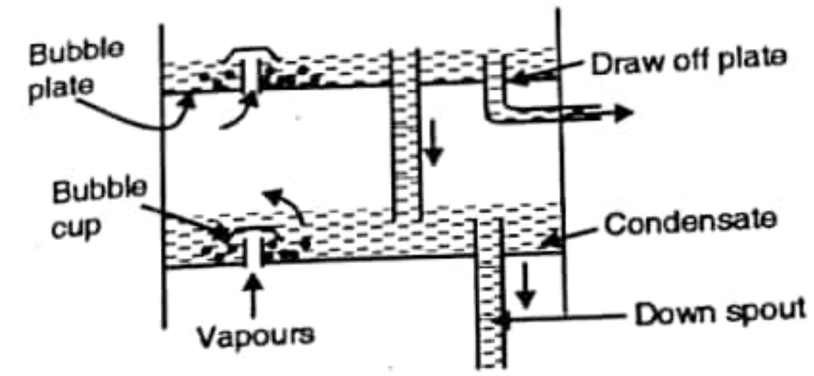


Fig. 3.6.3(b) : Portion of fractionating tower

The various petroleum fractions have calorific value about 11000 cal/gm. Their composition, boiling range and uses are given in Table 3.6.1.

Composition table

Table 3.6.1 : Products of fractional distillation of crude oil

Sr. No.	Name of fraction	Boiling range	Composition of hydrocarbon	Uses
1.	Uncondensed gases	Below 40° C	C_1 to C_4	Domestic and industrial fuel under 'LPG' name.
2.	Aviation fuel or petroleum other	40-70° C	C_5 to C_7	Fuel for aeroplane, helicopters, as solvent.
3.	Petrol or gasoline	60° C - 120° C	C_5 to C_8	Fuel for petrol engines, dry cleaning, as solvent.
4.	Naphtha or solvent spirit	120° C - 180° C	C_7 to C_{10}	As solvent and for dry cleaning, for chemicals.
5.	Kerosene	180° C - 250° C	C_{10} to C_{16}	For illumination, domestic fuel, for oil gas and fuel of jet engines.
6.	Diesel	250° C - 320° C	C_{15} to C_{18}	Diesel engine fuel.
7.	Heavy oil	320° C-400° C	C_{17} to C_{30}	For making petrol by cracking.
	(a) Lubricating oils	–	C_{18} to C_{20}	Lubricating purposes,
	(b) Vaselines	–	C_{20} to C_{22}	Cosmetics, medicines, ointments, lubricant.
	(c) Greases	–	C_{22} to C_{26}	Lubrication.
	(d) Wax	–	C_{26} to C_{30}	Candles, boot polish, tarpaulin cloth, wax paper, etc.
8.	Residue		above C_{30}	Road making, water proofing of roofs. As fuel, for arc light rods.
	(a) asphalt	–		
	(b) petroleum coke	–		

By above conversion, the insoluble mercaptides giving bad odour to the petrol are converted to disulphide, which are soluble in petrol and do not have bad odours, but still their presence in petrol is undesirable.

- The refined petroleum thus obtained does not satisfy all the characteristics upto the requirement especially octane number of petrol.
- Any such drawbacks are compensated by adding the additives to improve the properties.
- Generally, the petroleum with lower octane value is mixed with petroleum with higher octane value; so as to have proper octane value of the blend. Further, it is mixed with tetraethyl lead (TEL) which acts as an anti-knocking agent.

Syllabus topic

Cracking- Definition, Types of crackingI) Thermal cracking – (i) Liquid phase thermal cracking (ii) Vapour phase thermal cracking. II) Catalytic cracking- (i) Fixed-bed catalytic cracking (ii) Moving-bed catalytic cracking. Advantages of Catalytic cracking.

➤ **Topics covered :** All above, Comparison between Thermal and Catalytic Cracking, Comparison of liquid phase and vapour phase thermal cracking, Comparison of fixed bed and moving bed catalytic cracking

3.7 Cracking of Heavy Oil

Generally, on cracking a mixture of hydrocarbon is obtained which is allowed to undergo fractional condensation to separate gasoline.

3.7.1 Definition

MU - May 2012, Dec. 2012, Dec. 2013, Dec. 2014, May 2015, Dec. 2015

- *Cracking is a process of converging heavy oil with higher molecular weight hydrocarbons to the oil with lower molecular weight hydrocarbon which is known as gasoline.*
- *Thus, heavy oil is heated at a high temperature under pressure or in the presence of catalyst to obtain gasoline.*

e.g. $\underset{(Decane)}{C_{10}H_{22}} \xrightarrow{\text{Cracking}} \underset{\text{n-pentane}}{C_5H_{12}} + \underset{\text{Pentene}}{C_5H_{10}}$

$C_{16}H_{34} \xrightarrow{\text{Cracking}} \underset{\text{octane}}{C_8H_{18}} + \underset{\text{octene}}{C_8H_{16}}$

Thus, n-pentane or octane along with other lower hydrocarbon is used as gasoline.

Table 3.7.1 : Comparison between Thermal and Catalytic Cracking

Sr. No.	Thermal cracking	Catalytic cracking
(1)	Heavy oils are cracked by simply heating them to high temperature and pressure.	Heavy oils are cracked using small quantity of catalyst.
(2)	It is of two type - liquid or vapour phase.	It is of two types as - fixed bed or fluidised bed. (moving bed)
(3)	Temperature and pressure is of high range as, (a) Liquid phase : T = 420-550°C P = 15 to 100 kg/cm² (b) Vapour phase : T = 600 to 650° C P = 15 to 20 kg/cm²	Temperature and pressure is of low range, due to catalyst (a) Fixed bed : T = 425-540°C P = 1.5 kg/cm² (b) Fluidized bed: T = 550-570° C P = very low
(4)	Octane value of product ranges 60 - 80	Octane value of product is high, ranges from 80 - 90.
(5)	Cracking is not specific.	Cracking is specific and hence can give good quality of gasoline.
(6)	Yield % of gasoline is low (app. 50-60%)	Yield % of gasoline is high (app. > 75%)
(7)	Efficiency is low and not commonly used in refineries	Efficiency is high and used in modern refineries.
(8)	Initial and operating cost is high.	Initial cost high, but operating cost is low.

3.7.2 Types of Cracking

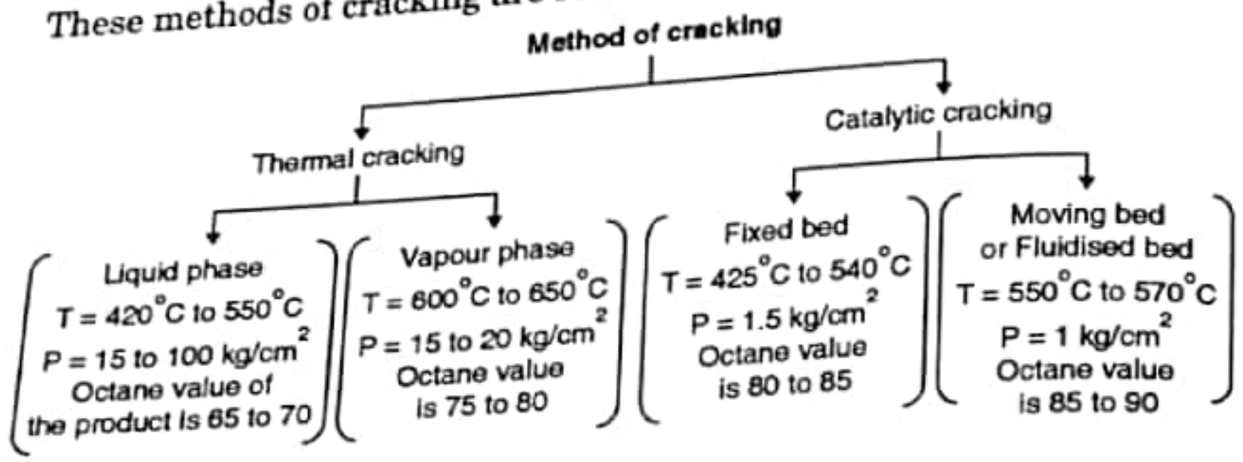
There are two methods for cracking :

i) Thermal cracking which may be

a) In liquid phase or b) In vapour phase

ii) Catalytic cracking which may be
a) Fixed bed b) Moving bed

These methods of cracking are summarised which are as follows :



3.7.2.1 Thermal Cracking

(a) Liquid phase thermal cracking

- By this method, any type of oil can be cracked. In this method, the oil is pumped into the coil kept at 420° C to 550° C under a pressure of 15 to 100 kg/cm². As the temperature increases, a better quality of gasoline is produced.
- The octane value of this gasoline is low, i.e. 65 to 70. Therefore, it is mixed with higher octane value gasoline and then used in engine.

(b) Vapour phase thermal cracking

- In this method, the heavy oil is heated in the heater at 400°C to convert it into the vapours and then these vapours are passed to the reaction chamber which is maintained at 600°C to 650°C and under a pressure of 10 to 20 kg/cm².
- At this stage, the higher hydrocarbons are converted into lower hydrocarbons easily and the octane value of petrol is usually 75 to 80.

Comparison of liquid phase and vapour phase thermal cracking

Sr. No.	Characteristic	Liquid Phase Thermal Cracking	Vapour Phase Thermal Cracking
1.	Cracking temperature	Moderate i.e. 420°C – 550°C	600°C – 650°C
2.	Pressure	High ≈ 15 to 100 kg/cm²	Low ≈ 15 – 20 kg/cm²
3.	Yield percentages	50 – 60%	–

Sr. No.	Characteristic	Liquid Phase Thermal Cracking	Vapour Phase Thermal Cracking
4.	Octane rating	65 – 70	> 70 (75 – 80)
5.	Pre-requirement for process	Any type of heavy oil can be used	Oil has to be vaporised readily
6.	Time required	Comparatively more	Comparatively less

3.7.2.2 Catalytic Cracking

MU - May 2012, Dec. 2012, Dec. 2013, May 2015

Catalytic cracking is a process in which heavy-oil is heated in the presence of a catalyst. Generally used catalysts are crystalline substances. e.g. bauxite, zeolite, crystalline alumino silicate, bentonite etc.

The temperature is adjusted just apt as where heavy oil gets vaporised. During the process heavy oil gets cracked and forms lower hydrocarbons – one saturated and other unsaturated.

e.g. n-hexadecane $\xrightarrow{\text{cracking}}$ octane + octene.

There are two types of catalytic crackings as :

(a) Fixed bed catalytic cracking

(b) Moving / fluidised bed catalytic cracking.

(a) Fixed bed catalytic cracking

MU - May 2014, May 2016

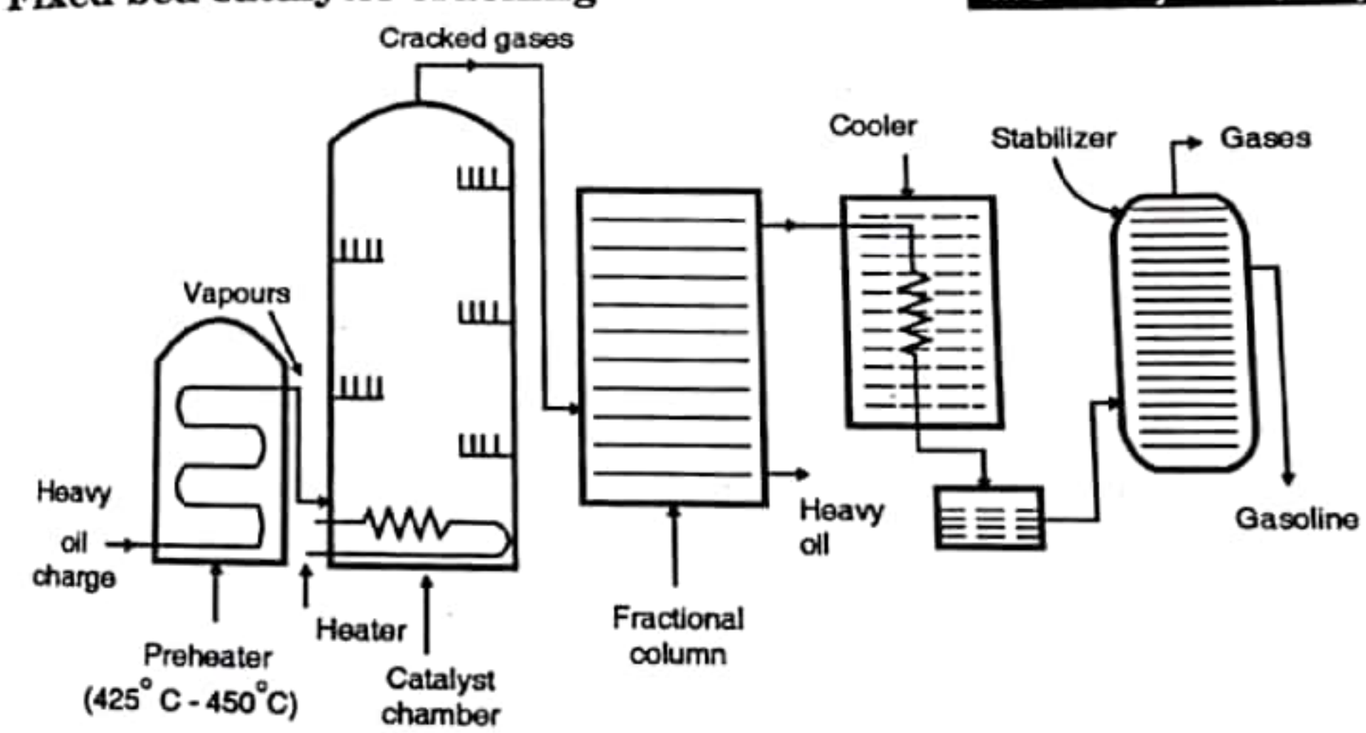


Fig. 3.7.1 : Fixed bed catalytic cracking

- In this method, vapours of the heavy oil are heated in the presence of catalyst due to which a better yield of petrol is obtained. The flow sheet of this method is shown in Fig. 3.7.1.
- In this method, heavy oil is vaporised by heating in an electrical heater. Then the vapours are passed over a series of trays containing catalyst. Generally, the catalyst used are *crystalline alumino-silicate, bentonite, bauxite and zeolites.*
- The reaction chamber is maintained at 425°C to 540°C and under a pressure of 1.5 kg/cm².
- The cracked gases are taken out from the top of the reaction chamber (cracker) and allowed to pass into fractionating tower, where gasoline fraction is collected. The octane value of this gasoline is about 80 – 85.
- During the cracking, free carbon is also formed which deposits on catalyst, then the flow of vapours of heavy oil is passed over the second set of reaction chamber and the catalyst in earlier chamber is regenerated by burning the carbon deposits with the help of air and reused.

(b) Moving bed or fluidised bed catalytic cracking principle

MU - Dec. 2013

- In fluidised bed catalytic cracking, a fine powder of catalyst is circulated through the cracker along with the vapours of heavy oil (Higher hydrocarbon).
- The catalyst accelerates and directs the cracking efficiently to form gasoline and other lower hydrocarbons.

For example

$$\underset{\text{n-octadecane}}{C_{18}H_{38}} \xrightarrow{\text{Cracking}} \underset{\text{n-decane}}{C_{10}H_{22}} + \underset{\text{Octene}}{C_8H_{16}}$$

$$\underset{\text{n-hexadecane}}{C_{16}H_{34}} \xrightarrow{\text{Cracking}} \underset{\text{n-hexane}}{C_6H_{14}} + \underset{\text{Decene}}{C_{10}H_{20}}$$

or

$$\underset{\text{n-hexadecane}}{C_{16}H_{34}} \xrightarrow{\text{Cracking}} \underset{\text{Octane}}{C_8H_{18}} + \underset{\text{Octene}}{C_8H_{16}}$$

Process

- In the modern refineries, mostly fluidised bed catalytic cracking is used.
- The major part of the process involves crackers and regenerators, which are kept side by side.

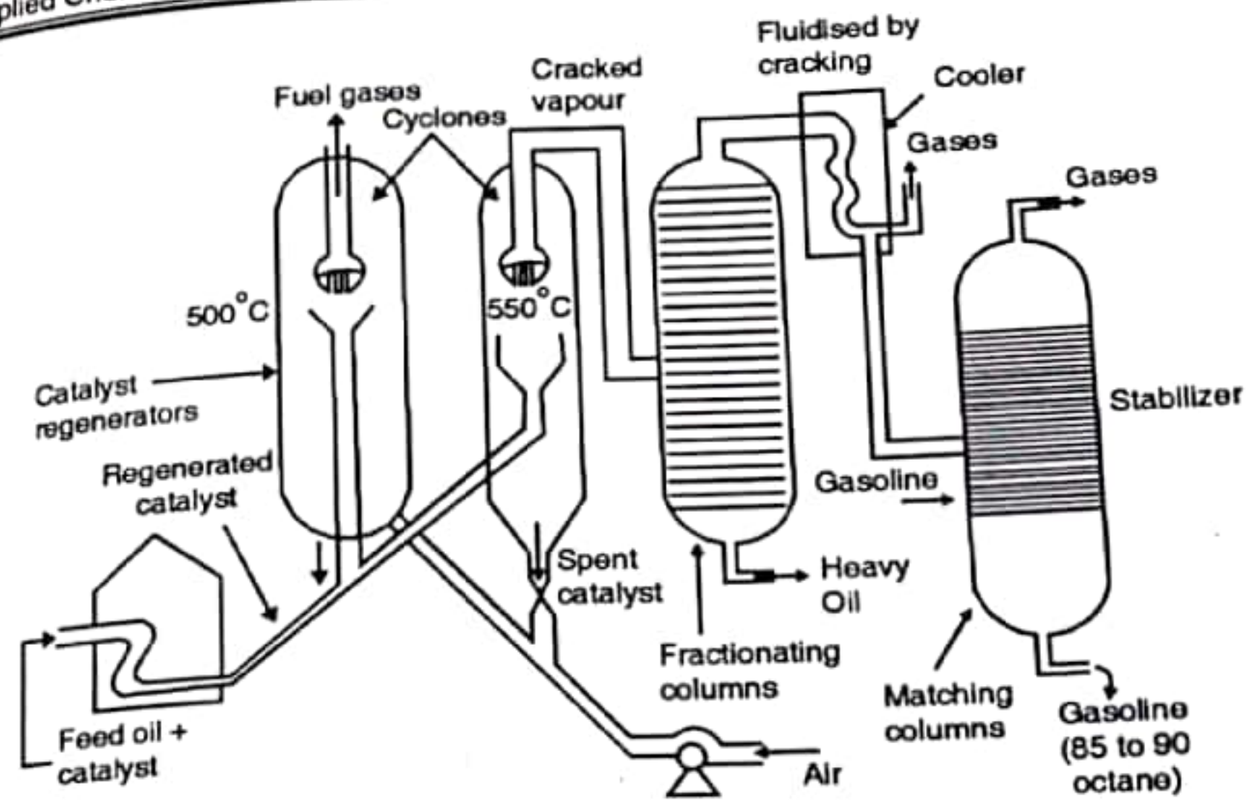


Fig. 3.7.2 : Moving/Fluidised bed catalytic cracking

- In this method, a mixture of heavy oil and catalyst is heated in the still to convert the heavy oil into vapours.
- These vapours along with hot catalyst are brought to the cracker. The cracker is maintained at a temperature of 550°C to 570°C and atmospheric pressure.
- In the cracker, the vapours of the heavy oil and hot catalyst come in intimate contact with each other and the breaking of higher molecular weight hydrocarbons into lower hydrocarbon (Gasoline) takes place.
- The low boiling hydrocarbons move up to the top of the cracker which are passed through the cyclone separator while the catalyst remains in the cracker.
- These cracked gases are further passed through the fractionating column to have three major fractions.

  a) Gasoline b) Middle oil c) Heavy oil
- The gasoline is further cooled and purified to remove the impurities of sulphur, unsaturated hydrocarbons and colouring matter; if present. The catalyst performs two function.

  (i) To get a better quality gasoline during cracking process.

  (ii) To carry heat during process.

Regeneration of exhausted catalyst

- Catalyst gets deactivated due to the deposition of free carbon on catalyst.
- The deactivated catalyst is taken from the bottom of the cracker and brought into regenerator where it is heated to about 500°C in the presence of hot air to burn carbon dioxide which is taken out from the top of the regenerator.
- The regenerated catalyst in hot condition is taken down to the vapours of heavy oil and recirculated in the cracker.

3.7.2.3 Advantages of Catalytic Process

MU - May 2014, Dec. 2014, May 2016

i) The cracking reaction can be carried out at lower temperature and pressure.

ii) The cracking is specific in nature and can give proper quality of gasoline.

iii) The octane value of gasoline is higher by catalytic process, hence better for petrol engine.

Comparison of fixed bed and moving bed catalytic cracking

Sr. No	Characteristic	Fixed Bed Catalytic Cracking	Moving Bed or Fluidised Bed Catalytic Cracking
1.	Chamber Reaction temperature	i.e. 425°C – 540°C	550°C – 570°C
2.	Pressure	1.5 kg/cm²	Around 1 kg/cm²
3.	Octane value	80 – 85	85 – 90

Syllabus topic

Petrol- Refining of petrol, unleaded petrol (use of MTBE), Catalytic converter, Power alcohol, Knocking, Octane number, Cetane number, Antiknocking agents.

3.8 Petrol [Gasoline]

3.8.1 Refining of Petrol [Reformulating / Reforming of gasoline]

MU - May 2013, May 2014, Dec. 2015

The gasoline obtained after fractionation of crude oil / cracking / synthesis may contain the following impurities :

(i) Some sulphur compounds

(ii) Some polyolefins [easily oxidisable hydrocarbons]

Therefore, such gasoline is treated chemically to purify it further, by removing impurities.

- Gasoline is made free from sulphur compounds by treating it with either of agents as sodium plumbite, sodium hypochlorite or by converting it to simpler compound like H_2S which can be oxidised to give free sulphur etc.
- other agents are $CuCl_2$, Fuller's earth, sodium iso-butyrate, sodium naphthenate, activated bauxites etc.
- Gasoline is made free from other polyolefins by "Fractionating" in a tower. This step is known as "stabilization of gasoline".
- Now it is blended with suitable hydrocarbon to improve its octane number (Refer 3.8.6).

3.8.2 Unleaded Petrol

MU - May 2012

- This is practically zero lead quantity gasoline supplied for motor fuels.
- In car exhaust, if catalytic converter is connected, leaded petrol cannot be used; because, lead destroys the active sites of catalyst.
- In catalytic converter, two types of catalysts are used as,
  (a) Reduction catalyst
  (b) Oxidation catalyst
- Catalyst helps to reduce emissions of harmful gases by following reactions.
- Reduction catalyst contains Pt or Rh, which can reduce NO_x as,

$$2\,NO_x \rightarrow N_2 + xO_2$$

- Oxidation catalyst helps treating unburnt hydro carbons oxidation catalyst unburnt hydrocarbons and carbon monoxide, due to presence of Pd or Pt,

$$x\,CO + \frac{x}{2}\,O_2 \rightarrow x\,CO_2$$

$$x\,HC + x\,O_2 \rightarrow \frac{x}{2}\,H_2O + \frac{x}{2}\,CO_2$$

- Engine is connected with computerised oxygen sensors, and signals are indicated to adjust the requirement of oxygen which is adjusted.

3.8.2.1 Advantages of Unleaded Petrol (ULP)

1. It is fuel without Lead which is a heavy metal and very harmful.

2. The use of ULP helps in controlling knocking in engines as it supports the use catalytic converters attached to exhaust in automobiles.
3. Octane Rating can be further improved by adding small amount of MTBE which supports combustion also.
4. ULP also allows use of atalysts like Rhodium which converts exhaust gases like CO and NO to CO_2 and N_2. Rhodium also converts unburnt hydrocarbons to CO_2 and H_2O.

3.8.3 MTBE Use of Catalytic Converter

- For gasoline, octane number was increased by adding benzene / toluene / xylene etc.
  But use of these hydrocarbons is restricted due to following reasons,
  (i) Benzene is carcinogenic
  (ii) Toluene / xylene show photochemical reactions.
- Recently, due to above problems, the aromatic hydrocarbons are avoided, and are replaced by "oxygenates".
- Generally following oxygenates are used to greater extent.
  (i) Alcohols : e.g. CH_3OH or C_2H_5OH
  (ii) Ethers : MTBE or ETBE
- These oxygenates possess octane ratings higher than 100
- C_2H_5OH is preferred over MTBE, in countries where corn/molasses are available in large quantity.
- MTBE (Methyl Tertiary Butyl Ether) is widely accepted as oxygenate by oil refineries because,
- It can be produced by simple reaction of iso-butylene with methanol.
- It helps to avoid disadvantages of methanol, rather provides alternative with safety and efficiency.
- Industry does not depend on corn crop for production of MTBE.

3.8.3.1 Advantages of MTBE

1. It contains "oxygen" in the form of ether group. It has low photochemical reaction with hydroxyl radical.
2. This oxygen in MTBE supports combustion of petrol in I.C.engine.
3. Due to presence of oxygen, formation of "peroxy" compounds is reduced, and thus "octane rating" is enhanced.

4. Thus use of lead containing compounds is avoided and excellent results are obtained.
5. Protection of environment is achieved.

3.8.3.2 Disadvantages of MTBE

- MTBE needs to be blended with gasoline at refinery (cannot be added later).
- MTBE is poisonous, hence may contaminate ground waters if gasoline leaks.

3.8.4 Power Alcohol

- When ethyl alcohol is used as fuel in internal combustion engine, it is called as power alcohol. Generally, ethyl alcohol is used as its 5-25% mixture with petrol.
- India has started mixing 5% ethyl alcohol in petrol from year 2003, but countries like Brazil use 25% ethyl alcohol in petrol from 1970.
- Use of ethyl alcohol in petrol reduces our dependence for petrol on foreign countries and even 5% ethyl alcohol blending in petrol, saves our foreign reserves by about Rs. 5000 crores/annum.
- Further it gives boost to the indigenous manufacturers of ethyl alcohol and farmers get better price of their grains produce.
- Ethyl alcohol is mainly manufactured by fermentation of molasses, starch, carbohydrates on a large scale and cheaply.

$$\underset{\text{starch}}{(C_6H_{10}O_5)_n} + \frac{n}{2}H_2O \xrightarrow[\text{enzyme}]{\text{diastase}} \frac{n}{2}\underset{\text{maltose}}{C_{12}H_{22}O_{11}} \xrightarrow{\text{maltase}} \underset{\text{glucose}}{n\,C_6H_{12}O_6}$$

$$\underset{\text{sucrose in molasses}}{C_{12}H_{22}O_{11}} \xrightarrow[H_2O]{\text{invertase}} \underset{\text{glucose}}{C_6H_{12}O_6} + \underset{\text{fructose}}{C_6H_{12}O_6}$$

$$\underset{\text{glucose/fructose}}{C_6H_{12}O_6} \xrightarrow{\text{Zymase}} 2\,C_2H_5OH + 2\,CO_2$$

- The starch or sucrose in molasses is converted into ethyl alcohol by fermentation as in above reactions. The ethyl alcohol obtained contains 95.5 % alcohol and 4.5% water. This 4.5% water from ethyl alcohol is separated either by use of suitable dehydrating agent or by distilling it alongwith benzene.

Advantages of power alcohol

i) Ethyl alcohol has good antiknocking property and its octane number is 90, while the octane number of petrol is about 65. Therefore addition of ethyl alcohol to petrol, increases its octane number.

ii) Alcohol has property of absorbing any traces of water if present in petrol.

iii) If a specially designed engine with higher compression ratio is used, then the disadvantage of lower C.V. of ethyl alcohol can be overcome.

iv) Ethyl alcohol contains 'O' atoms, which help for complete combustion of power alcohol and the polluting emissions of CO, hydrocarbon, particulates are reduced largely.

v) Use of ethyl alcohol in petrol reduces our dependence on foreign countries for petrol and saves foreign currency considerably.

vi) Power alcohol is cheaper than petrol.

Disadvantages of power alcohol

i) Ethyl alcohol has C.V. 7000 cal/gm, much lower than C.V. of petrol 11500 cal/gm. Use of power alcohol reduces power output upto 35%.

ii) Ethyl alcohol has high surface tension and its atomisation, especially at lower temperatures is difficult causing starting trouble.

iii) Ethyl alcohol may undergo oxidation to form acetic acid, which corrodes engine parts.

iv) Ethyl alcohol obtained by fermentation process directly cannot be mixed with petrol but it has to be dehydrated first.

v) As ethyl alcohol contains 'O' atoms, the amount of air required for complete combustion of power alcohol is lesser and therefore carburettor needs to be adjusted / modified.

3.8.5 Knocking

MU - May 2012, May 2014, Dec. 2014, Dec. 2015

- Knocking is a term related to the internal combustion engine working on petrol.
- In internal combustion engine, a mixture of gasoline vapours and air is used as a fuel. The combustion or burning of a fuel is initiated by a spark in the cylinder as shown in Fig. 3.8.1.
- Due to combustion, gases are formed which move the piston down the cylinder. The rate of combustion and movement of piston depend upon the composition of fuel, temperature and design of the engine.

- The movement of the piston must be even uniform without any vibration.
- But sometimes, the rate of combustion becomes so great that the fuel on ignition, instantaneously produces sudden increase in the gaseous volume which causes uneven movement of the piston with rattling noise in the engine. It is called as knocking of the engine. The knocking results in the loss of efficiency of I.C. engine.

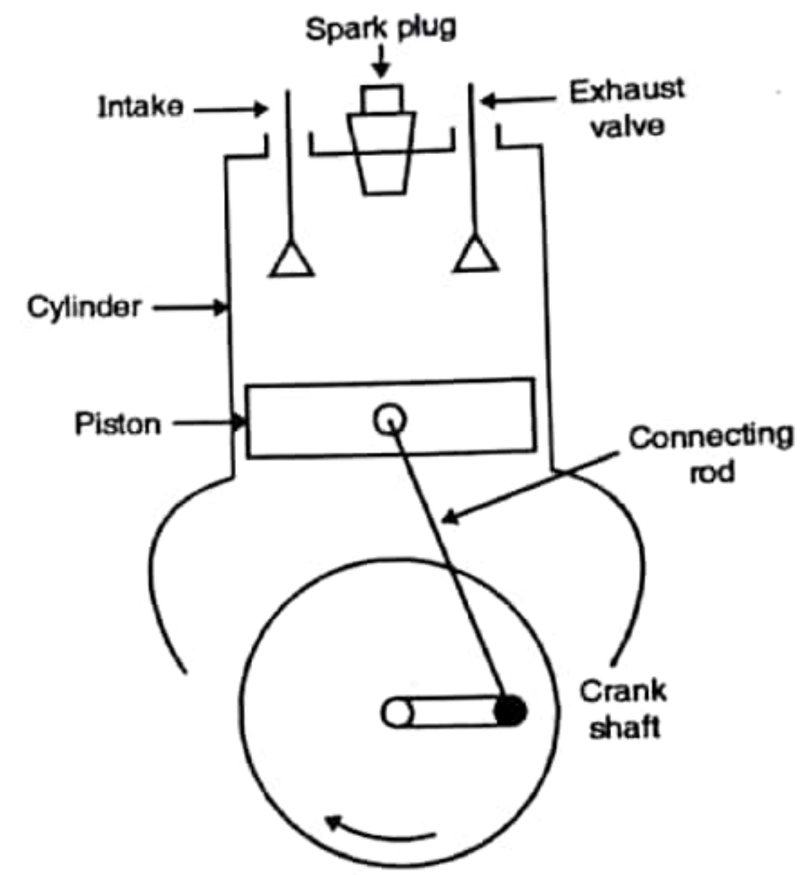


Fig. 3.8.1 : Spark in engine initiating combustion

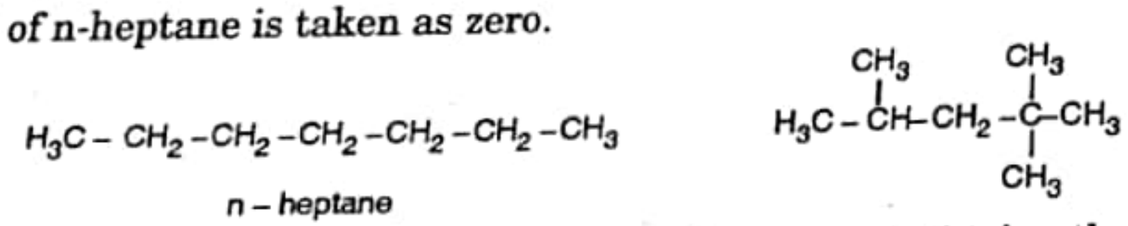
- Thus knocking can be defined as, "a sharp metallic sound similar to rattling of hammer, which is produced in the internal combustion engine due to immature ignition of the air-gasoline mixture".
- Knocking causes (i) loss of large amount of energy (ii) damage to the piston and cylinder.
- The knocking tendency of a fuel increases with the composition i.e. more the carbon length in paraffins, the knocking is high.
- The petrol is a mixture of various lower hydrocarbons and the knocking of the engine depends upon the structure of hydrocarbons, present in the petrol.
- It is observed that the sudden burning of hydrocarbons, which produces a large volume in short time, causes knocking.
- Thus, the straight chain saturated hydrocarbons have more knocking tendency than the straight chain unsaturated hydrocarbons, as it burns with a little difficulty.
- Further, the cyclic compounds have less tendency to knock than the straight chain compounds.

- The presence of double bond and aromaticity is also important. The aromatic hydrocarbons burn uniformly, thus it has a little tendency towards knocking. The position of double bond also matters, hydrocarbons having double bond near the centre of chain have less knocking property.

