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CONCEPT OF ELECTROCHEMISTRY

SYLLABUS

- Introduction, concept of electrode potential, Nernst equation, types of electrochemical cells, concept of standard electrode with examples
- Electrochemical series, simple numericals.

3.1 INTRODUCTION

Electrochemistry is a branch of chemistry that studies chemical reactions which take place in a solution at the interface of an electron conductor (the electrode) and an ionic conductor (the electrolyte), and which involve electron transfer between the electrode and the electrolyte. Chemical reactions where electrons are transferred between molecules are called oxidation/reduction (redox) reactions. In general, electrochemistry deals with the study of electrodes, electrochemical cells, conversion of chemical energy into electrical energy and vice versa.

3.2 ELECTRO CHEMICAL CELL

An electrochemical cell is a device consisting of two electrodes, each in contact with a solution of its own ions and transforms the free energy change of the redox reaction at the electrodes into electrical energy. In a redox reaction, the energy released in a reaction due to the movement of charged particles gives rise to a potential difference. The maximum potential difference is called the electromotive force (EMF) in volts. It should be apparent from the above that the potential difference between the electrodes of a cell is the major factor of the tendency for the cell reaction to take place. The more positive is the cell potential, the greater is the tendency for the reaction to proceed to spontaneity.

The electrochemical cells are classified as, (i) Voltaic cell (Galvanic cell), (ii) Electrolytic cell, (iii) Concentration cell, (iv) Fuel cell.

(i) Voltaic cell (Galvanic cell) :

The free energy change in a galvanic cell must be negative and the potential difference of the electrodes (cell voltage) must be positive. Energy is released from spontaneous redox reaction. System does work on load/surrounding. In galvanic cell the free energy change of electrode redox reaction is converted into electric energy; that is $\Delta G = -nFE$. The examples of galvanic cells are primary irreversible cells (dry cells) and secondary cells (lead storage batteries).

Dissimilar metals

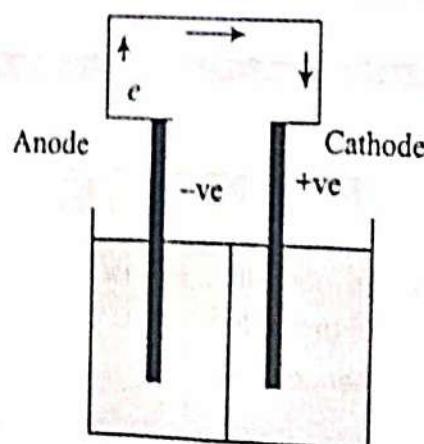


Fig. 3.1 : A galvanic cell

(ii) Electrolytic cell :

It is device in which electrical energy from an external source can be used to produce chemical reactions. Energy is absorbed to drive non-spontaneous redox reaction. Surroundings (power supply) do work on system (cell). In electrolytic cells, the reaction is being driven in the non-spontaneous direction by external electrical force and free energy change is positive.

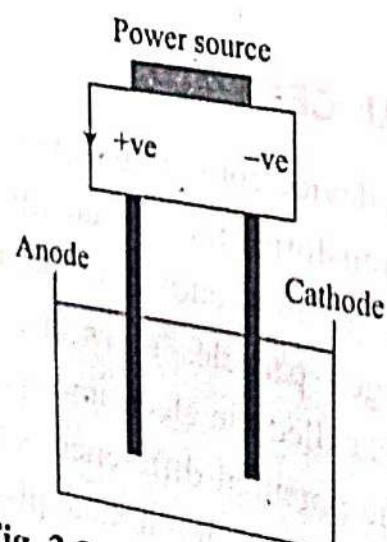


Fig. 3.2 : An electrolytic cell

(iii) Concentration cell :

A concentration cell is also an electrochemical device that generates electrical energy when two electrodes of the same metal are in contact with solutions of its ions at different concentrations. In a concentration cell, too, the free energy change of electrode reactions is converted into electric energy.

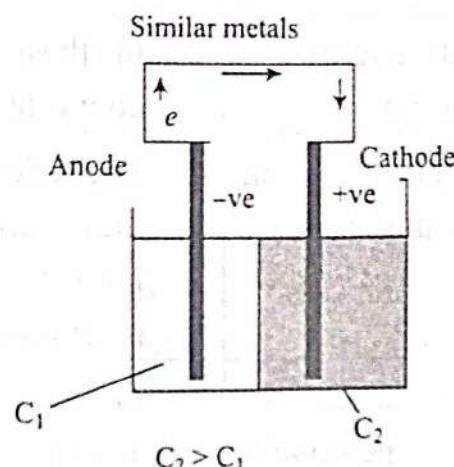


Fig. 3.3 : A concentration cell

(iv) Fuel cell :

A fuel cell is also an electrochemical device, which operates with continuous replenishment of the fuel at the electrode and no charging is required. In a fuel cell, the free energy change of electrode redox reactions is converted into electric energy.

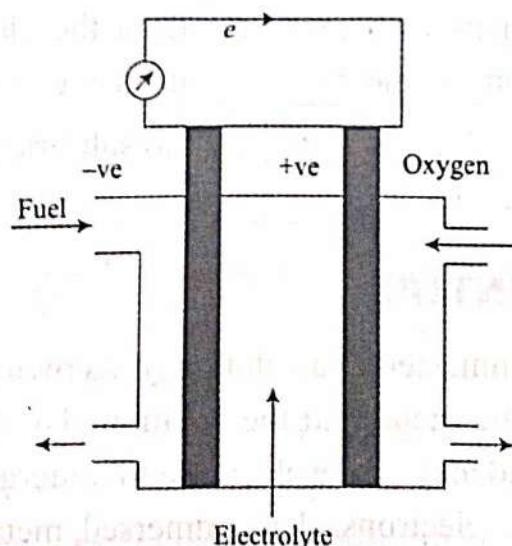


Fig. 3.4 : A fuel cell

Applications of Electrochemical cells :

- They are used in electro-refining of many non-ferrous metals. They are used in electro-winning of these metals.
- The production of high purity lead, zinc, aluminium and copper involves their use.
- Metallic sodium can be extracted from molten sodium chloride by placing it in an electrolytic cell and passing an electric current through it.

- Many commercially important batteries are made up of galvanic cell.
- Fuel cells are an important class of electro chemical cells that serve as a source of clean energy in several remote locations.

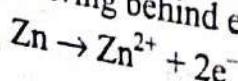
Comparison :

Galvanic Cell	Electrolytic Cell
1. In these cells, chemical energy is converted into electrical energy.	1. In these cells, electrical energy is converted into chemical energy.
2. The redox reactions that take place in these cells are spontaneous in nature.	2. The redox reactions that take place in these cells are non-spontaneous. An input of energy is required for redox reactions to proceed in these cells.
3. In these cells the anode is negatively charged and cathode is positively charged.	3. These cells feature positively charged anode and negatively charged cathode.
4. The electrons originate from the species that undergoes oxidation.	4. Electrons originate from an external source.
5. Electrodes are of dissimilar metals.	5. Electrodes used may be of dissimilar or same metals.
6. Electrode is immersed in its own ions and both have separate compartments.	6. Both the electrodes are immersed in the same electrolyte solution.
7. The two electrolyte solutions are connected by a salt bridge.	7. No salt bridge is required.

3.3 ELECTRODE POTENTIAL

When a piece of metal is immersed in a solution of its own ions, a potential difference is created at the interface of the metal and the solution. The magnitude of the potential difference is a major of the tendency of the electrode to undergo oxidation or reduction or the tendency to loose or gain electrons. The immersed metal is an electrode and the potential due to reaction at the interface of the electrode and the solution is called the electrode potential.

In order to understand the origin of electrode potential, consider a zinc electrode consists of zinc strip dipped in $ZnSO_4$. Nernst proposed that in the electrode there will be two tendencies – oxidation and reduction. If oxidation tendency occurs then Zn atoms on the metal surface undergo oxidation, leaving behind electrons on the surface.



The Zn^{2+} ions pass into the solution and the metal strip becomes negatively charged. The positively charged metal ions accumulate around the metal as shown in the Fig. 3.5.

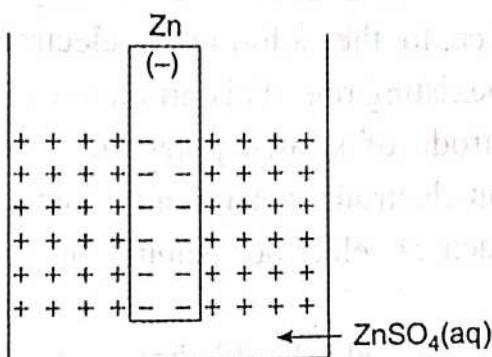
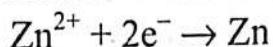


Fig. 3.5 : Origin of electrode potential (oxidation)

If the reduction tendency occurs, then Zn^{2+} ion in the solution undergo reduction by accepting electrons from the metallic surface.



Thus the metallic surface becomes positively charged and the negatively charged ions accumulate around the metal as shown in the Fig. 3.6.

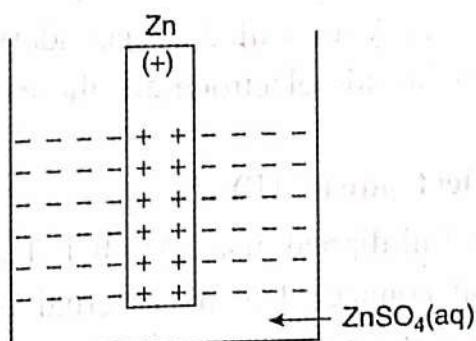


Fig. 3.6 : Origin of electrode potential (reduction)

The two tendencies happen simultaneously on the same electrode. Hence, an electrical double layer called Helmboltz electrical double layer (HED) is established at the metal-aqueous solution interface. Across the HED layer, there is movement of charges. This results in the potential called electrode potential. It is defined as the potential that exists between the metal or the gas and its ions in aqueous solution, at their equilibrium when they are in contact with each other. The electrode potential of a metal is thus a major of its tendency to lose or gain electrons when in contact with a solution of its own salt.

Standard Electrode Potential (E°) :

It is defined as the potential that exists between the metal or the gas and its aqueous solution of unit concentration at 298°K when the sum of all partial pressures of the gaseous reactants and products, if any, is equal to 1 atm pressure. This value is considered to compare the relative abilities of different electrodes to undergo oxidation or reduction.

3.4 REFERENCE ELECTRODE

The potential of an electrode cannot be accurately measured. It is not feasible to connect a measuring device to the solution of electrode, as it may lead to another equilibrium along with the existing one. This problem can be overcome if the electrode is connected to another electrode of known potential which can be termed as reference electrode. The criteria for an electrode to act as a reference electrode are:

1. The potential of such an electrode should be known, under the conditions of utility.
2. The potential of the electrode should show minimum variation with temperature. In other words, the potential gradient with respect to temperature should be minimum.