3.8.6 Octane Number of Petrol

MU - May 2012, May 2013, Dec. 2013, May 2014, Dec. 2014, Dec. 2015

- A petrol engine produces cracking noise and vibration together called as 'knocking' if petrol vapours entered in engine alongwith air, burns instantly (small explosion) with the firing of spark.
- The tendency to knock depends not only upon the quality of petrol but also on the engine design and conditions of engine run, compression ratio.
- *The knocking tendency of a petrol can be measured by using standard engine, run under set conditions. The knocking character of a petrol is expressed as "octane number". The knocking reduces efficiency and increases maintenance of engine.*
- It is found that *iso-octane* liquid has very good combustion characters and it produces a very little knock.
- On the contrary, *n-heptane* liquid detonates and produces high knocking in the engine. Therefore, the octane number of iso-octane is taken as 100 and that of n-heptane is taken as zero.



n – heptane

Iso-octane or 2, 2, 4 trimethyl pentane

Definition of octane number :

Octane number of a petrol sample is defined as, "the % of iso-octane in the mixture of iso-octane and n-heptane, which has similar knocking to the petrol sample".

Explanation

- For example, if a sample of petrol gives as much knocking as the mixture of 65% iso-octane and 35% n-heptane, then the octane number of petrol is 65.
- Octane number of some hydrocarbons is given here,

Benzene, toluene	100 +	n-pentane	62
Neopentane	90	2,2 dimethyl pentane	80
Cyclohexane	77	n-butane	70
Iso-octane	100	n-heptane	00

The relation between octane number of a hydrocarbon and its structure can be given as below,

Aromatics > Cycloalkane > alkene > branched alkane > Straight chain alkane.

- *Standard requirements* : Octane number of petrol should be at least 85 for motor cycles and cars. O.N. of petrol should be well above 100 for aeroplane and helicopter.
- This is achieved by using blend of isooctane with TEL (Anti knocking agent) and then mixing this blend with hydrocarbon. Benzene or toluene are widely used as their O.N. is high.
- The straight run petrol obtained from a refinery directly, has octane number below 60 while the petrol after catalytic reforming has O.N. above 85.
- The petrol obtained by catalytic cracking of heavy oil fraction has octane number above 85. (The octane numbers above 100 are rated by comparison with the mixture of iso-octane and tetraethyl lead. The O.N. of such very very low knocking mixture is obtained by extrapolation).

Increasing octane number of petrol

Octane number of a petrol can be increased by,

i) Addition of anti-knocking agents like *tetraethyl lead* litre (but this doping causes air pollution).

ii) Addition of *alkylate fraction* to petrol i.e. branched chain alkane of higher molecular weight.

iii) Adjusting compression ratio suitably (ratio of volume of engine cylinder at the end of suction stroke to the volume at the end of compression stroke).

iv) Addition of *benzene* or *toluene* to petrol.

Table 3.8.6.1 : Comparison between octane and cetane number

Sr. No.	Octane number	Cetane number
(1)	"Octane Number" expresses knocking character of petrol.	"Cetane Number" expresses knocking character of diesel.
(2)	Definition = "It is % of iso-octane in the mixture of iso-octane and n-heptane, which has similar knocking to the petrol sample"	Definition = "It is % of n-hexa-decane in the mixture of n-hexadecane and 2-methyl naphthalene which has same ignition character like the ignition character of the diesel under test."
(3)	Octane number of good petrol should be atleast 85 for motor cycles and cars 100 for aeroplanes and helicopters.	Cetane number of good diesel should be 25 for low speed engine, 35 for medium speed engine and 45 for high speed engines.
(4)	Octane number of petrol can be increased by adjusting compression ratio suitably, or by adding benzene or toluene, or alkylate fraction etc.	Cetane number of diesel can be increased by adding organic compounds containing oxygen atom, e.g. ethyl nitrate / nitrite, isoanry / nitrate, acetone peroxide etc.

3.8.6.1 Antiknocking Agents/Compounds **MU - Dec. 2013, Dec. 2014, Dec. 2015**

- Antiknocking agents are the compounds which help to increase the octane number of the fuel, decreasing the knocking.
- By the addition of these agents, the gasoline/petrol can be improved in its quality. Some of the compounds normally used are TEL, i.e. Tetra Ethyl Lead [$(C_2H_5)_4Pb$].
- The process of addition/mixing of any such antiknock agents to improve the quality of gasoline is known as doping.
- TEL is prepared by reacting ethyl chloride with lead sodium alloy at a temperature of 70°C.

$$4\,PbNa + 4\,C_2H_5Cl \rightarrow Pb\,(C_2H_5)_4 + 4\,NaCl$$

- The reaction mixture is cooled upto 40°C and tetra ethyl lead is further purified. Similarly, other antiknocking agents normally used are TML (Tetra Methyl Lead), Iron Carbonyl etc.

- About 0.5 ml. Of TEL per litre is added for motor petrol and about 1 ml. Of TEL per litre is generally added for aviation petrol.
- TEL is a colourless liquid with sweet odour, having specific gravity of 1.62.
- It boils at 200°C with decomposition. It is highly poisonous.
- TEL / any other substances, get converted into cloud of fine oxide of metal i.e.either lead oxide or whichever metal present. These fine particles react with hydrocarbon in petrol forming corresponding compounds like hydrocarbon peroxides molecules.
- This reaction reduces/slows down the chain oxidation reactions and thus delays "detonation".
- Disadvantages of TEL / other substances used are as follows,
  - (i) It is extremely harmful for the engine, because when Leaded petrol burns, PbO (litharge) is formed, which gets deposited on inner wall/lining of engine cylinder and
  - (ii) Also piston of engine gets jammed.
- Alternatively, to improve Octane number, other safe compounds are added, e.g. iso-pentane, iso-octane, ethyl benzene, iso propyl benzene, methyl tertiary butyl ether(MTBE) etc.
- The octane value of the gasoline may be increased by addition of fuel having higher octane value, such as benzol and alcohol.

(i) Scavanger

- Scavanger is a Greek word meaning *cleaning agent*. Generally, tetra ethyl lead is used as an antiknocking agent in gasoline.
- The lead forms PbO_2 or free Pb in the cylinder which deposits on the walls of cylinder and damages the inner surface of I.C. engine.
- To avoid this, a small amount of ethylene-di-bromide (Scavanger) is added. Ethylene di-bromide reacts with Pb or PbO_2 at 200°C-300°C to form $PbBr_2$.
- This $PbBr_2$ being volatile, gets removed from I.C. engine along with exhaust gases of engine. Thus, accumulation of lead in I.C. engine is avoided, but it pollutes the air with lead-bromide. Hence, an attempt is made to avoid the use of TEL in petrol and petrol is available under the name *unleaded petrol*. [Refer 3.8.2 for details]

3.8.7 Diesel

- Diesel is a fraction obtained between 250-320° C.
- The composition of diesel is saturated hydrocarbon between C_{15} to C_{18}, i.e. $C_{15}H_{32}$ to $C_{18}H_{38}$, having density between 0.86 – 0.95.
- Its calorific value is about 11000 kcal/kg.
- Diesel fuels are rated from their cetane number. If cetane number is 100 as in cetane the diesel considered as best and it would have highest spontaneous ignition temperature.

If Cetane number is zero as in case of 2-methyl naphthalene, the lowest spontaneous ignition temperature is observed.

Diesels are classified as :

(a) High speed diesel [number 45 and above]

(b) Medium speed diesel [number 35 and above]

(c) Low speed diesel [number 25 and above]

Cetane number can be improved by using additives as alkyl nitrates, diethylethers, butadienes, acetylenes, acetone, methyl alcohols, nitronaphthalenes etc. Generally the percentage of additives varies from 1% to 5%.

Properties (Advantages over gasoline)

1) Low price fuel.
2) Higher thermal efficiency about (30-35%).
3) Exhaust gases emitted contain less percentage of pollutants such as NO_x, CO_2, hydrocarbons etc.
4) Low consumption per unit of power produced.

Disadvantages

1) Its combustion requires heavy equipment to compress air.
2) Its combustion requires a complex and more expensive fuel injection device.

Uses

Diesel is used as fuel in engine.

3.8.8 Cetane Number of Diesel

MU - May 2013, Dec. 2014

- Combustion of diesel takes place under compression and heat conditions :

i) First only air is forced in cylinder and compressed to produce 500 - 700° C.

ii) Then the oil droplets are injected into the cylinder. The oil droplets absorb heat, oil molecules get decomposed and *atomisation* takes place.

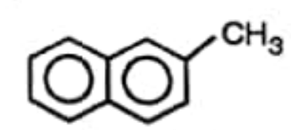
iii) The atomised oil chemically combines with O_2 to produce more heat, expansion of combustion gases, push on the piston.

For example,

$$8\,C + 18\,H + 25\,O \rightarrow 8\,CO_2 + 9\,H_2O$$

Step (ii) should be as fast as possible (1/500 sec. for fast speed) otherwise if there is time lag then the diesel knock is produced.

- The ignition lag depends upon the engine design, type of injector and mainly on chemical nature of fuel.
- A diesel having mostly straight chain alkane molecules and minimum branched chain alkanes, negligible aromatic hydrocarbons, has least diesel knock.
- The suitability of a diesel is determined in terms of cetane number. 2-methyl naphthalene liquid has maximum ignition lag and its cetane number is taken as zero. n-hexadecane burns in diesel engine smoothly without ignition lag and its cetane number is taken as 100.
- A standard diesel engine is taken for the study of cetane number of a diesel.
- *Cetane number of a diesel is defined as the % of n-hexadecane in the mixture of n-hexadecane and 2-methyl naphthalene which has same ignition character like the ignition character of the diesel under test.*



2-methyl naphthalene
(C.N. = Zero)

$H_3C-(CH_2)_{14}-CH_3$

n - hexadecane or cetane
(C.N. = 100)

- The cetane number and structure of the hydrocarbon are related as follow :

n-alkanes > cycloalkanes > alkenes > branched alkanes > aromatics.

- **Requirements :** The cetane number requirements are 25 for low speed engine, 35 for medium speed engine and above 45 for high speed engines.
- **Increasing cetane number :** The cetane number of a diesel can be increased by mixing diesel with oxygen atoms containing additives e.g. ethyl nitrite, ethyl nitrate, isoamyl-nitrate, acetone peroxide etc. These additives reduce surface tension of diesel, help finer spray and atomisation easier.

- **Remarks :** In petrol engine sudden combustion of petrol vapour causes knocking while delayed combustion of diesel in diesel engine causes knocking.
- We can say that an oil of low cetane number has high octane number. Further, a crude oil on fractionation, if gives high octane number petrol, gives diesel of low cetane number.
- **The cetane number of some of the diesels are as follows :**

  High speed diesel → 45

  Medium speed diesel → 35

  Low speed diesel → 25.

Syllabus topic : Combustion- Calculations for requirement of only oxygen and air (by weight and by volume only) for given solid & gaseous fuels.

➢ **Topics covered :** Definition of combustion, combustion reactions for solid fuels, and gaseous fuels,

3.9 Combustion

- *Combustion* is a process in which oxygen from the air reacts with the elements or compounds to give heat.
- As the elements or compounds combine in indefinite proportions with oxygen, we need to calculate what is minimum oxygen or air required for the complete combustion of compounds.
- The commonly involved combustion reactions are :

i) $C + O_2 \rightarrow CO_2$

ii) $2H_2 + O_2 \rightarrow 2H_2O$ **OR** $H_2 + (O) \rightarrow H_2O$ **OR** $H_2 + \frac{1}{2} O_2 \rightarrow H_2O$

iii) $S + O_2 \rightarrow SO_2$

iv) $2CO + O_2 \rightarrow 2CO_2$ **OR** $CO + (O) \rightarrow CO_2$ **OR** $CO + \frac{1}{2} O_2 \rightarrow CO_2$

v) $CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$

vi) $2C_2H_6 + 7O_2 \rightarrow 4CO_2 + 6H_2O$ **OR** $C_2H_6 + 3.5\ O_2 \rightarrow 2\ CO_2 + 3H_2O$

vii) $C_2H_4 + 3O_2 \rightarrow 2CO_2 + 2H_2O$

viii) $2C_2H_2 + 5O_2 \rightarrow 4CO_2 + 2H_2O$ **OR** $C_2H_2 + 2.5\ O_2 \rightarrow 2\ CO_2 + H_2O$

3.9.1 Calculation of Quantity of Air Required for Combustion of Fuel

By weight and volume

1) A substance and oxygen combine in definite proportion as per moles concept.

	C	+	O_2	→	CO_2	Mass proportions of C, O_2 and CO_2 are 12 : 32 : 44.
by weight	12		32		44	
by volume	1 Vol.		1 Vol.		1 Vol.	
	$2\ H_2$	+	O_2	→	$2\ H_2O$	Mass proportions of H_2, O_2, H_2O are 4 : 32 : 36.
by weight	4		32		36	
by volume	2 Vol.		1 Vol.		2 Vol.	

Nitrogen, ash (mineral matter) and CO_2 are not combustible.

2) At STP conditions, 22.4 litres of a gas is one gram-mole.

3) Air contains 21% oxygen by volume and 23% oxygen by mass.

4) Molar mass of air is taken as 28.94 gm/mole.

5) Oxygen required for combustion = theoretical O_2 required – Oxygen present in fuel.

6) Out of the total % of hydrogen in fuel, if some part is in the form of H_2O, then only the rest of the part combines with O_2.

7) When % of elements in a fuel is given, then calculate quantity by formula;

$$O_2 \text{ quantity} = \left[\frac{32}{12}C + 8\left(H - \frac{O}{8}\right) + S\right] \text{kg}$$

where C, H, S, O are masses of the elements.

$$\text{Quantity of air} = \frac{\text{Oxygen quantity} \times 100}{23} \text{ kg}$$

$$\text{Volume of air} = \frac{\text{volume of oxygen} \times 100}{21} \text{ m}^3$$

Syllabus topics : Biodiesel - Method to obtain Biodiesel from Vegetable Oils (Trans-esterification), Advantages and Disadvantages of Biodiesel.

➤ **Topics covered :** Trans-esterification process, Method/steps to obtain biodiesel-a green fuel, advantages and disadvantages of biodiesel.

3.10 Biodiesel (By Trans-esterification)

MU - Dec. 2012, May 2013, Dec. 2013, Dec. 2014, May 2015

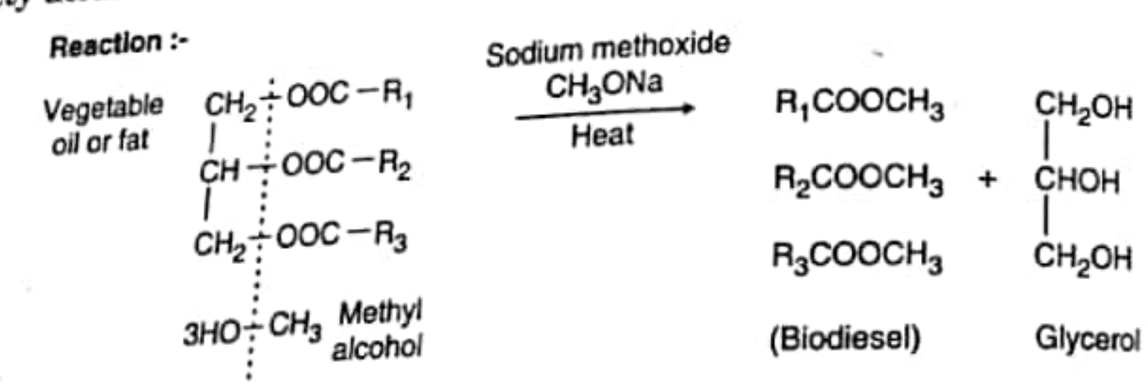
Chemical nature : Chemically biodiesel is *the methyl esters of long chain carboxylic acids*. Biodiesel is obtained by transesterification of vegetable oil or animal fats with methyl alcohol using sodium metal or sodium methoxide, as catalyst.

Transesterification

Transesterification is the process of converting one ester to another ester.

- A molecule of oil or fat is the triester of glycerol and three molecules of long chain carboxylic acids. This triester is converted into methyl esters of the fatty acids.

Reaction :-



- During the chemical conversion of vegetable oil to biodiesel we get water soluble glycerol and a small amount of sodium soaps.
- The water soluble part can be easily separated from biodiesel by washing the mixture with water.
- The alkaline sodium methoxide catalyst, saponifies some small amount of oil to give soap.
- Compounds present in biodiesel are like,

methyl palmitate	$H_3C-(CH_2)_{14}-COOCH_3$
methyl stearate	$H_3C-(CH_2)_{16}-COOCH_3$
methyl oleate	$H_3C-(CH_2)_7-CH=CH-(CH_2)_7-COOCH_3$
methyl linoleate	$H_3C-(CH_2)_5(CH=CH_2)-(CH_2)_7-COOCH_3$

3.10.1 Method / Steps to obtain Biodiesel – A Green Fuel

MU - Dec. 2012, May 2013, Dec. 2013, Dec. 2014, May 2015

i) Filter the cheap or waste vegetable oil / fat.
ii) Heat it at 110° C with stirring to remove any water from it.
iii) Prepare sodium methoxide from sodium metal and methanol. Add the sodium methoxide about 2% by weight to the vegetable oil or fat.
iv) Add methanol about 20% by volume to the mixture.
v) Heat the mixture with stirring for 30 minutes.
vi) Cool and mix sufficient water, stir well. The glycerol and soap dissolve in water phase.
vii) Separate the water insoluble phase (biodiesel) from water phase.
viii) Add antioxidant to the biodiesel to avoid it to become gummy due to oxidation and polymerisation.

- Biodiesel can be obtained from various vegetable oils like soyabeen oil, palm oil, groundnut oil, cottonseed oil, musturd oil, sunflower oil etc. and also from animal fats.
- The product is given name 'biodiesel' on account of that it is obtained from biological product and it is *biodegradable material* or Green Fuel.

3.10.2 Advantages of Biodiesel

MU - Dec. 2012, May 2013, Dec. 2013, Dec. 2014, May 2015

Biodiesel can be used as a good fuel for diesel engines but generally it is used as its 20% mixture with diesel.

i) Biodiesel is cheaper.
ii) It has high cetane numbers *46 to 54* and high C.V. of about 40 kJ/gm.
iii) It is regenerative and environment friendly.
iv) It does not give out particulate and CO pollutants.
v) It has certain extent of *lubricity*.
vi) Its use provides good market to vegetable oils and reduces our dependence for diesel on foreign countries, saving currency.
vii) It is clean to use biodiesel in diesel engines.

Syllabus topics : Fuel cell- Definition, types and applications.

➤ **Topics covered :** All above + Advantages of fuel cells over conventional power plants.

3.11 Fuel cell- Definition, Types and Applications

Fuels cells

- Fuel cells convert the chemical energy produced by a chemical reaction into usable electric power/electrical energy.
- Fuel cells produce electricity as long as fuel (hydrogen) is supplied, and the charge is not reduced/lost.
- Fuel cells produce direct current (DC) power, not alternating current (AC) power similar to a battery.

Definition of fuel cell

- A fuel cell is an electro-chemical device in which the chemical energy of fuel is continuously converted into electric energy. This conversion of energy takes place at constant pressure and temperature.
- The important feature of a fuel cell is that the fuel and the oxidant are combined in the form of ions.
  e.g. hydrogen (H_2) – Oxygen (O_2) called hydrox fuel cell.
- The main components of a fuel cell are :
  1. Anode comprising of fuel.
  2. Cathode comprising of an oxidant, (Which is also a fuel material)
  4. Container with inlets and outlets for H_2 to O_2.
  3. An electrolyte (a solution of H_2SO_4 for acidic fuel cell and KOH for alkali fuel cells).
  5. Separators.
  6. Sealing material.

Types of Fuel cells

1. Alkaline fuel cell
2. Proton Exchange Membrane FC (PEMFC)
3. Phosphoric Acid FC (PAFC)
4. Molten Carbonate FC.(MCFC)
5. Solid Oxide FC (SOFC)
6. Direct Methanol Fuel Cell (DMFC)

Applications of fuel cells.

Fuel cells have variety of application few are listed below :

1. These are used to supply power to
   a. All types of devices, such as hand held to portable generators.
   b. All types of vehicles, such as trucks, buses, marine transport etc.
   c. Space programmes.
2. Fuel cells as, "Stationary Power Stations". distribute power generation, and cogeneration (in which excess heat released. Stationary fuel cells can be used for backup power, power for remote locations, during electricity generation is used for other applications).

Advantages of Fuel Cells Over Conventional Power Plants

1. Simple in operation and less polluting, as the by-product is pure water.
2. Space requirement is much less.
3. Cooling water is not needed.
4. Energy conversion efficiency is higher, especially for H_2-powered fuel cells,
5. Heat generated is rejected directly to atmosphere, the process being isothermal
6. Fuel cells can be installed at the point of use thus reducing power losses during the transmission and distribution.almost 3 times of traditional combustion technology.
7. By using series – parallel combination of fuel cells, the output power rating at any voltage and current can be obtained.
8. The capacity can be increased as the demand grows.
9. It has long life.
10. Fuel cells operate quietly, have fewer moving parts and are well suited for a variety of applications.

3.12 Solved Numericals (GCV, NCV Calculations by Dulong Formula)

Example 3.12.1 : *A sample of coal has following composition by mass C = 70%, O = 8%, H = 10%, N = 3%, S = 2%, Ash = 7%. Calculate H.C.V. and L.C.V. using Dulong formula.*

Solution :

$$H.C.V = \frac{1}{100}\left[8080\,C + 34500\left(H - \frac{O}{8}\right) + 2240\,S\right]$$

$$= \frac{1}{100}\left[8080 \times 70 + 34500\left(10 - \frac{8}{8}\right) + 2240 \times 2\right]$$

$$= \frac{1}{100}[565600 + 34500\,(10 - 1) + 2240 \times 2]$$

$$= \frac{1}{100}[565600 + 310500 + 4480] = \frac{1}{100}[880580]$$

$$= 8805.80 \text{ kcal/kg.}$$

$$\text{L.C.V.} = \left[\text{H.C.V} - \frac{9}{100}\text{H} \times 587\right] \text{kcal/kg.}$$

$$= \left[8805.80 - \frac{9}{100} \times 10 \times 587\right] = [8805.80 - 528.30]$$

$$= 8277.50 \text{ kcal/kg.}$$

Ans. : *H.C.V. = 8805.80 kcal/kg.*
L.C.V. = 8277.50 kcal/kg.

Example 3.12.2 : *A sample of coal contains C = 61%, O = 32%, H = 6%, S = 0.5%, N = 0.2% and Ash = 0.3%. Calculate its G.C.V and N.C.V by Dulong and Petits formula.*

Solution :

$$\text{H.C.V} = \frac{1}{100}\left[8080\,\text{C} + 34500\left(\text{H} - \frac{\text{O}}{8}\right) + 2240\,\text{S}\right]$$

$$= \frac{1}{100}\left[8080 \times 61 + 34500\left(6 - \frac{32}{8}\right) + 2240 \times 0.5\right]$$

$$= \frac{1}{100}[492880 + 34500\,(6 - 4) + 2240 \times 0.5]$$

$$= \frac{1}{100}[492880 + 69000 + 1120] = \frac{1}{100}[563000]$$

$$= 5630.00 \text{ kcal/kg.}$$

$$\text{L.C.V.} = \left[\text{H.C.V} - \frac{9}{100}\text{H} \times 587\right] \text{kcal/kg.}$$

$$= \left[5630.00 - \frac{9}{100} \times 6 \times 587\right] = [5630.00 - 316.98]$$

$$= 5313.02 \text{ kcal/kg.}$$

Ans. : *H.C.V. = 5630.00 kcal/kg*
L.C.V. = 5313.02 kcal/kg

Example 3.12.3 : *A sample of coal contains, C = 70%; O = 20%; H = 8%; S = 0.5%; N = 0.2%; Ash = 1.0%. Calculate the gross and net calorific value of the coal.*

Solution

$$\text{G.C.V/H.C.V} = \frac{1}{100}\left[8080\,\text{C} + 34500\left(\text{H} - \frac{\text{O}}{8}\right) + 2240\,\text{S}\right]$$

$$= \frac{1}{100}\left[8080 \times 70 + 34500\left(8 - \frac{20}{8}\right) + 2240 \times 0.5\right]$$

$$= \frac{1}{100}\left[8080 \times 70 + 34500\left(\frac{44}{8}\right) + 2240 \times 0.5\right]$$

$$= \frac{1}{100}[565600 + 189750 + 1120] = 7564.7 \text{ kcal/kg.}$$

$$\text{N.C.V/L.C.V} = [\text{H.C.V.} - 0.09 \times \%\text{H} \times 587]$$

$$= [7564.7 - 0.09 \times 8 \times 587] = 7564.7 - 422.64$$

$$\textbf{N.C.V} = \textbf{7142.06 kcal/kg.}$$

...Ans.

Example 3.12.4 : *Analysis of a sample of coal gave the following information, C = 80%; H = 6%; O = 8%; S = 2.5%; Ash = 3.5%. Calculate the gross and net calorific value of coal. Also calculate the minimum quantity of air needed for complete combustion of 1 kg. of the above coal.*

Solution

$$\text{H.C.V.} = \frac{1}{100}\left[8080\,\text{C} + 34500\left(\text{H} - \frac{\text{O}}{8}\right) + 2240\,\text{S}\right]$$

$$= \frac{1}{100}\left[8080 \times 80 + 34500\left(6 - \frac{8}{8}\right) + 2240 \times 2.5\right]$$

$$= \frac{1}{100}[646400 + 172500 + 5600]$$

$$= 8245 \text{ kcal/kg.}$$

$$\text{L.C.V} = \text{H.C.V.} - (0.09 \times \%\,\text{H} \times 587)$$

$$= 8245 - 0.09 \times 6 \times 587 = 8245 - 316.98$$

$$= 7928.02 \text{ kcal/kg.}$$

Quantity of Air Required,

$$\text{C} + \text{O}_2 \rightarrow \text{CO}_2 \qquad \text{C} = 80\,\% = 0.80 \text{ kg}$$

$12 + 32 = 44$

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

$2 + 16 = 18$

$S + O_2 \rightarrow SO_2$

$32 + 32 = 64$

$H = 6\% = 0.06$ kg

$O = 8\% = 0.08$ kg

$S = 2.5\% = 0.025$ kg

Calculation of oxygen needed for 1 kg coal

Element	%	Weight per kg. of coal	Weight of O_2 in kg.
C	80	0.80	$0.80 \times \frac{32}{12} = 2.133$
H	6	0.06	$0.06 \times \frac{16}{2} = 0.48$
O	8	0.08	–
S	2.5	0.025	$0.025 \times \frac{32}{32} = 0.025$
			Total = 2.638

Weight of oxygen required = Weight of O_2 needed – weight of O_2 present

$= 2.638 - 0.08$

$= 2.558$ kg.

Weight of air required for complete combustion [∵ Air contains 23% O_2 by weight]

$= 2.558 \times \frac{100}{23}$ kg

$= 11.12$ kg.

Ans. : *H.C.V. = 8245 kcal/kg.*
L.C.V. = 7928.02 kcal/kg.
Weight of oxygen needed = 2.638 kg.
Weight of air required for complete combustion =11.12 kg.

Example 3.12.5 : *A coal is having the following composition by weight, C = 90%; O = 0.3%; S = 0.5%; N = 0.5%; Ash = 2.5%. Net calorific value was found to be 8965.28 k.cal/kg. Calculate the percentage of hydrogen and higher calorific value of coal.*

LCV

HCV

Solution

$$N.C.V. = G.C.V. - \left[\frac{9}{100} \times H \times \text{Latent heat}\right]$$

$$N.C.V. = \frac{1}{100}\left[8080C + 34500\left(H - \frac{O}{8}\right) + 2240\,S\right] - \frac{9H}{100} \times \text{Latent heat}$$

Thus,

$$\therefore 8965.28 = \frac{1}{100}\left[(8080 \times 90) + 34500\left(H - \frac{0.3}{8}\right) + (2240 \times 0.5)\right] - \frac{9}{100} \times H \times 587$$

solved to find the value of hydrogen.

Ans. : *% of hydrogen = 6.2%*
G.C.V. = 9292.83 kcal/kg

GCV = HCV
NCV = LCV

Example 3.12.6 : *A sample of coal contains :*
C = 60% O = 33% H = 6%
S = 0.5% N = 0.3% Ash = 0.2%
Calculate the gross and net calorific values.

Solution

$$HCV = \frac{1}{100}\left[8080\,C + 34500\left(H - \frac{O}{8}\right) + 2240\,S\right]$$

$$= \frac{1}{100}\left[8080 \times 60 + 34500\left(6 - \frac{33}{8}\right) + 2240 \times 0.5\right]$$

$$= \frac{1}{100}\left[484800 + 34500\,(6 - 4.13) + 1120\right]$$

$$= \frac{1}{100}\left[484800 + 34500\,[1.87] + 1120\right]$$

$$= \frac{1}{100}\left[484800 + 64515 + 1120\right]$$

$$= 5504.35 \text{ kcal/ kg.}$$

$$NCV = \left[HCV - \frac{9 \times H}{100} \times 587\right]$$

$$= \left[5504.35 - \frac{9 \times 6}{100} \times 587\right]$$

$$= [5504.35 - 316.98] = 5187.37 \text{ kcal/kg.}$$

Ans. : *HCV = 5504.35 kcal/kg*
NCV = 5187.37 kcal/kg

Example 3.12.7 : *Calculate the gross and net calorific value of coal having following composition : C = 80%, H = 7%, O = 3%, S = 3.5%, N = 2.1% and ash = 4.4%.*

Solution

$$H.C.V = \frac{1}{100}\left[8080\,C + 34500\left(H - \frac{O}{8}\right) + 2240\,S\right]$$

$$= \frac{1}{100}\left[8080 \times 80 + 34500\left(7 - \frac{3}{8}\right) + 2240 \times 3.5\right]$$

$$= \frac{1}{100}\,[646400 + 34500\,(7 - 0.38) + 2240 \times 3.5]$$

$$= \frac{1}{100}\,[646400 + 228390 + 7840]$$

$$= \frac{1}{100}\,[882630]$$

$$= 8826.30 \text{ kcal/kg.}$$

$$L.C.V. = \left[H.C.V - \frac{9}{100}H \times 587\right] \text{kcal/kg.}$$

$$= \left[8826.30 - \frac{9}{100} \times 7 \times 587\right]$$

$$= [8826.30 - 369.81]$$

$$= 8456.49 \text{ kcal/kg.}$$

Ans. : *H.C.V. = 8826.30 kcal/kg.*
L.C.V. = 8456.49 kcal/kg.

Example 3.12.8 : *The % composition of mass of a sample of coal is as follows. C = 80%, H = 6%, O = 8%, S = 1.5%, N = 1%, ash = rest. Calculate the gross and net calorific value of Fuels.*

Solution :

$$\text{Gross Calorific Value} = \frac{1}{100}\left[8080\,C + 34500\left(H - \frac{O}{8}\right) + 22405\right]$$

$$= \frac{1}{100}\left[8080 \times 80 + 34500\left(6 - \frac{8}{8}\right) + 2240 \times 1.5\right]$$

$$= 8222.60 \text{ kcal/kg.}$$

$$\text{Net Calorific Value} = [HCV - (0.09 \times \%\,H \times 587)]$$

$$= [-(0.09 \times 6 \times 587)]$$

$$= 7905.62 \text{ kcal/kg}$$

Ans. : *HCV = 8222.60 kcal/kg*
NCV = 7905.62 kcal/kg

Example 3.12.9 : *Calculate the Gross and Net calorific value of coal sample having the following composition : C – 85%, H – 7%, O – 3%, S – 3.5%, N – 2.1% and Ash – 4.4%.*

Solution

Given data :

C = 85% S = 3.5%
H = 7% N = 2.1%
O = 3% Ash = 4.4%

To calculate GCV and NCV of coal sample

$$GCV = \frac{1}{100}\left[8080\,C + 34500\left(H - \frac{O}{8}\right) + 22405\right]$$

$$= \frac{1}{100}\left[8080 \times 85 + 34500\left(7 - \frac{3}{8}\right) + 2240 \times 3.5\right]$$

$$= \frac{1}{100}\,[686800 + 228562.5 + 7840]$$

$$= \frac{1}{100}\,[923202.5] = 9232.025$$

$$\therefore \; \mathbf{GCV = 9232.03 \text{ kcal / kg}}$$ **...Ans.**

$$\text{Now } NCV = GCV - (0.09 \times \%\,H \times 587)$$

$$= 9232.03 - (0.09 \times 7 \times 587)$$

$$= 9232.03 - 369.81$$

$$= \mathbf{8862.22 \text{ kcal / kg}}$$ **...Ans.**

Example 3.12.10 : *Calculate the gross and net calorific value of coal having following composition.*
C = 80%, H = 7%, O = 3%, S = 3.5%, N = 2.1% and ash = 4.4%.

Solution :

$$GCV = \frac{1}{100}\left[8080\,C + 34500\left(H - \frac{O}{8}\right) + 2240\,S\right]$$

$$= \frac{1}{100}\left[8080 \times 80 + 34500\left(7 - \frac{3}{8}\right) + 2240 \times 3.5\right]$$

$$= \frac{1}{100}\ [646400 + 226562.5 + 7840]$$

$$= \frac{1}{100}\ [880802.5]$$

$\therefore$ GCV = **8808 Kcals/kg**

$\therefore$ NCV = GCV – (0.09 H × 587)

= 8808 – (0.09 × 7 × 587) = 8808 – (369.81)

$\therefore$ NCV = **8438.2 kcal/kg**

Example 3.12.11 : *A sample of coal has the following composition by mass.*
C = 85%, H = 6%, O = 8%
S = 0.5%, and Ash = 0.5%
Calculate the H.C.V. and L.C.V. using Dulong's formula.

Solution :

Dulong's Formula

$$H.C.V = 1/100\ (8080\ C + 34500\ (H - \frac{O}{8}) + 2240\ S)$$

$$L.C.V = H.C.V - 0.09 \times H \times 587$$

Numerical solution

$$H.C.V = 1/100\ (8080 \times 35 + 34500\ (6 - \frac{8}{8}) + 2240 \times 0.5)$$

$$= 1/100\ (686800 + 172500 + 1120)$$

$$= 1/100\ (860420)$$

$$= 8604.2\ K\ Cal/kg$$

$$L.C.V = 8604.2 - 0.09 \times 6 \times 587$$

$$= 8604.2 - 316.98$$

$$= 8287.22\ K\ Cal/kg$$

H.C.V = 8604.2 K Cal/kg
L.C.V = 8287.22 K Cal/kg

Example 3.12.12 : *A sample of coal constrains - C = 70%, O = 23%, H = 5%, S = 1.5 %, N = 0.4%, ash = 0.1%. Calculate G.C.V. and N.C.V. of this fuel.*

Solution :

Given : C = 70 % S = 1.5 % O = 23 %
N = 0.4 % H = 5 % Ash = 0.1 %

To calculate GCV and NCV

$$GCV = \frac{1}{100}\left[8080 \times C + 34500\ (H - \frac{O}{8}) + 2240 \times S\right] Kcal/kg$$

$$= \frac{1}{100}\left[8080 \times 70 + 34500\ (5 - \frac{23}{8}) + 2240 \times 1.5\right] Kcal/kg$$

$$= \frac{1}{100}\ [565600 + 95625 + 3360]\ Kcal/kg$$

GCV = 6615.61 Kcal/kg **...Ans.**

$$NCV = GCV - \left[\frac{9H}{100} \times 587\right] = 6615 - \left[\frac{9 \times 5}{100} \times 587\right]$$

$$= 6615.61 - 264.15$$

NCV = 6351.46 Kcal/kg **...Ans.**

Example 3.12.13 : *A sample of coal has the following composition – C = 90%, H = 8%, N = 2%, S =1.5%, O = 5% and remaining ash. Calculate the GCV and LCV (Latent heat of condensation of steam = 587 cal/g)* **MU - May 2012, 4 Marks**

Solution :

$$G.C.V. = \frac{1}{100}\left[8080 \times C + 34500\left(H - \frac{O}{8}\right) + 2240S\right] Kcal/kg$$

$$= \frac{1}{100}\left[8080 \times 90 + 34500\left(8 - \frac{5}{8}\right) + 2240 \times 1.5\right] Kcal/kg$$

$$= \frac{1}{100}\ [727200 + 254437.5 + 3360]\ Kcal/kg$$

$$= \frac{1}{100}\ [984997.5]\ Kcal/kg$$

$\therefore$ G.C.V. = 9849.975 K.cal/kg

LCV = G.C.V. – [0.09 × H × 587] kcal/kg

= 9849.975 – [0.09 × 8 × 587] kcal/kg

$= [9849.975 - 422.84]$ kcal/kg

$\therefore$ L.C.V. $= 9427.335$ kcal/kg

Ans. : ***G.C.V. = 9849.975 kcal.kg***
L.C.V. = 9427.335 kcal/kg

Example 3.12.14 : *A sample of coal has the following composition by weight : C = 82%, H = 6%, O = 8%, S = 0.5%, N = 3% and Ash = 0.5%. Calculate the Gross and Net Calorific value using Dulong's formula.* **MU - Dec. 2013, 5 Marks**

Solution :

To Calculate Gross and Net calorific value,

Dulong formula,

$$G.C.V = \frac{1}{100}\left[8080\,C + 34500\left(H - \frac{O}{8}\right)\right] + 2240\,S)\ \text{kcal\kg.}$$

$$= \frac{1}{100}\left[8080 \times 82 + 34500\left(6 - \frac{8}{8}\right) + 2240 \times 0.5\right]\ \text{kcal\kg}$$

$$= \frac{1}{100}[662560 + 172500 + 1120]\ \text{kcal/kg}$$

$$= \frac{1}{100}[836180] = \boxed{8361.80\ \text{kcal/kg}}$$

$$G.C.V = 8361.80\ \text{kcal/kg}$$ ...Ans.

$$\text{Net Calorifc Value} = G.C.V. - \left[\frac{9 \times H}{100} \times 587\right]\ \text{kcal\kg.}$$

$$= 8361.80 - \left[\frac{9 \times 6}{100} \times 587\right]\ \text{kcal/kg}$$

$$= 8361.80 - 316.98$$

$$N.C.V = \boxed{8044.82\ \text{kcal\kg.}}$$

Example 3.12.15 : *A sample of coal has the following composition by mass : C = 80%, H = 4%, O = 6%, S = 3%, N = 2% and Ash = 5%. Calculate gross and net calorific value using Dulong's formula.* **MU - May 2014, 5 Marks**

Solution :

$$GCV = \frac{1}{100}\left[8080\,C + 34500\left(H - \frac{O}{8}\right) + 2240\,S\right]$$

$$= \frac{1}{100}\left[8080 \times 80 + 34500\left(4 - \frac{6}{8}\right) + 2240 \times 3\right]$$

$$= \frac{1}{100}[646400 + 112125 + 6720] = \frac{1}{100}[765245]$$

$\therefore$ GCV $= \boxed{7625.45\ \text{Kcal / Kg}}$

$\therefore$ NCV $=$ GCV $- (0.09\ H \times 587)$

$= 7625.45 - (0.09 \times 4 \times 587) = 7625.45 - (211.32)$

$\therefore$ NCV $= \boxed{7414.13\ \text{Kcal /Kg}}$

Ans. : ***G.C.V. = 7625.45 kcal/kg.***
N.C.V. = 7414.13 kcal/kg.

Example 3.12.16 : *A sample of coal has the following coraposition by mass : C = 75%, H = 7%, O = 8%, S = 4%, N = 2% and Ash = 4 %. Calculate Gross Calorific value of the fuel using Dulong's formula.* **MU - Dec. 2014, 3 Marks**

Solution :

$$H.C.V = \frac{1}{100}\left[8080\,C + 34500\left(H - \frac{O}{8}\right) + 2240\,S\right]$$

$$= \frac{1}{100}[8080 \times 75 + 34500\{7 - 8/8\} + 2240 \times 4]$$

$$= \frac{1}{100}[606000 + 34500\{7 - 1\} + 8960]$$

$$= \frac{1}{100}[606000 + 207000 + 8960]$$

$$= \frac{1}{100}[821960] = \boxed{8219.60\ \text{kcal/kg.}}$$

$$L.C.V. = \left[H.C.V - \frac{9}{100}H \times 587\right]\ \text{kcal/kg.}$$

$$= [8219.60 - 0.09 \times 7 \times 587]$$

$$= [8219.60 - 369.81] = \boxed{7849.79\ \text{kcal/kg.}}$$

Ans. : ***H.C.V. = 8219.60 kcal/kg.***
L.C.V. = 7849.79 kcal/kg.

3.13 Solved Numericals : Combustion of Solid Fuels - Requirement of weight and Volume of O_2 and Air

Example 3.13.1 : *Calculate the weight and volume of air required for complete combustion of 5 kg. coal with following compositions, C = 85%; H = 10%; O = 5%.*

Solution

Combustion reactions :

$$C + O_2 \rightarrow CO_2 \qquad C = 85\% = 0.85 \text{ kg}$$

$$12 + 32 \rightarrow 44 \qquad H = 10\% = 0.10 \text{ kg}$$

$$H_2 + \frac{1}{2} O_2 \rightarrow H_2O \qquad 5\% = 0.05 \text{ kg}$$

$$2 + 16 \rightarrow 18$$

Calculation of O_2 needed for 1 kg coal

Elements = Weight in kg	Weight of O_2 required for complete combustion in kg.
C = 0.85	$0.85 \times \frac{32}{12} = 2.26$ kg.
H = 0.1	$0.1 \times 8 = 0.8$ kg.
O = 0.05	–
	Total oxygen = 3.06 kg.

Weight of oxygen required

= Weight of oxygen needed – weight of oxygen present

$= 3.06 - 0.05 = \boxed{3.01 \text{ kg}}$

∴ *Weight of Air required for complete combustion*

[∵ Air contains 23% O_2 by weight]

$$= 3.01 \times \frac{100}{23} = \boxed{13.08 \text{ kg. per 1 kg. coal.}}$$

∴ *Air required for 5 kg. of coal*

$$= 13.08 \times 5 = \boxed{65.40 \text{ kg.}}$$

Volume of Air

∵ 28.94 kg. of air = 22,400 ml volume at NTP

$$\therefore \quad 65.4 \text{ kg. of air} = \frac{22400 \times 65.4}{28.94} = 50620.6 \text{ ml. air}$$

$$= \boxed{50.6206 \text{ litres of air}}$$

Ans. : Weight of air required = 65.4 kg.

Volume of air required = 50.62 litres.

Example 3.13.2 : *Calculate the weight of air needed for complete combustion of 1 gm of coal containing : C = 72%, H = 10%, O = 9%, N = 3% and remaining being ash.*

Solution : **Combustion reactions**

$$C + O_2 \rightarrow CO_2 \qquad C = 72\% = 0.72 \text{ kg}$$

$$12 \quad 32 \quad 44 \qquad H = 10\% = 0.10 \text{ kg}$$

$$H_2 + \frac{1}{2} O_2 \rightarrow H_2O \qquad O = 9\% = 0.09 \text{ kg}$$

$$2 \quad 16 \quad 18 \qquad N = \text{No combustion reaction}$$

Calculation of O_2 needed in kg for 1 kg coal.

Element	Weight	O_2 required for complete combustion
C	0.72	$0.72 \times \frac{32}{12} = 1.92$ kg
H	0.10	$0.1 \times \frac{16}{2} = 0.8$ kg
O	0.09	–
N	0.03	–
		Total oxygen = 2.72 kg

∴ Weight of oxygen required = Weight of oxygen needed – Weight of oxygen present

$= 2.72 - 0.09$

$= \boxed{2.63 \text{ kg}}$

$\therefore$ Weight of air required for complete combustion $= 2.63 \times \frac{100}{23}$

$= \boxed{11.43 \text{ kg per 1 kg coal}}$

Ans. : *Weight of air required for complete combustion = 11.43 kg*

Example 3.13.3 : *A sample of coal has the following percentage composition by mass :*

C = 70% H = 10% O = 5%

N = 2% S = 3% and remaining ash

Calculate the minimum amount of air needed for complete combustion of 1 kg of coal.

Solution :

Data given : C = 70 % H = 10 % O = 5 % N = 2 % S = 3 %

Reaction :

$$\underset{12}{C} + \underset{32}{O_2} \rightarrow \underset{44}{CO_2}$$

$$\underset{2}{H_2} + \frac{1}{2}O_2 \rightarrow \underset{18}{H_2O}$$

$$\underset{32}{S} + \underset{32}{O_2} \rightarrow \underset{64}{SO_2}$$

C = 70% = 0.70 kg
H = 10% = 0.10 kg
S = 3% = 0.03 kg
O = 5% = 0.05 kg

Calculation of O_2 needed for 1 kg coal.

Element weight in kg	Weight of O_2 required for complete combustion
C = 0.70	$0.70 \times \frac{32}{12} = 1.87$
H = 0.10	$0.1 \times \frac{16}{2} = 0.80$
S = 0.03	$0.03 \times \frac{32}{32} = 0.03$
O = 0.05	–
Total O_2	2.7 kg

$\therefore$ Weight of O_2 required = Weight of O_2 needed – Weight of O_2 present

$= 2.70 - 0.05$

$= \boxed{2.65 \text{ kg}}$

Weight of air $= 2.65 \times \frac{100}{23}$ kg

$= \boxed{11.52 \text{ kg}}$

Ans. : *Weight of air = 11.52 kg*

Example 3.13.4 : *Calculate the volume of air containing 25 % oxygen by volume at 27° C and 760 mm pressure which will be required for complete combustion of 3 kg fuel containing, C = 75%; H = 23%; and Ash = 2%.*

Solution :

Calculation of O_2 needed for 1 kg coal.

Components	% Composition	Weight of elements per kg. of fuel	Weight of O_2 in kg for 1 kg fuel
Carbon	75	0.75	$\frac{32}{12} \times 0.75 = 2.00$
Hydrogen	23	0.23	$\frac{16}{2} \times 0.23 = 1.84$
Ash	2	–	–
			–
		Total O_2	3.84 kg

$\therefore$ Weight of O_2 required per 3 kg of fuel = 11.5275 kg.

Volume of oxygen at NTP

$\because$ 32 kg. of $O_2 \rightarrow$ 22.4 cu.m. of O_2

$\therefore$ 11.5275 kg of $O_2 = \frac{22.4 \times 11.5275}{32} = 8.06$ cu.m.

Now $\therefore \frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$

$$\frac{760 \times 8.06}{273} = \frac{760 \times V_2}{300}$$

$$V_2 = \frac{1837680}{207480}$$

$\therefore V_2 = 8.857$ cu.m. O_2

But, air contains 25% O_2 by volume.

∴ 25 cu.m. of O_2 is present in 100 cu.m. of air.

∴ 8.857 cu.m. of O_2 is present in $\frac{8.857 \times 100}{25}$ = **35.43 cu.m. of air.**

Ans. : *Volume of air = 35.43 cu.m*

Example 3.13.5 : *A sample of coal requires 20% excess air for complete combustion. Calculate weight of air for 250 gm of the coal, if its composition is,*

C = 81%, H = 4%, N = 1.5%, S = 1.2%, O = 3%, ash = 9.3%.

Solution : *Let us calculate the O_2 required for 1 kg of coal first.*

$$\text{Weight of carbon} = \frac{81}{100} \times 1 = 0.81 \text{ kg}$$

$$\text{Weight of hydrogen} = \frac{4}{100} \times 1 = 0.04 \text{ kg}$$

$$\text{Weight of sulphur} = \frac{1.2}{100} \times 1 = 0.012 \text{ kg}$$

$$\text{Weight of oxygen} = \frac{3}{100} \times 1 = 0.03 \text{ kg}$$

Calculation of O_2 needed for 1 kg coal.

Reactions	Weight of O_2 required
$C + O_2 \rightarrow CO_2$ 12 32	$0.81 \times \frac{32}{12} = 2.16$ kg
$2\,H_2 + O_2 \rightarrow 2\,H_2O$ 4 32	$0.04 \times \frac{32}{4} = 0.32$ kg
$S + O_2 \rightarrow SO_2$ 32 32	$0.012 \times \frac{32}{32} = 0.012$ kg
	Total O_2 required = 2.492 kg Less O_2 available = – 0.03
	Net O_2 required = 2.462 kg

$$\text{Weight of air required} = \frac{\text{weight of } O_2 \times 100}{23} = 10.7 \text{ kg air.}$$

As 20% excess is required for complete combustion, then practically required weight of air

$$= \frac{10.7 \times 120}{100} = 12.845 \text{ kg air.}$$

As 1000 gm of coal requires 12.845 kg air.

∴ 250 gm of coal requires = $\frac{250}{1000} \times 12.845$ = **3.211 kg air.**

Example 3.13.6 : *A petrol sample contains 14% H and 86% C. Calculate volumes of oxygen and air required for complete combustion of 1 kg of the petrol, at STP conditions.*

Solution :

Given data : Weight of petrol = 1 kg, weight of C = $\frac{86}{100} \times 1$ = 0.86 kg.

Weight of H = $\frac{14}{100} \times 1$ = 0.14 kg, O % = 0

Calculation of O_2 needed for 1 kg coal

Reactions	Weight of oxygen required
$C + O_2 \rightarrow CO_2$	$\frac{32}{12} \times 0.86 = 2.293$ kg
$2\,H_2 + O_2 \rightarrow 2\,H_2O$	$\frac{32}{4} \times 0.14 = 1.12$ kg
	Total O_2 = 3.413 kg

As 32 gm O_2 at STP occupies 22.4 lit.

∴ 3.413 × 1000 gm O_2 at STP will occupy $\frac{3.413 \times 1000 \times 22.4}{32}$ lit.

= **2389.3 litres oxygen gas.**

Volume of air at STP = Volume of $O_2 \times \frac{100}{21}$ = **11377.8 litres air.**

Ans. : *Volume of O_2 = 2389.3 liters*

Volume of air = 11377.8 liters

Example 3.13.7 : *A sample of coal contains C = 65%, H = 13%, O = 6%, S = 4%, N = 2%, and ash = remaining. Calculate the minimum amount of air needed for complete combustion of 1 kg. of coal.*

Solution :

Given data :

C = 65%, H = 13%, O = 6%

S = 4%, N = 2%

ash = Remaining

wt of coal = 1 kg

To calculate = minimum amount of air.

Combustion reactions

$C + O_2 \rightarrow CO_2$ C = 65% = 0.65 kg

$12 + 32 \rightarrow 44$ H = 13% = 0.13 kg

$H_2 + \frac{1}{2} O_2 \rightarrow H_2O$ O = 6% = 0.06 kg

$2 + 16 \rightarrow 18$ S = 4% = 0.04 kg

Calculation of O_2 need for 1 kg coal

elements	Wt of O_2 required for complete combustion of 1 kg coal
C = 0.65	$0.65 \times \frac{32}{12} = 2.26$ kg
H = 0.13	$0.13 \times 8 = 1.04$ kg
O = 0.06	= 0.06 kg
S = 0.04	$0.04 \times \frac{32}{32} = 0.04$ kg
N = 0.02	–

Total oxygen needed = 3.34 kg.

∴ Weight of oxygen required = weight of oxygen needed – weight of oxygen present

= 3.34 – 0.06

= **3.28 kgs**

∴ Weight of air required for complete combustion = $3.28 \times \frac{100}{23}$

= **14.26 kg for 1 kg coal.**

∴ Volume of air

∵ 28.94 kg of air = 22400 ** at NTP

∴ 14.26 kg of air = $\left[\frac{22400 \times 14.26}{28.94}\right]$ ml of air

= **11.03 litres of air**

Ans. : *Weight of air required = 14.26 kg*

Volume of air required = 11.03 litres

Example 3.13.8 : *A coal sample has the following composition by weight. C = 84 %, H = 6%, S = 1%, O = 8% and remaining ash. Calculate the minimum quantity of air required both by weight and volume for the complete combustion of 2 kg of this fuel. (Mol. Wt. of air = 28.94).*

Solution

Given Data :

Weight of coal sample = 2 kg

C = 84 % H = 6 %

S = 1 % O = 8%

Ash = Remaining

To calculate : Minimum quantity of air by weight and volume.

Calculation of O_2 needed for 1 kg coal

Element	%	Weight per kg of coal	Weight of O_2 in kg
C	84	0.84	$0.84 \times \frac{32}{12} = 2.24$
H	6.0	0.06	$0.06 \times \frac{16}{2} = 0.48$
O	8.0	0.08	–
S	1.0	0.01	0.01*32/32=0.01
		Total O_2	2.73 kg

∴ Weight of oxygen required = weight of O_2 needed – weight of O_2 present

= 2.72 – 0.08 = **2.64 kg**

∴ Weight of air required = Amount of O_2 needed $\times \frac{100}{23}$

for 1 kg coal

$$= 2.64 \times \frac{100}{23} = \boxed{11.48 \text{ kgs}}$$

$\therefore$ for 2 kgs $= 2 \times 11.48 = 22.96$ kgs

$\therefore$ Volume of air = No. of moles of air × 22.4 litres required for 1 kg coal

$$= \frac{11.48}{28.94} \times 22.4$$

$$= \boxed{8.89 \text{ litres}}$$

$\therefore$ for 2 kgs $= 2 \times 8.89 = \boxed{17.78 \text{ litres}}$

Ans. : *Weight of air = 22.96 kgs*
Volume of air = 17.78 litres

Example 3.13.9 : *A sample of coal contains C = 75%, H = 12 %, O = 6%, S = 4%, remaining being other impurities and ash. Calculate the minimum amount of air by volume and weight required for complete combustion of 5 kg. of fuel.*

Solution :

Given : C = 75%, H = 12 %, O = 6%, S = 4%, Weight of fuel = 5 kg

To calculate minimum amount of air for complete combustion - by volume and weight

Calculation of O_2 needed for 1 kg coal

Component Weight in Kg	Combustion reaction	Weight of O_2 required in Kg.
C = 0.75	$C + O_2 \rightarrow CO_2$ $12 + 32 \rightarrow 44$	$0.75 \times \frac{32}{12} = 2.00$
H = 0.12	$H_2 + \frac{1}{2} O_2 \rightarrow H_2O$	$0.12 \times \frac{16}{2} = 0.96$
S = 0.04	$S + O_2 \rightarrow SO_2$	$0.04 \times \frac{32}{32} = 0.04$
	Total = 3.00 Kg.	
O = 0.06	Total required $O_2 = 3.00 - 0.06 = 2.94$ Kg.	

$\therefore$ O_2 required for 5 Kg fuel $= 2.94 \times 5$

$$\boxed{= 14.70 \text{ Kg}}$$

Now minimum weight of air required

for 5 Kg of fuel $= 14.70 \times \frac{100}{23}$

$$\boxed{= 63.91 \text{ Kg}}$$

Volume of air required

If 28.94 Kg of air ≡ 22400 ml. at NTP

Then 63.91 Kg of air $\equiv \left[\frac{63.91 \times 22400}{28.94}\right]$ ml. at NTP

$$= \boxed{\textbf{49467.31 ml. or 49.47 litres at NTP.}}$$

Example 3.13.10 : *A coal sample has the following composition by weight C = 85%, H = 5%, S = 2%, O = 5% and Ash = 3%. Calculate the minimum quantity of air required both by weight and volume for the complete combustion of 2 kgs of coal.*

Solution :

Calculation of weight of O_2 needed for 1 kg coal

Reaction	Wt. of O_2 required.
$\underset{12}{C} + \underset{32}{O_2} \rightarrow CO_2$	$0.85 \times \frac{32}{12} = 2.67$
$\underset{4}{2H_2} + \underset{32}{O_2} \rightarrow 2H_2O$	$0.05 \times \frac{32}{4} = 0.40$
$\underset{32}{S} + \underset{32}{O_2} \rightarrow SO_2$	$0.02 \times \frac{32}{32} = 0.02$
O_2	= 0.05 kg.
Total O_2 required O_2 present	3.09 kg. 0.05 kg.

$\therefore$ O_2 needed = 3.04 kg.

$\therefore$ Weight of air required $= 3.04 \times \frac{100}{23}$

$= 13.217$ kg.

$\therefore$ For 2 kg coal $=$ **26.434 kg of air**

Volume of Air :

$\because$ 28.94 kg air $=$ 22400 ml. volume at NTP.

$\therefore$ 26.434 kg air $= \dfrac{22400 \times 26.434}{28.94}$ ml.

$= 20460.92$ ml.

$=$ **20.461 litres of air**

Example 3.13.11 : *Calculate the weight and volume of air needed for complete combustion of 1 kg of coal containing,*
C = 65%, H = 4%, O = 7 %, N = 3.0%
Moisture = 15% and remaining is Ash.
Molecular weight of air = 28.949

Solution :

Constituents	% by Weight	Weight of each per kg.
C	65	0.65
H	04	0.04
O	07	0.07
N	03	–
Moisture	15	–

(i) Weight of air required $= \dfrac{100}{23}(2.67C + 8H + S - O)$ kg

$= \dfrac{100}{23}(2.67 \times 0.65 + 8 \times 0.04 + 0 - 0.07)$ kg

$= \dfrac{100}{23}(1.733 + 0.32 - 0.07)$ kg

$= \dfrac{100}{23}(1.9833)$ kg

$\therefore$ ***Weight of air required*** $=$ **8.623 kg**

(ii) Volume of air required :

Molecular weight of air $=$ 28.949 g.

$\because$ 28.949 kg of air occupies $=$ 22.4 m^3 of air

$\therefore$ 8.623 kg of air occupies $= \dfrac{8.623}{28.949} \times 22.4$

$=$ **6.672 m^3 of air**

Ans. : *Weight of air required = **8.632 kg***

*Volume of air required = **6.679 kg***

Example 3.13.12 : *Calculate the weight and volume of air required for complete combustion of 1 kg of coal containing ; C = 65%, H = 4%, O = 7%, N = 3%, moisture = 15% and remaining is ash. (molecular weight of air = 28.94g)*

MU - Dec. 2012, 6 Marks

Solution :

% element	Wt. in kg.	Combustion Reaction	Wt. of O_2 required (kg)
C = 65 %	0.65 Kg.	$C + O_2 \rightarrow CO_2$ 12 32	$0.65 \times \dfrac{32}{12} = 1.73$
H = 4 %	0.04 Kg.	$H_2 + \dfrac{1}{2} O_2 \rightarrow H_2O$ 2 16	$0.04 \times \dfrac{16}{2} = 0.32$
O = 7 %	0.07 Kg.	-	0.07
Moisture 15 %	-	-	-
N = 3 %	0.03 Kg.	No reaction	-
		Total O_2 required	2.05
		O_2 present	– 0.07
		O_2 needed	1.98

$\therefore$ Weight of air required $= 1.98 \times \dfrac{100}{23}$

$=$ **8.6087 Kg.**

$\therefore$ Volume of air required =

$\because$ 28.94 Kg air $\equiv$ 22400 ml Volume at NTP

$\therefore$ 8.6087 Kg air $\equiv \left[\frac{22400 \times 8.6087}{28.94}\right] = 6663.27$ ml

$= \boxed{6.663 \text{ litres.}}$

Ans. : *Wt. of air needed = 8.6087 Kg.*
Volume of air needed = 6.663 litres.

Example 3.13.13 : *A Coal sample has the following composition by weights : C = 82%, H = 3%, O = 8%, S = 2%, N = 2% and Ash = 3%. Calculate the minimum amount of air required both by weight and volume for complete combustion of 2 kg of coal. (Molecular weight of air = 28.949 gm)*

MU - May 2013, 6 Marks

Solution :

Calculation of Weight of O_2 needed for 1 Kg of coal

% Constituent	Weight in kg.	Combustion Reaction	Weight of O_2 in kg.
C = 82	0.82	$C + O_2 \rightarrow CO_2$ 12 32	$0.82 \times \frac{32}{12} = 2.187$
H = 3	0.03	$H_2 + \frac{1}{2} O_2 \rightarrow H_2O$ 2 16	$0.03 \times \frac{16}{2} = 0.240$
S = 2	0.02	$S + O_2 \rightarrow SO_2$ 32 32	$0.02 \times \frac{32}{32} = 0.020$
O = 8	0.08	–	0.08
		Total O_2 Required	= 2.447
		Oxygen available	– 0.080
		$\therefore$ Oxygen needed	2.367 kg.

$\therefore$ Weight of air needed $= 2.367 \times \frac{100}{23}$ Kg.

$= 10.29$ kg.

$\therefore$ Weight of air for 2 kg coal $= (10.29 \times 2)$

$= \boxed{20.58 \text{ kg}}$

To calculate volume of air for 2 kg coal,

$\because$ 28.949 kg air $\equiv$ 22.4 Litres

$\therefore$ 20.58 kg air $\equiv \left(\frac{22.4 \times 20.58}{28.949}\right)$ Litres

$\equiv \boxed{15.92 \text{ Litres}}$

Ans. : *Weight of air = **20.58 kg***
*Volume of air = **15.92 L***

Example 3.13.14 : *1.5 g of a coal sample was burnt in a cumbustion apparatus and the products of Combustion were collected in previously weighted KOH bulb and C_aCl_2 tube. The increase in Weights of KOH bulb and C_aCl_2 tube were found to be 3.92g and 1.25 g respectively. Calculate percentage carbon and hydrogen in the sample.*

MU – Dec. 2015, 3 Marks

Solution :

wt. of coal sample = 1.5 gm

Change of wt. of $CaCl_2$ tube = 1.25 gm

Change of wt. of KOH tube = 3.92 gm

To calculate : % C, % H

Reactions :

$C + O_2 \rightarrow CO_2$ ...(Absorbed on KOH)

12 32 44

$2H_2 + O_2 \rightarrow 2H_2O$ ...(Absorbed on $CaCl_2$)

4 32 36

or 2 16 18

Hence wt. of CO_2 obtained = 3.92 gms.

and wt. of H_2O obtained = 1.25 gms

Thus if 44 gm CO_2 ≡ 12 gm Carbon

∴ 3.92 gm CO_2 ≡ 3.92 * 12/44 = 1.07 gm Carbon

Thus 1.5 gm sample of coal contain 1.231 gm carbon.

∴ % Carbon in coal = 1.07 * 100/1.5

= 71.3 %

Similarly,

If 18 gm H_2O ≡ 2 gm Hydrogen

∴ 1.25 gm H_2O ≡ $\frac{1.25 \times 2}{18}$ gm Hydrogen

≡ 0.139 gm Hydrogen

Thus 1.5 gm sample of coal contains 0.139 gm H_2.

∴ % Hydrogen = $\frac{0.139 \times 100}{1.5}$ = **9.26 %**

Ans. : *% C in coal = 71.3 %*

% H in coal = 9.26%

Example 3.13.15 : *A sample of coal has the following composition by mass : C =70 %, H = 10% O = 4% S=2%, N=2% and Ash = 12%. Calculate Gross and Net calorific value using Dulong's formula.*

MU – Dec. 2015, 5 Marks

Solution :

Given data :

C = 70% S = 2%

H = 10% N = 2%

O = 4% Ash = 12%

To calculate GCV and NCV of coal sample

$$GCV = \frac{1}{100}\left[8080\,C + 34500\left(H - \frac{O}{8}\right) + 22405\right]$$

$$= \frac{1}{100}\,[8080 * 70 + 34500\,(10 - 4/8) + 2240 * 2]$$

$$= \frac{1}{100}\,[565600 + 327750 + 4480] = \frac{1}{100}\,[897830]$$

= 8978.30 kcal/kg

∴ **GCV = 8978.30 kcal / kg** **...Ans.**

Now NCV = GCV – (0.09 × % H × 587)

= 8978.30 – (0.09 × 10 × 587)

= 8978.30 – 528.7

= **8449.6 kcal / kg** **...Ans.**

3.14 Solved Numericals : Combustion of Gaseous Fuels – Requirement of Oxygen and Air [Volume and Weight] :

Example 3.14.1 : *A gaseous fuel has following composition by volume – CH_4 = 35%, CO = 10%, H_2 = 6%, C_3H_8 = 10%. Calculate the weight of air required for complete combustion. (Given : Molecular weight of air = 28.94)*

Solution :

Given data :

Volume of gas fuel = 1 m^3, Volume of H_2 = 0.06 m^3

Volume of CH_4 = 0.35 m^3, Volume of CO = 0.1 m^3

Volume of C_3H_8 = 0.1 m^3

Calculation of Volume of O_2 needed for 1m^3 of fuel

Reactions	Volume of O_2 required
$2\,H_2 + O_2 \rightarrow 2\,H_2O$ 2 vol. 1 vol.	1/2 × 0.06 = 0.03m^3
$CH_4 + 2\,O_2 \rightarrow CO_2 + 2\,H_2O$ 1 vol. 2 vol.	2/1 × 0.35= 0.7 m^3
$CO + 0.5\,O_2 \rightarrow CO_2$	0.5 × 0.1 = 0.05 m^3
$C_3H_8 + 5\,O_2 \rightarrow 3CO_2 + 4\,H_2O$	5 × 0.1 = 0.5 m^3
Total O_2 required	= 1.28 m^3
O_2 present in sample	nil

Total O_2 required = 1.28 m^3

$$\text{Volume of air} = \text{Volume of } O_2 \times \frac{100}{21} = 1.28 \times \frac{100}{21}$$

$$= 6.095 \text{ m}^3 \text{ of air} = 6.095 \text{ litres air}$$

$\therefore$ weight of air

$\because$ 22.4 litres = 28.94 kg air

$\therefore$ 6.095 litres = $\left(\frac{6.095 \times 28.94}{22.4}\right)$ kg of air = **7.874 kg of air**

Ans. : *Volume of air = 6.095 m³ or 6095 litres air*
Weight of air = 7.874 kg

Example 3.14.2 : *A gaseous fuel has following composition by volume. H_2 = 35.00%, CH_4 = 7.00%, C_2H_6 = 4.00%, CO = 6.00%, N_2 = 8.00% Calculate the volume of air required for complete combustion of one cubic meter of this fuel.*

Solution :

Given data

Volume of gas fuel = 1 m³,
Volume of CH_4 = 0.07 m³,
Volume of C_2H_6 = 0.04 m³
Volume of H_2 = 0.35 m³
Volume of CO = 0.06 m³
Volume of N_2 = 0.08m³

Calculation of Volume of O_2 needed for 1m³ of fuel

Reactions	Volume of O_2 required
$2\,H_2 + O_2 \rightarrow 2\,H_2O$ 2 vol. 1 vol.	$\frac{1}{2} \times 0.35 = 0.175$ m³
$CH_4 + 2\,O_2 \rightarrow CO_2 + 2\,H_2O$ 1 vol. 2 vol.	$2/1 \times 0.07 = 0.14$ m³
$C_2H_6 + 3.5\,O_2 \rightarrow 2\,CO_2 + 3\,H_2O$ 1 vol. 3.5 vol.	$3.5 \times 0.04 = 0.14$ m³
$CO + 0.5\,O_2 \rightarrow CO_2$	$0.5 \times 0.06 = 0.03$ m³
Total O_2 required	= 0.485 m³
O_2 present in sample	nil

Total O_2 required = 0.485 m³

$$\text{Volume of air} = \text{Volume of } O_2 \times \frac{100}{21} = 0.485 \times \frac{100}{21}$$

$$= 2.309 \text{ m}^3 \text{ of air} = \boxed{23090 \text{ litres air.}}$$

Ans. : *Volume of air required = 2.309 m³ or 23090 litres air*

Example 3.14.3 : *A gas has following composition by volume : CH_4 = 40%, C_2H_6 = 20%, C_3H_8 = 10%, H_2 = 10%, CO = 10%, N_2 = 10%. Calculate weight of air required per m³ of gas. (Mol wt of air = 28.94)*

Solution : Given data

Volume of gas fuel = 1 m³,
Volume of CH_4 = 0.4 m³,
Volume of C_2H_6 = 0.2 m³
Volume of C_3H_8 = 0.1 m³
Volume of H_2 = 0.1 m³
Volume of CO = 0.1 m³
Volume of N_2 = 0.1 m³

Calculation of Volume of O_2 needed for 1m³ of fuel

Reactions	Volume of O_2 required
$2\,H_2 + O_2 \rightarrow 2\,H_2O$ 2 vol. 1 vol.	$\frac{1}{2} \times 0.1 = 0.05$ m³
$CH_4 + 2\,O_2 \rightarrow CO_2 + 2\,H_2O$ 1 vol. 2 vol.	$2/1 \times 0.4 = 0.8$ m³
$C_2H_6 + 3.5\,O_2 \rightarrow 2\,CO_2 + 3\,H_2O$ 1 vol. 3.5 vol.	$3.5 \times 0.2 = 0.7$ m³
$CO + 0.5\,O_2 \rightarrow CO_2$	$0.5 \times 0.1 = 0.5$ m³
$C_3H_8 + 5\,O_2 \rightarrow 3CO_2 + 4\,H_2O$	$5 \times 0.1 = 0.5$ m³
N_2 (No reaction)	–
Total O_2 required	= 2.55 m³
O_2 present in sample	nil

Total O_2 required = 2.55 m³

$$\text{Volume of air} = \text{Volume of } O_2 \times \frac{100}{21} = 2.55 \times \frac{100}{21}$$

$$= 12.14 \text{ m}^3 \text{ of air} = \boxed{12140 \text{ litres air.}}$$

Ans. : *Weight of air required = 12.14 m³ or12140 litres air*

Example 3.14.4 : *A gas has the following composition by volume H_2 = 20%, CH_4 = 6%, CO = 22%, CO_2 = 4%, O_2 = 4% and N_2 = 44%. Find the volume of air actually supplied per m^3 of this gas.*

Solution :

(i) Calculations for minimum air for complete combustion

Volume of CH_4 in 1 m^3 gas = 0.06 m^3

Volume of CO in 1 m^3 gas = 0.22 m^3

Volume of H_2 = 0.2 m^3

Volume of N_2 = 0.44 m^3

Volume of CO_2 = 0.04 m^3

and Volume of O_2 = 0.04 m^3

Calculation of volume of O_2 needed for 1m^3 of fuel

Reaction	Volume of O_2 required m^3
$CH_4 + 2\,O_2 \rightarrow CO_2 + H_2O$	$2 \times 0.06 = 0.12$
$CO + 0.5\,O_2 \rightarrow CO_2$	$0.5 \times 0.22 = 0.110$
$H_2 + 0.5\,O_2 \rightarrow H_2O$	$0.5 \times 0.2 = 0.10$
CO_2 (no reaction)	–
N_2 (no reaction)	–
Total O_2 required	= 0.33
O_2 in sample	= 0.04
	Total O_2 required = 0.29 m^3

Volume of air = 0.29 × 100/21 = **1.381 m^3**

Ans. : Volume of air = 1.381 m^3

Example 3.14.5 : *Calculate volume of air required for complete combustion of 1 cu.m. of gaseous fuel having following compositions by @volume. H_2 = 25%; C_2H_4 = 10%; CH_4 = 30%; CO = 32%; N_2 = 2% and water vapour = 1%.*

Solution :

Compounds	% By volume	Per cu.m.
H_2	25	0.25
C_2H_4	10	0.10
CH_4	30	0.30
CO	32	0.32
N_2	2	0.02
Water Vapour	1	0.01

Equation involved

1) $2H_2 + O_2 \rightarrow H_2O$

2 vol. 1 vol.