The most commonly used reference electrode is the hydrogen electrode. The potential of all other electrodes are measured with respect to the hydrogen electrode which is also called a primary reference electrode. There are few more reference electrodes which are standardized using standard hydrogen electrodes and then can be used as reference electrodes. They are called as secondary reference electrodes. Calomel electrode and Silver-Silver Chloride electrode are the examples of secondary reference electrodes.

[A] Standard Hydrogen Electrode (SHE) :

It consists of a platinum foil dipped in 1.0 M HCl. The platinum foil is enclosed in a thick walled glass tube and connected to an external contact wire. Pure hydrogen is passed into the container at 1 atm pressure through the inlet at the top. Excess hydrogen leaves the electrode through the outlet at the bottom as shown in the Fig. 3.7

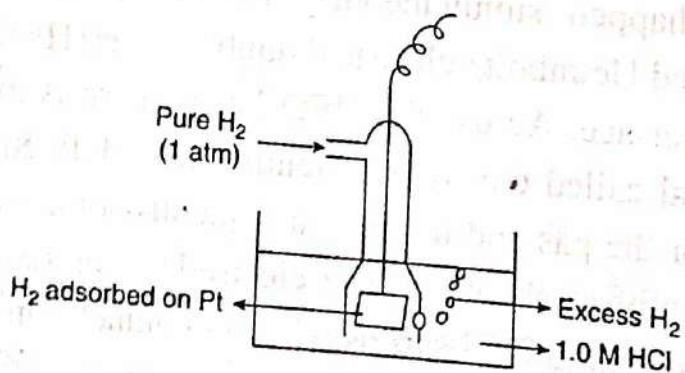
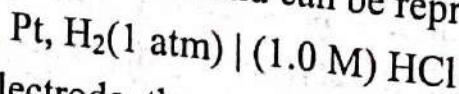
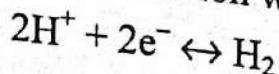


Fig. 3.7 : Standard Hydrogen Electrode

Pure hydrogen gets adsorbed on the platinum surface and is in contact with H^+ ions in the solution. It forms a reversible electrode and can be represented as:



If reduction occurs at the electrode, the reaction will be:



As the potential cannot be measured directly, it is assumed to be zero at 298K. Since E° of SHE is assumed to be zero, the potential of the second electrode can be obtained. The potential of an electrode measured at standard condition is known as standard electrode potential. The electrode potential is a measure of reduction potential of an electrode with respect to SHE.

Limitations of SHE :

1. SHE cannot be used in presence of strong oxidizing and reducing agents.
2. It is difficult to maintain unit molar concentration of hydrogen throughout and to pass hydrogen at 1 atm pressure.
3. Presence of arsenic compounds would get adsorbed on platinum foil and poisons the surface thereby affecting equilibrium of the reaction.

[B] Calomel Electrode :

It consists of a thin layer of pure mercury at the bottom of the container. It is covered with a paste of Hg, Hg_2Cl_2 and KCl of known concentration. The rest of the container is filled with KCl solution of known concentration, saturated with Hg_2Cl_2 as shown in the Fig. 3.8.

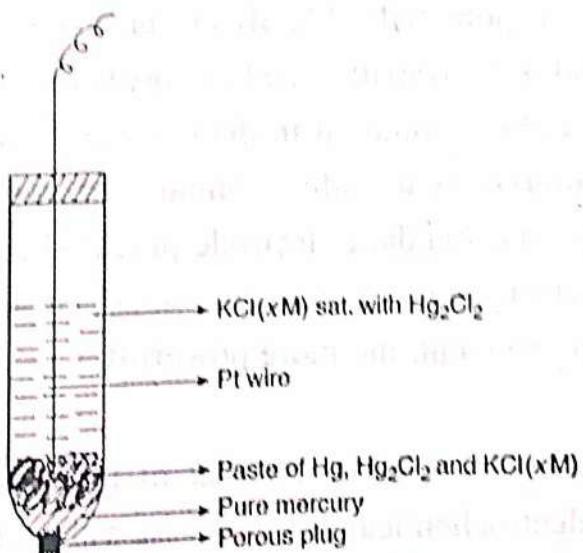
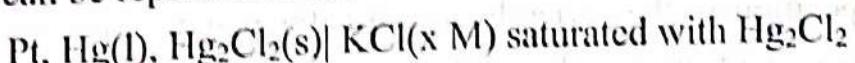


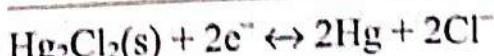
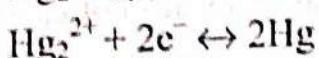
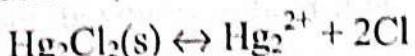
Fig. 3.8: Calomel Electrode

The electrode can be represented as:



The potential of this electrode depends on the concentration of KCl. It is a reversible electrode.

If reduction occurs at this electrode, the reaction can be shown as:



Nernst's equation for the Calomel electrode is:

$$E_{\text{Hg}_2\text{Cl}_2} = E^\circ_{\text{Hg}_2\text{Cl}_2} - \frac{2.303RT}{nF} \log [\text{Cl}^-]^2$$

Calomel electrode with saturated KCl and 1.0 M KCl have potential values of 0.2412V and 0.28V respectively.

Advantages of Calomel Electrode:

1. It is used in corrosion studies.
2. It is easy to construct and easy to transport.
3. It provides constant potential value with varying temperature.
4. It finds application in laboratories for measuring potential of an electrode.

3.5 ELECTRO CHEMICAL SERIES

The standard electrode potential for all metals can be obtained by preparing the cells in which one electrode is standard hydrogen electrode while the other is metal immersed in a solution of its ions of normal activity. The standard electrode potentials are also known as standard oxidation potentials. Metals are arranged in the increasing order of electrode potential. A metal will normally displace any other metal below it in the series from solutions of its salts and precipitate it in the metallic form. Thus, Mg, Al, Zn or Fe will displace Cu from solutions of its salts. Similarly Pb will displace Cu, Hg or Ag; while Cu will displace Ag. The standard electrode potential is a quantitative measure of the readiness of the element to act as a reducing agent in aqueous solution; the more negative the potential of the element, the more powerful is its action as a reducing agent.

Table 3.1)

The elements arranged in the increasing order of their standard electrode potential constitute a series called electrochemical series. These values are measured with respect to standard hydrogen electrode at 25°C. The greater the negative value of the potential, the greater is the tendency of the metal to pass into solution in the ionic state. Elements occupying higher position in the series have a greater negative potential are said to be highly electropositive and those placed lower in the series are said to be highly electronegative. Metals occupying top positions in the series hold their valence electrons rather loosely and hence exhibit greater tendency to lose electrons. Consequently such metals are highly electropositive and readily oxidized and corroded. On the other hand metals occupying lower positions in the series do not easily lose electrons and hence not corroded easily. All metals standing above in the electrochemical series will have a tendency to displace all metals standing below from dilute solutions containing their ions.

The characteristics of electrochemical series:

1. Lithium is the first member of the series.
2. Highly reactive metal systems which are good reducing agents are at the top of the series.
3. Good oxidizing agents are at the bottom of the series.
4. Hydrogen system is at the middle of the series. All the elements which displace hydrogen from dilute acids are placed above it.

The applications of electrochemical series:

1. Higher the reduction potential, greater is the tendency of the element to get reduced. Hence the relative oxidizing and reducing abilities of the elements can be compared easily. For instance, among Zn and Cu systems, zinc system has lower reduction potential (-0.76 V) than Cu (+0.34 V). So, zinc system has more reducing ability than Cu. Lower the reduction potential, greater is the reducing ability.
2. A metal placed higher in the series is anodic to other metals which lie below it. An element can displace all elements that lie below it in the series, from their salt solutions. For example, zinc added to a hot saturated solution of CuSO_4 can displace copper from the salt. Thus displacement reactions can be predicted.
3. Knowledge of electrochemical series helps in selection of electrode assemblies, to construct the galvanic cells of desired EMF.
4. The polarity of the electrode system and electrode reaction can be easily predicted.
5. Spontaneity and feasibility of the cell under construction can be easily predicted.

Table 3.1 : Standard electrode potentials of metals

(The values given refer to the normal activity of ions at a standard temperature of 25°C)

Metal ion electrode system	Electrode reaction (Acid solution)	Standard electrode potential (E_0) in volts
Li / Li ⁺	$\text{Li}^+ + \text{e}^- = \text{Li}$	-3.045 (Reactive metals)
K / K ⁺	$\text{K}^+ + \text{e}^- = \text{K}$	-2.925
Ca / Ca ⁺⁺	$\text{Ca}^{+2} + 2\text{e}^- = \text{Ca}$	-2.866
Na / Na ⁺	$\text{Na}^+ + \text{e}^- = \text{Na}$	-2.714
Mg / Mg ⁺⁺	$\text{Mg}^{+2} + 2\text{e}^- = \text{Mg}$	-2.363
Al / Al ⁺⁺⁺	$\text{Al}^{+3} + 3\text{e}^- = \text{Al}$	-1.662
Mn / Mn ⁺⁺⁺	$\text{Mn}^{+2} + 2\text{e}^- = \text{Mn}$	-1.180
Zn / Zn ⁺⁺	$\text{Zn}^{+2} + 2\text{e}^- = \text{Zn}$	-0.763
Cr / Cr ⁺⁺⁺	$\text{Cr}^{+3} + 3\text{e}^- = \text{Cr}$	-0.744
Fe / Fe ⁺⁺	$\text{Fe}^{+2} + 2\text{e}^- = \text{Fe}$	-0.041
Cd / Cd ⁺⁺	$\text{Cd}^{+2} + 2\text{e}^- = \text{Cd}$	-0.441
Co / Co ⁺⁺	$\text{Co}^{+2} + 2\text{e}^- = \text{Co}$	-0.277
Ni / Ni ⁺⁺	$\text{Ni}^{+2} + 2\text{e}^- = \text{Ni}$	-0.25
Sn / Sn ⁺⁺	$\text{Sn}^{+2} + 2\text{e}^- = \text{Sn}$	-0.136
Pb / Pb ⁺⁺	$\text{Pb}^{2+} + 2\text{e}^- = \text{Pb}$	-0.126
$\text{H}_2 / 2\text{H}^+$	$2\text{H}^{+2} + 2\text{e}^- = \text{H}_2$	0.00 Reference
Cu / Cu ⁺⁺	$\text{Cu}^{+2} + 2\text{e}^- = \text{Cu}$	0.337
Cu / Cu ⁺	$\text{Cu}^+ + \text{e}^- = \text{Cu}$	0.522
Hg / Hg ⁺	$\text{Hg}^+ + \text{e}^- = \text{Hg}$	0.799
Ag / Ag ⁺	$\text{Ag}^+ + \text{e}^- = \text{Ag}$	0.80
Hg / Hg ⁺⁺	$\text{Hg}^{++} + 2\text{e}^- = \text{Hg}$	0.854
Pd / Pd ⁺⁺	$\text{Pd}^{+2} + 2\text{e}^- = \text{Pd}$	0.987
Pt / Pt ⁺⁺	$\text{Pt}^{+2} + 2\text{e}^- = \text{Pt}$	1.2
Au/Au ⁺⁺⁺	$\text{Au}^{+3} + 3\text{e}^- = \text{Au}$	1.42 (Noble metals)