∴ 0.25 vol. Of H_2 required $\frac{0.25}{2}$ = **0.125 cu.m. of O_2.**

2) $C_2H_4 + 3O_2 \rightarrow 2CO_2 + 2H_2O$

1 vol. 3 vol.

∴ 0.1 vol. Of C_2H_4 = **0.3 cu.m. of O_2.**

3) $CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$

1 vol. 2 vol.

∴ 0.3 vol. of CH_4 = **0.6 cu.m. of O_2.**

4) $2CO + O_2 \rightarrow 2CO_2$

2 vol. 1 vol.

∴ 0.32 vol. of CO = $\frac{0.25}{2}$ = **0.3 cu.m. of O_2.**

∴ Total O_2 = 0.125 + 0.3 + 0.6 + 0.16

= **1.185 cu.m. of oxygen.**

Air contains 21 percentage O_2 by volume.

∴ 21 cu.m. of O_2 = 100 cu.m. of air

∴ 1.185 cu.m. of O_2 = $\frac{100}{21}$ (1.185)

= **5.64 cu.m.**

Ans. : ***Volume of air required = 5.64 cu.m.***

Example 3.14.6 : *A gas has following compounds by volume. H_2 = 20%; CH_4 = 10%, CO = 25%; O_2 = 5%; CO_2 = 15%; N_2 = 20%. Calculate volume of air at 25 °C and 750 mm. Pressure for complete combustion of 1 cu.m of fuel.*

Solution :

Compounds	% By volume	Per cu.m
H_2	20	0.2
CH_4	10	0.1
CO	25	0.25
CO_2	15	0.15
O_2	5	0.05
N_2	20	0.2

$$2H_2 + O_2 \rightarrow H_2O$$

2 Vol. 1 Vol.

$\therefore$ 0.2 cu.m H_2 = **0.1 cu.m of O_2.**

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$$

1 Vol. 2 Vol.

$\therefore$ 0.1 cu.m CH_4 = **0.2 cu.m of O_2**

$$2CO + O_2 \rightarrow 2CO_2$$

2 Vol. 1 Vol.

$\therefore$ 0.25 cu.m CO = **0.125 cu.m of O_2.**

$$\text{Total } O_2 = [(0.1 + 0.2 + 0.125) - 0.05] \text{ Cu.m}$$

$$= \mathbf{0.375 \text{ cu.m}}$$

$$\frac{P_0 V_0}{T_0} = \frac{P_1 V_1}{T_1}$$

$$\therefore \frac{760 \times 0.375}{273} = \frac{750 \times V_1}{298}$$

$$\therefore V_1 = 0.414 \text{ cu.m}$$

Volume of O_2 in air = 21%

21 cu.m $O_2 \rightarrow$ 100 cu.m air

$$0.414 \text{ cu.m } O_2 = \frac{100 \times 0.414}{21} = 1.975 \text{ cu.m}$$

Ans. : *Volume of air = 1.975 cu.m*

Example 3.14.7 : *A gaseous fuel contains H_2 = 50%, CH_4 = 30%, N_2 = 2%, CO = 7%, C_2H_4 = 3%, C_2H_6 = 5% and H_2O vapour = 3%. Calculate volume of air required for complete combustion of 1 m^3 of the gas.*

Solution :

Given data

Volume of gas fuel = 1 m^3, Volume of H_2 = 0.5 m^3

Volume of $CH_4 = \frac{30}{100} \times 1 = 0.3$ m^3, Volume of CO $= \frac{7}{100} \times 1 = 0.07$ m^3

Volume of $C_2H_4 = \frac{3}{100} \times 1 = 0.03$ m^3, Volume of $C_2H_6 = \frac{5}{100} \times 1 = 0.05$ m^3

Calculation of volume of O_2 needed for 1m^3 of fuel

Reactions	Volume of O_2 required
$2H_2 + O_2 \rightarrow 2H_2O$ 2 vol. 1 vol.	$\frac{1}{2} \times 0.5 = 0.25$ m^3
$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$ 1 vol. 2 vol.	$\frac{2}{1} \times 0.30 = 0.60$ m^3
$C_2H_4 + 3O_2 \rightarrow 2CO_2 + 2H_2O$ 1 vol. 3 vol.	$\frac{3}{1} \times 0.03 = 0.09$ m^3
$CO + 0.5O_2 \rightarrow CO_2$	$0.5 \times 0.07 = 0.035$
$C_2H_6 + 3.5O_2 \rightarrow 2CO_2 + 3H_2O$ 1 vol. 3.5 vol.	$\frac{3.5}{1} \times 0.05 = 0.175$ m^3

Total O_2 required = 1.150 m^3

$$\text{Volume of air} = \text{Volume of } O_2 \times \frac{100}{21} = 1.150 \times \frac{100}{21}$$

$$= 5.476 \text{ m}^3 \text{ of air}$$

$\therefore$ **Volume of air = 5476 litres air.**

Example 3.14.8 : *Calculate the volume of air required for complete combustion of 1 m³ of gaseous fuel which possess by volume : CH_4 = 35%, C_2H_4 = 5%, CO = 15%, H_2 = 40%, N_2 = 1%, Water Vapour = 4%.*

Solution :

Volume of fuel = 1 m³

Volume of CH_4 = 0.35 m³

Volume of C_2H_4 = 0.05 m³

Volume of CO = 0.15 m³

Volume of H_2 = 0.4 m³

Volume of N_2 = 0.01 m³ } No combustion reaction

Volume of Vapours = 0.04 m³

Calculation of Volume of O_2 needed for 1m³ of fuel.

Reaction	Vol. of O_2 m³ required
$CH_4 + 2O_2 \rightarrow CO_2 + H_2O$	$2 \times 0.35 = 0.7$ m³
$CO + 0.5O_2 \rightarrow CO_2$	$0.5 \times 0.15 = 0.075$ m³
$H_2 + 0.5\ O_2 \rightarrow H_2O$	$0.5 \times 0.4 = 0.2$ m³
$C_2H_4 + 3O_2 \rightarrow 2CO_2 + 2H_2O$	$3 \times 0.05 = 0.15$ m³
Total oxygen	1.125

$$\text{Volume of air} = 1.125 \times \frac{100}{21} = 5.357 \text{ m}^3 = 5357 \text{ litres}$$

Ans. : Volume of air = 5.357 m³
= 5357 litres.

Example 3.14.9 : *A gaseous fuel has the following composition by volume. CH_4 = 35%, C_2H_4 = 5%, CO = 15%, H_2 = 40% N_2 = 1 water vapour = 4% Calculate volume and weight of air required for complete combustion of 1m³ of fuel. [molecular weight of air = 28.94]* **MU - May 2015, 5 Marks**

Ans. :
Given data : CH_4 = 35 %, C_2H_4 = 5 %, CO = 15%, O_2 = Nil
H_2 = 40 %, CO_2 = 2 % , N_2 = 1 %,
Water Vapours = 4 %

Calculate of quantity of O_2

Component	Reaction	Volume of O_2
CH_4 = 0.35 m³	$CH_4 + 2\ O_2 \rightarrow CO_2 + 2\ H_2O$	$0.35 \times 2 = 0.7$ m³
C_2H_4 = 0.05 m³	$C_2H_4 + 3\ O_2 \rightarrow 2\ CO_2 + 2\ H_2O$	$0.05 \times 3 = 0.15$ m³
CO = 0.15 m³	$CO + \frac{1}{2}\ O_2 \rightarrow CO_2$	$0.15 \times \frac{1}{2} = 0.075$ m³
H_2 = 0.4 m³	$H_2 + \frac{1}{2}\ O_2 \rightarrow H_2O$	$0.4 \times \frac{1}{2} = 0.2$ m³

Volume of (Total) O_2 required = 1.125 m³

O_2 available in fuel = 0.00

∴ Net O_2 required = 1.125 m³

∴ Volume of air required = 1.125 × 100 / 21 m³
= 5.357 m³
= 5357 Ltrs

∴ Weight of air
∴ 22.4 litres = 28.94 kg air
∴ 5357 litres = 5357 × 28.94 / 22.4] kg of air
= 6921 kg of air

Ans. : Volume of air = 5.357 m³ or 5357 litres
Weight of air = 6921 kg

Example 3.14.10 : *The composition of gas was found to be H_2 = 10%, CH_4 = 16%, C_2H_6 = 20%, N_2 = 6%, CO = 22%, CO_2 = 18%, O_2 = Rest. Calculate the volume of air required for complete combustion of 10 m³, of this gas.*

Solution :

Given data :

Volume of gas fuel = 10 m³, Volume of H_2 = 0.1 m³
Volume of CH_4 = 0.16 m³, Volume of CO = 0.22 m³

Volume of C_2H_6 = 0.2 m^3 Volume of CO_2 = 0.18 m^3 } No combustion reaction

Volume of O_2 = 0.08 m^3 Volume of N_2 = 0.06 m^3

Calculation of volume of O_2 needed for 1m^3 of fuel.

Reactions	Volume of O_2 required
$2\,H_2 + O_2 \rightarrow 2\,H_2O$ 2 vol. 1 vol.	$\frac{1}{2} \times 0.1 = 0.05\ m^3$
$CH_4 + 2\,O_2 \rightarrow CO_2 + 2\,H_2O$ 1 vol. 2 vol.	$2/1 \times 0.16 = 0.32\ m^3$
$C_2H_6 + 3.5\,O_2 \rightarrow 2\,CO_2 + 3\,H_2O$ 1 vol. 3.5 vol.	$3.5 \times 0.2 = 0.7\ m^3$
$CO + 0.5\,O_2 \rightarrow CO_2$	$0.5 \times 0.22 = 0.110\ m^3$
Total O_2 required	$= 1.18\ m^3$
O_2 present in sample	$= 0.08\ m^3$

Total O_2 required = 1.10 m^3

$$\text{Volume of air} = \text{Volume of } O_2 \times \frac{100}{21} = 1.10 \times \frac{100}{21}$$

$$= 5.238\ m^3 \text{ of air}$$

$\therefore$ **Volume of air = 5238 litres air.** ...Ans.

Example 3.14.11 : *The composition of a gas was found to be H_2 = 10%, CH_4 = 16%, C_2H_6 = 20%, N_2 = 6%, CO = 22%, CO_2 = 18%, O_2 = rest. Calculate the volume of air required for complete combustion of 1 m^3 of this gas.*

Solution :

Given data :

Volume of gas = 1 m^3, Volume of H_2 = 0.10 m^3

Volume of CH_4 = 0.16 m^3, Volume of C_2H_6 = 0.20 m^3

Volume of N_2 = 0.06 m^3, Volume of CO = 0.22 m^3

Volume of CO_2 = 0.18 m^3, Volume of O_2 = remaining 8% = 0.08 m^3

Calculation of volume of O_2 needed for 1m^3 of fuel

Reactions	Volume of O_2 required
$2H_2 + O_2 \rightarrow 2H_2O$ 2 vol 1 vol.	$\frac{1}{2} \times 0.10 = 0.05\ m^3$
$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$ 1 vol 2 vol.	$2 \times 0.16 = 0.32\ m^3$
$C_2H_6 + 3.5O_2 \rightarrow 2CO_2 + 3H_2O$ 1 vol + 3.5 vol.	$3.5 \times 0.2 = 0.70\ m^3$
$CO + \frac{1}{2}\,O_2 \rightarrow CO_2$, 1 vol $\frac{1}{2}$ vol	$\frac{1}{2} \times 0.22 = 0.11\ m^3$
N_2 and CO_2 (No reaction)	–
Total O_2 required	**1.18 m^3**
O_2 present in sample	**0.08 m^3**

Total O_2 needed = 1.10 m^3

$$\text{Volume of air} = \text{volume of } O_2 \times \frac{100}{21}\ m^3$$

$$= 1.10 \times \frac{100}{21}\ m^3$$

$$= \boxed{5.238\ m^3}$$

$$= 5238 \text{ litres}$$

Ans. : **Volume of air required = 5.238 m^3 or = 5238 litres**

Example 3.14.12 : *A gas has following composition by volume H_2 = 20%, CH_4 = 6%, CO = 22%, CO_2 = 4%, O_2 = 4% and N_2 = 44%, find the volume of air actually required per m^3 for complete combustion of this gas.*

Solution :

Given :

H_2 = 0.20 m^3, O_2 = 0.04 m^3

CH_4 = 0.06 m^3, N_2 = 0.44 m^3

CO = 0.04 m^3

Calculation of volume of O_2 needed for $1m^3$ of fuel

Reaction	Volume of O_2 reqd.	
$2H_2 + O_2 \rightarrow 2H_2O$ 2 Vol 1 Vol	$\frac{1}{2} \times 0.2 = 0.1\ m^3$	
$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$ 1 Vol 2 Vol	$\frac{2}{1} \times 0.06 = 0.12\ m^3$	
$CO + \frac{1}{2} O_2 \rightarrow CO_2$	$\frac{1}{2} \times 0.22 = 0.11\ m^3$	
CO_2, N_2	No reaction	
O_2	$= 0.04\ m^3$	
$\therefore$ O_2 required O_2 present	$0.33\ m^3$ $0.04\ m^3$	$\therefore$ **O_2 needed = 0.29 m^3**

$$\text{Volume of air} = \text{Vol. of } O_2 \times \frac{100}{21}$$

$$= 0.29 \times \frac{100}{21}$$

Ans. : **Volume of air = 1.381 m^3 of air or**
= 1381 litres of air

Example 3.14.13 : *The composition of gas was found to be H_2 =10%, CH_4 = 20%, C_2H_6 = 16%, N = 6%, CO = 18%, CO_2 = 22%. O_2 = rest. Calculate volume of air required for $1m^3$ of this gas.*

Solution :

Given :

$H_2 = 10\ \% = 0.1\ m^3$ N = 6 % O_2 = remaining (8 %) = 0.08 m^3

$CH_4 = 20\ \% = 0.2\ m^3$ CO = 18 % = 0.18 m^3

$C_2H_6 = 16\ \% = 0.16\ m^3$ CO_2 = 22 % = 0.22 m^3

To calculate volume of air required for $1m^3$ gas.

Reactions and calculation of oxygen required.

Reactions	Volume of oxygen required, m^3
$H_2 + \frac{1}{2} O_2 = H_2O$ 1 0.5	$0.1 \times 0.5 = 0.05$
$CH_4 + 2O_2 = CO_2 + 2H_2O$ 1 2	$0.2 \times 2 = 0.40$
$C_2H_6 + 3.5O_2 = 2CO_2 + 3H_20$ 1 3.5	$0.16 \times 3.5 = 0.56$
$CO + \frac{1}{2} O_2 = CO_2$ 1 0.5	$0.18 \times 0.5 = 0.09$

CO_2 and N = No reaction

Total oxygen required	= 1.10 m^3
Oxygen present in sample	= 0.08
$\therefore$ Total O_2 required	= 1.02 m^3

$\therefore$ Volume of air = $1.02 \times \frac{100}{21}$ = **4.86m^3**

Ans. : **Volume of air = 4.86 m^3 or**
= 4860 L

Example 3.14.14 : *A gaseous fuel has the following composition by volume : H_2 = 35%, CH_4 = 45% C_2H_6 = 6%, CO=12% and remaining N_2. Calculate the minimum amount of air required a 27 °C and 760 mm Hg pressure for the complete combustion of 1 cu.m of the fuel.* **MU - May 2012, 4 Marks**

Solution :

H_2 = 0.35 m^3 , C_2H_6 = 0.06 m^3

CH_4 = 0.45 m^3 , CO = 0.12 m^3

Calculate of O_2 required

Sr. No.	Reaction	Volume of O_2 required
1.	$H_2 + \frac{1}{2} O_2 \longrightarrow H_2O$ 1 vol. 0.5 vol.	$0.35 \times 0.5 = 0.175\ m^3$
2.	$CH_4 + 2\ O_2 \longrightarrow CO_2 + 2\ H_2O$ 1 vol. 2 vol.	$0.45 \times 2 = 0.90\ m^3$
3.	$C_2H_6 + 3.5\ O_2 \longrightarrow 2CO_2 + 3\ H_2O$ 1 vol. 3.5 vol.	$0.06 \times 3.5 = 0.210\ m^3$
4.	$CO + \frac{1}{2} O_2 \longrightarrow CO_2$ 1 vol. 0.5 vol.	$0.12 \times 0.5 = 0.06\ m^3$
5.	N_2 No reaction.	–
	∴ Total O_2 required	$= 1.345\ m^3$
	O_2 present in fuel.	Nil

$$\therefore \quad \text{Volume of air required} = \text{Volume of } O_2 \times \frac{100}{21}$$

$$= \left(1.345 \times \frac{100}{21}\right) m^3$$

$$= 6.4048\ m^3$$

$$= 6.4048 \text{ litres of air}$$

$$\therefore \quad \text{Weight of air} = \because 22.4 \text{ litres air} \equiv 28.94 \text{ kg}$$

$$\therefore 6.4048 \text{ litres air} \equiv$$

$$= \boxed{8.274 \text{ kg}}$$

$$\text{Now,} \quad \frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$

$$\therefore \quad \frac{760 \times 6.4048}{273} = \frac{760 \times V_2}{273}$$

$$\therefore \quad V_2 = \frac{6.4048 \times 300}{273} = \boxed{7.038 \text{ litres air}}$$

Weight of air at 760 mm and 27°C :

$\because$ 22.4 litres air ≡ 28.94 kg

$\therefore$ 7.038 litres air ≡ 9.092 kg

Ans. : ***Volume of air = 7.038 Litres***
Weight of air = 9.092 kg

Example 3.14.15 : *A gaseous fuel has the following composition by volume : H_2 = 10%, CH_4 = 30%, C_3H_8 = 20%, CO = 20%, CO_2 = 15%, N_2 = 5%. Calculate the volume of air required for complete combustion of 1m³ of this gas.* **MU - May 2013, 5 Marks**

Solution :

Calculation of volume of O_2 required for complete combustion of 1m³ of gaseous fuel.

% Constitute	Volume of constituent (m³)	Combustion Reaction	Volume of O_2 required m³
H_2 = 10	0.10 m³	$H_2 + \frac{1}{2} O_2 \rightarrow H_2O$ 1 0.5	$0.10 \times 0.5 = 0.05$
CH_4 = 30	0.30 m³	$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$ 1 2	$0.30 \times 2 = 0.60$
C_3H_8 = 20	0.20 m³	$C_3H_8 + 5\ O_2 \rightarrow 3\ CO_2 + 4\ H_2O$ 1 5	$0.20 \times 5 = 1.00$
CO = 20	0.20 m³	$CO + \frac{1}{2} O_2 \rightarrow CO_2$ 1 0.5	$0.20 \times 0.5 = 0.10$
CO_2 and N_2	No Combustion Reaction		
	∴ Total O_2 required		**1.75 m³**

$\therefore$ Volume of air = Volume of $O_2 \times \frac{100}{21}$

$= \left(1.75 \times \frac{100}{21}\right) m^3$

$= \boxed{8.333\ m^3}$

$= \boxed{8333 \text{ litres}}$

Ans. : Volume of air required = 8333 L

Example 3.14.16 *: A gaseous fuel has the following composition by volume : $H_2 = 50\%$, $CO = 10\%$, $CH_4 = 30\%$, $C_2H_4 = 5\%$, $N_2 = 1\%$, $O_2 = 2\%$ and $CO_2 = 2\%$. Calculate volume and weight of air required for complete combustion of $1m^3$ of fuel. (Molecular weight of air = 28.949)*

MU - Dec. 2013, 6 Marks

Solution :

Calculation of volume of O_2 in m^3 for 1 m^3 of gaseous fuel

Sr. No.	Constituent %	Constituent Volume – m^3	Combustion Reaction	Volume of O_2
1.	$H_2 = 50$	0.5	$H_2 + \frac{1}{2} O_2 \rightarrow H_2O$ 1 1/2	$0.5 \times 0.5 = 0.25$
2.	$CO = 10$	0.1	$CO + \frac{1}{2} O_2 \rightarrow CO_2$ 1 $\frac{1}{2}$	$0.1 \times 0.5 = 0.05$
3.	$CH_4 = 30$	0.30	$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$ 1 2	$0.3 \times 2.0 = 0.60$
4.	$C_2H_4 = 5$	0.05	$C_2H_4 + 3O_2 \rightarrow 2\ CO_2 + 2\ H_2O$ 1 3	$0.05 \times 3 = 0.15$
5.	N_2 and CO_2	No reaction	**Total O_2 required**	**1.05**
6.	$O_2 = 2$	0.02	**O_2 available in fuel**	**0.02**
			$\therefore$ O_2 needed	**1.03 m^3**

$\therefore$ Volume of air needed $= \left(\text{Volume of } O_2 \text{ needed} \times \frac{100}{21}\right) m^3$

$= 1.03 \times \frac{100}{21}$

$= 4.904\ m^3 = \boxed{4904 \text{ litres}}$

$\therefore$ Weight of air :

$\because$ 22.4 litres air $\equiv$ 28.94 kg

$\therefore$ 4904 litres air $\equiv \left[\frac{4904 \times 28.94}{22.4}\right]$ kg air.

$\equiv \boxed{6338 \text{ kg air}}$

Ans. : Volume of air needed = 4905 L
Weight of air needed = 6338 kg

Example 3.14.17 *: A gaseous fuel has the following composition by volume. $H_2 = 55\%$, $CH_4 = 30\%$, $C_2H_4 = 5\%$, $CO = 5\%$, $N_2 = 1\%$, $CO_2 = 2\%$ and $O_2 = 2\%$. Calculate volume and weight of air required for complete combustion of $1m^3$ of fuel. (Molecular weight of air = 28.949)*

MU - May 2014, 6 Marks

Solution :

Calculation of volume of O_2 in m^3 for 1 m^3 of gaseous fuel

Sr. No.	Constituent %	Constituent Volume – m^3	Combustion Reaction	Volume of O_2
1.	$H_2 = 55$	0.55	$H_2 + \frac{1}{2} O_2 \rightarrow H_2O$ 1 1/2	$0.55 \times 0.5 = 0.275$
2.	$CO = 5$	0.05	$CO + \frac{1}{2} O_2 \rightarrow CO_2$ 1 $\frac{1}{2}$	$0.05 \times 0.5 = 0.025$
3.	$CH_4 = 30$	0.30	$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$ 1 2	$0.3 \times 2.0 = 0.60$
4.	$C_2H_4 = 5$	0.05	$C_2H_4 + 3O_2 \rightarrow 2\ CO_2 + 2\ H_2O$ 1 3	$0.05 \times 3 = 0.15$

Sr. No.	Constituent %	Constituent Volume – m^3	Combustion Reaction	Volume of O_2
5.	N_2 and CO_2	No reaction	Total O_2 required	1.05
6.	$O_2 = 2$	0.02	O_2 available in fuel	0.02
			∴ O_2 needed	1.03 m^3

$$\therefore \text{Volume of air needed} = \left(\text{Volume of } O_2 \text{ needed} \times \frac{100}{21}\right) m^3$$

$$= 1.03 \times \frac{100}{21}$$

$$= 4.904\ m^3 = \boxed{4904 \text{ litres}}$$

∴ Weight of air :

$$\because \quad 22.4 \text{ litres air} \equiv 28.94 \text{ kg}$$

$$\therefore \quad 4904 \text{ litres air} \equiv \left[\frac{4904 \times 28.94}{22.4}\right] \text{ kg air.}$$

$$\equiv \boxed{6338 \text{ kg air}}$$

Ans. : **Volume of air needed = 4905 L**

Weight of air needed = 6338 kg

Example 3.14.18 : *A gaseous fuel has the following composition by volume : H_2 = 40%, CH_4 = 30%, CO = 10%, C_3H_8 = 12%, N_2 = 3%, O_2 = 2% and CO_2 = 3%. Calculate volume and weight of air required for complete combustion of 1m³ of fuel. (Molecular Weight of air = 28.949)* **MU - Dec. 2014, 6 Marks**

Solution :

Calculation of volume of O_2 required for complete combustion of 1m³ of gaseous fuel.

% Constitute	Volume of constituent (m^3)	Combustion Reaction	Volume of O_2 required m^3
$H_2 = 40$	0.40 m^3	$H_2 + \frac{1}{2} O_2 \rightarrow H_2O$ 1 0.5	$0.40 \times 0.5 = 0.20$

% Constitute	Volume of constituent (m^3)	Combustion Reaction	Volume of O_2 required m^3
$CH_4 = 30$	0.30 m^3	$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$ 1 2	$0.30 \times 2 = 0.60$
$C_3H_8 = 12$	0.12 m^3	$C_3H_8 + 5\ O_2 \rightarrow 3\ CO_2 + 4\ H_2O$ 1 5	$0.12 \times 5 = 0.60$
$CO = 10$	0.10 m^3	$CO + \frac{1}{2} O_2 \rightarrow CO_2$ 1 0.5	$0.10 \times 0.5 = 0.05$
CO_2 and N_2	No combustion reaction		
$O_2 = 2$	minus		0.02
	∴ Total O_2 required		**1.42 m^3**

$$\therefore \text{Volume of air} = \text{Volume of } O_2 \times \frac{100}{21}$$

$$= [1.42 \times 100/21]\ m^3$$

$$= \boxed{6.762\ m^3}$$

$$= \boxed{6762 \text{ litres}}$$

∴ Weight of air :

$$\because \quad 22.4 \text{ litres air} \equiv 28.94 \text{ kg}$$

$$\therefore \quad 6762 \text{ litres air} \equiv 6762 \times 28.94 / 22.4 \text{ kg air.}$$

$$\equiv \boxed{8736.26 \text{ kg air}}$$

Ans. : ***Volume of air needed = 6762 L***

Weight of air needed = 8736.26 kg

Example 3.14.19 : *A gaseous fuel has the following composition by volume. CO = 40%, H_2 = 42%, C_3H_8 = 4%, CH_4 = 4%, N_2 = 4% and O_2 = 6%. Calculate volume and weight of air required for complete combustion of 1m³ of fuel (Molecular weight of air = 28.949)* **MU – May 2016, 6 Marks**

Solution :

Calculation of volume of O_2 in m^3 for 1 m^3 of gaseous fuel

Sr. No.	Constituent %	Constituent Volume – m^3	Combustion Reaction	Volume of O_2
1.	$H_2 = 42$	0.42	$H_2 + \frac{1}{2} O_2 \rightarrow H_2O$ 1 1/2	$0.42 \times 0.5 = 0.21$
2.	$CO = 40$	0.40	$CO + \frac{1}{2} O_2 \rightarrow CO_2$ 1 $\frac{1}{2}$	$0.40 \times 0.5 = 0.20$
3.	$CH_4 = 4$	0.04	$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$ 1 2	$0.04 \times 2.0 = 0.08$
4.	$C_3H_8 = 4$	0.04 m^3	$C_3H_8 + 5\,O_2 \rightarrow 3\,CO_2 + 4\,H_2O$ 1 5	$0.04 \times 5 = 0.20$
5.	N_2 and CO_2	No reaction	Total O_2 required	0.69
6.	$O_2 = 6$	0.06	O_2 available in fuel	0.06
			$\therefore$ O_2 needed	0.63 m^3

$$\therefore \text{Volume of air needed} = \left(\text{Volume of } O_2 \text{ needed} \times \frac{100}{21}\right) m^3$$

$$= 0.63 \times \frac{100}{21}$$

$$= 3.00\ m^3 = 3000 \text{ litres}$$

$\therefore$ Weight of air :

$\because$ 22.4 litres air $\equiv$ 28.94 kg

$\therefore$ 3000 litres air $\equiv$ 3000 * 28.94 / 22.4 kg air.

$\equiv$ **3875 kg air**

Ans. : **Volume of air needed = 3000 L**
Weight of air needed = 3875 kg

Example 3.14.20 : *A gaseous fuel has the following composition by volume.*
$CO = 46\%$ $H_2 = 30\%$
$CH_4 = 10\%$
$C_2H_4 = 4\%$ $N_2 = 1\%$
$CO_2 = 2\%$ and $O_2 = 7\%$
Calculate volume and weight of air required for complete combustion of 1m³ of fuel. (Mol.wt of air=28.949).

MU – Dec. 2015, 6 Marks

Solution :

Calculation of volume of O_2 in m^3 for 1 m^3 of gaseous fuel

Sr. No.	Constituent %	Constituent Volume – m^3	Combustion Reaction	Volume of O_2
1.	$H_2 = 30$	0.3	$H_2 + \frac{1}{2} O_2 \rightarrow H_2O$ 1 1/2	$0.3 \times 0.5 = 0.15$
2.	$CO = 46$	0.46	$CO + \frac{1}{2} O_2 \rightarrow CO_2$ 1 $\frac{1}{2}$	$0.46 \times 0.5 = 0.23$
3.	$CH_4 = 10$	0.10	$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$ 1 2	$0.1 \times 2.0 = 0.20$
4.	$C_2H_4 = 4$	0.04	$C_2H_4 + 3O_2 \rightarrow 2\,CO_2 + 2\,H_2O$ 1 3	$0.04 \times 3 = 0.12$
5.	N_2 and CO_2	No reaction	**Total O_2 required**	**0.70**
6.	$O_2 = 7$	0.07	**O_2 available in fuel**	**0.07**
			$\therefore$ O_2 needed	**0.63 m^3**

$$\therefore \text{Volume of air needed} = \left(\text{Volume of } O_2 \text{ needed} \times \frac{100}{21}\right) m^3$$

$$= 0.63 \times \frac{100}{21}$$

$$= 3.00\ m^3 = \boxed{3000 \text{ litres}}$$

∴ Weight of air :

∵ 22.4 litres air ≡ 28.94 kg

∴ 3000 litres air ≡ 3000 * 28.94 / 22.4 kg air.

≡ **3875 kg air**

Ans. : **Volume of air needed = 3000 L**
Weight of air needed = 3875 kg

3.15 Solved Numericals : Proximate and Ultimate Analysis

Example 3.15.1 : *By Kjeldahl's method 1.5 gm. of a sample of coal was analyzed. The ammonia evolved was absorbed in 50 ml. of 0.1 N H_2SO_4. After absorption the excess H_2SO_4 required 35 ml. of 0.1 N NaOH for neutralization. Calculate the percentage nitrogen.*

Solution :

Given : Weight of sample = 1.5 gms

NaOH consumed = 35 ml

Normality of H_2SO_4 and KOH = 0.1 N

Quantity of H_2SO_4 = 50 ml.

Amount of H_2SO_4 used = (50 – 35) ml. = 15 ml.

Equivalents of H_2SO_4 = $15 \times 0.1 = 1.5 = 1.5 \times 10^{-3}$ milli equivalents

∴ Weight of Nitrogen = $1.5 \times 10^{-3} \times 14 = 0.0021$ gms

$$\therefore \% \text{ Nitrogen} = \frac{\text{Weight of Nitrogen}}{\text{Weight of Coal sample}} \times 100$$

$$= \frac{0.0021}{1.5} \times 100$$

$$= \boxed{1.4\ \%}$$

Ans. : Percentage of nitrogen in coal sample = 1.4%.

Example 3.15.2 : *1.56 gm of the coal was Kjeldahlized and NH_3 gas thus evolved was absorbed in 50.0 ml of 0.1 N H_2SO_4. After absorption the excess (residual) acid required 6.25ml of 0.1 N NaOH for exact neutralization. 2.60 gm of the coal sample in a qualitative analysis gave 0.1755 gm of $BaSO_4$. Calculate the percentage of N and S in the coal sample.*

Solution :

(a) Calculation of % Nitrogen

Data : Weight of coal = 1.56 gm.

Volume of H_2SO_4 = 50 ml.

Volume of NaOH = 6.25 ml.

Normality of H_2SO_4 and NaOH = 0.1 N.

H_2SO_4 consumed = 50 – 6.25 = 43.75 ml.

Equivalents of H_2SO_4 = $43.75 \times 0.1 = 4.375 \times 10^{-3}$ milli equivalent

% Nitrogen = $N_2 = 4.375 \times 10^{-3} \times 14$ gm.

$$= \frac{\text{wt. of Nitrogen}}{\text{wt.of coal sample}} \times 100$$

$$= \frac{4.375 \times 10^{-3} \times 14}{1.56} \times 100 = \boxed{3.93\%}$$

(b) Calculation of % sulphur

Data : Weight of coal = 2.60 gm

Weight of $BaSO_4$ formed = 0.1755 gm

$$\% \text{ S} = \frac{\text{Wt. of } BaSO_4 \text{ formed}}{\text{Wt.of coal sample}} \times \frac{32}{233} \times 100$$

$$= \frac{0.1755}{2.60} \times \frac{32}{233} \times 100 = \frac{561.6}{605.8} = \boxed{0.93\%}$$

Ans. : *% N = 3.93 %*
% S = 0.93 %

Example 3.15.3 : *By Kjeldahl's method, 3.5 gms of the coal sample was analysed. The NH_3 gas evolved was absorbed in 50 ml of 0.1 N H_2SO_4. After the absorption, the residual (excess) H_2SO_4 required 15 ml. of 0.1 N NaOH for neutralization. Calculate the percentage of nitrogen in the sample of coal.*

Solution :

Given : Weight of sample = 3.5 gms

NaOH consumed = 15 ml

Normality of H_2SO_4 and NaOH = 0.1 N

Quantity of H_2SO_4 = 50 ml.

Amount of H_2SO_4 used = (50 – 15) ml.

= 35 ml.

Equivalents of H_2SO_4 = $35 \times 0.1 = 3.5$

= 3.5×10^{-3} milli equivalents

$\therefore$ Weight of Nitrogen = $3.5 \times 10^{-3} \times 14 = 0.05$ gms

$$\therefore \text{ \% Nitrogen} = \frac{\text{Weight of Nitrogen}}{\text{Weight of Coal sample}} \times 100$$

$$= \frac{3.5 \times 10^{-3} \times 14}{3.5} \times 100$$

$$= \frac{3.5 \times 14}{3.5 \times 1000} \times 100 = \frac{3.5 \times 14}{3.5} = \boxed{1.4\%}$$

Ans. : *Percentage of nitrogen in coal sample = 1.4%.*

Example 3.15.4 : *1.5 g of a sample of coal was taken for C and H estimation by combustion method. The increase in weights of tube containing anhydrous $CaCl_2$ and bulb containing KOH was found to be 1.25 g and 4.88 g respectively. Calculate the percentage of C and H.*

Solution :

Given Data :

wt. of coal sample = 1.5 gm

Change of wt. of $CaCl_2$ tube = 1.25 gm

Change of wt. of KOH tube = 4.88 gm

To calculate : % C

% H

Reactions :

$$C + O_2 \rightarrow CO_2 \quad \text{...(Absorbed on KOH)}$$

12 32 44

$$2H_2 + O_2 \rightarrow 2H_2O \quad \text{...(Absorbed on } CaCl_2\text{)}$$

4 32 36

or 2 16 18

Hence wt. of CO_2 obtained = 4.88 gms.

and wt. of H_2O obtained = 1.25 gms

Thus if 44 gm CO_2 ≡ 12 gm Carbon

$$\therefore \quad 4.88 \text{ gm } CO_2 \equiv \frac{4.88 \times 12}{44}$$

= 1.231 gm Carbon

Thus 1.5 gm sample of coal contain 1.231 gm carbon.

$$\therefore \quad \text{\% Carbon in coal} = \frac{1.231 \times 100}{1.5}$$

$$= \boxed{88.7\ \%}$$

Similarly,

If 18 gm H_2O ≡ 2 gm Hydrogen

$$\therefore \quad 1.25 \text{ gm } H_2O \equiv \frac{1.25 \times 2}{18} \text{ gm Hydrogen}$$

≡ 0.139 gm Hydrogen

Thus 1.5 gm sample of coal contains 0.139 gm H_2.

$$\therefore \quad \text{\% Hydrogen} = \frac{0.139 \times 100}{1.5} = \boxed{9.26\ \%}$$

Ans. : *% C in coal = 88.7%*

% H in coal = 9.26%

Example 3.15.5 : *1.95 g of a coal sample was taken for nitrogen estimation by Kjeldahl method. The ammonia liberated required 9.5 ml of 0.4N H_2SO_4 for neutralization. The same sample of coal weighting 1.5 g in a Bomb calorimeter experiment produced 0.35 g of $BaSO_4$. Calculate percentage of N and S.*

Solution :

Given Data :

Weight of coal sample for Nitrogen analsysis = 1.95 gm

Volume of H_2SO_4 = 9.5 gm

Normality of H_2SO_4 = 0.4 N

Weight of coal sample = 1.5 gms in Bomb calorimeter

Weight of $BaSO_4$ = 0.35 gms

To calculate : percentage N

$$N\ \% = \frac{\text{Volume of acid consumed} \times \text{Nacid} \times 1.4}{\text{Weight of coal sample}}$$

$$= \frac{9.5 \times 0.4 \times 1.4}{1.95} = 2.73\ \%$$

$$S\ \% = \frac{\text{Weight of } BaSO_4 \text{ ppt.} \times 32 \times 100}{\text{weight of coal sample} \times 233}$$

$$= \frac{0.35 \times 32 \times 100}{1.5 \times 233} = \frac{1120}{349.5}$$

$$\therefore\ S\ \% = \boxed{3.20\ \%}$$

Ans. : *N % = 2.73 %*
S % = 3.20 %

Example 3.15.6 : *3g of coal was heated in Kjeldahl's flask and NH_3 gas evolved was absorbed in 40 ml of 0.5 N H_2SO_4. After absorption, the excess acid required 18.5 ml of 0.5 N KOH for exact neutralization. 2.3 g of coal sample in quantitative analysis gave 0.35 g $BaSO_4$. Calculate the of N and S in the sample.*

Solution :

Percentage of N :

Volume of H_2SO_4 = 40 ml

Normality of H_2SO_4 = 0.5 N

Volume of KOH = 18.5 ml

Normality of KOH = 0.5 N

Weight of coal = 3 g

$$\therefore \text{Volume of } H_2SO_4 \text{ used} = (40 - 18.5)\ ml.$$

$$= 22.5\ ml$$

$$\%\ N = \frac{\text{Volume of } H_2SO_4 \text{ used} \times N_{H_2SO_4} \times 1.4}{\text{Weight of coal sample}}$$

$$= \frac{22.5 \times 0.5 \times 1.4}{3}$$

$$\%\ N = \boxed{5.25\ \%}$$

$$\%\ S = \frac{\text{Weight of } BaSO_4}{\text{Weight of Coal}} \times \frac{32}{233} \times 100$$

$$= \frac{0.35}{2.3} \times \frac{32}{233} \times 100 = \boxed{2.089\ \%}$$

Example 3.15.7 : *2.5 gms of coal sample was taken in Silica Crucible and heated in oven maintained at 110°C for one hour. The weight after heating was 2.368 gms. The same sample was analysed for volatile matter, and weight obtained was 1.75 gms. The sample was further treated to get a fixed weight of 0.95 gms. Calculate percentage of moisture, V.M., ash and F.C. for this sample.*

Solution :

Weight of moisture = 2.500 – 2.368 gm

= 0.132 gms.

Weight of volatile matter = 2.368 – 1.750

= 0.618 gms

Weight of ash = 0.95 gms

$$\therefore\ \%\ \text{moisture} = \frac{0.132}{2.5} \times 100 = \boxed{5.28\ \%}$$

$$\%\ \text{Volatile matter} = \frac{0.618}{2.5} \times 100 = \boxed{24.72\ \%}$$

$$\%\ \text{ash} = \frac{0.95}{2.5} \times 100 = \boxed{38.00\ \%}$$

$$\% \text{ Fixed carbon} = 100 - [5.28 + 24.72 + 38.00]$$
$$= 100 - [68.00]$$

$$\therefore \quad \% \text{ Fixed carbon} = \boxed{32\ \%}$$

Example 3.15.8 : *By Kjeldahle's method, 2.3 gms of coal sample was anlaysed for nitrogen content. The liberated ammonia was neutralized by 12.5 ml. of 0.5 N H_2SO_4 solution. The same weight of sample gave 0.64 gms of $BaSO_4$ precipitate. Calculate percentage of nitrogen and sulphur in the sample.*

Solution :

Percentage of N

Method 1

$$\text{Normality of } H_2SO_4 = 0.5 \text{ N}$$
$$\text{Volume of } H_2SO_4 \text{ used} = 12.5 \text{ ml.}$$
$$\therefore \quad M_{eq.} \text{ of } H_2SO_4 = (12.5 \times 0.5 \times 10^{-3}) = 6.25 \times 10^{-3}\ M_{eq.}$$
$$\therefore \quad \text{Weight of } N_2 = (6.25 \times 10^{-3} \times 14) \text{ gms}$$
$$= (87.5 \times 10^{-3}) \text{ gms}$$
$$\therefore \quad \% N = \frac{\text{Weight of Nitrogen}}{\text{Weight of coal}} \times 100$$
$$= \frac{87.5 \times 10^{-3}}{2.3} \times 100 = \boxed{3.80\ \%}$$

Method 2

$$\text{Volume of } H_2SO_4 \text{ used} = 12.5\%$$
$$\text{Normality of } H_2SO_4 = 0.5 \text{ N}$$
$$\therefore \quad \% N = \frac{\text{Volume of } H_2SO_4 \text{ used} \times N_{H_2SO_4} \times 1.4}{\text{Weight of coal sample}}$$
$$= \frac{12.5 \times 0.5 \times 1.4}{2.3} = \boxed{3.80\ \%}$$
$$\% S = \frac{\text{Weight of } BaSO_4}{\text{Weight of coal sample}} \times \frac{32}{233} \times 100$$

$$= \frac{0.64}{2.3} \times \frac{32}{233} \times 100$$
$$= \frac{20.48}{535.9} \times 100$$
$$\therefore \quad \% S = \boxed{3.82\ \%}$$

Example 3.15.9 : *3.2 gms of coal in Kjeldahl's experiment evolved NH_3 which was absorbed in 40 ml of 0.5 N H_2SO_4. After absorption, the excess acid required 16 ml of 0.5 N KOH for complete neutralization. 2.5 gms of coal sample in quantitative analysis gave 0.42 gm $BaSO_4$. Calculate the % of N and S in the sample.*

Solution :

$$\text{Weight of coal sample for } N_2 \text{ analysis} = 3.2\text{g}$$
$$\text{Volume of } H_2SO_4 = (40 \text{ ml} - 16) = 24 \text{ ml}$$
$$NH_2SO_4 = 0.5 \text{ N}$$
$$\text{Weight of coal sample in Bomb calorimeter} = 2.5 \text{ g.}$$
$$\text{Weight of } BaSO_4 \text{ ppt} = 0.42 \text{ g.}$$

To Calculate N%

$$= \frac{\text{Volume of acid consumed} \times N_{acid} \times 1.4}{\text{Wt. of coal sample}}$$
$$= \frac{24 \times 0.5 \times 1.4}{3.2}$$
$$= \boxed{5.25\ \%}$$

To Calculate S%

$$= \frac{\text{Weight of } BaSO_4 \text{ ppt}}{\text{Weight of Coal Sample}} \times \frac{32}{233} \times 100$$
$$= \frac{0.42}{2.5} \times \frac{32}{233} \times 100$$
$$= \frac{13.44}{582.5} \times 100$$
$$\therefore \quad S\% = \boxed{2.31\ \%}$$

Example 3.15.10 : *1.95 g of a coal sample was taken for Nitrogen estimation by Kjeldahl method. The ammonia liberated required 9.5 ml of 0.4 NH_2SO_4 for neutralization. The same sample of coal weighing 1.5 g in a Bomb's calorimeter experiment produced 0.35 g of $BaSO_4$. Calculate the percentage of N and S.*

Solution :

$$\% N = \frac{\text{Volume of acid consumed} \times 1.4}{\text{Weight of coal sample}}$$

$$= \frac{9.5 \times 0.4 \times 1.4}{1.95}$$

$$= \boxed{2.73\ \%}$$

$$\% S = \frac{\text{Weight of } BaSO_4 \text{ ppt} \times 32 \times 100}{\text{Weight of coal sample} \times 233}$$

$$= \frac{0.35 \times 32 \times 100}{1.55 \times 233}$$

$$= \boxed{3.20\ \%}$$

Ans. : ∴ % N = 2.73 %
∴ % S = 3.20 %

Example 3.15.11 : *2.5 of air dried coal sample was taken in a silica crucible, after heating it in an electric oven at 105° – 110°C for 1 hour, the residue was weighed 2.410g, The residue was heated in a silica crucible covered with vented lid at a temperature 950 ± 20°C for exactly 7 minutes. After cooling the weight of residue was found to be 1.78g. The residue was then ignited at 750°C to a constant weight of 0.246g. Calculate the percentage of fixed carbon in a coal sample.*

Solution :

(1) Weight of coal taken = 2.5 g

Mass of moisture in coal = 2.5 – 2.415

= 0.085 g.

$$\therefore \% \text{ of moisture} = \frac{\text{Loss in weight of coal}}{\text{weight of coal taken}} \times 100 = \frac{0.085 \times 100}{2.5}$$

$$= \boxed{3.4\ \%}$$

Mass of U. Matter = 2.415 – 1.78 = 0.635 g

(2) $$\% \text{ of volume Matter} = \frac{0.635 \times 100}{2.5}$$

$$= \boxed{25.4\ \%}$$

(3) Mass of residue after ignition = 0.246 g

$$\% \text{ of Ash} = \frac{\text{Weight of ash left}}{\text{Weight of coal taken}} \times 100 = \frac{0.246 \times 100}{2.5}$$

$$= \boxed{9.8\ \%}$$

(4) % of Fixed Carbon

= 100 – (% Moisture + V. M + Ash)

= 100 – (3.4 + 25.4 + 9.8)

= 100 – 38.6

$$= \boxed{61.4\ \%}$$

Ans. :
∴ % Moisture = 3.4 %
∴ % Volatile matter = 25.4 %
% Ash = 9.8%
% Fixed Carbon = 61.4%

Example 3.15.12 : *1kg of coal sample was used for determination of Nitrogen by Kjeldhal's method. The ammonia evolved was passed into 50 ml of 0.1N sulphuric acid. The excess acid required 42ml of 0.1N NaOH for neutralization. Calculate the percentage of N_2.*

MU - May 2012, 3 Marks

Solution :

Given data :

Weight of coal = 1 kg, Volume of H_2SO_4 = 50 ml.

Normality of H_2SO_4 = 0.1 N, Volume of NaOH = 4.2 ml.

Normality of NaOH = 0.1 N

To calculate % N in coal sample

$$\% N = \frac{\text{Volume of acid cosumed} \times \text{Normality of acid} \times 1.4}{\text{Weight of coal sample}}$$

Here, Volume of acid consumed = (50 – 42) ml.

$= 8$ ml.

$\therefore$ Equivalents of $H_2SO_4 = 8 \times 0.1$

$= 0.8$ milli equivalents.

$\therefore$ Weight of $N_2 = (0.8 \times 14)$ gms

$= 11.2$ gm

$$\therefore \% N_2 = \frac{\text{Weight of } N_2}{\text{Weight of coal sample}} \times 100$$

$$\therefore \% N_2 = \frac{11.2}{1000} \times 100 = \boxed{1.12}$$

Ans. : Volatile matter in coal = 1.12

Example 3.15.13 : *An air dried sample of coal weighing 2.9 g was taken for volatile matter determination. After losing volatile matter the coal sample weighed 1.96 g. If it contains 4.5% moisture, Find the percentage volatile matter in it.*

MU - May 2012, 4 Marks

Solution :

Given data :

Weight of coal = 2.9 gm

After losing volatile matter = 1.96 gm

% moisture = 4.5 %

To calculate % volatile matter.

Let us calculate weight of coal after losing moisture,

Let the weight be X gms.

$$\% \text{ moisture} = \frac{\text{Loss in weight after heating in oven}}{\text{weight of coal}} \times 100$$

$$\therefore 4.5 = \frac{2.9 - X}{2.9} \times 100$$

$$\therefore \frac{4.5 - 2.9}{100} = 2.9 - X$$

$$\therefore X = 2.9 - 0.1305$$

$$= 2.7695 \text{ gm}$$

Now,

$$\% \text{ Volatile matter} = \frac{\text{Loss in weight due to V.M.}}{\text{Weight of coal}} \times 100$$

$$= \frac{2.7695 - 1.9600}{2.9} \times 100$$

$$= \frac{0.8095}{2.9} \times 100$$

$$= \boxed{27.91\%}$$

Ans. : Volatile matter in coal = 27.91 %

Example 3.15.14 : *In a Kjeldahl's apparatus, 3.5g of the coal sample was analysed. The NH_3 gas evolved was absorbed in 50 ml of 0.1N H_2SO_4. The residual H_2SO_4 required 15 ml of 0.1N NaOH for neutralisation. Calculate percentage of nitrogen in the sample.*

MU - Dec. 2012, 3 Marks

Solution :

Weight of coal sample for N_2 analysis = 3.5 gms.

Volume of H_2SO_4 = 50ml

$N_{H_2SO_4}$ = 0.1 N.

Volume of NaOH = 15 ml.

N_{NaOH} = 0.1 N

To calculate N %

Here volume of acid consumed (0.1 NH_2SO_4) = (50 – 15) ml.

$= 35$ ml

$$\% N = \frac{\text{Volume of acid consumed} \times N_{acid} \times 1.4}{\text{Weight of coal}}$$

$$= \frac{35 \times 0.1 \times 1.4}{3.5} = \boxed{1.4\ \%}$$

Ans. : % N in coal Sample = 1.4 %

Example 3.15.15 : *2.499 gms of coal sample was taken in silica crucible and heated in oven maintained at 110 °C for one hour. The weight after heating was 2.368 gms. The same sample was analysed for volatile matter and weight obtained was 1.75g, the sample as further treated to get fixed wieght of 0.95 gms. Calculate the percentage of moisture, volatile matter, ash and fixed carbon for this sample.*

MU - Dec. 2012, 5 Marks

Solution :

Given data

Weight of coal Sample : 2.499 gms. = w_1

Weight of coal after heating at 110°C : 2.388 gms. = w_2

Weight of coal after heating for V.M. : 1.75 gms. = w_3

Fixed weight obtained = 0.95 gms. = w_4

$$\text{To calculate \% moisture} = \frac{\text{Loss in Weight}}{\text{Weight of coal}} \times 100$$

$$= \frac{w_1 - w_2}{w_1} \times 100$$

$$= \frac{0.111}{2.499} \times 100 = \boxed{4.44\ \%}$$

$$\text{To calculate \% V.M.} = \frac{\text{Loss in weight due to V.M.}}{\text{Weight of coal}} \times 100$$

$$= \frac{w_2 - w_3}{w_1} \times 100$$

$$= \frac{2.388 - 1.75}{2.499} \times 100 = \boxed{25.53\ \%}$$

$$\text{\% Ash} = \frac{\text{Constant weight}}{\text{Weight of coal}} \times 100$$

$$= \frac{0.95}{2.499} \times 100 = \boxed{38\ \%}$$

$$\text{\% Fixed carbon} = 100 - [\text{\% moisture} + \text{\% V.M.} + \text{\% Ash}]$$

$$= 100 - [4.44 + 25.53 + 38]$$

$$= 100 - [68.97]$$

$$\therefore \text{ \% Fixed carbon} = \boxed{31.03\ \%}$$

Ans. :

∴ % Moisture = 4.44 %
∴ % Volatile matter = 25.53 %
% Ash = 38.00 %
% Fixed Carbon = 31.03 %

Example 3.15.16 : *A coal sample was subjected to ultimate analysis, 0.6 gm of coal on combustion in a Bomb colorimeter, produces 0.05 gm $BaSO_4$. Calculate the percentage of 'S' in coal sample.*

MU - May 2013, 3 Marks

Solution :

Weight of coal sample = 0.6 gms.

Weight of $BaSO_4$ = 0.05 gms.

To calculate % S

$$\text{\% S} = \frac{\text{Weight of } BaSo_4 \text{ ppt}}{\text{Weight of Coal Sample}} \times \frac{32}{233} \times 100$$

$$= \frac{0.05}{0.6} \times \frac{32}{233} \times 100$$

$$= \frac{1.6}{139.8} \times 100$$

$$\therefore \text{ \% S} = \boxed{1.14\ \%}$$

Ans. : **∴ % S = 1.14 %**

Example 3.15.17 : *A coal sample was subjected to ultimate analysis. 1.5g of coal on combustion in a Bomb calorimeter gave 0.42g of $BaSO_4$. Calculate percentage sulphur in the coal sample.*

MU - Dec. 2013, 3 Marks

Solution :

Weight of Coal Sample = 1.5 gms.

Weight of $BaSO_4$ ppt = 0.42 gms.

To calculate % S in coal sample,

$$\text{\% S} = \frac{\text{Weight of } BaSO_4 \text{ ppt}}{\text{Weight of coal sample}} \times \frac{32}{233} \times 100$$

$$= \frac{0.42}{1.5} \times \frac{32}{233} \times 100$$

$$= \frac{13.44}{349.5} \times 100$$

$$\therefore \text{ \% S} = \boxed{3.85\ \%}$$

Ans. : **∴ % S = 3.85 %**

Example 3.15.18 : *A coal sample was subjected to ultimate analysis 1.5g of coal on combustion in a Bomb calorimeter gave 0.24g of $BaSO_4$. Calculate percentage sulphur in the coal sample.*

MU - May 2014, 3 Marks

Solution :

$$\% S = \frac{\text{Weight of } BaSO_4}{\text{Weight of coal sample}} \times \frac{32}{233} \times 100$$

$$= [0.24 \div 1.5] \times \frac{32}{233} \times 100$$

$$= [7.68 \div 349.5] \times 100$$

$$\therefore \% S = \boxed{2.197\ \% \sim 2.2\ \%}$$

Ans. : ∴ % S = 2.197 % ~ 2.2 %

Example 3.15.19 : *2.5 g. of a coal sample was analysed for nitrogen content by Kjeldahl's method. The liberated ammonia required 12.7 ml of 0.5N H_2SO_4 solution for neutralization. In a separate experiment, using Bomb calorimeter, 1.5 g of coal sample gave 0.28g of $BaSO_4$. Calculate percentage Nitrogen and Sulphur in the sample.*

MU - Dec. 2014, 5 Marks

Solution :

Given Data :

Weight of coal sample for Nitrogen analysis = 2.5 gm

Volume of H_2SO_4 = 12.7 ml

Normality of H_2SO_4 = 0.5 N

Weight of coal sample = 1.5 gms in Bomb calorimeter

Weight of $BaSO_4$ = 0.28 gms

To calculate : percentage N

$$N\ \% = \frac{\text{Volume of acid consumed} \times \text{N acid} \times 1.4}{\text{Weight of coal sample}}$$

$$= [12.7 \times 0.5 \times 1.4 \div 2.5]$$

$$= \boxed{3.56\ \%}$$

$$S\ \% = \frac{\text{Weight of } BaSO_4 \text{ ppt.} \times 32 \times 100}{\text{weight of coal sample} \times 233}$$

$$= \frac{0.35 \times 32 \times 100}{1.5 \times 233} [0.28 \times 32 \times 100] \div [1.5 \times 233]$$

$$= \frac{1120}{349.5} [896 \div 349.5]$$

$$\therefore S\ \% = \boxed{2.56\ \%}$$

Ans. : N % = 3.56 %
S % = 2.56 %

Example 3.15.20 : *2.5 gm of air dried coal sample was taken in a silica crucible, after heating it in an electric oven at 110° C for 1 hr the residue was weighed 2.41 gm. The residue was heated in Silica crucible covered with vented lid at a temperature 925 ± 25° C for exactly 7 minutes. After cooling the weight of residue was found to contain 1.98 gm. The residue was then ignited to a constant weight of 0.246 gm. Report the results of above analysis.*

MU - May 2015, 5 Marks

Solution :

(1) Weight of coal taken = 2.5 g

Mass of moisture in coal = 2.5 – 2.41

= 0.09 g.

$$\therefore \% \text{ of moisture} = \frac{\text{Loss in weight of coal}}{\text{weight of coal taken}} \times 100$$

$$= [0.09 \times 100 \div 2.5]\ \% = \mathbf{3.6\ \%}$$

(2) Mass of Volatile Matter = 2.41 – 1.78 = 0.63 g

% of volume Matter = [0.635 × 100 ÷ 2.5] = **25.4 %**

(3) Mass of residue after ignition = 0.246 g

$$\% \text{ of Ash} = \frac{\text{Weight of ash left}}{\text{Weight of coal taken}} \times 100 = \frac{0.246 \times 100}{2.5}$$

$$= \mathbf{9.8\ \%}$$

(4) % of Fixed Carbon = 100 – (% Moisture + V. M + Ash)

= 100 – (3.6 + 25.4 + 9.8) = 100 – 38.8 = **61.2 %**

Example 3.15.21 : *1.5 g of a coal sample was analysed for nitrogen content by Kjeldahl's method. The liberated ammonia required 14ml OF 0.1N H_2SO_4 solution for neutralization. In a separate experiment using Bomb Calorimeter, 1,5g of the same sample gave 0.3 g of $BaSO_4$. Calculate percentage nitrogen and sulphur in the sample.* **MU – May 2016, 5 Marks**

Solution :

Given Data :

Weight of coal sample for Nitrogen analysis = 1.5 gm

Volume of H_2SO_4= 14 ml

Normality of H_2SO_4 = 0.1 N

Weight of coal sample =1.5 gms in Bomb calorimeter

Weight of $BaSO_4$ = 0.3 gms

To calculate : percentage N

$$N\ \% = \frac{\text{Volume of acid consumed} \times \text{N acid} \times 1.4}{\text{Weight of coal sample}}$$

$$= [14 \times 0.1 \times 1.4 \div 1.5]$$

$$= \boxed{1.30\ \%}$$

$$S\ \% = \frac{\text{Weight of } BaSO_4 \text{ ppt.} \times 32 \times 100}{\text{weight of coal sample} \times 233}$$

$$= [0.3 \times 32 \times 100] \div [1.5 \times 233]$$

$$= [960 \div 349.5]$$

$$\therefore \quad S\ \% = \boxed{2.74\ \%}$$

Ans. : N % =1.30%

S % =2.74 %

Important Terms and Definitions

- *Fuels are all those substances which on combustion give large amount of heat energy.*

- Fuels can also be defined as substances which undergo combustion in the presence of air to produce a large amount of heat that can be used economically for domestic and industrial purpose.
- This definition does not include nuclear fuel because it cannot be used easily by a common man.
- Calorific value : Number of units of heat evolved during complete combustion of unit weight of the fuel.
- Calorific value can also be defined as, the number of parts of water which gets heated through 1°C by the heat evolved by the complete combustion of one unit weight of fuel (unit volume for gaseous fuels) under the conditions such as, (i) whole of heat evolved is absorbed by water (ii) the products formed leave the system at atmospheric temperature and pressure.
- A British Thermal Unit may be defined as, the heat required to raise the temperature of one pound of water from 60° F to 61° F.
- The Calorie, a unit of heat may be defined as, the heat required to raise the temperature of one kg of water from 15°C to 16°C.
- High calorific value may be defined as, the total amount of heat products when one unit of the fuel has been burnt completely and the products combustion have been cooled to 16°C or 60°F.
- Low calorific value may be defined as, the net heat produced when unit mass or volume of fuel is completely burnt and products are allowed to escape.
- The calorific value of fuels (e.g. Coal) is determined theoretically by Dulong formula, or I.A. Davies formula.
- Dulong formula can be expressed as,

$$Q = \frac{1}{100}\left[8080\ C + 34500\left(H - \frac{O}{8}\right) + 2240\ S\right]$$

Where, Q = Calorific value in K.C.U/kg

C = % Carbon

H = % Hydrogen

O = % Oxygen

S = % Sulphur

- The same formula in terms of H.C.V and L.C.V can be expressed as,

$$H.C.V = \frac{1}{100}\left[8080\ C + 34500\left(H - \frac{O}{8}\right) + 2240\ S\right]$$

and $L.C.V = \left[H.C.V - \frac{9}{100} H \times 587\right]$

Experimentally the calorific value of solid and liquid fuels is determined by using Bomb calorimeter.

- Proximate analysis is the study or analysis of coal sample in which
  a) moisture % b) volatile matter %
  c) ash % and d) fixed carbon % are determined.
- The analysis of coal in which percentages of C, H, N, S and O elements are found out, is known as ultimate analysis.

$$C\% = \frac{\text{Weight of } CO_2 \text{ formed} \times 12 \times 100}{\text{Weight of coal sample} \times 44}$$

$$H\% = \frac{\text{Weight of } H_2O \text{ formed} \times 2 \times 100}{\text{Weight of coal sample} \times 18}$$

$$N\% = \frac{\text{Volume of acid consumed} \times \text{normality of acid} \times 1.4}{\text{Weight of coal sample}}$$

OR $$N\% = \frac{\text{Volume of acid} \times \text{change in normality of acid} \times 1.4}{\text{Weight of coal sample}}$$

$$S\% = \frac{\text{Weight of } BaSO_4 \text{ ppt.} \times 32 \times 100}{\text{Weight of coal sample} \times 233}$$

O % : **It is obtained by difference,**

$$O\% = 100 - (C\% H\% + N\% + ash\% + S\%)$$

- The liquid fuels are generally the products obtained from petroleum refining.
- The main constituents of crude of raw petroleum are paraffin (C_nH_{2n+2}) naphthalene (C_nH_{2n}) and aromatic hydrocarbons (C_nH_{2n-4}). The concentrations of all these vary.
- Refining or fractionation is the process of separation of various fractions from crude oil, on the basis of fractional distillation.
- Cracking is a process of converging heavy oil with higher molecular weight hydrocarbons to the oil with lower molecular weight hydrocarbon which is known as gasoline.
- Knocking is a sharp metallic sound similar to rattling of hammer, which is produced in the internal combustion engine due to immature ignition of the air-gasoline mixture.

- Antiknocking agents are the compounds which help to increase the octane number of the fuel, decreasing the knocking.
- Scavanger is a Greek word meaning cleaning agent
- Octane number of a petrol sample is defined as the % of iso-octane in the mixture of iso-octane and n-heptane, which has similar knocking to the petrol sample.
- The knocking character of a petrol is expressed as "octane number".
- Cetane number of a diesel is defined as the % of n-hexadecane in the mixture of n-hexadecane and 2-methyl naphthalene which has same ignition character like the ignition character of the diesel under test.
- The suitability of a diesel is determined in terms of cetane number.

Unsolved Problems

Prob. 1 : Determine the gross and net calorific value of the fuel which on ultimate analysis gave following results. C = 92%; H = 4%; O = 2%; N = 1%; S = 0.3%; Ash = 0.7%. Assume latent heat of condensation of steam as 580 kcal/kg.

(Ans. : G.C.V. = 8734.07 kcal/kg, N.C.V. = 8525.27 kcal/kg)

Prob. 2 : A sample coal contains C = 76%; O = 16%; H = 5%; N = 1.5%; S = 0.3%; Ash = 1.0%. Calculate the higher and lower calorific value of coal.

(Ans. : G.C.V. = 7182.52 kcal/kg, N.C.V. = 6918.37 kcal/kg)

Prob. 3 : A sample of coal has following composition by mass C = 75%; H = 6%; O = 8%; Ash = 7.0%.and nitrogen to make 100%. Calculate H.C.V. and L.C.V.. Given that H.C.V. of C = 8080 kcal/kg. H = 34500 kcal/kg and S = 2240 kcal/kg. **(Ans. : H.C.V. =7785.00 kcal/kg , L.C.V. = 7468.02 kcal/kg)**

Prob. 4 : Calculate weight of the air needed for complete combustion of 5 kg of coal having C = 86%, H = 5%, S = 2.5%, N = 1.5%, remaining ash.

(Ans. : 59.02 kg.)