3.6 GALVANIC SERIES

Table 3.2 : Galvanic series (on the basis of relative oxidation potentials in sea water)

More Anodic or Active (or Corroded end)	Active or more anodic
Magnesium	Zinc
Magnesium alloys	Aluminium
Aluminium alloys	Low carbon steel
Cast iron	Stainless steel (active)
Lead-tin alloys	Tin
Lead	Brass
Copper	Bronze
Inconel	Copper-Nickel alloys
Silver	Monel
Stainless steel	Graphite
Platinum	Titanium
	Gold
	Noble (cathodic)

Although electrochemical series gives very useful information regarding chemical reactivity of metals, it may not be able to provide sufficient information in predicting the corrosion behavior in a particular set of environmental conditions. However, in practical situations many side reactions may take place which influence the corrosion reactions. In view of this, oxidation potential measurements of various metals and alloys in common use have been made using standard calomel electrode as the reference electrode and

immersing the metals and alloys in sea water. These are arranged in decreasing order of their activity and this series is known as 'galvanic series'. (Table 3.2)

Where as in the electrochemical series, metals are arranged from top to bottom in increasing order of their reduction potential. A metal high in the series is more anodic and undergoes corrosion faster than metal below it. However, some exceptions to this generalization are known. For example, in Zn - Al couple, Zn (below than Al) corrodes as Al develops oxide layer and resists corrosion. Such a behavior is well explained by considering the positions of these metals in galvanic series. The galvanic series provide more accurate information regarding the relative tendency of common metals and alloys to undergo corrosion and is more reliable than those based on electrochemical series. In the galvanic series more active metals are given higher place and corrode readily. The metals at the lower end do not easily react and therefore do not corrode so easily under atmospheric condition. When two metals are in electrical contact and an electrolyte is present, the one higher up in the galvanic series corrodes and the other is protected. The greater the difference in their positions in the galvanic series show less tendency to corrode corrosion. Metals close to each other in the galvanic series show when in contact with each other.

Comparison :

Electrochemical series	Galvanic series
1. Electrode potentials are measured by dipping pure metals in their salt solution of 1M concentration, without any oxide film on them.	1. This series was developed by studying corrosion of metals and alloys in unpolluted sea water, without their oxide films, if any removed.
2. The position of a given metal in electrochemical series is fixed.	2. The positions of given metal may shift in galvanic series.
3. It gives no information regarding positions of alloys.	3. Since alloys are included in galvanic series so their corrosion can be studied from this series.
4. The position of a metal in this series is permanently fixed.	4. The position of a metal when present in the form of an alloy, is different from pure metal
5. This series comprises of metals and non-metals.	5. This series comprises of metals and alloys
6. It predicts the relative corrosion tendencies.	6. It predicts the relative corrosion tendencies.

In an electrochemical cell, the electrode potential depends on the nature of the electrode, concentration of the electrolyte and temperature. Nernst derived a fundamental equation relating the free energy change of any electrode processes to the potential developed at the electrode along with the concentration of ions in the solutions and its temperature.

Derivation :

Consider an electrode assembly undergoing a spontaneous reaction.



The equilibrium constant (K) for this system in equilibrium can be evaluated as

$$K = \frac{[M]}{[M^{n+}]}$$

Some amount of electrical work is done and is maximum at equilibrium referred to as W_{\max} .

$W_{\max} = (\text{Number of Coulombs of charge flowing across the HED}) \times (\text{Energy available per Coulombs of charge})$

$$W_{\max} = nEF$$

As the reaction is spontaneous, there is decrease in the free energy. Also the decrease in free energy appears as work done (W_{\max}).

Therefore,

$$-\Delta G = W_{\max} = nEF$$

Under standard conditions, $-\Delta G^0 = nE^0 F$

The decrease in free energy change for the above mentioned reaction can be expressed as,

$$\Delta G = \Delta G^0 + 2.303 RT \log_{10} \frac{[M]}{[M^{n+}]}$$

Substituting the values of ΔG and ΔG^0 ,

$$-nEF = -nE^0 F + 2.303 RT \log_{10} \frac{[M]}{[M^{n+}]}$$

Dividing by $-nF$ we get,

$$E = E^0 - \frac{2.303 RT}{nF} \log_{10} \frac{[M]}{[M^{n+}]}$$

For a Galvanic cell the EMF is given as,

$$E_{\text{cell}} = E^0_{\text{cell}} - \frac{2.303 RT}{nF} \log_{10} K$$

Where, K is the equilibrium constant for the reaction.

Applications of Nernst Equation:

- The potential of an electrode and EMF of a cell can be calculated at any temperature and concentration.
- The concentration of the reactants can be calculated by knowing the potential of an electrode.
- The pH of a solution can be calculated by measuring the EMF.
- The concentration of a solution in the galvanic cell can be determined.

NUMERICALS ON NERNST EQUATION

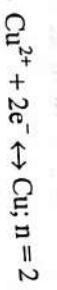
- Calculate the electrode potential of copper, if the concentration of CuSO_4 is 0.206 M at 23.1°C . Given that $E^0_{\text{Cu}^{2+}/\text{Cu}} = +0.34 \text{ V}$.

Solution :

Given that

$$[\text{CuSO}_4] = 0.206; T = 296.1^\circ\text{K}$$

The reaction taking place is



According to Nernst's equation,

$$\begin{aligned} E_{\text{Cu}^{2+}/\text{Cu}} &= E^0_{\text{Cu}^{2+}/\text{Cu}} - \frac{2.303RT}{nF} \log_{10} \frac{1}{[\text{Cu}^{2+}]} \\ &= +0.34 - \frac{2.303 \times 8.314 \times 296.1}{2 \times 96500} \times \log_{10} \frac{1}{0.206} \\ &= 0.31984 \text{ V} \end{aligned}$$

Ans. : $E_{\text{Cu}^{2+}/\text{Cu}} = 0.31984 \text{ V}$

- Calculate the concentration of NiCl_2 in the nickel electrode having a potential of -0.16942 V at 24.9°C . Given that $E^0_{\text{Ni}^{2+}/\text{Ni}} = -0.14 \text{ V}$.

Solution :

- According to Nernst's equation,

$$E_{\text{Ni}^{2+}/\text{Ni}} = E^0_{\text{Ni}^{2+}/\text{Ni}} - \frac{2.303RT}{nF} \log_{10} \frac{1}{[\text{Ni}^{2+}]}$$

Here $n = 2$. So,

$$-0.16942 = -0.14 + \frac{2.303 \times 8.314 \times 297.9}{2 \times 96500} \times \log_{10}(x);$$

$$\begin{aligned} -0.16942 &= -0.14 + (0.02955) \times \log_{10} x \\ -0.02942 &= 0.02955 \times \log_{10} x \end{aligned}$$

We get $x = [\text{NiCl}_2] = 0.1010 \text{ M}$

Ans. : Concentration of $\text{NiCl}_2 = 0.1010 \text{ M}$

- Calculate the standard electrode potential of lead electrode, if the electrode potential is -0.18025 V at 301 K and a concentration of Pb^{2+} solution is 0.0096 M .

Solution :

Given $[\text{Pb}^{2+}] = 0.0096 \text{ M}$; $E_{\text{Pb}^{2+}/\text{Pb}} = -0.18025 \text{ V}$; $T = 301 \text{ K}$.

According to Nernst's equation,

$$\begin{aligned} E_{\text{Pb}^{2+}/\text{Pb}} &= E^0_{\text{Pb}^{2+}/\text{Pb}} - \frac{2.303RT}{nF} \log_{10} \frac{1}{[\text{Pb}^{2+}]} \\ E^0_{\text{Pb}^{2+}/\text{Pb}} &= E_{\text{Pb}^{2+}/\text{Pb}} + \frac{2.303RT}{nF} \log_{10} [\text{Pb}^{2+}] \\ &= -0.18025 - \frac{2.303 \times 8.314 \times 301}{2 \times 96500} \times \log_{10}(0.0096) \\ &= -0.18025 - 0.02986 \times (-2.0177) \\ &= 0.1200 \text{ V} \end{aligned}$$

Ans. : $E^0_{\text{Pb}^{2+}/\text{Pb}} = 0.1200 \text{ V}$

3.8 REVIEW QUESTIONS

- Explain the origin of electrode potential.
Ans. Refer Section 3.3.
- Define Standard Electrode Potential.
Ans. Refer Section 3.3.
- Calomel electrode is a reference electrode. Justify.
Ans. Refer Section 3.4.
- Give the advantages of Calomel electrode.
Ans. Refer Section 3.4.
- Write a note on Calomel electrode.
Ans. Refer Section 3.4.
- What is a reference electrode?
Ans. Refer Section 3.4.

7. What are the limitations of SHE?

Ans. Refer Section 3.4.

8. Explain Standard Hydrogen electrode.

Ans. Refer Section 3.4.

9. Presence of impurities in the hydrogen gas poisons the SHE. Justify.

Ans. Refer Section 3.4.

10. Write a note on electrochemical cell.

Ans. Refer Section 3.2.

11. Give the different types of electrochemical cells.

Ans. Refer Section 3.2.

12. Distinguish between galvanic cell and electrolytic cell.

Ans. Refer Section 3.2.

13. Give the applications of electrochemical cell.

Ans. Refer Section 3.2.

14. Explain the characteristics of electrochemical series.

Ans. Refer Section 3.5.

15. Give the applications of electrochemical series.

Ans. Refer Section 3.5.

16. Write a note on galvanic series.

Ans. Refer Section 3.6.

17. Differentiate between galvanic series and electrochemical series.

Ans. Refer Section 3.6.

18. Derive Nernst equation.

Ans. Refer Section 3.7.

19. Give the applications of Nernst equation.

Ans. Refer Section 3.7.

20. A zinc rod is placed in a 0.1M solution of zinc sulphate at 25°C. Calculate the potential of the electrode at this temperature, assuming 96% dissociation of ZnSO_4 and $E^{\theta}_{\text{Zn}^{2+}/\text{Zn}} = 0.76 \text{ V}$.

Ans. $E_{\text{Zn}^{2+}/\text{Zn}} = 0.1200 \text{ V}$

21. Calculate the potential of the following electrochemical cell at 25°C.

$\text{Cu}(\text{s}) | \text{Cu}^{2+}(\text{aq}) (0.50 \text{ M}) || \text{H}^+(\text{0.01}) | \text{H}_2(0.95 \text{ atm}) ; \text{Pt}$

Ans. $E_{\text{cell}} = -0.449 \text{ V}$

FUELS AND COMBUSTION

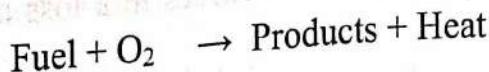
SYLLABUS

- Definition, classification, characteristics of a good fuel
- Units of heat (no conversions), Calorific value - Definition, Gross or Higher calorific value & Net or lower calorific value, Dulong's formula & numerical for calculations of Gross and Net calorific values.
- Solid fuels- Analysis of coal - Proximate and Ultimate Analysis- numerical problems and significance.
- Liquid fuels- Petrol - Knocking, Octane number, Cetane number, Antiknocking agents, unleaded petrol, oxygenates (MTBE), catalytic converter.
- Combustion - Calculations for requirement of only oxygen and air (by weight and by volume only) for given solid & gaseous fuels.

6.1 INTRODUCTION

A fuel can be defined as a combustible substance, containing carbon as main constituent, which on proper burning gives large amount of heat, which can be used economically for domestic and industrial purposes. Wood, charcoal, coal, kerosene, petrol, diesel, producer gas, oil gas etc are some of the fuels.

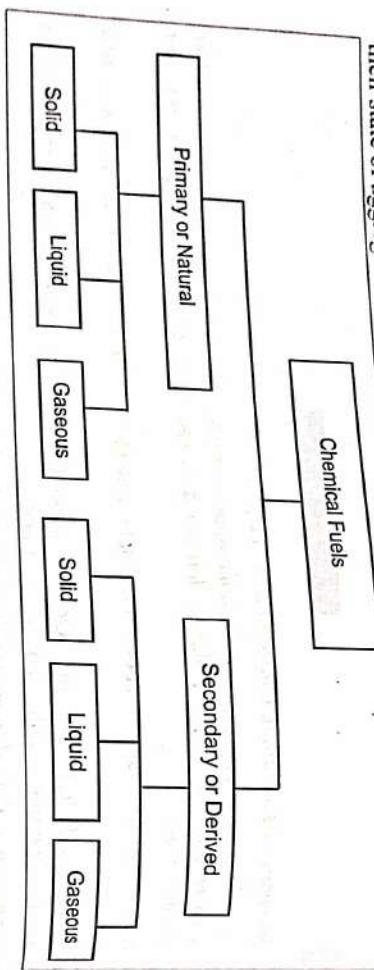
During the process of combustion of a fuel (like coal), the atoms of carbon, hydrogen etc. combine with oxygen with the simultaneous liberation of heat at a rapid rate. This energy is liberated due to the "rearrangement of valence electrons" in these atoms which results in the formation of new compounds (like CO_2 , H_2O etc.). These new compounds have less energy in them and therefore the energy released during the combustion process is the difference in the energy of the reactants (C, H and O etc. of fuel) and that of the products formed.



Coal and crude petroleum are referred to as fossil fuels as they result from fossilized remains of plants and animals. They may be considered as stored fuels or stored energy. They are primary or main source of fuel.

6.2 CLASSIFICATION OF FUELS

The fossil fuels have been classified according to the first classification (and preparation) and (2) the state of aggregation. According to the first classification, we have (a) natural or primary fuels which are found in nature as such e.g. wood, peat, coal, petroleum, natural gas etc. (b) artificial or secondary fuels are those which are prepared from the primary fuels. For example, charcoal, coke, diesel oil, kerosene oil, petrol, gas, producer gas, blast furnace gas etc. The second method of classification is based on their state of aggregation as solid, liquid and gaseous fuels.



6.3 CHARACTERISTICS OF A GOOD FUEL

While selecting a good fuel for a particular purpose, we have to consider the different aspects of fuel. A good fuel should have the following characteristics :

- (1) **High Calorific value** : As the amount of heat generated and temperature attained thereby depends upon the calorific value of the fuel, so a fuel should possess high calorific value.
- (2) **Moderate ignition temperature** : Ignition temperature is the temperature at which the fuel must be pre-heated so that it starts burning smoothly. Low ignition temperature is dangerous for storage and transport of fuel, since it can cause fire hazards. High ignition temperature causes difficulty in igniting the fuel but the fuel is safe during storage, handling and transport. Hence, an ideal fuel should have 'moderate' ignition temperature.
- (3) **Low moisture content** : Fuel should have low moisture content because presence of moisture reduces its heating value and involves in a loss of money as it is paid for the same rate as the fuel.

6.4 CALORIFIC VALUE

Calorific value is most important property of the fuel. The efficiency of the fuel is judged by its calorific value. Calorific value is also known as heat of combustion and generally expressed in terms of calories/gm. This is the amount of heat obtained by complete combustion of unit quantity of fuel. The amount of heat given out is expressed in calories. Calorific value of the fuel is defined as the amount of heat liberated by complete combustion of a unit mass of the fuel. Calorific value of solid and liquid fuels are usually expressed in calories per gram (cal/gm) or kilocalories per kilogram (kcal/kg) or British thermal units /lb. In case of gaseous fuel, the units used are kilocalorie per cubic meter (kcal/m³) or B.Th.U/cubic feet (B.Th.U/ ft³).

6.4.1 Units of Heat

The units of heat generally employed are calories, kilogram calories, British therm units and centigrade heat units.

(4) **Low non-combustible matter content** : The non-combustible matter remains in the form of ash after combustion. The presence of non-combustible matter reduces the calorific value of the fuel. It is said that each percent of non combustible matter reduces the calorific value by about 1.5 percent. It also increases cost of storage, handling and disposal of waste products. Hence, a good fuel should have low non combustible matter content.

(5) **Moderate velocity of combustion** : If the rate of combustion is low, then the required high temperature is not attained and high rate of combustion is not desirable. A good fuel should have moderate velocity of combustion.

(6) **Products of combustion** : Fuel, on burning, should not give out objectionable and harmful gases. In other words, the gaseous products of combustion should not pollute the atmosphere. CO, SO₂, H₂S, PH₃ etc are some of the harmful gases.

(7) **Low cost** : A good fuel should be readily available in bulk at a cheap rate.

(8) **Transportation** : Fuel must be easy to handle, store and transport at a low cost. Solid and liquid fuels can easily be transported from one place to another. Transportation of gaseous fuels is costly and can even cause fire hazards.

(9) **Should not undergo spontaneous combustion** : It should not undergo spontaneous combustion.

(10) **Combustion should be easily controllable** : i.e. combustion of the fuel should be easy to start or stop, when required.

(11) **Storage cost in bulk should be low**.

(12) **Efficiency** : Fuel should burn in air with efficiency, without much smoke.

(13) **In case of solid fuel, the size should be uniform so that combustion is regular.**

(a) Calorie (cal) or gram calorie (g.cal) : For all practical purposes, the calorie or gram calorie may be defined as the amount of heat required to raise the temperature of one gram of water through one degree centigrade. (i.e. from 15°C to 16°C) 1 calorie = 4.185 joules.

(b) Kilocalorie or kilogram calorie or kg cal : K.C.U.)

This is equal to 1000 calories and thus is the amount of heat required to raise the temperature of one kilogram of water through 1°C (from 15°C to 16°C)

$$1 \text{ kcal} = 1000 \text{ cal.}$$

(c) British thermal unit :

A British thermal unit is the amount of heat required to raise the temperature of water through 1°F (more precisely from 60°F to 61°F).

$$1 \text{ B.Th.U} = 1,054.6 \text{ Joules} = 1,054.6 \times 10^7 \text{ ergs.}$$

$$1 \text{ B.Th.U} = 252 \text{ cals} = 0.252 \text{ kcal}$$

$$1 \text{ kcal} = 3.968 \text{ B.Th.U.}$$

(d) Centigrade heat unit (C.H.U.) :

The centigrade heat unit is the amount of heat required to raise the temperature of water through 1°C .

$$1 \text{ kcal} = 3.968 \text{ B.Th.U.} = 2.2 \text{ C.H.U.}$$

This unit can be interconverted as follows :

$$1 \text{ kcal/kg} = 1.8 \text{ B.Th.U./lb}$$

$$1 \text{ kcal/m}^3 = 0.1077 \text{ B.Th.U./ft}^3$$

$$1 \text{ B.Th.U./ft}^3 = 9.3 \text{ kcal/m}^3.$$

The calorific value of a fuel can be considered in two ways :

- (1) Higher calorific value or gross calorific value.
- (2) Lower calorific value or net calorific value.

6.4.2 Higher Calorific Value or Gross Calorific Value

Usually, hydrogen is present in almost all the fuels. When the fuel containing hydrogen is burnt the hydrogen present undergoes combustion and gets converted to steam. If the products of combustion are condensed to the room temperature (15°C or 60°F) the latent heat of condensation of steam is evolved. This latent heat of condensation of steam so liberated also gets included in the total heat and as a result more amount of heat is available. As this amount of heat is included in gross calorific value, the GCV is always more than net calorific value. The calorific value determined by bomb calorimeter gives gross or higher calorific value.

The gross calorific value or higher calorific value is defined as the total amount of heat produced when a unit mass/volume of fuel is burnt completely and the products of combustion have been cooled to room temperature. (i.e. 15°C or 60°F)

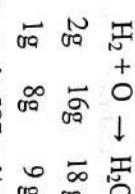
6.4.3 Net Calorific Value or Lower Calorific Value

In actual use of any fuel, the water vapour, moisture etc. are not condensed and escape with hot combustion gases. Hence latent heat of steam is not measured or included in the net or lower calorific value of the fuel. The net or lower calorific value of the fuel is defined as the net amount of heat produced when a unit mass of fuel is burnt completely and the products of combustion are allowed to escape into the atmosphere.

Net or lower calorific value = Gross calorific value - Latent heat of condensation of water vapour formed.

= Gross calorific value - (Mass of hydrogen per unit weight of the fuel burnt \times 9 \times Latent heat of vaporization of water)

1 part by weight of hydrogen gives 9 parts by weight of water as follows :



The latent heat of steam is 587 cal/g (or kcal/kg) or 1060 B.Th.U./lb of water vapour produced.

$$\text{Net calorific value} = \text{Gross calorific value} - 9 \times \frac{H}{100} \times 587$$

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

where H = percentage of hydrogen in the fuel.

In actual practical use, of a fuel, it is rarely feasible to cool the combustion products to the room temperature to allow the condensation of water vapour formed and utilized that latent heat, hence the water vapour formed also is allowed to escape along with the hot combustion gases.

6.5 THEORETICAL CALCULATION OF CALORIFIC VALUE OF FUEL

The calorific value of fuel can be approximately computed by knowing percentage of the constituent elements of the fuel. Ultimate analysis gives the percentages of the elements like C, H, N, S and O. According to Dulong, the calorific value of different sum of the calorific values of its constituent elements. The calorific value of different elements is given as follows.