Prob. 5 : The percentage analysis of coal contains 85% carbon, 5% hydrogen, 1% suphur, 1% oxygen and remaining ash. Calculate weight and volume of air required for complete combustion of 4 kg of coal. **(Ans. : 46.44 kg and 35.95 cu.m.)**

Prob. 6 : The percentage composition of coal sample was C = 84%, H = 6.5%, O = 5.5%, N = 1%, S = 2.0%. Calculate the quantity of oxygen on volume basis required at 27° C and one atmosphere pressure for combustion of 1.5 kg of coal.

(Ans. : 3.47 cu.m.)

Prob. 7 : A gas used in internal combustion engine has 45% H_2, 35% CH_4, 15% CO and 5% N_2. Find the volume of air needed for the complete combustion of one cu.m. of gas. **(Ans. : 4.76 cu.m.)**

Prob. 8 : A gaseous fuel has following composition : H_2 = 40%, CH_4 = 30%, C_2H_6 = 20% and N_2 = 9%. Calculate the volume of air per cu.m. of gas if 30% excess of air is supplied. **(Ans. : 9.282 cu.m.)**

Prob. 9 : A gaseous fuel has following composition by volume, CH_4 = 40%, H_2 = 40%, C_2H_6 = 6%, N_2 = 1%. Calculate the volume for air required if 20% excess air is used for complete combustion. **(Ans. : 7.44 m^3)**

Review Questions

Q. 1 Define fuels. How are they classified ?

Q. 2 Distinguish clearly between
- (a) Peat and anthracite
- (b) Coal and coke
- (c) Octane number and cetane number.
- (d) Thermal and catalytic cracking.
- (e) Proximate analysis and ultimate analysis.

Q. 3 Compare the advantages of gaseous fuels over liquid fuels.

Q. 4 How is proximate analysis of coal conducted? What is its significance?

Q. 5 How is ultimate analysis carried out? What is its significance?

Q. 6 Define Gross and Net calorific value of a fuel.

Q. 7 Differentiate between Gross and Net calorific value of a fuel.

Q. 8 What are the characteristics of an ideal fuel ?

Q. 9 Write informative notes on :
- (a) Origin of petroleum
- (b) Mixing of petroleum
- (c) Separation and purification of petroleum

3.16 University Questions and Answers

May 2012

Q. 1 What is knocking ? Define octane number. What is unleaded petrol ? (4 Marks)
(Ans. : Refer sections 3.8.5, 3.8.6 and 3.8.2)

Q. 2 What is cracking ? Discuss the fixed bed catalytic cracking method in detail. (6 Marks)
(Ans. : Refer sections 3.7.1 and 3.7.2.2(a))

Dec. 2012

Q. 1 Give the characteristics of good fuel. (3 Marks)
(Ans. : Refer section 3.4)

Q. 2 Define cracking. Explain catalytic cracking. Discuss fixed-bed catalytic cracking. (5 Marks)
(Ans. : Refer sections 3.7.1, 3.7.2.2 and 3.7.2.2(a))

Q. 3 What is Bio-diesel ? Explain the trans-esterification method for production of Bio-diesel from vegetable oil. What are its advantages ? (6 Marks)
(Ans. : Refer sections 3.10, 3.10.1 and 3.10.2)

May 2013

Q. 1 Define Octane number and Cetane number. Give their significance. (3 Marks)
(Ans. : Refer sections 3.8.6 & 3.8.8)

Q. 2 Explain refining of petroleum with suitable diagram. (5 Marks)
(Ans. : Refer section 3.8.1)

Q. 3 What is bio-diesel ? Explain the method to obtain bio-diesel from vegetable oil. Give advantages of bio-diesel as a fuel. (6 Marks)
(Ans. : Refer sections 3.10, 3.10.1 and 3.10.2)

Dec. 2013

Q. 1 Define Octane number of gasoline, Name any two anti-knock agents. (3 Marks)
(Ans. : Refer sections 3.8.6 and 3.8.6.1)

Q. 2 What is Biodiesel ? Give 'Trans-estinification reaction in preparation of Biodisel from vegetable oils. What are the advantages of Biodiesel ? (5 Marks)
(Ans. : Refer sections 3.10, 3.10.1 and 3.10.2)

Q. 3 What is cracking ? With a schematic diagram, explain any one method of catalytic cracking. (6 Marks)
(Ans. : Refer sections 3.7.1 and 3.7.2.2(a) or (b))

May 2014

Q. 1 Define octane number of gasoline. How is knocking tendency of gasoline related to chemical structure of hydrocarbons present ? (3 Marks)
(Ans. : Refer sections 3.8.6 & 3.8.5)

Q. 2 With a suitable diagram, explain process of refining of petroleum. (5 Marks)
(Ans. : Refer section 3.8.1)

Q. 3 With a schematic diagram, explain fixed bed catalytic cracking. Mention any two advantages of catalytic cracking over thermal cracking. (6 Marks)
(Ans. : Refer sections 3.7.2.2(a) and 3.7.2.3)

Dec. 2014

Q. 1 What is 'cracking' of heavy oil ? Mention any four advantages of catalytic cracking over thermal cracking. (3 Marks)
(Ans. : Refer sections 3.7.1 and 3.7.2.3)

Q. 2 What is meant by 'Knocking' in internal combustion engine ? Define Octane number and Cetane number. Name any two anti-knock agents. (4 Marks)
(Ans. : Refer sections 3.8.5, 3.8.6, 3.8.6.1 and 3.8.8)

Q. 3 What is biodiesel ? Explain method to obtain biodiesel from vegetable oil. What are the advantages of biodiesel ? (6 Marks)
(Ans. : Refer sections 3.10, 3.10.1 and 3.10.2)

May 2015

Q. 1 What is cracking? Explain fixed bed catalytic cracking with diagram. (5 Marks)
(Ans. : Refer sections 3.7.1 and 3.7.2.2)

Syllabus topics : Biodiesel- Method to obtain Biodiesel from vegetable oils (Trans-esterification), advantages and disadvantages of biodiesel.

Q. 1 What is Bio-diesel ? Explain the trans-esterification method for production of Bio-diesel from vegetable oil. What are its advantages ?

(Ans. : Refer sections 3.10, 3.10.1 and 3.10.2)

(May 2012, Dec. 2013, Dec.2014, May 2015)

Q. 2 What is bio-diesel ? Explain the method to obtain bio-diesel from vegetable oil. Give advantages of bio-diesel as a fuel.

(Ans. : Refer sections 3.10, 3.10.1 and 3.10.2) **(May 2013)**

Syllabus topic - Calorific Value – GCV and NCV

Q. 1 Refer Example 3.3.2 **(May 2016)**

Syllabus Topic : Solid Fuels

Q. 2 Refer Example 3.5.4 **(May 2015)**

Solved Numericals (GCV, NCV Calculations by Dulong Formula)

Q. 1 Refer Example 3.12.13 **(May 2012)**

Q. 2 Refer Example 3.12.14 **(Dec.2013)**

Q. 3 Refer Example 3.12.15 **(May 2014)**

Q. 4 Refer Example 3.12.16 **(Dec.2014)**

Syllabus Topic : Solved Numericals : Combustion of Solid Fuels - Requirement of weight and Volume of O_2 and Air

Q. 1 Refer Example 3.13.12 **(Dec. 2012)**

Q. 2 Refer Example 3.13.13 **(May 2013)**

Syllabus Topic : Solved Numericals : Combustion of Gaseous Fuels – Requirement of Oxygen and Air [Volume and Weight] :

Q. 1 Refer Example 3.14.9 **(May 2015)**

Q. 2 Refer Example 3.14.14 **(May 2012)**

Q. 3 Refer Example 3.14.15 **(May 2013)**

Q. 4 Refer Example 3.14.16 **(Dec. 2013)**

Q. 5 Refer Example 3.14.17 **(May 2014)**

Q. 6 Refer Example 3.14.18 **(Dec. 2014)**

Q. 7 Refer Example 3.14.19 **(May 2016)**

Q. 8 Refer Example 3.15.12 **(May 2012)**

Q. 9 Refer Example 3.15.13 **(May 2012)**

Q. 10 Refer Example 3.15.14 **(Dec.2014)**

Q. 11 Refer Example 3.15.15 **(Dec.2012)**

Q. 12 Refer Example 3.15.16 **(May 2013)**

Q. 13 Refer Example 3.15.17 **(Dec.2013)**

Q. 14 Refer Example 3.15.18 **(May 2014)**

Q. 15 Refer Example 3.15.19 **(Dec.2014)**

Q. 16 Refer Example 3.15.20 **(May 2015)**

Q. 17 Refer Example 3.15.21 **(May 2016)**

□□□

CHAPTER 4

MODULE 4

Composite Materials

Syllabus

Introduction, Constitution- i) Matrix phase ii) Dispersed phase. Characteristic properties of composite materials. Classification- (A) Particle - reinforced composites- i) Large – particle reinforced composites ii) Dispersion - strengthened composites. (B) Fiber – reinforced composites- i) Continuous - aligned ii) Discontinuous - aligned (short)- (a) aligned (b) randomly oriented (C) Structural Composites- i) Laminates (ii) Sandwich Panels.

Syllabus Topic : Introduction

➢ **Topics covered :** What are composite material ? Defination of composited

4.1 Introduction

MU - May 2012

- *Composites are engineered materials,* comprising of *metals, ceramics, glasses and polymers.* The relationship between these three constituents with respective examples is shown in Fig. 4.1.1.
- The composites obtained using respective material exhibits *unique properties or qualities.*
- The composites show *better characteristics as compared to* those possessed by its *constituents.*
- Sometimes all together new/different characteristic is observed to be possessed by composite material which is not present in either of its constituents.

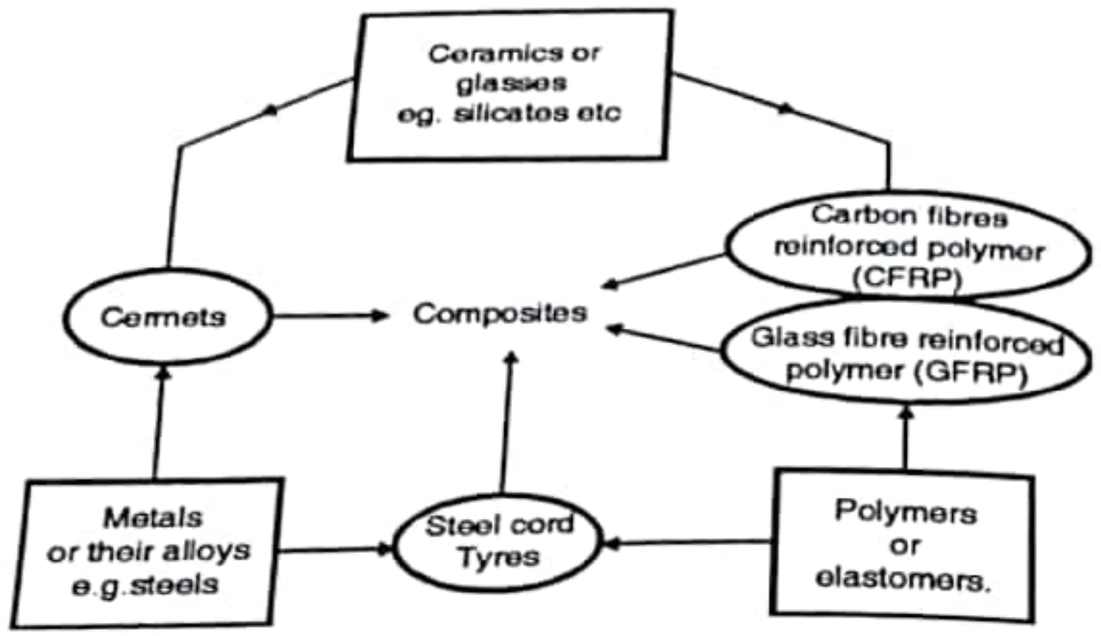


Fig. 4.1.1 : Engineering materials forming composites

- The combination of two or more existing materials is brought about by physical means. A composite in true sense must show *matrix material surrounding its reinforcing material* completely, in which the *two phases*, not only exist, but *act together* so as to produce the *desired characteristics*.

Examples

- Natural composite such as,
  - Wood or many other plant tissues contain cellulose chain polymer in a matrix of lignin.
  - Bone which contain soft but strong protein collagen and hard and brittle material apatite.
- Synthetic composites such as,
  - Rain proof cloth (cloth impregnated with waterproof material),
  - Packing paper impregnated with bitumen or wax,
  - Reinforced concrete,
  - Insulating tape are some examples.

4.1.1 Definition of composite

MU - Dec. 2012, Dec. 2014, May 2015, Dec. 2015

- Thus composite may be defined as, "A multiphase product made by using two or more existing materials which exhibits properties of its constituents as well as shows certain unique properties of its own."

- The properties of composite solely depend upon the composition of its constituents. Thus it is possible to form newer composites as per demand of technologies, such as in the field of :
  (i) Aerospace
  (ii) Marine
  (iii) Transportation
- For aerospace applications, the material with certain specific properties is required. Such a material should have following properties :
  (i) Low density
  (ii) High stiffness
  (iii) High strength
  (iv) High resistance to abrasion.
- All above properties are *contradictory* to each other like *to have high strength, density has to be high*. But *if* we combine a material of *low density* with other one with high strength and other properties, we can make a new material having all above properties. Such a new material is prepared by composing, hence called as *"composites"*.

Syllabus Topic : Constitution of composites

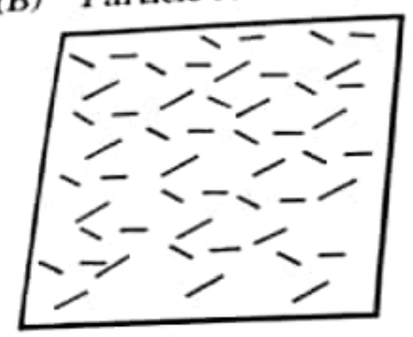
➢ **Topics covered :** phases of composites- matrix phase and its functions, & Dispersed phase.

4.2 Constitution of Composites

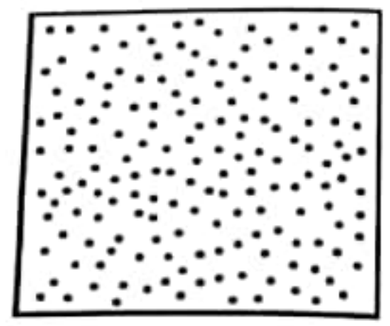
- Most of composites are made by using minimum two phases. The phases are namely :
  (a) Matrix phase
  (b) Dispersed phase.

  e.g. polymer composites in which matrix is of polymer and particles of metals/ceramic/fibre serves as dispersed phase.
- A *polymer* and a *reinforcing material* as a two phase mixture, with interfaces between them, is known as polymer composite.
- The polymer composite has properties of both the materials in combination.
- The polymer phase is called as *matrix* phase and the composite used for mixing is known as *dispersed phase*. The boundaries between the matrix and dispersed phase, are known as *inter phase*.

- On the basis of the dispersed phase used in the matrix, the polymer composites are of two types :
  (A) Fibre reinforced
  (B) Particle reinforced.



(A) Fibre reinforcement (fibres in polymer matrix)



(B) Particle reinforcement (particles in polymer matrix)

Fig. 4.2.1

4.2.1 Matrix Phase

MU - Dec. 2013, Dec. 2014, May 2015, May 2016

- *Matrix material* should have the properties such as :
  1. It should have adequate ductility.
  2. Its should possess lower *elastic modulus* as compared to that of the fibre used.
  3. It should *get bonded to fibre* very strongly, but with minimum pull out of fibre.
- The matrix material is selected on the basis of the properties mentioned in combination of the fibre. The proper choice of matrix and fibre gives *strong bonding* and ultimately a *good composite material.*

Examples

Metals such as Al, Cu which show high ductility bonded to the polymers such as thermoplastics and thermosets are most widely used as matrix material.

4.2.2 Functions of Martix

MU - Dec. 2013, Dec. 2014, May 2016

Functions of matrix constituent in polymer composite are,

(i) *To bind* the reinforcing particles/fibres *strongly.*

(ii) It acts as medium for distribution of applied load to the dispersed phase.

(iii) It keeps the reinforcing *fibres in proper orientation* for the high strength development.

(iv) It *prevents* propagation of *cracks* due to its plasticity.

MU - May 2015

4.2.3 Dispersed Phase

The dispersed phase comprises of fibres, normally with small diameter preferred to bulk ones. A special type of fibres, widely known as *Whiskers* are used.

- These fibres have following properties : [Properties of whiskers]
  1. They are very thin single crystal.
  2. They possess extremely large length/diameter ratios.
  3. They are flaw free
  4. They are small in size, hence the degree of crystalline perfection obtained is high.
  5. They are exceptionally strong.
- All above properties make *whiskers highly useful* as reinforcing fibres as dispersed phase. But still these are not used very commonly, due to following reasons,
  1. They are *costly.*
  2. The process of incorporating them in matrix phase is tedious.

Examples of whiskers are *oxides* (of Al), *carbides* and *nitrides* (of Si), *Graphite etc.*

The other simple fibre materials used as *dispersed phase* are :

1. Polycrystalline polymers or ceramics.
2. Amorphous polymers or ceramics.

Both above generally have *small diameters*, hence *preferred.*

Some important dispersed phase examples and their characteristics are given below :

(a) **Glass fibres**

- The glass fibres are produced by passing a glass melt through small orifices (holes) and cooled.
- Glass fibres are popular reinforcing materials. It offers very high tensile strength, higher thermal stability, high toughness and impact strength, to the polymer matrix.
- Polymers are filled with 20% to 40% glass fibres.

(b) **Carbon fibres**

- They are prepared from carbon by oxidation under tension at low temperature and then carbonization at 1000°C.

- These fibres are stiff, strong, even at high temperature.

(c) Aramid fibres

- Aramid is the aromatic polyamide e.g. Nomex, Kevlar.
- It has liquid-crystal polymer property.
- Its parallel arranged polymer chains for a long distance can be obtained from melt during drawing.
- The fibres have very high tensile strength, impact resistance, high thermal stability.

(d) Particles

- Metal powders, metal oxides, carbon black, metal carbides, silica powder, mica, salts, can be intimately mixed with the polymer matrix to make the composite.
- These materials offer high abrasion resistance, higher mechanical strength, better performance at higher temperature to the composite and may modify thermal and electrical conductivity of polymer.
- It is necessary that *the dispersed phase* should have *good compatibility* with the *polymer matrix* and there should be *strong interfacial bond* between the dispersed phase *and matrix phase,* otherwise the *composite* may *have low durability* and *easier failure* during working.

(e) Metallic wires such as *Molybdenum, Tungsten* or *High carbon* steel are also used as *dispersed phase.* These are more suitable for automobile tyres, wire wound high pressure hoses or filament wound rocket casting. Their specific uses are due to large diameter in wire form.

Syllabus Topic : Characteristic Properties of Composite Materials

4.3 Characteristic Properties of Composite Materials

MU - Dec. 2014, Dec.2015

Composits are made from combination of metals, polymers and ceramics or only metals, and ceramics. They possess following unique characteristics over individually metal / polymers / ceramics.

(1) They possess

(i) Low specific gravity

(ii) High specific strength

(iii) High specific stiffness

(iv) Low Thermal expansion

(v) High corrosion resistance

(vi) High oxidation resistance

(2) They can retain their strength at high temperature

(3) They show better toughness, impact and thermal shock resistace.

(4) They show better fatigue strength, and low thermal expansion and electrical conductivity.

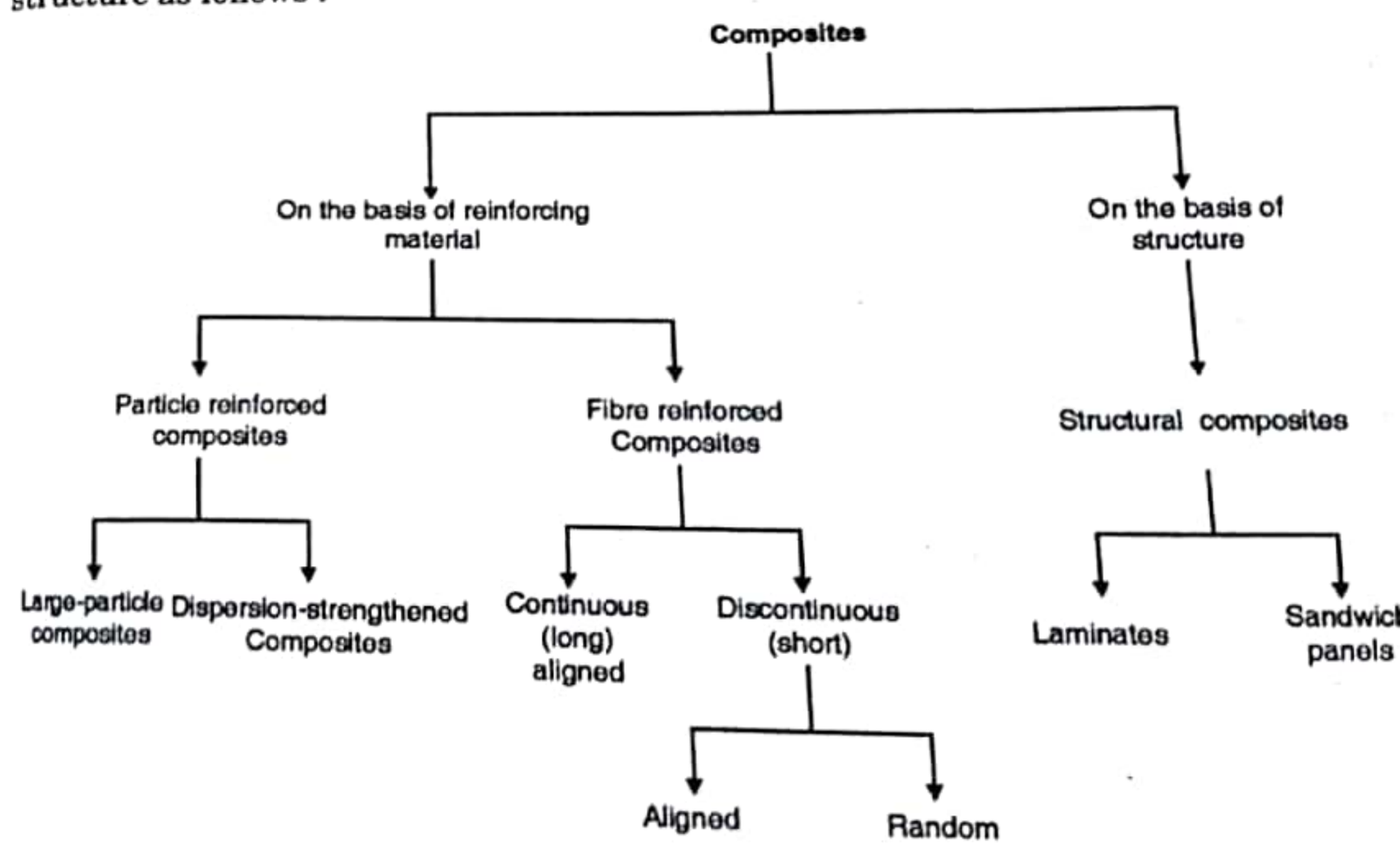
Syllabus Topic

Classification of Composites : Classification- (A) Particle - reinforced composites- i) Large – particle reinforced composites ii) Dispersion – strengthened composites. (B) Fiber – reinforced composites- i) Continuous – aligned ii) Discontinuous – aligned (short)- (a) aligned (b) randomly oriented (C) Structural Composites- i) Laminates (ii) Sandwich Panels

4.4 Classification of Composites

MU - May 2012, May 2013, May 2014, May 2016

The composites are classified on the basis of reinforcing material or structure as follows :



4.4.1 Particle-reinforced Composites

In this type of composites, the size of particles in dispersed phase are of nearly the same in all direction.

Large particle composites

In this sub-type of composites, the particulate phase should have following characteristics.

(a) *Stiffer* and *harder* as compared to matrix phase.

(b) It acts as reinforcing material.

(c) It *restrains the movement* of matrix surrounding to itself.

(d) The bond strength between two phases governs *mechanical properties* of *composite.*

Table 4.4.1 : Examples of particle reinforced composites

Material	Matrix phase	Particulate phase	Properties
1. Concrete	Cement	Sand and gravels	1. R.C.C. is harder than ordinary cement. 2. Sets well on surface thereby holding structures.
2. Cermets (a) Oxide based	Cr	Al_2O_3	1. Good strength. 2. Very good thermal shock resistance.
(b) Carbide based	Co or Ni	Tungsten Carbide (WC) Or Titanium carbide (TiC)	1. Very hard 2. Very high surface hardness *Application :* In wire drawing dyes, valves and machine parts.
	Co or Ni	Or Chromium carbide (CrC)	High abrasion and corrosion resistance *Application :* In valves, spray nozzle pump parts etc.

Dispersion-strengthened composites

- In this type of composite, the particles size is smaller (10 to 100 nm).
- The metal or alloys are made into extremely small particle size in given range and are dispersed in the matrix phase. This is achieved by appropriate heat treatment. The process is called as *"precipitation hardening"* or *"Age hardening"*, the former term given because the new phase of materials obtained in process is known as *"precipitates"*, where as latter term is suitable because composite increases its hardness as alloy ages.

e.g. Alloys such as, *Cu – Sn, Mg – Al, Cu – Be, Al–Cu,* some ferrous *alloys* are hardened and made into composite materials with *ceramics.*

4.4.2 Fibre Reinforced Composites

MU - May 2012, Dec. 2012, May 2016

Constitution

These are composite materials made up of

(a) A polymer matrix

(b) A filament

(c) A bonding agent (which ties fibre filaments to polymers)

Commonly used fibres are *glass or metallic.* These fibres are employed either in continuously or discontinuously as staples or whiskers.

Properties of fibre reinforced composites

The fibre reinforced composites possess,

(1) High tensile strength

(2) High specific gravity

(3) High elastic modulus

(4) They are stiff.

(5) They possess lower overall density.

Factors governing properties of fibre-reinforced composites are :

(1) Nature of fibres and matrix

(2) Properties of fibres and matrix

(3) Relative volume fraction of fibre and matrix

(4) Orientation and distribution of fibres in matrix phase.

(5) Length to diameter ratio of fibres

(6) Strength of interfacial bond between fibre phase and matrix.

Few important types of fibre reinforced composites, are given in Table 4.4.2, with properties and application.

Table 4.4.2 : Important fiber reinforced composites

Composite	Fibre phase	Matrix phase	Properties	Application	Limitation
1. Glass fibre reinforced polymer composite	Glass fibres (long as well as short)	Ploymers such as nylons, polyester etc.	1. Lower density 2. Higher tensile strength 3. Higher impact resistance 4. High resistance to corrosion and chemicals	1. Automobile parts 2. Pipes 3. Transportation industries 4. Industrial flooring 5. Storage tanks.	1. They can be used in low temperature service conditions; because polymers matrixes get deteriorated at higher temperatures. 2. The stiffness is comparatively low, hence cannot be employed as structural components.
2.Carbon fibre reinforced polymer composite	Glass fibres (long as well as small)	Polymers such as nylons, polyester etc.	1. Higher density 2. Excellent resistance to corrosion 3. Dimensional stability even at high temperature	1. Used to make structural components e.g. body or wings of aircraft helicopter. 2. Sports materials or fishing rods	High cost, hence used generally for specific purposes only.

Composite	Fibre phase	Matrix phase	Properties	Application	Limitation
3. Aramid fibre-reinforced polymer composite.	(a) Short aramid fibres or discontinuous	Polymeric material	1. High surface area. 2. High aspect ratio 3. Toughness to strength 4. Heat stability 5. High resistance to wear.	In automobile brakes and clutches.	Price is high, due to high cost of raw materials Note : These are about 4 times more in performance than that containing asbestos. Hence are best substitutes in place of asbestos containing material which is banned due to its ill effect on health
	(b) Long aramid fibres continuous	Polymeric material	1. Ductile like metals 2. It can sustain stresses.	1. In commercial aircrafts 2. Helicopter parts like rotor blades, motor housing 3. Business aircrafts as structural material 4. Protective apparel (thermal or ballistics)	Practically on limitations except cost. Note : In latest commercial aircrafts (like Boing –747 and Airbus 320), about 3-5% composites containing aramid or its hybrid fibres with carbon are employed.
4. Alumina and /or carbon fibre-reinforced metal composite	(a) Al_2O_3 or Carbon fibres	Aluminium Alloy	1. Low density 2. Resistant to thermal distortion 3. Resistant to wear 4. Creep resistant	To make engine components in automobile industry	
	(b) Al_2O_3or W (tungsten)	Ni and cobalt based alloy	1. Excellent strength 2. Resistant to creep and rupture at high temperature.	To make components of turbine engine	

4.4.3 Structural Composites or Layered Composites

MU - Dec. 2012

A structural composite consists of both homogeneous and composite materials. Their properties depend upon, the characteristic properties of the constituent materials as well as the geometric design.

Structural composites are of two types such as,

(a) Laminar composite : e.g. *plywood*

(b) Sandwich panel : e.g. *honeycomb core*

4.4.3.1 Laminar Composites

MU - May 2013, Dec. 2014

- It consists of *panels or sheets* which are two dimensional. These panels possess *preferred directions to achieve high strength.*

  e.g. plywood in which wood and continuous aligned fibre reinforced plastics are in preferred directions.
- Such successively oriented layers are stacked one above other with preferred directions (Fig. 4.4.1) and then are cemented. Such an arrangement or orientation ensures varying high strength with each successive layer.
- Plywood is a laminated composite containg thin layers of wood where layers are alternatively glued together. This type of layering brings grain of each layer at right angles of its neighboring layer.
- Use of fabric material such as cotton, paper or woven glass fibres dispersed in suitable plastic matrix is also in practice to make laminar composites.

Properties

Properties of these composites depend upon :

(a) The properties of its constituents

(b) The geometrical design

Generally such composites are :

(1) Strong in both directions of reinforcement

(2) Low shear strength

Applications

These composites are used in many familiar applications, such as :

(1) Interiors in premises

(2) False ceilings for diffused lighting etc.

(3) Furniture making.

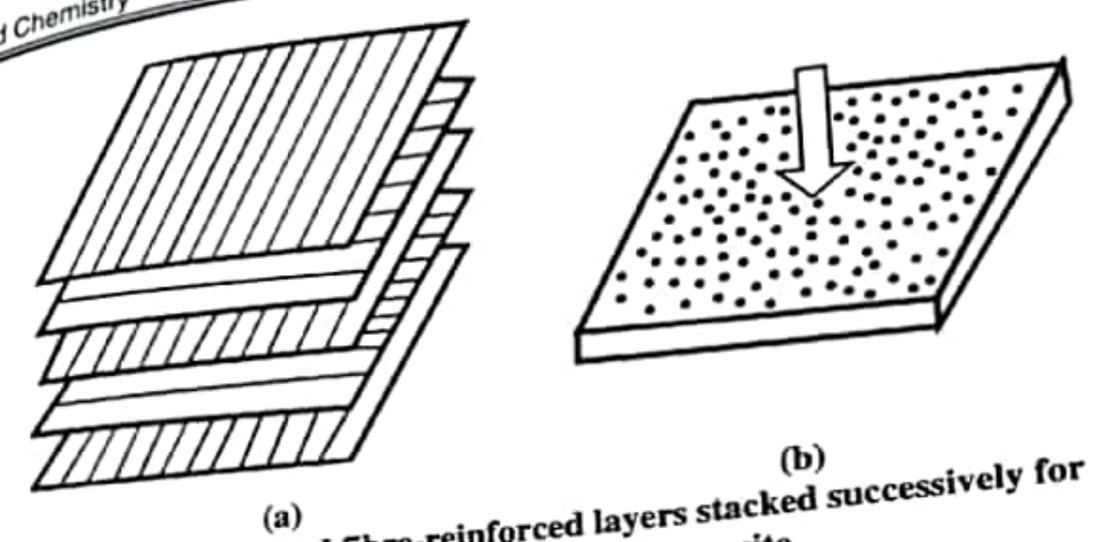


Fig. 4.4.1 : Oriented fibre-reinforced layers stacked successively for producing a laminar composite

4.4.3.2 Sandwich Panel

MU - Dec. 2013, May 2014, May 2015, Dec. 2015

This is another type of *layered composite.* It consists of

(1) *"Faces"* are formed by two strong outer sheets.

e.g Titanium, steel, aluminium alloys, plywood, fibre reinforced plastic material.

(2) *"Core"* which is layer of less dense material.

e.g. Synthetic rubbers, foamed polymers, inorganic cementing material etc.

All above three layers are joined together with an adhesive.

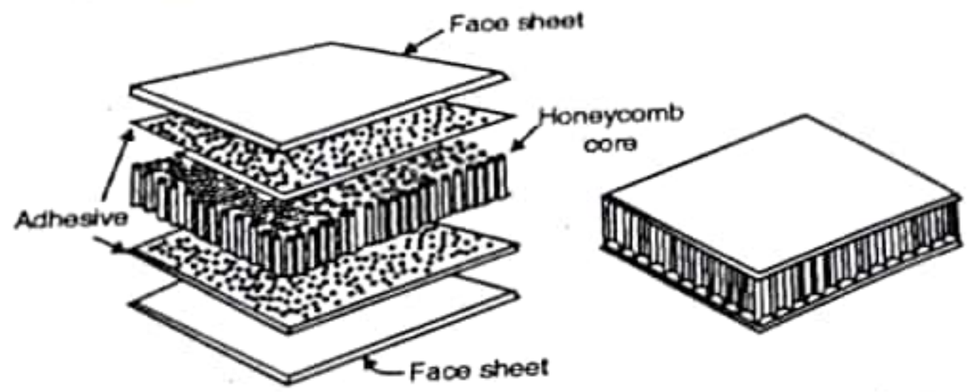
In these *"faces"* are capable of bearing *transverse bending stresses.* The *'core'* performs functions related to structural properties.

(i) Separation of faces from each other.

(ii) Resisting deformations perpendicular to the face plane.

(iii) Providing certain degree of shear rigidity along above planes which are perpendicular to the 'faces'.

With increase in thickness of core, its stiffness increases. The Fig. 4.4.2 shows 'honeycomb' structure which contain thin foils forming interlocked hexagonal cells with their axes oriented at right angles in the direction of face sheet.



(a) Honeycomb core sandwich panel : Construction (b) Sandwich panel : Fabricated

Fig. 4.4.2 : Schematic diagram

Properties

These have following properties :

(1) Excellent dimensional stability

(2) Resistant to abrasion and corrosion

(3) High tensile strength

(4) Low density

(5) High elasticity modulus

Application

These are used in :

(1) *Aircraft* for wings, fuselage and skins of tailpane.

(2) *In roofs,* walls and floor of buildings.

4.5 Application of Composite Materials

MU - Dec. 2012

The composite materials find variety of applications in all those areas where, high mechanical strength, dimension stability, thermal stability, corrosion resistance, abrasion resistance etc. is desirable. They find application in following industries,

(a) Construction

(b) Electrical and electronics and telecommunication

(c) Transportation

(d) Agriculture

(e) Sport goods

(f) Automobile

(g) Aviation industry

(h) Mobiles

Composites, in short are extremely useful and more research work is going on to develop newer materials to cater to various industries.

Important Terms and Definitions

- *Composites are engineered materials,* comprising of metals, ceramics, glasses and polymers.
- *Natural composits are the materials occurring in mature* e.g.Wood or many other plant tissues contain cellulose chain polymer in a matrix of lignin. This is example of natural composite.
- *Synthetic composites* such as, rain proof cloth (cloth impregnated with waterproof material), packing paper impregnated with bitumen or wax, reinforced concrete, insulating tape are some examples.
- Thus composite may be defined as, "A multiphase product made by using two or more existing materials which exhibits properties of its constituents as well as shows certain unique properties of its own."
- Most of composites are made by using minimum two phases. The phases are namely :

  (a) Matrix

  (b) Dispersed phase.

  e.g. polymer composites in which matrix is of polymer and particles of metals/ceramic/fibre serves as dispersed phase.
- The polymer phase is called as *matrix* phase and the composite used for mixing is known as *dispersed phase*. The boundaries between the matrix and dispersed phase, are known as *inter phase*.

Review Questions

Q.1 What are composites ? Give examples ?

Q.2 Explain the role of composites in aviation industry.

Q.3 Write a note on constitution of composites; giving suitable example.

Q.4 Explain the term

(i) Matrix and (ii) Dispersed Phase.

Q. 5 Name two types of composites based on dispersed phase.

Q. 6 List out ideal characteristics of matrix material

Q. 7 What are the main function of a matrix material in polymer composite ?

Q. 8 What are whiskers ? What are their special properties ? Give few examples.

Q. 9 List some important dispersed phase constituents. Discuss their features.

Q. 10 How are composites classified on the basis of reinforcing materials ?

Q. 11 Write notes on :

(i) Large particle reinforced composites.

(ii) Dispersion strengthened composites.

Q. 12 Which are the constituents of fibre reinforced composites ?

Q. 13 List out properties of fibre reinforced composites.

Q. 14 Which are the factors governing properties of fibre reinforced composites ?

Q. 15 Write notes on, giving phases, properties, use and limitations.

(a) Glass fibre reinforced polymer composites

(b) Carbon fibre reinforced polymer composites

(c) Aramid fibre reinforced polymer composites

(d) Alumina /carbon fibre reinforced polymer composites

Q. 16 Write a note on different "Layered composites."

Q. 17 Explain "Laminar composites" with suitable example.

Q. 18 Explain "Sandwich panel" with suitable example.

Q. 19 What are important application of composites ?

Q. 20 "Composites may be materials for future". Comment.

4.6 University Questions and Answers

May 2012

Q. 1 Give the classification of composite materials. (3 Marks)
(Ans. : Refer section 4.4)

Q. 2 What are composite materials ? Describe fiber reinforced composites. (5 Marks)
(Ans. : Refer sections 4.1.1 & 4.4.2)

Dec. 2012

Q. 1 What are composite materials ? What are the applications of composites. (3 Marks)
(Ans. : Refer section 4.1.1 and 4.5)

Q. 2 Explain structural composites. (5 Marks)
(Ans. : Refer section 4.4.3)

Q. 3 What are fibre-reinforced composites. (4 Marks)
(Ans. : Refer section 4.4.2)

May 2013

Q. 1 Give classification of composite material. (3 Marks)
(Ans. : Refer section 4.4)

Q. 2 Explain Laminar composite with suitable example. (4 Marks)
(Ans. : Refer section 4.4.3.1)

Dec. 2013

Q. 1 Define 'matrix phase' of composite material. State functions of matrix phase. (3 Marks)
(Ans. : Refer section 4.2.1 & 4.2.2)

Q. 2 Write a note on 'sandwich panel' type layered composites. (4 Marks)
(Ans. : Refer section 4.4.3.2)

May 2014

Q. 1 Give classification of composite materials. (3 Marks)
(Ans. : Refer section 4.4)

Q. 3 Explain 'sandwpich panel' type layered composites with a suitable diagram. Mention their applications. (4 Marks)
(Ans. : Refer section 4.4.3.2)

Dec. 2014

Q. 1 What are composite materials ? Mention any four characteristic properties of composite materials. (3 Marks)
(Ans. : Refer sections 4.1.1 and 4.3)

Q. 2 Explain laminar composites with suitable example. (4 Marks)
(Ans. : Refer section 4.4.3.1)

Q. 3 Define matrix phase of composite material. State functions of matrix phase. (4 Marks)
(Ans. : Refer sections 4.2.1 and 4.2.2)

May 2015

Q. 1 Define terms : (5 Marks)

(i) Composite material
(Ans. : Refer section 4.1.1)

(ii) Matrix phase
(Ans. : Refer section 4.2.1)

(iii) Dispersed phase
(Ans. : Refer section 4.2.3)

Q. 2 Write a note on 'Sandwitch panel' type layered composites. (4 Marks)
(Ans. : Refer section 4.4.3.2)

Dec. 2015

Q. 1 What are composite materials ? Mention any four characteristic of composite matierals (3 Marks)
(Ans. : Refer section 4.1.1 and 4.3)

Q. 2 Expalin 'sandwich panel' type layered structural composites, with a suitable diagram. Mention their application. (4 Marks)
(Ans. : Refer section 4.4.3.2)

May 2016

Q. 1 Give classification of composite materials. (3 Marks)
(Ans. : Refer section 4.4)

Q. 2 What are glass fibre reinforced composites ? Outline their properties, application and limitations. (4 Marks)
(Ans. : Refer section 4.4.2)

Q. 3 Define matrix phase of composite material. State functions of matrix phase. (4 Marks)
(Ans. : Refer sections 4.2.1 and 4.2.2)

e-book

Note :

- *Exact syllabus topic wise answers to the following questions are available in e book.* ***Please download as per instructions given.***

Syllabus Topic : Introduction

Q. 1 What are composite materials ? Describe fiber reinforced composites.
(Ans. : Refer sections 4.1.1 and 4.4.2)
(May 2012, Dec. 2012, Dec. 2014, May 2015)

Q. 2 Give classification of composite material.
(Ans. : Refer section 4.4) **(May 2012, May 2013, May 2014, May 2016)**

Syllabus Topic : Constitution of composites

Q. 1 Define 'matrix phase' of composite material. State functions of matrix phase.
(Ans. : Refer section 4.2.1 & 4.2.2)
(Dec. 2013, Dec. 2014, May 2015, May 2016)

Q. 2 Define term : Dispersed phase *(Ans. : Refer section 4.2.3)* **(May 2015)**

Syllabus Topic : Characteristic Properties of Composite Materials

Q. 1 Mention any four characteristic properties of composite materials.
(Ans. : Refer section 4.3) **(Dec. 2014)**

Syllabus Topic : Classification of Composites : Classification - (A) Particle - reinforced composites- i) Large – particle reinforced composites ii) Dispersion – strengthened composites. (B) Fiber – reinforced composites- i) Continuous – aligned ii) Discontinuous – aligned (short)-
(a) aligned (b) randomly oriented (C) Structural Composites- i) Laminates (ii) Sandwich Panels

Q. 1 What are the applications of composites.
(Ans. : Refer section 4.5) **(Dec. 2012)**

Q. 2 Explain structural composites. *(Ans. : Refer section 4.4.3)* **(Dec. 2012)**

Q. 3 Explain Laminar composite with suitable example.
(Ans. : Refer section 4.4.3.1) **(May 2013, Dec. 2014)**

Q. 4 Explain 'sandwpich panel' type layered composites with a suitable diagram. Mention their applications. *(Ans. : Refer section 4.4.3.2)*
(Dec. 2013, May 2014, May 2015, Dec. 2015)

Q. 5 What are glass fibre reinforced composites ? Outline their properties, application and limitations. *(Ans. : Refer section 4.4.2)* **(May 2012, Dec.2012, May 2016)**

□□□

CHAPTER 5

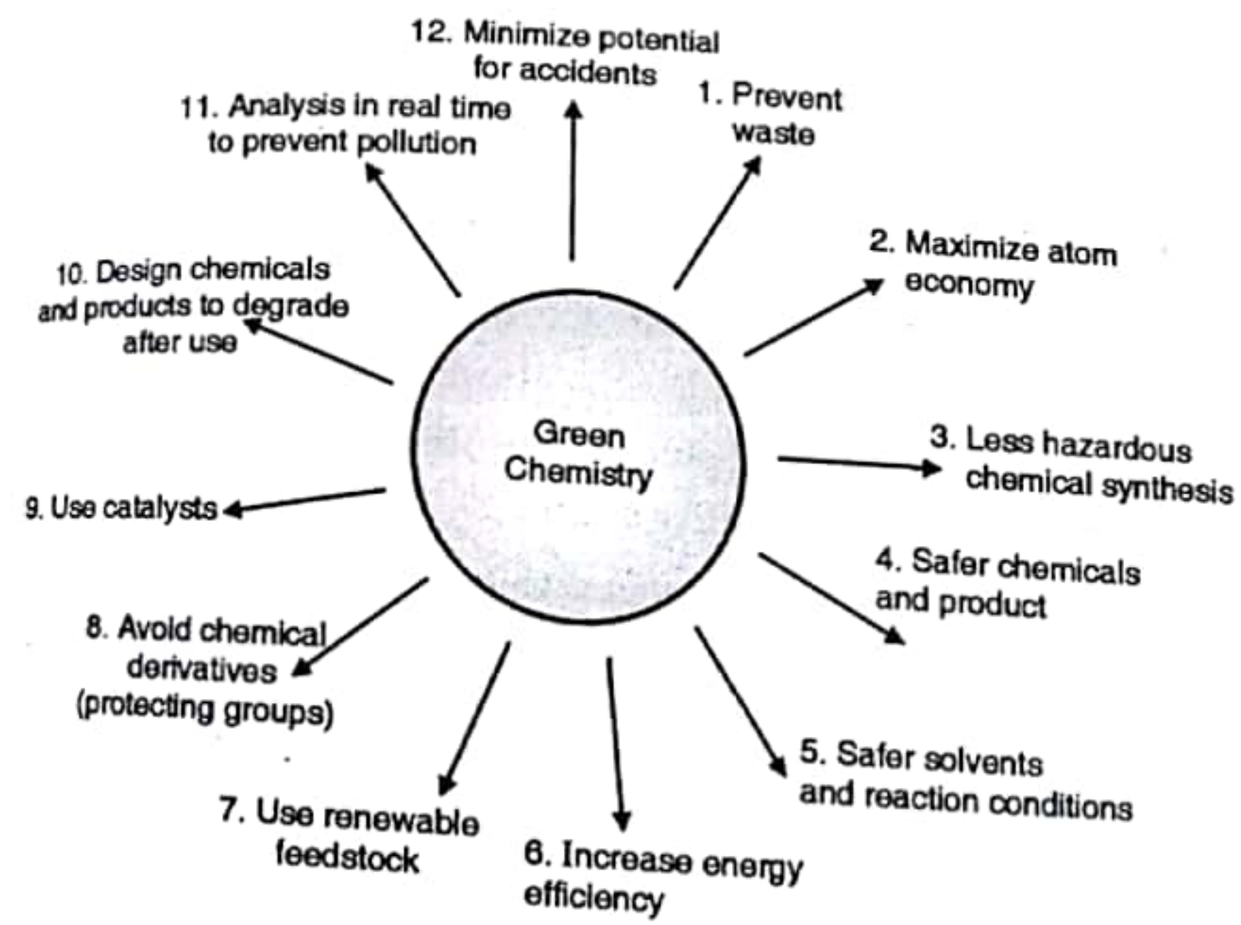
MODULE 5

Green Chemistry

Syllabus

Green Chemistry

Introduction, Twelve Principles of Green chemistry, numerical on atom economy, Conventional and green synthesis of Adipic acid, Indigo, Ibuprofen and Carbaryl. Green solvents (water,supercritical CO2) and products from natural materials.



Syllabus Topic : Green Chemistry Introduction

➢ **Topics covered :** Introduction of Green Chemistry

5.1 Introduction

MU - Dec. 2012, May 2013

- The *knowledge of chemistry* and all the developments in different branches of chemistry during last few decades have given many useful products to mankind, e.g. *medicines, fabrics, insecticides, drugs, dyes, rubber, petrol, etc are few to mention.*
- The *dependence of humans* on all these formulations/products is *increasing* day by day and hence with growing populations *more* number of *industries* are established to produce *these products in large quantity.*
- The *chemical reactions* involved are always associated with certain *by-products* which are *harmful for the environment* and cause severe pollution problems.
- In fact all the *chemicals are toxic in varying extent.* Hence, to *minimize* the problems of *environmental pollution and hazardous waste* it became necessary to *review and modify* all the chemical processes used for manufacture.
- Thus design of harmless processes to produce various products has emerged as a new branch commonly known as "clean chemistry" or *"Green Chemistry" or "Environmentally benign chemistry".*
- *Green Chemistry* came into existence more than a decade back is now *becoming very popular.*
- It includes any chemical process or technology that improves the environment and thus our quality of life.
- Green chemistry is a highly *effective approach* to pollution prevention because it applies innovative scientific solutions to real-world environmental situations.
- The 12 Principles of Green Chemistry, originally suggested by *Paul Anastas and John Warner, are well accepted* by the chemists *all over the world.*

Syllabus Topic : Twelve Principles of Green chemistry

Topics covered : List of twelve principles of green chemistry with explaination.

5.2 The Twelve Principles of Green Chemistry

MU - Dec. 2012, May 2013

1. Prevention of waste
2. Maximise Atom economy
3. Non-hazardous chemical
4. Safer chemical
5. Auxiliary Substances
6. Energy efficiency
7. Renewable feedstocks
8. Derivatisation
9. Catalysts
10. Degradable products
11. New Analytical methods
12. Accident prevention

We will discuss each of these principles in brief,

5.2.1 Prevention of Waste

MU - Dec. 2013, May 2014,Dec.2015

"Prevention is better than the cure"

- It is better to prevent waste than to treat and clean up waste after it is formed.
- It has been a common practice to *dump* waste on land or in water or released in air. This resulted in soil, water and air pollution.
- This made the legislation to be stringent on industries and hence there was compulsion to have waste treatment and disposal units attached to the manufacturing plants. Thus the cost of process increased considerably.
- Thus green chemistry involves to design chemical syntheses in such a way that the process involves pathway to give products, leaving no waste to treat or clean up.

5.2.2 Maximize Atom Economy

- The design of the synthesis of the product should be such that all the chemicals/materials used in the process gets converted into the products to the maximum extent.
- It is common observation that most of the *organic reactions release undesired products* along with the useful products of the reaction.

- The unutilized material is considered as waste which causes trouble and the process becomes uneconomical.
- Green chemistry requires that new processes should be designed such that the most of the starting material gets converted into product. This is called as *Maximising atom economy.*

5.2.3 Non-hazardous Chemical Synthesis

MU - Dec. 2014

- The synthetic method should be designed wherever possible to use and generate substances having little or no toxicity to human health and the environment.
- The starting material selected should be least toxic. Thus e.g. pyridine, or β-naphthyl amine being known to be carcinogenic should be avoided as starting materials.
- The reactions in which intermediates or reagents or products are toxic, should not be followed. In stead alternative pathways should be used for synthesis.
- **For example :** In 1984, due to leakage of MIC at Bhopal there was major casualty and the after effects of the same are still suffered by many. This compound MIC is an intermediate in manufacture of agricultural pesticides and was known to be highly poisonous.
- Hence green chemistry recommends the design of synthesis to use and generate substances with little or no toxicity to humans and the environment.
- Other example is of synthesis of indigo as given below

5.2.4 Design Safer Chemicals and Products

- The chemical products should be designed to preserve the efficiency of desired function while reducing toxicity.
- When any medicinal formulations are to be put in market , they are put first on trials to check their toxic effects on humans.
- If found to be toxic then alternatives are prepared keeping in mind the function of the medicine but only toxicity reduced.
- Similarly in many insecticides like *DDT, gamaxane, aldrin* etc which are found to be *toxic to humans*, the use of these is *curtailed* and alternatively *biological pesticides* are more in use.

- *Thus green chemistry emphasizes to design chemical products to be fully effective, yet have little or no toxicity.*

5.2.5 Auxiliary Substances (Use Safer Solvents and Reaction Conditions)

- The use of auxiliary substances like solvents, separating agents etc. should be made unnecessary wherever possible and innocuous when used.
- Avoid using carcinogenic solvents, separation agents, or other auxiliary chemicals. If these chemicals are necessary, use innocuous chemicals.
- The solvents such as **acetone, benzene, ether** being highly inflammable should be *avoided.*
- Other chemicals such as CCl_4, $CHCl_3$, carry health risk hence should be *avoided.*
- If a solvent is necessary, *water is a good medium* as well as certain *eco-friendly solvents* that do not contribute to smog formation or destroy the ozone.
- **For example :** For *drycleaning* the fabrics, the toxic solvent like *perchloroethylene* was used, which is *replaced* during recent years by *liquid* CO_2.

5.2.6 Energy Efficiency

MU - Dec. 2014

- The energy requirements of chemical processes should be minimized considering their environmental and economic impacts. The synthetic methods should be carried out at ambient temperature and pressure wherever possible.
- The aim of green chemistry is to increase energy efficiency.
- This can be achieved by use of catalysts, and by stopping the use of fossil / gaseous fuels which release solid or gaseous pollutants.
- The recently found substitutes are microwave radiations and ultra sound, which are used in the processes requiring very less energy.
- The energy efficiency of process can be increased by :
  a) *proper heat transfer and*
  b) *minimal wastage of energy during the process.*
- Many chemical are produced by *fermentation* process where energy requirement is low and also the products are less harmful

5.2.7 Use Renewable Feedstock (Waste Utilisation) MU - May 2012, May 2014

- The raw materials should be renewable rather than depleting, wherever technically and economically feasible.
- Renewable feedstock are often made from agricultural products or are the wastes of other processes; depleting feedstock are made from fossil fuels (petroleum, natural gas, or coal) or are mined.
- **For example :** A new method is developed to prepare adipic acid from glucose obtained from corn starch or cellulose. This is green process because it *replaces benzene* as starting material for production of same product. *Benzene* is a known *carcinogen*.

5.2.8 Avoid Chemical Derivatives

- During synthesis unnecessary derivatisation such as blocking or protecting groups or any temporary modifications should be avoided, if possible.
- The use of derivatives *increases the steps* of the process
- The additional reagents are required
- It generates more waste products
- To avoid these effects, alternative reagents are to be used which are more *selective*.
- **Example :** *Synthesis of Ibuprofen* is given below where in traditional pathway larger number of steps are involved, and atom economy is low. This has been modified to increase atom economy.

5.2.9 Use Catalysts, not Stoichiometric Reagents

- The catalytic reagents which are selective in their reaction, are preferred
- over stoichiometric reagents.
- Minimize waste by using *catalytic reactions*.
- Many times *catalysts* are used in small amounts and can carry out a single reaction
- They are preferable to *stoichiometric reagents,* which are used in excess and work *only once.*
- Catalytic *reactions are faster* and hence require less energy.
- In recent years many processes are been developed which use *non toxic recoverable catalysts and also biocatalysis.*

5.2.10 Design Chemicals and Products to Degrade after use

Chemical products should be designed such that they break down to environment innocuous substances after use so that they do not accumulate in the

Examples

1. *DDT* when used as pesticide, its residues remain in *soil* for many years causing pollution. The alternative to this is biological insecticides biodegradable and cause solid waste. The alternative to this the
2. The packaging material such as plastics or polystyrene are non biodegradable plastics containing cellulose and the packing pellets made up of starch are used.

5.2.11 New Analytical Methods : (Analyze in Real Time to Prevent Pollution)

New analytical processes have to be developed to allow on-line monitoring and control prior to the formation of hazardous substances.

Example : *Preparation of ethylene glycol*, in which if reaction conditions are not monitored perfectly, toxic substances are produced at higher temperature.

5.2.12 Minimize the Potential for Accidents

The substances and its forms used in chemical process should be chosen to minimize the potential for the chemical releases, accidents, explosions and fire catalysts helps in minimizing the potential of accidents which is desirable. The use of safer chemicals, minimizing temperature, pressure and using.

Syllabus Topics : Numerical on Atom Economy

Topics covered : Explaination of Atom Economy, Theoretical yield, Percentage yield, Atom economy %, numerical : 1. Calculation of % atom economy for preparation of n-propyl bromide from n-propyl alcohol.2. preparation of maleic anhydride.

5.3 Atom Economy-Explaination

The theoritical yield for every reaction can be calculated as,

$$\text{Theoretical yield} = \text{Stoichiometric ratio} \times \left[\frac{\text{Molecular weight of the desired product}}{\text{Molecular weight of limiting reagent}}\right] \times \text{weight of limiting reagent}$$

On conducting the reaction the experimental or actual yield of the process is obtained. From this percentage yield is calculated.

$$\text{Percentage yield} = \left[\frac{\text{Actual yield}}{\text{Theoritical yield}}\right] \times 100$$

5.3.1 Example : Preparation of n-propyl bromide from n-propyl alcohol (0.6 g)

$$CH_3CH_2CH_2\text{-}OH + NaBr + H_2SO_4 \quad CH_3CH_2CH_2Br + NaHSO_4 + H_2O$$

Mol Wt = 60 103 98 Mol Wt. 123 ⟶ 120 18

Thus 1 mole of reactant gives one mole of product

Hence

$$\text{Theoritical yield} = \text{Stoichiometric ratio} \times \left[\frac{\text{Molecular weight of the desired product}}{\text{Molecular weight of limiting reagent}}\right] \times \text{Weight of limiting reagent}$$

$$= \frac{1}{1} \times \left[\frac{123}{60}\right] \times 0.6$$

$$= 1.23 \text{ gms}$$

But actually yield of the above reaction is found to be 0.99 gms

$$\text{Hence percentage yield} = \frac{0.99}{1.23} \times 100 = 80.49\ \%$$

Atom economy can be calculated by using following formula,

$$\%\ \text{Atom economy} = \frac{\text{Molecular weight of product}}{\text{Total molecular weight of reactants}} \times 100$$

∴ In above reaction, % atom economy can be calculated as,

$$\%\ \text{Atom economy} = \frac{\text{Molecular weight of n-propyl bromide}}{\text{Molecular weight of (n-propanol + NaBr)}} \times 100$$

$$= \frac{123}{60 + 103} \times 100$$

$$= \frac{123}{163} \times 100$$

$$= 75.5\%$$

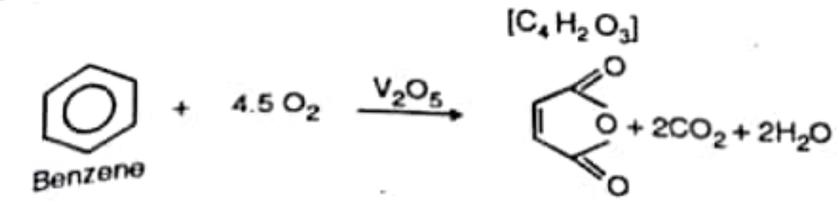
Other examples for understanding the efficiency of reaction is given here,

5.3.2 Preparation (synthesis) of Maleic Anhydride

Maleic Anhydride can be prepared by oxidation of

a) Benzene b) Butene c) Butane

(I) i)



Mol.wt. 78 4.5 x 32 = 144 98

$$\%\ \text{Atom economy} = \frac{98}{78 + 144} \times 100$$

$$= \frac{98}{222} \times 100$$

$$\boxed{\therefore\ \%\ \text{Atom economy} = 44.1\%}$$

(II)

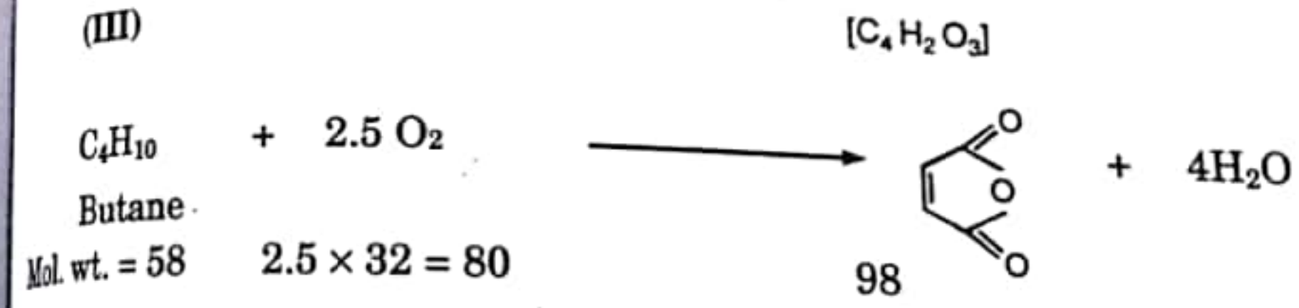
Mol. Wt. = 56 3 × 32 = 96 98

$$\%\ \text{Atom economy} = \frac{98}{56 + 96} \times 100$$

$$= \frac{98}{152} \times 100$$

$$\boxed{\therefore\ \%\ \text{Atom economy} = 64.5\ \%}$$

(III)



Mol. wt. = 58 2.5 × 32 = 80 98

$$\%\ \text{Atom economy} = \frac{98}{58 + 80} \times 100$$

$$= \frac{98}{138} \times 100$$

$$\therefore\ \boxed{\%\ \text{Atom economy} = 71.0\ \%}$$

Thus for different reaction atom economy can be calculated and thus the process giving maximum atom economy can be selected.

The processes with *90 % yield* and *higher atom* economy are considered as *excellent* and those with *20 % yield* and *lower atom economy* are *poor*.

Thus it becomes essential to design synthesis so that the final product contains the maximum proportion of the desired product thereby increasing the atom economy. There should be few, if any, wasted atoms.

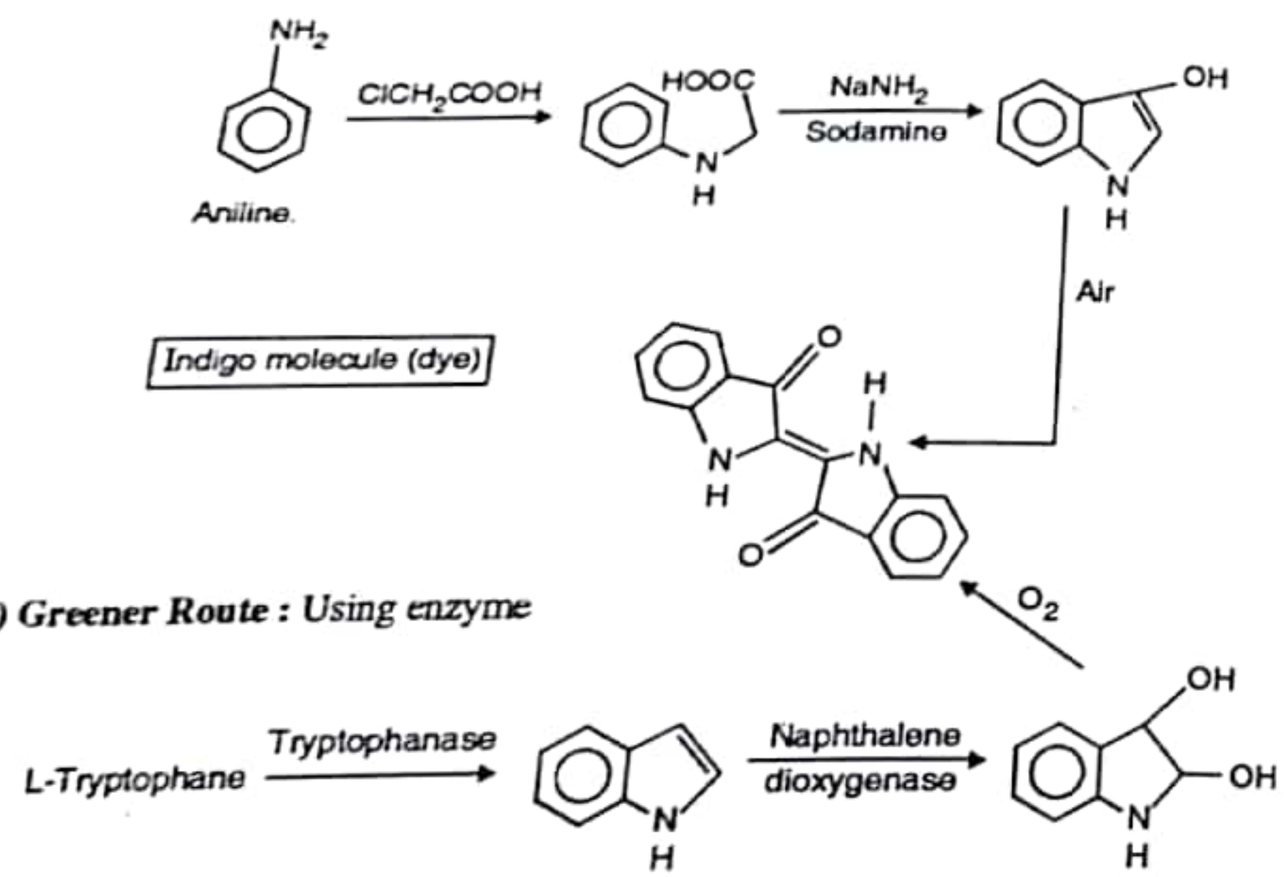
Syllabus Topic : Conventional and Greener Synthesis of Indigo

➢ **Topics covered :** Synthesis of Indigo a) using aniline b) using an enzyme

MU - May 2013, Dec. 2014, Dec.2015, May 2016

5.4 Synthesis of Indigo

(A) Conventional Route using hazardous Aniline



(B) Greener Route : Using enzyme

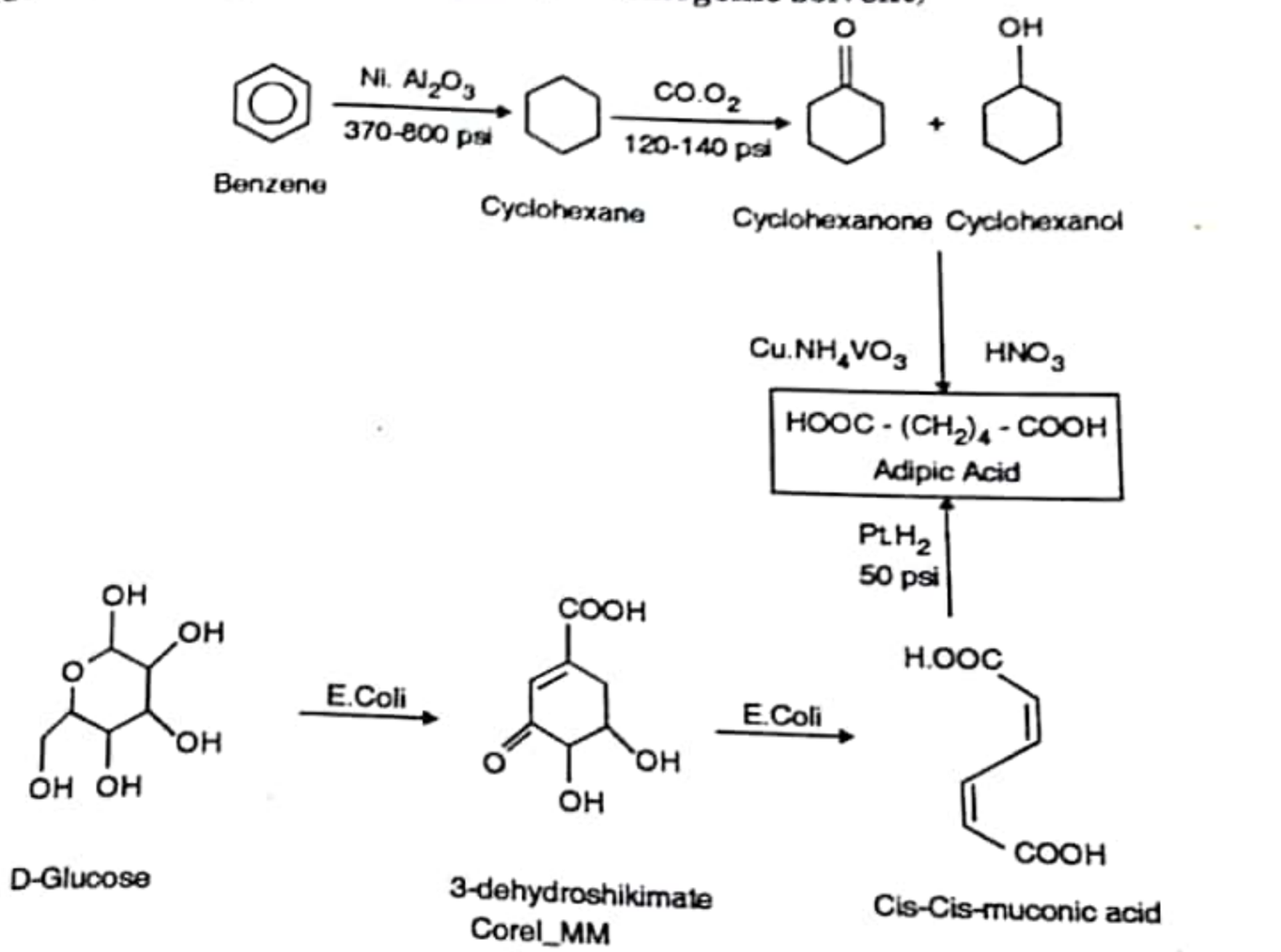
Syllabus Topic : Conventional and Green Synthesis of Adipic Acid