Calorific value of carbon = 8080 cal/g

Calorific value of hydrogen = 34500 cal/g

Calorific value of sulphur = 2240 cal/g

In case, oxygen is also present, it is assumed to be present in the combined form

i.e. as H_2O .

Thus, the Dulong's formula for calculating the calorific value from the chemical composition of fuel is

$$HCV = \frac{1}{100} [8080 C + 34500 (H - O/8) + 2240 S] \text{ kcal/kg}$$

where C, H, O and S represent the percentage of the corresponding elements

$$LCV = HCV - 0.09 H \times 587$$

$$LCV = [HCV - 0.09 H \times 587] \text{ kcal/kg.}$$

This is based on the fact that 1 part of H by mass gives 9 parts by H_2O and latent heat of steam is 587 cal/g.

NUMERICALS ON GCV AND NCV :

- A coal sample contains C = 60%, O = 33%, H = 6%, S = 0.5%, N = 0.3%. Calculate the gross calorific value of the coal.

Solution :

Using Dulong's formula,

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

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

$$= \frac{1}{100} [484800 + 6487.5 + 1120]$$

$$= \frac{1}{100} [550607.5]$$

$$= 5506.075 \text{ kcal/kg}$$

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

$$= 5506.075 - (0.09 \times 6 \times 587)$$

$$= 5506.075 - 316.98$$

Ans. : HCV = 5506 kcal/kg

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

1. A sample of coal contained C = 66%, O = 28%, H = 4%, S = 1.5%, N = 0.8% and Ash = 0.2%. Calculate the higher and lower calorific values of coal.

Solution : Using Dulong's formula :

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

$$= \frac{1}{100} [8080 \times 66 + 34500 (4 - \frac{28}{8}) + 2240 \times 1.5]$$

$$= \frac{1}{100} [533280 + 17250 + 3360]$$

$$= 553890$$

$$= 5538.90 \text{ kcal/kg.}$$

$$L.C.V. = [H.C.V. - (0.09 \times H \times 587)]$$

$$= 5538.9 - 0.09 \times 4 \times 587$$

$$= 5327.58 \text{ kcal/kg}$$

Ans. : HCV = 5538.90 kcal/kg

$$LCV = 5327.58 \text{ kcal/kg}$$

3. Calculate the percentage of hydrogen and HCV of a coal containing C = 85%, S = 1%, O = 2%, N = 2.5%, and Ash = 3.5% and that coal is having L.C.V of 8490.5 kcal/kg.

Solution :

$$L.C.V. = H.C.V. - 0.09 H \times 587 \text{ Kcal/Kg}$$

$$8490.5 \text{ kcal/kg} = H.C.V. - 0.09 H \times 587$$

$$H.C.V. = 8490.5 + 0.09 H \times 587$$

$$H.C.V. = 8490.5 + 52.8 H \text{ kcal/kg}$$

Using Dulong's formula :

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

$$= \frac{1}{100} [8080 \times 85 + 34500 (H - \frac{2}{8}) + 2240 \times 1]$$

$$= \frac{1}{100} [686800 + 34500 H - 8625 + 2240]$$

$$= [6868 + 345H - 86.25 + 22.4] \text{ kcal/kg}$$

or

$$H.C.V. = (6804.15 + 345H) \text{ kcal/kg}$$

$$\begin{aligned} \text{F.E. Sem-II Engineering Chemistry-II} \\ &= (6804.15 + 345 H) \text{ kcal/kg} \\ &= (6804.15 + 345 \times 5.77) \text{ kcal/kg} \\ &= 8490.5 + 52.8 H \text{ kcal/kg} \\ \therefore & 345H - 52.8H = 1686.35 \\ \therefore & 292.2H = 1686.35 \\ H &= 5.77\% \\ \text{H.C.V.} &= 8490.5 + 52.8 \times 5.77 \\ &= 8795.15 \text{ kcal/kg.} \end{aligned}$$

Now,

$$\begin{aligned} \text{Ans. : HCV} &= 8795.15 \text{ kcal/kg} \\ \% \text{H} &= 5.77 \end{aligned}$$

4. Find the gross and net calorific value of a fuel which on ultimate analysis gives the following results :

$$\begin{aligned} \text{C} &= 80\%, \text{H} = 6\%, \text{O} = 8\%, \text{S} = 1.5\%, \text{N} = 1.0\%. \\ \text{Solution :} & \end{aligned}$$

Using Dulong's formula :

$$\begin{aligned} \text{H.C.V.} &= \frac{1}{100} [8080 \text{C} + 34500 (\text{H} - \frac{\text{O}}{8}) + 2240 \text{S}] \\ &= \frac{1}{100} [8080 \times 80 + 34500 (6 - \frac{8}{8}) + 2240 \times 1.5] \\ &= \frac{1}{100} [646400 + 172500 + 3360] \end{aligned}$$

$$= \frac{1}{100} [822260]$$

$$= 8222.6 \text{ kcal/kg}$$

$$\text{L.C.V.} = [\text{H.C.V.} - (0.09 \times \text{H} \times 587)]$$

or

$$\begin{aligned} \text{N.C.V.} &= 8222.6 - 0.09 \times 6 \times 587 \\ &= 7905.62 \text{ kcal/kg} \end{aligned}$$

$$\begin{aligned} \text{Ans. : HCV} &= 8222.6 \text{ kcal/kg} \\ \text{LCV} &= 7905.62 \text{ kcal/kg} \end{aligned}$$

5. A sample of coal contains C = 70%, O = 20%, H = 6%, S = 2.5%, N = 1.5% Calculate the gross and net calorific value of the coal.

Solution :

Using Dulong's formula :

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

$$\begin{aligned} &= \frac{1}{100} [8080 \times 70 + 34500 (6 - \frac{20}{8}) + 2240 \times 2.5] \\ &= \frac{1}{100} [8080 \times 70 + 34500 (6 - \frac{20}{8}) + 2240 \times 2.5] \\ &= \frac{1}{100} [565600 + 120750 + 5600] \\ &= \frac{1}{100} [686215] \end{aligned}$$

[May 2010]

$$\begin{aligned} \text{Ans. : HCV} &= 6919.5 \text{ kcal/kg} \\ \text{LCV} &= 6602.52 \text{ kcal/kg} \end{aligned}$$

6. A sample of coal has the following composition by mass, C = 85%, H = 7%, O = 3%, S = 3.5%, N = 2.1% and Ash = 4.4%. Calculate H.C.V. and L.C.V. using Dulong formula.

Solution :

Using Dulong's formula :

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

$$\begin{aligned} &= \frac{1}{100} [8080 \times 85 + 34500 (7 - \frac{3}{8}) + 2240 \times 3.5] \\ &= \frac{1}{100} [686800 + 228562.5 + 7840] \end{aligned}$$

[May 2010]

$$\begin{aligned} \text{L.C.V.} &= [\text{H.C.V.} - (0.09 \times \text{H} \times 587)] \\ &= 9232.025 \text{ kcal/kg} \end{aligned}$$

$$\begin{aligned} \text{L.C.V.} &= [\text{H.C.V.} - (0.09 \times \text{H} \times 587)] \\ &= 9232.025 - 0.09 \times 7 \times 587 \\ &= 8862.215 \text{ kcal/kg} \end{aligned}$$

Using Dulong's formula :

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

$$\begin{aligned} \text{Ans. : HCV} &= 9232.025 \text{ kcal/kg} \\ \text{LCV} &= 8862.215 \text{ kcal/kg} \end{aligned}$$

7. A sample of coal has the following composition by mass, C = 80%, H = 4.4%, O = 3%, S = 3.5%, N = 2.1% and Ash = 4.4%. Calculate H.C.V. and L.C.V. using Dulong formula.

Solution :

Using Dulong's formula :

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

$$= \frac{1}{100} [8080 \times 80 + 34500 (7 - \frac{3}{8}) + 2240 \times 3.5]$$

$$= \frac{1}{100} [646400 + 228562.5 + 7840]$$

[Dec. 2011]

$$= \frac{1}{100} [882802.5]$$

$$= 8828.025 \text{ kcal/kg}$$

$$\text{L.C.V.} = [\text{H.C.V.} - (0.09 \times \text{H} \times 587)]$$

$$= 8828.025 - 0.09 \times 7 \times 587$$

$$= 8828.025 - 369.81$$

$$= 8458.215 \text{ kcal/kg}$$

Ans. : HCV = 8828.025 kcal/kg
LCV = 8458.215 kcal/kg

8. A sample of coal has the following composition by mass, C = 85%, H = 6%, O = 8%, S = 0.5% and Ash = 0.5%. Calculate H.C.V. and L.C.V. using Dulong formula. [May 2011]

Solution :

Using Dulong's formula :

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

$$= \frac{1}{100} [8080 \times 85 + 34500 (6 - \frac{8}{8}) + 2240 \times 0.5]$$

$$= \frac{1}{100} [686800 + 172500 + 1120]$$

$$= \frac{1}{100} [860420]$$

$$= 8604.2 \text{ kcal/kg}$$

10. A solid fuel coal containing 90% carbon, 8% hydrogen, 1.5% sulphur, 2% Nitrogen, 5% oxygen and remaining ash. Calculate the high and low calorific value of the solid fuel. [May 2012]

Solution : Using Dulong's formula :

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

$$\text{L.C.V.} = [\text{H.C.V.} - (0.09 \times \text{H} \times 587)]$$

$$= 8604.2 - 0.09 \times 8 \times 587$$

$$= 8287.22 \text{ kcal/kg}$$

9. A sample of coal contains C = 70%, O = 23%, H = 5%, S = 1.5%, N = 0.4% and Ash = 0.1%. Calculate the gross and net calorific value of the coal. [Dec. 2011]

Solution :

Using Dulong's formula :

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

$$= \frac{1}{100} [8080 \times 70 + 34500 (5 - \frac{23}{8}) + 2240 \times 1.5]$$

$$= \frac{1}{100} [565600 + 73312.5 + 3360]$$

$$= \frac{1}{100} [642272.5]$$

$$= 6422.725 \text{ kcal/kg.}$$

$$\text{L.C.V.} = [\text{H.C.V.} - (0.09 \times \text{H} \times 587)]$$

$$= 6422.725 - 0.09 \times 5 \times 587$$

$$= 6422.725 - 264.15$$

$$= 6158.575 \text{ kcal/kg.}$$

Ans. : HCV = 6422.725 kcal/kg
LCV = 6158.575 kcal/kg

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$$= \frac{1}{100} [8080 \times 90 + 34500 (8 - \frac{5}{8}) + 2240 \times 1.5]$$

$$= \frac{1}{100} [727200 + 34500 (59/8) + 3360]$$

$$= \frac{1}{100} [727200 + 254437.5 + 3360] \text{ kcal/kg}$$

$$= \frac{1}{100} [984997.5]$$

$$= 9849.975 \text{ kcal/kg}$$

$$= [H.C.V. - (0.09 \times H \times 587)]$$

$$= 9849.975 - 0.09 \times 8 \times 587$$

$$= 9849.975 - 422.64$$

$$= 9427.335 \text{ kcal/kg}$$

Ans. : HCV = 9849.975 kcal/kg
LCV = 9427.335 kcal/kg

11. A coal sample 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.

Solution : Using Dulong's formula :

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

$$= \frac{1}{100} [8080 \times 82 + 34500 (6 - \frac{8}{8}) + 2240 \times 0.5]$$

$$= \frac{1}{100} [662560 + 34500 (5) + 1120]$$

$$= \frac{1}{100} [662560 + 172500 + 1120] \text{ kcal/kg}$$

$$= \frac{1}{100} [836180]$$

$$= 8361.8 \text{ kcal/kg}$$

$$\text{L.C.V.} = [\text{H.C.V.} - (0.09 \times \text{H} \times 587)]$$

$$= 8361.8 - 0.09 \times 6 \times 587$$

$$= 8361.8 - 316.98 = 8044.82 \text{ kcal/kg}$$

Ans. : HCV = 8361.8 kcal/kg
LCV = 8044.82 kcal/kg

Fuels And Combustion
Q2. A coal sample has the following composition by weight C=80%, H=4%, O=6%, S=3%, N=2% and Ash=5%. Calculate the gross and net calorific value using Dulong's formula.