➢ **Topic covered :** Synthesis of Adipic Acid a) using benzene & b) using glucose

MU – May 2012, Dec.2012, Dec.2013, May 2014, May 2015

5.5 Synthesis of Adipic Acid

Traditional pathway : Using Benzene (Carcinogenic solvent)



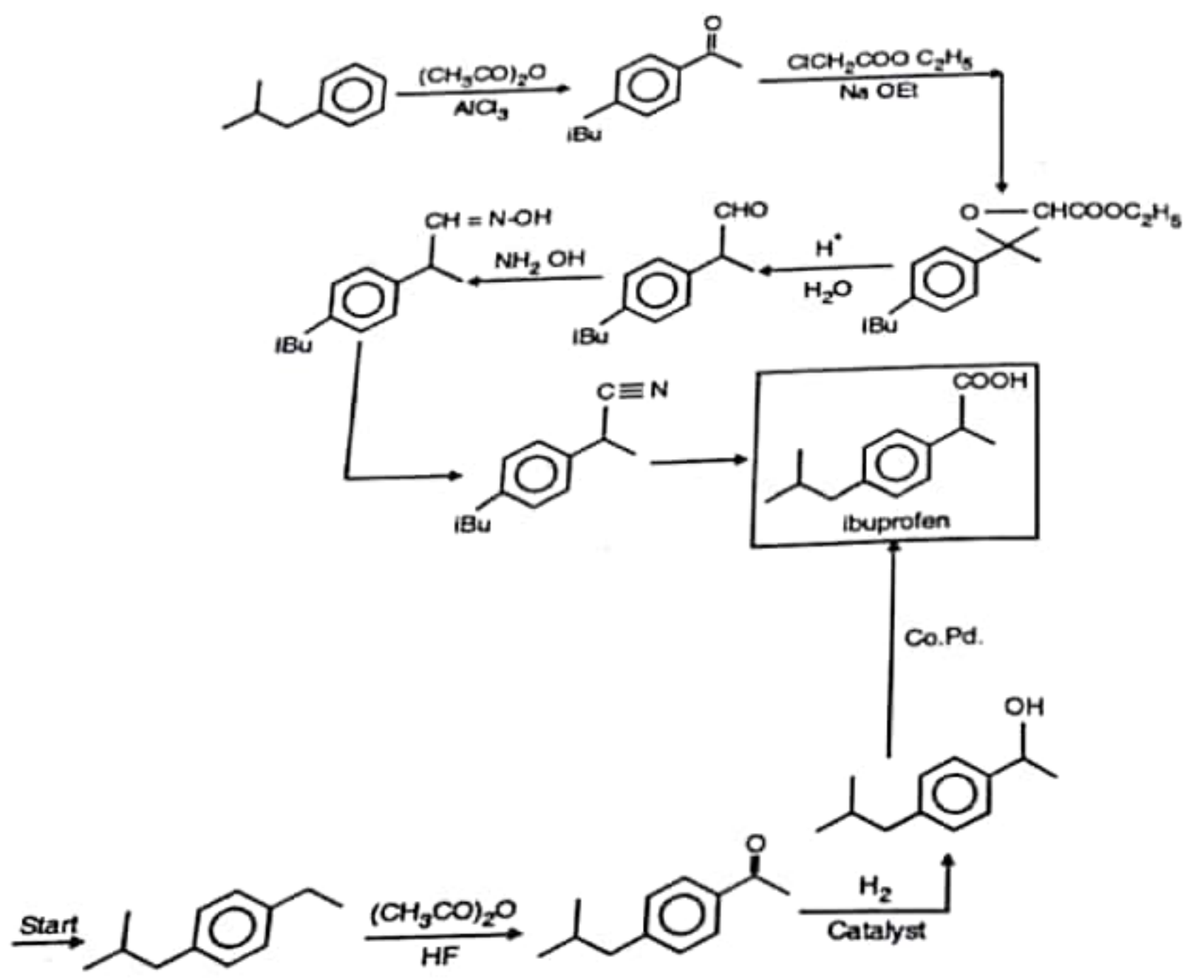
Greener pathway : Using glucose (absolutely safe)

Syllabus Topic : Conventional and Greener Route for Synthesis of IBU Profen

➢ **Topics covered :** Synthesis of Ibuprofen a. Using bezene derivative b) using natural/greener material

5.6 Synthesis of Ibu Profen

(A) Traditional method : With larger number of steps (Atom economy = 40 %)



(B) Alternative Synthesis

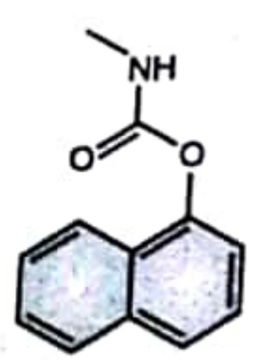
With the atom economy = 77 % and recoverable catalyst.

Syllabus Topic : Conventional and Greener Route of Synthesis of Carbaryl

➤ ***Topics covered :*** structural formula of carbaryl; synthesis of carbaryl - a) Using conventionsl route with 1-naphthol b) by greener route using 1-naphthol.

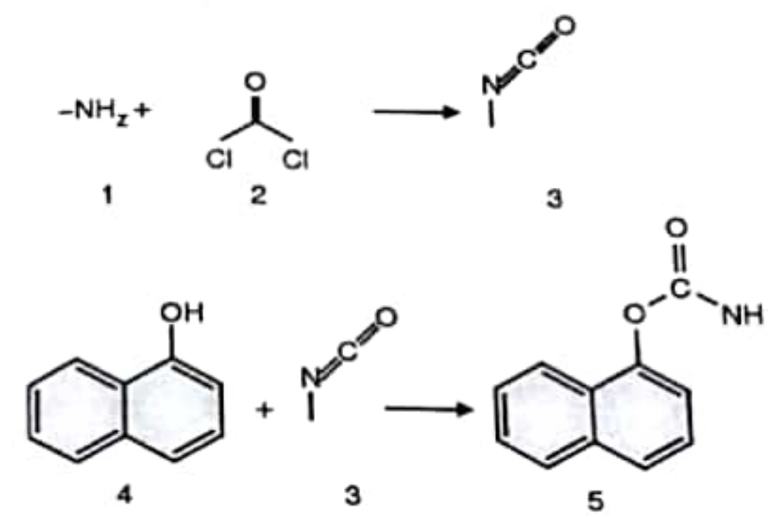
5.7 Synthesis of Carbaryl

Structure of Carbaryl



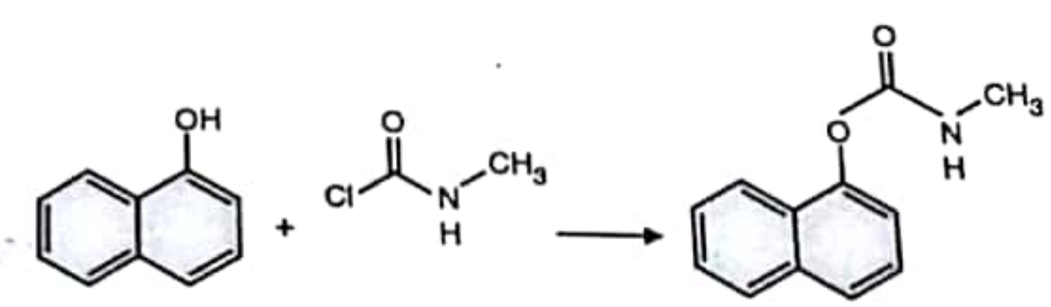
(I) Traditional route

Carbaryl is prepared on large scale by treating methyl-isocyanate [compound 3] with 1-naphthol [compound 4], Amine is treated with Phosgene to get methyl-isocyanate. Carbaryl is produced by treating methyl isocyanate (3) with 1-naphthol (4).



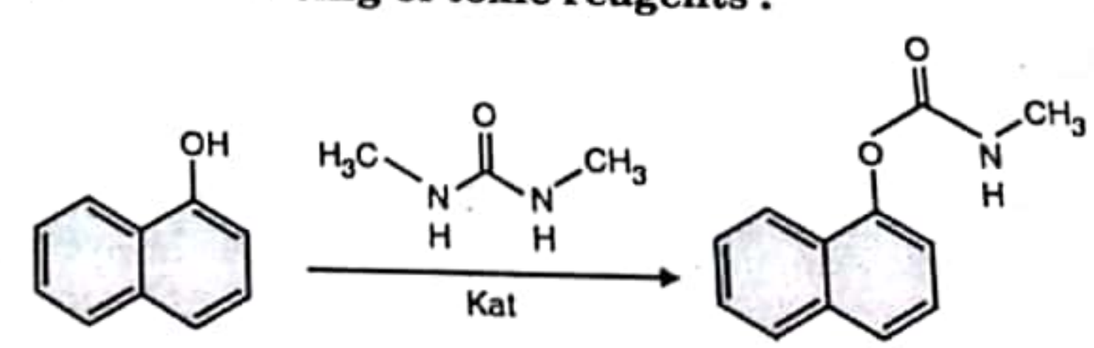
Note : This process was carried out in Bhopal, by Union Carbide where leakage of MIC mishap took place in 1984

(II) With using naphtol-1 and methylcarbamoyl chloride :



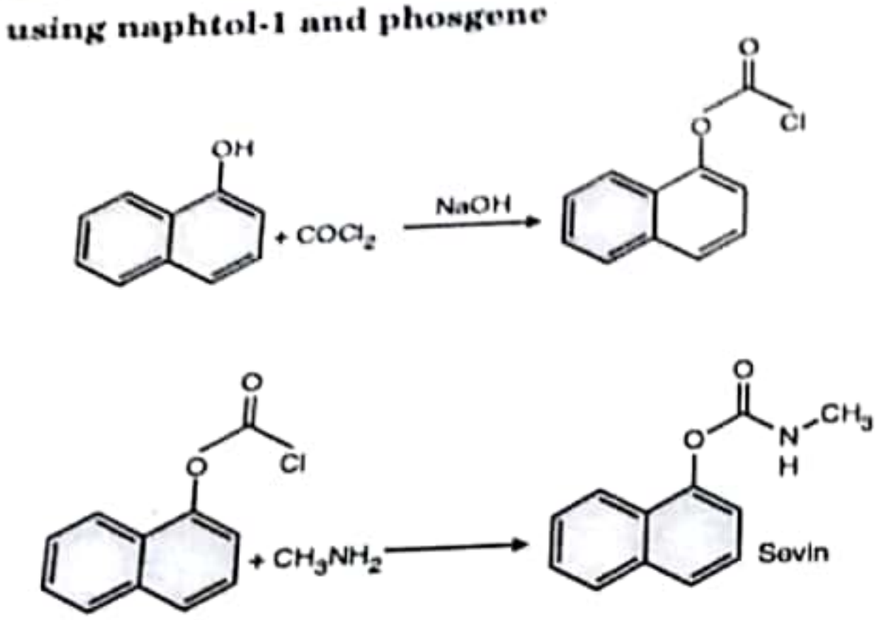
In these routes of synthesis of Carbaryl highly roxic substance such as phosgene, methyl isocyanate and methylcarbamoyl chloride are used.

We have developed a new and cost-effective approach to sevin synthesis without using of toxic reagents :



Routes of sevin synthesis :

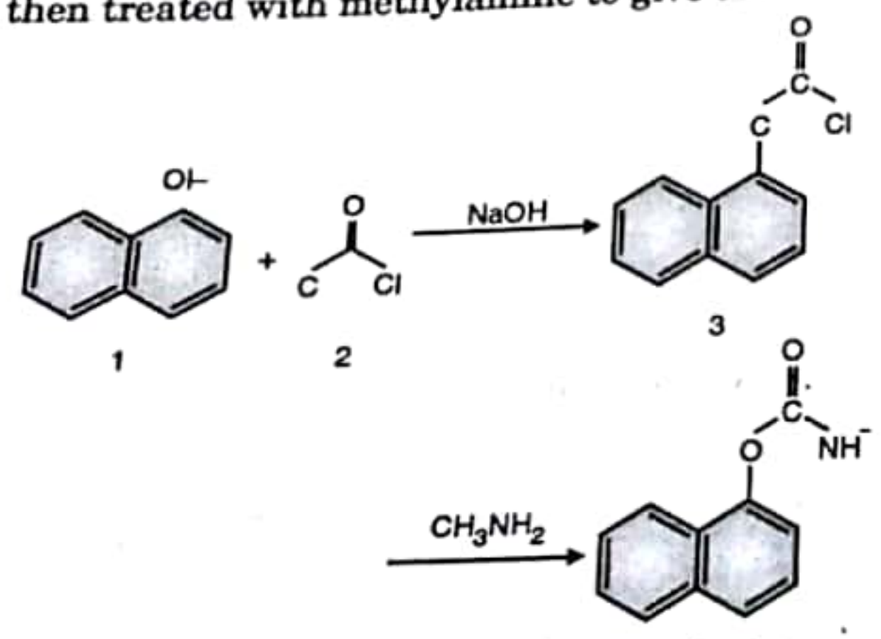
(I) With using naphtol-1 and phosgene



(II) Green route

1-naphthol [compound 1] treated directly with equal quantity of phosgene [compound 2] in alkaline medium to get chloroformate [compound 3], which is then treated with methylamine to give carbary [compound 4]

Alternatively, 1-naphothol (1) is first converted to its chloroformate (3), which is then treated with methylamine to give the desired product (4).



Greener route synthesis also uses exactly the same reagents, but these are taken in a different sequence. Hence, this synthesis avoids the preparation of methyl isocyanate.

But use of phosgene and methyl amine is still needs to be avoided. Research is in progress

5.8 Numerical Problems on Atom Economy / Solved University Examples

Example 5.8.1 : *Calculate the percentage atom economy for the following reaction with respect to Allyl chloride.*

$$CH_3 - CH = CH_2 + Cl_2 \longrightarrow Cl - CH_2 - CH = CH_2 + HCl$$

Propene *Allyl chloride*

MU - Dec. 2014, 4 Marks

Solution :

Reaction given :

$$CH_3 - CH = CH_2 + Cl_2 \longrightarrow Cl - CH_2 - CH = CH_2 + HCl$$

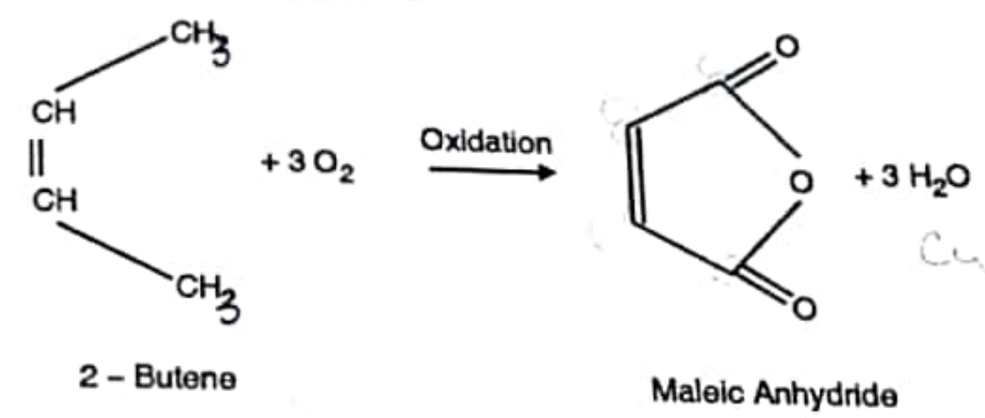
Propene 42 71 Allyl chloride (76.5) 36.5

$$\% \text{ Atom economy} = \frac{\text{Molecular weight of product}}{\text{Total molecular wt. of reactants}} \times 100$$

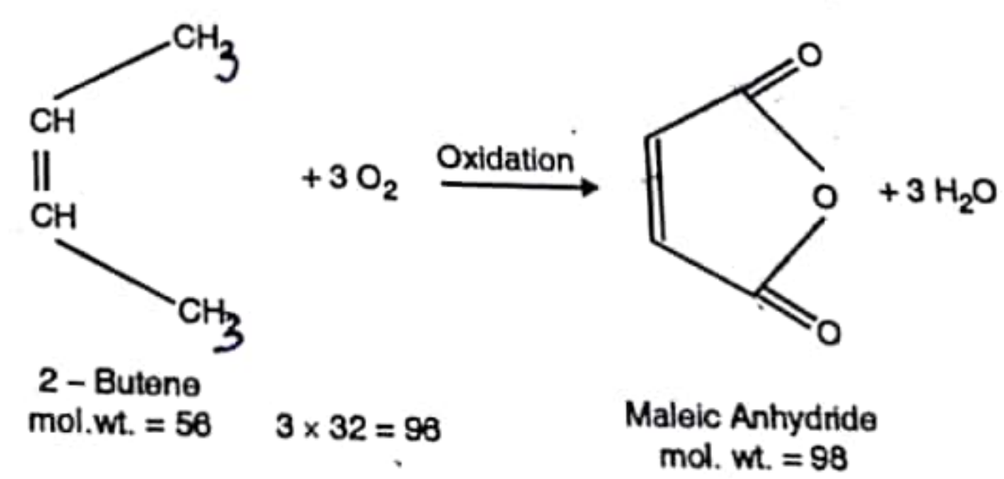
$$= \frac{76.5}{42 + 71} \times 100 = \frac{76.5}{113} \times 100 = 67.7\ \%$$

Ans. : $\boxed{\% \text{ Atom economy} = 67.7\%}$

Example 5.8.2 : *Calculate the atom economy for the following reaction, to prepare maleic anhydride.*



Solution



$$\% \text{ Atom economy} = \frac{\text{Molecular weight of product}}{\text{Total molecular weight of reactants}} \times 100$$

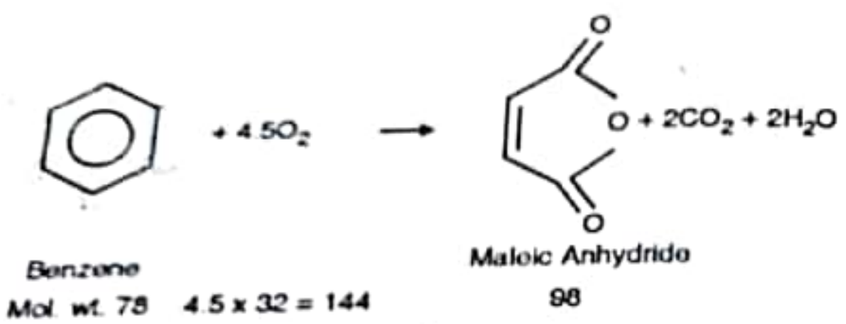
$$= \frac{98}{56 + 96} \times 100 = \frac{98}{152} \times 100 = 64.5\ \%$$

Ans. : *% Atom economy = 64.5%*

Example 5.8.3 : *Calculate the atom economy for the following reaction.*

Solution :

Given data



$$\therefore \% \text{ Atom economy} = \frac{98}{78 + 144} \times 100$$

$$= \frac{98}{222} \times 100 = \mathbf{44.1\ \%}$$ **...Ans.**

Ans. : *% Atom economy = 44.1%*

Example 5.8.4 : *Calculate the percent atom economy for the following reactions –*

(i) $CH_3CH = CH_2 + H_2 \xrightarrow{Ni} CH_3CH_2CH_3.$

(ii) $C_6H_6 + CH_3CI \xrightarrow{AlCl_3} C_6H_5CH_3 + HCI.$

Solution

(i) $CH_3CH = CH_2 + H_2 \xrightarrow{Ni} CH_3CH_2CH_3.$

Molecular weight = 42 2 44

$$\% \text{ Atom economy} = \frac{\text{Molecular weight of product}}{\text{Total molecular weight of reactants}} \times 100$$

$$= \frac{44}{42 + 2} \times 100$$

$$= \frac{44}{44} \times 100 = 100\ \%$$

(ii) $C_6H_6 + CH_3CI \xrightarrow{AlCl_3} C_6H_5CH_3 + HCI.$

Molecular weight = 78 50.5 92

$$\% \text{ Atom economy} = \frac{\text{Molecular weight of product}}{\text{Total molecular weight of reactants}} \times 100$$

$$= \frac{92}{78 + 50.5} \times 100$$

$$= \frac{92}{128.5} \times 100$$

$$= 71.5\%$$

Ans. : *% Atom economy = (i) 100% (ii) 71.5%*

Example 5.8.5 : *Calculate the percentage atom economy for the following reaction with respect to acetanilide :*

$$C_6H_5NH_2 + (CH_3CO)_2O \longrightarrow \underset{\text{Acetanilide}}{C_6H_5NHCOCH_3} + CH_3COOH.$$

MU - May 2012, May 2014, 4 Marks

Solution :

Reaction given :

$$\underset{\text{Aniline}}{C_6H_5NH_2} + \underset{\text{Acetic Anhydride}}{(CH_3CO)_2O} \longrightarrow \underset{\text{Acetanilide}}{C_6H_5NHCOCH_3} + \underset{\text{Acedic acid}}{CH_3COOH.}$$

Mol. wt. = 93 102 92 123

$$\% \text{ Atom economy} = \frac{\text{Molecular weight of product}}{\text{Total molecular weight of reactants}} \times 100$$

$$= \frac{123}{(93 + 102)} \times 100$$

$$= \frac{92}{128.5} \times 100 = 51.5\%$$

$$= \frac{123}{195} \times 100 = 63.07\ \%$$

Ans. : *% Atom economy = 63.07 %*

Example 5.8.6 : *Calculate the atom economy of the following reaction.*

$$C_6H_6 + 4 \cdot 5O_2 \xrightarrow{V_2O_5} C_4H_2O_3 + 2CO_2 + 2H_2O$$

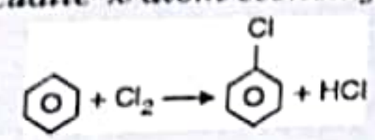
Solution :

$$C_6H_6 + 4.5\,O_2 \xrightarrow{V_2O_5} C_4H_2O_3 + 2CO_2 + 2\,H_2O$$

Benzene	4.5×32	Maleic
Mol. Weight 78	= 144	Anhydride
		Mol. Weight 98.

(Refer to example 5.4.3 for solution.)

Example 5.8.7 : *Calcualte % atom economy for following reactions :*



MU - May 2013, 4 Marks

Solution :

Benzene	Chlorine	Chlorobenzene
Mol.wt = 78	71	112.5

$$\% \text{ Alom Economy} = \frac{\text{Mol. Weight of product}}{\text{Total molecular weight of reactants}} \times 100$$

$$= \frac{112.5}{78 + 71} \times 100$$

$$= \boxed{75.5\ \%}$$

Example 5.8.8 : *Calculate percentage atom economy for the following reaction with respect to acetophenone :*

$$C_6H_6 + CH_3COCl \xrightarrow{AlCl_3} C_6H_5COCH_3 + HCl$$

benzene *acetophenone*

MU - Dec. 2013, 4 Marks

Solution :

$$C_6H_6 + CH_3COCl \xrightarrow{AlCl_3} C_6H_5COCl + HC1$$

	Benzene	Acetyl Chlorid	Acetophenone
Mol. wt. =	78	78.5	140.5

To Calculate % atom economy for reaction,

$$\% \text{ Atom Economy} = \frac{\text{Weight of product}}{\text{Total weight of Reactants}} \times 100$$

$$= \frac{140.5}{78 + 78.5} \times 100$$

$$= \boxed{89.78\ \%}$$

Example 5.8.9 : *Calculate percentage atom economy for the following reaction w.r. to methy iso-cyanate*

$$CH_3NH_2 + COCl_2 \rightarrow CH_3 - N = C = O + 2HCl$$

Methyl iso-cynate

MU - May 2015, 4 Marks

Solution :

$$\text{Molecular weight} = \underset{31}{CH_3NH_2} + \underset{99}{COCl_2} + \longrightarrow \underset{57}{CH_3\text{-}N = C = O} + 2HCl$$

$$\% \text{ Atom economy} = \frac{\text{Molecular weight of product}}{\text{Total molecular weight of reactants}} \times 100$$

$$= 57 \div [\,31 + 99\,] \times 100$$

$$= 57 / 130 \times 100 = 44\ \%$$

$$\% \text{ Atom economy} = \mathbf{44\ \%}$$

Ans. : % Atom economy = **44 %**

Example 5.8.10 : *Calculate percentage atom economy for the following reaction with respect to benzanilide ?* **MU – May 2016, 4 Marks**

Solution :

$$C_6H_5NH_2 + C_6H_5COC1 \rightarrow C_6H_5NHCOC_6H_5 + HCl$$

	Aniline	Benzoyl Chloride	Benzanilide
Mol. wt. =	93	140.5	196

To Calculate % atom economy for reaction,

$$\% \text{ Atom Economy} = \frac{\text{Weight of product}}{\text{Total weight of Reactants}} \times 100$$

$$= [196 / 93 + 140.5] \times 100 = \boxed{83.9\%}$$

Example 5.8.11 : *Calculate percentage atom economy for the following reaction withrespect to cinnamaldehyde.*

$$\underset{\text{benzaldehyde}}{C_6H_5CHO} + \underset{\text{acetaldehyde}}{CH_3CHO} \xrightarrow{NaOH} \underset{\text{cinnamaldehyde}}{C_6H_5CH{-}CHCHO} + H_2O$$

MU - Dec. 2015, 4 Marks

Solution :

	C_6H_5CHO +	CH_3CHO	$\longrightarrow$ $C_6H_5CH = CH.CHO$ + H_2O
Mol wt	106	44	132

$$\% \text{ Atom economy} = \frac{\text{Molecular weight of product}}{\text{Total molecular weight of reactants}} \times 100$$

$$= [132 / 106 + 44] \times 100$$

$$= 88\ \%$$

5.9 Green Solvents

MU - May 2012, Dec. 2012

The "Green solvents" – a newer concept involves the technology which has been popularly preferred over conventional solvent extraction process because of environmental concerns, such as the need to eliminate organic solvents and to find appropriate technologies for their disposal. e.g. Ionic liquid CO_2, propylene Glycol etc.

5.9.1 Ionic Liquid Supercritical CO_2

MU - May 2012, May 2016

Introduction

- Supercritical fluids possess properties of gases and liquids in an intriguing manner, which could offer a range of applications / possibilities in both synthetic and analytical chemistry.
- Supercritical / Ionic liquid carbon dioxide has found to be an energy conserving, selective and waste reducing alternatives to organic solvents and therefore is viewed as promising environmentally benign solvents. In addition, supercritical fluids can lead to reaction, which are difficult or even impossible to achieve in conventional solvents.
- Supercritical / Ionic liquid extraction is relatively new technology with a large potential for application in industry.

Principle

- The basic principle of Supercritical Fluid Extraction (SFE) technology is that when the *feed material is contacted* with a *supercritical fluid* then the *volatile substances* will *partition* into the *supercritical phase.*
- After the dissolution of soluble material the supercritical fluid containing the dissolved substances is removed from the feed material.
- The extracted component is then completely separated from the supercritical fluids (SCF) by means of a temperature and/or pressure change. The SCF may then be recompressed to the extraction conditions and recycled.

Choice of Solvents of Supercritical fluid Extraction

The choice of the SFE solvents is similar to a regular extraction. Principal considerations are as follow :

Good solvent property

Inert to the product

Easy separation from the product

Low cost

Carbon dioxide is the most commonly used *SCF*, primarily due to its low critical parameters (31.1°C, 73.8 bar), low cost and non-toxicity. However, several other SCF's have also been used in industrial processes.

5.9.2 Products from Natural Materials

Introduction

The biodiversity of plants and microbes is an unending resource for newer chemical templets. It provides information on the synergy of molecular tools like *genomics, proteomics* and *advanced bioanalytical technique* for development of new drugs or new molecules.

Plants as a Sources of New Drugs/Biomolecules

- Plants have been playing an important role in the field of pharmacy, not only in ancient times but also in the arena of modern drug discovery.
- The chemical diversity of plants gives the important clew for synthesis of different efficient pharmacophores in pharmaceutical drug design.
- Examples like Mepridine (Demerol), Pentazocine (Darvon), are totally synthetic drugs for which opiates such as morphine and codeine were the models.

- Japanese research group has recently isolated Stilbene derivative from the bark of a *Shorea hemsleyana* (dipterocarpeaceae) and roots of Cyphostemma bainessi (Vitaceae).
- The active compound identified is Hemsleyanol-D is a potent antibacterial agent Methicillin resistant staphylococcus aureus (MRSA) responsible for variety of human diseases.

Important Terms and Definitions

- The design of harmless processes to produce various products has emerged as a new branch commonly known as "clean chemistry" or "*Green Chemistry*" or "*Environmentally benign chemistry*".
- Atom economy can be calculated by using following formula,

$$\% \text{ Atom economy} = \frac{\text{Molecular weight of product}}{\text{Total molecular weight of reactants}} \times 100$$

Review Questions

Q. 1 What is this branch of "Green Chemistry" ?

Q. 2 Explain objectives of green chemistry.

Q. 3 Why is it called as clean chemistry ?

Q. 4 Why is it essential to have green processes ?

Q. 5 List the principles of green chemistry.

Q. 6 Explain the following principles of green chemistry with suitable example :

(i) Prevention of waste (ii) Maximise Atom economy
(iii) Non-hazardous chemical (iv) Safer chemical
(v) Auxiliary Substances (vi) Energy efficiency
(vii) Renewable feedstocks (viii) Derivatisation
(ix) Catalysts (x) Degradable products
(xi) New Analytica methods (xii) Accident prevention

Q. 7 Why is it essential to avoid derivatisation in reaction ?

Q. 8 How maximizing atom economy is beneficial ?

Q. 9 How prevention of waste is advantageous ?

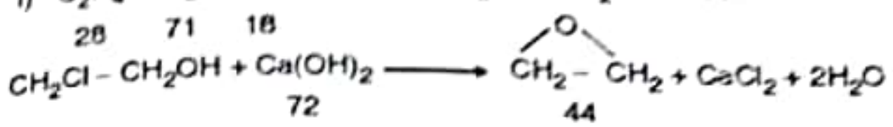
Q. 10 Discuss applications of green chemistry.

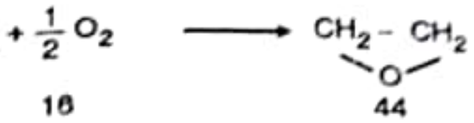
Q. 11 Write short note on : $SC\text{-}CO_2$

Q. 12 Calculate % atom economy for following reaction.

(a) Synthesis of ethylene oxide.

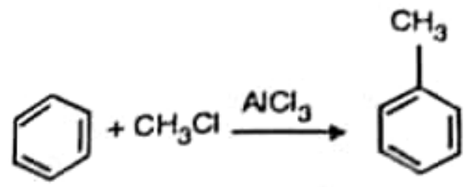
i) $C_2H_4 + Cl_2 + H_2O \longrightarrow CH_2Cl - CH_2OH + HCl$
(28, 71, 18)

$CH_2Cl - CH_2OH + Ca(OH)_2 \longrightarrow$  $+ CaCl_2 + 2H_2O$
(72, 44)

ii) $C_2H_4 + \frac{1}{2}O_2 \longrightarrow$ 
(28, 16, 44)

[Ans. : (i) 23 % (ii) 100 %]

(b) $CH_3CH_2CH_2Br + KOH \xrightarrow{\text{alcohol}} CH_3CH = CH_2 + KBr + H_2O$ **[Ans. : 27%]**

(c)  **[Ans. : 71.5%]**

(d) $CH_3CH_2Br + KOH \xrightarrow{H_2O} CH_3CH_2OH + KBr$ **[Ans. : 32.6 %]**

5.10 University Questions and Answers

May 2012

Q. 1 What are green solvents ? Give two industrial applications of green solvents. (3 Marks)
(Ans. : Refer section 5.9 and 5.9.1)

Q. 2 Explain conventional and green route of manufacturing Adipic acid. Also justify why the route is green. (6 Marks)
(Ans. : Refer section 5.5(A) and 5.4(B))

Dec. 2012

Q. 1 What is Green Chemistry ? Give the significance. (3 Marks)
(Ans. : Refer sections 5.1 and 5.2)

Q. 2 Explain the traditional and green route for production of adipic acid. (6 Marks)
(Ans. : Refer section 5.5)

Q. 3 Write a note on Green solvents. (5 Marks)
(Ans. : Refer section 5.9)

May 2013

Q. 1 What is Green chemistry ? List the 12 principles of Green chemistry. (3 Marks)
(Ans. : Refer sections 5.1 and 5.2)

Q. 3 Explain traditional and greener route of production of *Indigo dye*. By this reactions which principle of green chemistry is shown ? (5 Marks)
(Ans. : Refer section 5.4)

Dec. 2013

Q. 1 Explain 'prevenetion of waste' principle in Green Chemistry. (3 Marks)
(Ans. : Refer section 5.2.1)

Q. 2 Explain conventional and green chemistry route of production of adipic acid. Highlight the green chemistry principle involved. (5 Marks)
(Ans. : Refer section 5.5)