Solution : Using Dulong's formula :

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

$$= \frac{1}{100} [8080 \times 80 + 34500 (4 - \frac{6}{8}) + 2240 \times 3]$$

$$= \frac{1}{100} [646400 + 34500 (26/8) + 6720]$$

$$= \frac{1}{100} [646400 + 112125 + 6720] \text{ kcal/kg}$$

$$= \frac{1}{100} [765245]$$

$$= 7652.45 \text{ kcal/kg}$$

$$\text{L.C.V.} = [\text{H.C.V.} - (0.09 \times \text{H} \times 587)]$$

$$= 7652.45 - 0.09 \times 4 \times 587$$

$$= 7441.13 \text{ kcal/kg}$$

Ans. : HCV = 7652.45 kcal/kg
LCV = 7441.13 kcal/kg

13. A coal sample has the following composition by weight C=75%, H=7%, O=8%, S=4%, N=2% and Ash=4%. Calculate the gross calorific value using Dulong's formula.

Solution : Using Dulong's formula :

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

$$= \frac{1}{100} [8080 \times 75 + 34500 (7 - \frac{8}{8}) + 2240 \times 4]$$

$$= \frac{1}{100} [606000 + 34500 (6) + 8960]$$

$$= \frac{1}{100} [606000 + 207000 + 8960] \text{ kcal/kg}$$

$$= \frac{1}{100} [821960]$$

$$= 8219.60 \text{ kcal/kg}$$

[May 2014]

Ans. : HCV = 8219.60 kcal/kg

Dec 2011

Nov 2014

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14. A coal sample has the following composition by weight C=70%, H=10%, O=4%, S=2%, N=1% and Ash=12%. Calculate the gross and net calorific value of the fuel.

Solution: Using Dulong's formula :

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

using Dulong's formula :

$$\begin{aligned} \text{H.C.V.} &= \frac{1}{100} \left[8080 \times 70 + 34500 \left(10 - \frac{4}{8} \right) + 2240 \times 2 \right] \\ &= \frac{1}{100} \left[8080 \times 70 + 34500 \left(10 - \frac{4}{8} \right) + 2240 \times 2 \right] \\ &= \frac{1}{100} \left[8080 \times 70 + 34500 \left(\frac{76}{8} \right) + 4480 \right] \\ &= \frac{1}{100} \left[8080 \times 70 + 34500 \left(9.5 \right) + 4480 \right] \\ &= \frac{1}{100} [565600 + 327750 + 4480] \\ &= \frac{1}{100} [897830] \\ &= 8978.30 \text{ kcal/kg.} \end{aligned}$$

$$\text{L.C.V.} = [\text{H.C.V.} - (0.09 \times H \times 587)]$$

$$\begin{aligned} \text{L.C.V.} &= [\text{H.C.V.} - (0.09 \times H \times 587)] \\ &= 8978.3 - 0.09 \times 10 \times 587 \\ &= 8978.3 - 528.3 \\ &= 8450 \text{ kcal/kg.} \end{aligned}$$

Ans. : HCV = 8978.30 kcal/kg

[May 2016]

15. A coal sample has the following composition by mass. C=70%, H=9%, O=4%, S=2%, N=1% and Ash=14%. Calculate gross calorific value of the fuel using Dulong's formula.

Solution: Using Dulong's formula :

$$\begin{aligned} \text{H.C.V.} &= \frac{1}{100} \left[8080 C + 34500 \left(H - \frac{O}{8} \right) + 2240 S \right] \\ &= \frac{1}{100} \left[8080 \times 70 + 34500 \left(9 - \frac{4}{8} \right) + 2240 \times 2 \right] \\ &= \frac{1}{100} [565600 + 293250 + 4480] \\ &= \frac{1}{100} [863330] \\ &= 8633.3 \text{ kcal/kg.} \end{aligned}$$

Ans. : HCV = 8633.3 kcal/kg

F.E. Sem.-III Fuels And Combustion
A coal sample has the following composition by mass. C=70%, H=5.5%, O=8.4%, N=0.6% and S=1.5%. Calculate GCV and NCV of the fuel.

Solution: Using Dulong's formula :

$$\begin{aligned} \text{H.C.V.} &= \frac{1}{100} \left[8080 C + 34500 \left(H - \frac{O}{8} \right) + 2240 S \right] \\ &= \frac{1}{100} [8080 \times 84 + 34500 \left(5.5 - \frac{8.4}{8} \right) + 2240 \times 1.5] \\ &= \frac{1}{100} [8080 \times 84 + 34500 \left(\frac{35.6}{8} \right) + 2240 \times 1.5] \\ &= \frac{1}{100} [678720 + 153525 + 3360] \\ &= \frac{1}{100} [835605] \\ &= 8356.05 \text{ kcal/kg.} \end{aligned}$$

[Dec 2017]

17. A coal sample has the following composition by mass. C=84%, H=5.5%, O=8.4%, N=0.6% and S=1.5%. Calculate GCV and NCV of the fuel.

Solution : Using Dulong's formula :

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

$$\begin{aligned} \text{H.C.V.} &= \frac{1}{100} [8080 \times 84 + 34500 \left(5.5 - \frac{8.4}{8} \right) + 2240 \times 1.5] \\ &= \frac{1}{100} [8080 \times 84 + 34500 \left(\frac{35.6}{8} \right) + 2240 \times 1.5] \\ &= \frac{1}{100} [678720 + 153525 + 3360] \\ &= \frac{1}{100} [835605] \\ &= 8356.05 \text{ kcal/kg.} \end{aligned}$$

[May 2017]

$$\begin{aligned}
 L.C.V. &= [H.C.V. - (0.09 \times H \times 587)] \\
 &= 8356.05 - 0.09 \times 5.5 \times 587 \\
 &= 8356.05 - 290.565 \\
 &= 8065.485 \text{ kcal/kg.}
 \end{aligned}$$

Ans. : $HCV = 8356.05 \text{ kcal/kg}$
 $LCV = 8065.485 \text{ kcal/kg}$

18. A coal sample has the following composition. C=70%, H=5%, O=23%, S=1.5%, N=0.4% and Ash=0.1%. Calculate GCV of the fuel.

Solution : Using Dulong's formula:

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

$$= \frac{1}{100} [8080 \times 70 + 34500 (5 - \frac{23}{8}) + 2240 \times 1.5]$$

$$= \frac{1}{100} [8080 \times 70 + 34500 \frac{[17]}{8} + 3360]$$

$$= \frac{1}{100} [565600 + 73312.5 + 3360]$$

$$= \frac{1}{100} [642272.5]$$

$$= 6422.725 \text{ kcal/kg.}$$

$$L.C.V. = [H.C.V. - (0.09 \times H \times 587)]$$

$$= 6422.725 - 0.09 \times 5 \times 587$$

$$= 6422.725 - 264.15$$

$$= 6158.575 \text{ kcal/kg.}$$

Ans. : $HCV = 6422.725 \text{ kcal/kg}$
 $LCV = 6158.575 \text{ kcal/kg}$

19. A coal sample contains.

C=66%, H=4%, O=28%, N=0.8% and S=1.5% and Ash = 0.2%. Calculate GCV and NCV of the fuel.

Solution : Using Dulong's formula:

$$\begin{aligned}
 H.C.V. &= \frac{1}{100} [8080 C + 34500 (H - \frac{O}{8}) + 2240 S] \\
 &= \frac{1}{100} [8080 \times 66 + 34500 (4 - \frac{28}{8}) + 2240 \times 1.5]
 \end{aligned}$$

$$= \frac{1}{100} [533280 + 17250 + 3360]$$

$$= \frac{1}{100} [553890]$$

$$L.C.V. = [H.C.V. - (0.09 \times H \times 587)]$$

$$= 5538.9 - 0.09 \times 4 \times 587$$

Ans. : $HCV = 5538.90 \text{ kcal/kg}$
 $LCV = 5327.58 \text{ kcal/kg}$

[May 2019]

Ans. : $HCV = 7006.335 \text{ kcal/kg}$

[May 2019]

10. Calculate HCV of a coal sample containing C=85%, H=1%, N=1.5%, O=5%, S=0.4% and remaining being ash.

Solution : Using Dulong's formula:

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

$$= \frac{1}{100} [8080 \times 85 + 34500 (1 - \frac{5}{8}) + 2240 \times 0.4]$$

$$= \frac{1}{100} [686800 + 12937.5 + 896]$$

$$= \frac{1}{100} [700633.5]$$

$$= 7006.335 \text{ kcal/kg}$$

Ans. HCV = 7006.335 kcal/kg

6.6 ANALYSIS OF COAL AND ITS SIGNIFICANCE

Coal is a highly carbonaceous fuel which is formed in nature as the final product of a series of decompositions of vegetable matter under the influence of heat and pressure in a limited supply of air. It is chiefly composed of C, H, N, O and S besides non combustible inorganic matter.

The composition of coal varies widely according to source and age. Hence its analysis is necessary to interpret the results from the point of view of classification, price fixation and industrial utilization of coal.

In order to ascertain the quality of coal, it is subjected to the following two types of analysis:

- (1) Proximate analysis,
- (2) Ultimate analysis.

6.6.1 Proximate Analysis Determination of moisture content, volatile matter, content and fixed carbon in the coal. Although this analysis is empirical, it provides important information regarding commercial classification and determination of suitability of coal for a particular domestic or industrial use. The proximate analysis is carried out by using standard specifications. The proximate analysis is carried out as per standard specifications. The proximate analysis is known as free moisture of air dried sample. Moisture which is lost on air drying is surface moisture.

(1) Determination of moisture :

About 1g of finely powdered air dried coal sample is weighed in a crucible. The crucible is placed inside an electric hot air oven, which is maintained at 105°C - 110°C . The crucible is allowed to remain in oven for 1 hour. Then it is taken out with the help of a pair of tongs. It is then cooled in a desiccator and weighed. Loss in weight is reported as moisture on percentage basis.

$$\text{Percentage of moisture} = \frac{\text{Loss in weight}}{\text{Weight of air dried sample}} \times 100$$

Significance :

During combustion, a significant amount of liberated heat is wasted in evaporating the moisture and thus high percentage of moisture reduces the calorific value of the coal. Moreover, it quenches the fire in the furnace. Since moisture is transported at the same cost as coal, fuel becomes expensive. Due to excessive surface moisture, handling of coal becomes troublesome. However, small quantity of surface moisture upto 10% is desirable in coal as it improves yield and quantity of metallurgical coke. It also produces a more uniform fuel bed and reduces the amount of fly ash.

(2) Determination of volatile matter :

The moisture free coal sample left in the crucible (1) is then covered with a lid. It is then placed in an electric furnace (muffle furnace), maintained at $925^{\circ}\text{C} \pm 20^{\circ}\text{C}$. The crucible is taken out of the oven after 7 minutes of heating. The crucible is first cooled in air and then inside a desiccator and weighed again. Loss in weight is reported as volatile matter on percentage basis.

$$\text{Percentage of volatile matter} = \frac{\text{Loss in weight due to removal of volatile matter}}{\text{Weight of coal sample taken}} \times 100$$

Significance :

The volatile matter expelled is not present as such in the coal but results from its thermal decomposition. The volatile matter evolved consists of combustible gases like CO_2 , H_2 , CH_4 and other hydrocarbons and incombustible gases like CO_2 and N_2 .

The incombustible gases do not have any heating value and are undesirable. Some coals may have very high volatile matter (upto 50%) and on burning they produce a large amount of gas or vapour which also burn with production of flame. Thus coals with high volatile matter burn with long, smoky flame and have low heating value. Coals with low volatile matter burns with a shorter flame. Thus the information regarding space required depends upon the nature of the flame. Further, the percentage of volatile matter in a coal denotes that high proportion of which escapes unburnt. Hence lesser the volatile matter, better the rank of the coal.

(3) Determination of ash :

The residual coal left in crucible (2) is then heated without lid in a muffle furnace at $700 \pm 50^{\circ}\text{C}$ for half an hour. The crucible is then taken out. It is cooled in air and then in desiccator and weighed. The process of heating, cooling and weighing is repeated till a constant weight is obtained. The residue is reported as ash on percentage basis.

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

Significance :

The ash is a non combustible inorganic matter left after complete combustion of organic matter in the coal. The ash consists of silica, alumina, iron oxide and small quantities of magnesia as well as lime. The ash reduces heating value of coal. Moreover, ash causes the hindrance to the flow of air and heat, thereby lowering the temperature. It causes trouble during firing by forming clinkers blocking the interspace of the grate on which coal is being burnt. It causes obstruction to air supply, thereby the burning of coal becomes irregular. The ash increases transportation and storage cost of the coal. Since ash has to be removed from the furnace and disposed off, it increases labour cost. After mining, coal is washed in washeries so as to reduce the percentage of ash and thus high quality cooking coal is made available to steel plants. Washings of non coking coal reduces its transportation storage and labour cost. As coal/coke are used as reducing agents in several metallurgical operations, the composition of ash affects the slag and metal composition, its characteristics and it is the most important factor governing the selection of a proper flux.

(4) Fixed carbon :

$$\text{Percentage of fixed carbon} = 100 - \text{Percentage of (Moisture + Volatile matter + Ash)}$$

Significance :

Higher the percentage of fixed carbon, greater is its calorific value and better will be quality of fuel. Hence high percentage of carbon is desirable. It also helps in designing the furnace and shape of fire box because it is the fixed carbon that burns in solid state.

1. A coal sample was analyzed as follows :

Exactly 2.5g was weighed into silica crucible next covered with a vented lid and strongly heated for exactly seven minutes at $950 \pm 20^\circ\text{C}$. The residue weighed 2.415g, the crucible was then heated without cover at 700°C until a constant weight was obtained. The last residue was found to weigh 0.245g. Calculate the percentage results of above analysis.

Solution :

$$(i) \quad \text{Weight of coal taken} = 2.5\text{g}$$

$$\text{Mass of moisture in coal sample} = 2.5 - 2.415$$

$$= 0.085\text{g}$$

$$\therefore \text{Percentage of moisture} = \frac{\text{Loss in weight of coal}}{\text{Weight of coal taken}} \times 100$$

$$= \frac{0.085 \times 100}{2.5}$$

$$= 3.4\%$$

$$(ii) \quad \text{Mass of volatile matter} = 2.415 - 1.528$$

$$= 0.887\text{g}$$

$$\therefore \text{Percentage of volatile matter} = \frac{\text{Loss in weight due to volatile matter}}{\text{Weight of coal}} \times 100$$

$$= \frac{0.887 \times 100}{2.5}$$

$$= 35.48\%$$

$$(iii) \quad \text{Mass of ash} = 0.245\text{g}$$

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

$$= \frac{0.245 \times 100}{2.5}$$

$$= 9.8\%$$

$$(iv) \quad \text{Percentage of fixed carbon} = 100 - (\% \text{ Moisture} + \text{Volatile matter} + \text{Ash})$$

$$= 100 - (3.4 + 35.48 + 9.8)$$

$$= 100 - 48.68$$

$$= 52.32\%$$

$$\text{Ans. : \% Moisture} = 3.4$$

$$\% \text{ Volatile Matter} = 35.48$$

$$\% \text{ Ash} = 9.8$$

$$\% \text{ Fixed Carbon} = 52.32$$

NUMERICALS ON PROXIMATE ANALYSIS

1. One gram of air dried sample of coal on heating at 110°C for 1 hour produced a residue 0.72 g mass which on combustion at 950°C for 1 hour produced a air left 0.1g of non-combustible matter. Calculate the result of proximate analysis.

Solution : Weight of coal taken = 1 g

$$(i) \quad \text{Mass of moisture in coal sample} = 1.0 - 0.72$$

$$= 0.150\text{g}$$

$$\therefore \text{Percentage of moisture} = \frac{\text{Loss in weight of coal}}{\text{Weight of coal taken}} \times 100$$

$$= \frac{0.150 \times 100}{1}$$

$$= 15\%$$

$$(ii) \quad \text{Mass of volatile matter} = 0.850 - 0.720$$

$$= 0.13\text{g}$$

$$\therefore \text{Percentage of volatile matter} = \frac{\text{Loss in weight due to volatile matter}}{\text{Weight of coal}} \times 100$$

$$= \frac{0.13 \times 100}{1}$$

$$= 13\%$$

$$(iii) \quad \text{Mass of residue} = 0.1$$

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

$$= \frac{0.1 \times 100}{1}$$

$$= 10\%$$

$$(iv) \quad \text{Percentage of fixed carbon} = 100 - (\% \text{ Moisture} + \text{Volatile matter} + \text{Ash})$$

$$= 100 - (15 + 13 + 10)$$

$$= 100 - 38$$

$$= 62\%$$

$$\text{Ans. : \% Moisture} = 15$$

$$\% \text{ Volatile Matter} = 13$$

$$\% \text{ Ash} = 10$$

$$\% \text{ Fixed Carbon} = 62$$

3. A sample of coal was analyzed for content of moisture, volatile matter and ash. From the following data, calculate the percentage of the above quantities.

[Dec. 2009]

	Weight of coal taken	Weight of coal taken
(i)	Mass of moisture in coal sample = 2.5 g	2.5 g
(ii)	Percentage of moisture = $\frac{2.5 - 2.415}{2.5} \times 100 = 0.085\%$	0.085%
(iii)	Mass of volatile matter = 0.132 g	0.132 g
(iv)	Percentage of volatile matter = $\frac{0.132 \times 100}{2.5} = 5.28\%$	5.28%

- Solution :
- Weight of coal taken = 2.5 g
 - Weight of coal after heating at 100°C = 2.368 g
 - Weight of coal after heating covered crucible at $950 \pm 20^\circ\text{C}$ = 1.75 g
 - Constant weight obtained at the end of the experiment = 0.95 g.

	Weight of coal taken	Weight of coal taken
(i)	Mass of moisture in coal sample = 2.5 g	2.5 g
(ii)	Percentage of moisture = $\frac{2.5 - 2.415}{2.5} \times 100 = 0.085\%$	0.085%
(iii)	Mass of volatile matter = 0.132 g	0.132 g
(iv)	Percentage of volatile matter = $\frac{0.132 \times 100}{2.5} = 5.28\%$	5.28%

- Solution :
- Weight of coal taken = 2.5 g
 - Mass of moisture in coal sample = $2.5 - 2.368 = 0.132\text{ g}$
 - Percentage of moisture = $\frac{\text{Loss in weight of coal}}{\text{Weight of coal taken}} \times 100 = \frac{0.132 \times 100}{2.5} = 5.28\%$
 - Mass of volatile matter = $2.368 - 1.75 = 0.618\text{ g}$

- Percentage of volatile matter = $\frac{\text{Loss in weight due to volatile matter}}{\text{Weight of coal}} \times 100 = \frac{0.618 \times 100}{2.5} = 25.4\%$

	Weight of coal taken	Weight of coal taken
(i)	Mass of moisture in coal sample = 2.5 g	2.5 g
(ii)	Percentage of moisture = $\frac{2.5 - 2.415}{2.5} \times 100 = 0.085\%$	0.085%
(iii)	Mass of volatile matter = 0.132 g	0.132 g
(iv)	Percentage of volatile matter = $\frac{0.132 \times 100}{2.5} = 5.28\%$	5.28%

- Solution :
- Weight of coal taken = 2.5 g
 - Mass of moisture in coal sample = $2.5 - 2.368 = 0.132\text{ g}$
 - Percentage of moisture = $\frac{\text{Loss in weight of coal}}{\text{Weight of coal taken}} \times 100 = \frac{0.132 \times 100}{2.5} = 5.28\%$
 - Mass of volatile matter = $2.368 - 1.75 = 0.618\text{ g}$

$$\text{Percentage of volatile matter} = \frac{\text{Loss in weight due to volatile matter}}{\text{Weight of coal}} \times 100 = \frac{0.618 \times 100}{2.5} = 25.4\%$$

	Weight of coal taken	Weight of coal taken
(i)	Mass of moisture in coal sample = 2.5 g	2.5 g
(ii)	Percentage of moisture = $\frac{2.5 - 2.415}{2.5} \times 100 = 0.085\%$	0.085%
(iii)	Mass of volatile matter = 0.132 g	0.132 g
(iv)	Percentage of volatile matter = $\frac{0.132 \times 100}{2.5} = 5.28\%$	5.28%

- Ans. : % Moisture = 5.28
% Volatile Matter = 24.72
% Ash = 38

- Ans. : % Fixed Carbon = 61.2

5. 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 of volatile matter in it.

Solution :

4. 2.5 g of air dried coal sample was taken in a silica crucible, after heating it in an electric oven at $105\text{-}110^\circ\text{C}$ for 1 hour; the residue was weighed 2.410 g. The residue was heated in a silica crucible covered with vented lid at a temperature $950 \pm 20^\circ\text{C}$ for exactly 7 minutes. After cooling the weight of residue was found to be 1.78 g. The residue was then ignited at $700\text{-}750^\circ\text{C}$ to a constant weight of 0.246 g. Calculate the percentage of fixed carbon in a coal sample.

- Ans. : % Moisture = 4.5 %
% Volatile Matter = $\frac{2.9 - 1.96}{2.9} \times 100 = 41.0\%$
% Ash = 38

- Ans. : % Fixed Carbon = $\frac{0.246 \times 100}{2.9} = 8.4\%$

- Loss in weight of coal = $\frac{4.5 \times 2.9}{100} = 0.1305\text{ g}$

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6.24 Removal of moisture = $2.9 - 0.1305$
= 2.7695 g

(i) Weight of coal after removal of moisture = 2.7695 g

Weight of coal = $2.7695 - 1.96$

Mass of volatile matter = 2.7695 g

= $\frac{\text{Loss in weight due to volatile matter}}{\text{Weight of coal}} \times 100$

$$\text{Percentage of volatile matter} = \frac{0.8095 \times 100}{2.9}$$

$$= 27.91\%$$

Ans. : % Volatile Matter = 27.91

(6) 2.5 g of coal sample was taken in silica crucible and heated in oven maintained at 110 °C for one hour. The weight after heating was 1.98g. The sample was analysed for volatile matter and weight of 0.246g. Calculate the percentage of further heated to get fixed weight of ash and fixed carbon for this sample.

[May 2015]

Solution :

$$\text{Weight of coal taken} = 2.5\text{g}$$

$$\text{Mass of moisture in coal sample} = 2.5 - 2.41 = 0.09\text{g}$$

$$\therefore \text{Percentage of moisture} = \frac{\text{Loss in weight of coal}}{\text{Weight of coal taken}} \times 100$$

$$= \frac{0.09 \times 100}{2.5}$$

$$= 3.6\%$$

(ii) Mass of volatile matter = $2.41 - 1.98$

$$= 0.43\text{g}$$

Percentage of volatile matter = $\frac{\text{Loss in weight due to volatile matter}}{\text{Weight of coal}} \times 100$

$$= \frac{0.43 \times 100}{2.5}$$

$$= 17.2\%$$

(iii) Mass of residue after ignition at 700-750°C = 0.246 g

Weight of ash left

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

$$= \frac{0.246 \times 100}{2.5}$$

$$= 9.84\%$$

E.Sem.-II App.

6.25 % of fixed carbon = $100 - (\% \text{ Moisture} + \text{Volatile matter} + \text{Ash})$
= $100 - (3.6 + 17.2 + 9.84)$
= 69.36 %

Ans. : % moisture = 3.6
% volatile matter = 17.2
% ash = 9.84
% fixed carbon = 69.36.

6.6.2 Ultimate Analysis

Ultimate analysis is useful in classification of coal and in combustion calculations as it basically determines the percentage of elements. It includes the determination of carbon, hydrogen, nitrogen, sulphur, oxygen and ash. The ultimate analysis is required for detailed and accurate heat balance for the equipment in which the fuel is used.

Determination of carbon and hydrogen :

A known weight (about 1 – 2 g) of air dried coal is taken in a porcelain boat and coal is burnt in a combustion tube (about 90 cms in length and about 12-15 mm in diameter) which is packed with copper oxide and silver guaze. Copper oxide helps in ensuring a complete combustion of sample. Silver guaze retains the oxidation products of elements like sulphur and chlorine present in coal.

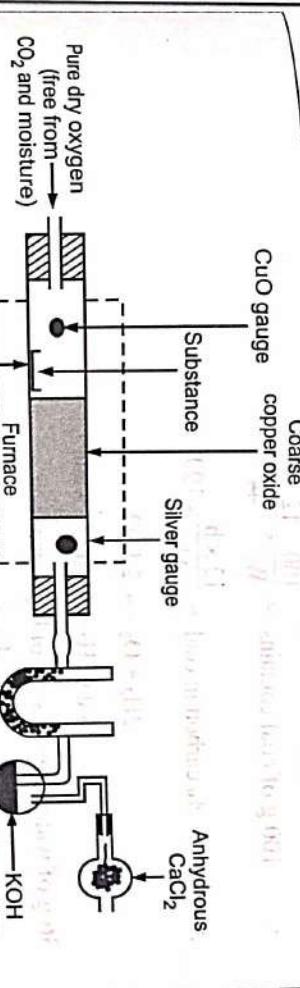


Fig. 6.1 : Combustion apparatus

The sample of coal is burnt in a combustion tube at 800°C in the presence of air free from carbon dioxide and moisture. Carbon and Hydrogen present in the coal gets converted into carbon dioxide and water respectively as per the following equations :



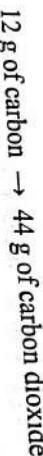
The products of combustion are passed through previously weighed U-tube containing anhydrous calcium chloride and a bulb containing potassium hydroxide solution. Carbon dioxide and water are absorbed in previously weighed potassium hydroxide bulb and calcium chloride U-tube respectively. The difference in weights of calcium chloride U-tube and potassium hydroxide bulb give the amount of water and carbon dioxide respectively. From these percentages of carbon and hydrogen calculated.

Calculations :

$$\text{Let the weight of coal} = W \text{ g}$$

$$\text{Weight of } H_2O \text{ (increase in weight of } CaCl_2 \text{ tube)} = a \text{ g}$$

$$\text{Weight of } CO_2 \text{ (increase in weight of KOH bulb)} = b \text{ g}$$



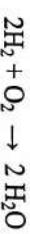
$$44 \text{ g of } CO_2 \text{ contain } 12 \text{ g of carbon}$$

$$\therefore b \text{ g of } CO_2 \text{ contain} = \frac{12 \times b}{44} \text{ g of carbon}$$

$$W \text{ g of coal contains} = \frac{12 \times b}{44} \text{ g of carbon}$$

$$\therefore 100 \text{ g of coal contains} = \frac{100}{W} \times \frac{12 \times b}{44}$$

$$\therefore \% \text{ carbon in coal} = \frac{12 \times b}{44} \times 100$$



$$4 \text{ g of } H_2 \rightarrow 36 \text{ g of water}$$

$$36 \text{ g of water contains } 4 \text{ g of hydrogen}$$

$$\therefore a \text{ g of water contains} = \frac{4 \times a}{36} \text{ g of hydrogen}$$

$$W \text{ g of coal contains} = \frac{4 \times a}{36} \text{ g of hydrogen}$$

$$\therefore 100 \text{ g of coal contains} = \frac{4 \times a}{36} \times \frac{100}{W}$$

$$\therefore \% \text{ of hydrogen in coal} = \frac{4 \times a}{36} \times \frac{100}{W}$$

Calorific value of a fuel is related to its carbon content. Higher the percentage of carbon, greater is the calorific value and better is the quality of coal.

Hydrogen is mainly present in combination with oxygen of coal and classification of coal. It also helps in the burning of coal and classification of coal. Higher the percentage of hydrogen, better is the quality of coal. Further hydrogen is associated with volatile matter of the coal and affects the use of coal.

Determination of Nitrogen

Nitrogen present in the fuel can be estimated by Duma's method or by Kjeldahl's method. The Kjeldahl's method is the most commonly used method as it gives better results.

In this method, a known weight (about 1 g) of coal is taken in a Kjeldahl's flask [Fig. 6.2]. It is treated with 20 ml of conc. H_2SO_4 and about 10 g of anhydrous potassium sulphate. 0.5 g of copper sulphate is used as a catalyst. The function of potassium sulphate is to raise the boiling point.

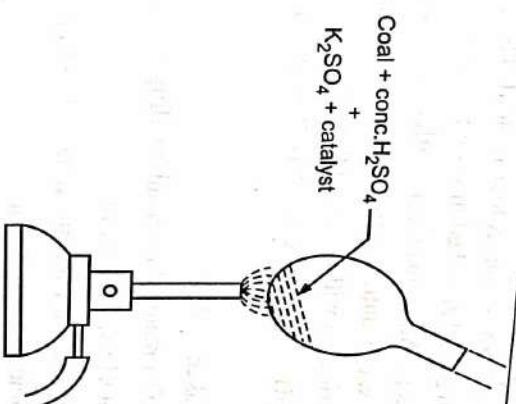


Fig. 6.2 : Kjeldahl's flask

Heating is carried out in a fuming cupboard until the nitrogen present in the coal is converted into ammonium sulphate. When the solution becomes almost colourless, the solution is then transferred to one litre round bottom flask. 30 ml of 40% NaOH is added slowly from the side of the flask. The round bottom flask is connected to a condenser through a trap as shown in Fig. 6.3.

$$100 \text{ g of coal contains} = \frac{1.4(y-x)}{1000} \times \frac{100}{W}$$

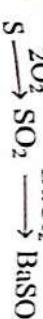
$$\% \text{ N} = \frac{\text{Volume of acid used} \times \text{Normality} \times 1.4}{\text{Weight of coal taken}}$$

Significance :

Nitrogen is an inert and incombustible gas and does not contribute any useful property. It is generally found in small amount.

Determination of sulphur :

A known weight of coal is burnt completely in a bomb calorimeter in a current of oxygen. During burning sulphur present in coal is oxidized and converted into sulphate. The ash formed is now extracted with dilute hydrochloric acid and the acid extract is treated with barium chloride solution to give a white precipitate of barium sulphate which is filtered, washed, dried and weighed.



Calculations :

32 g sulphur gives 233.4 g BaSO₄

Let weight of coal taken = W g

Weight of BaSO₄ formed = x g

∴ 233.4 g BaSO₄ contains 32 g of S

$$\therefore x \text{ g of BaSO}_4 \text{ contains } \frac{32 \times x}{233} \text{ g of S}$$

$$W \text{ g coal contains } \frac{32x}{233} \text{ g of S}$$

$$\therefore 100 \text{ g coal contains } \frac{32x}{W} \times \frac{100}{233}$$

$$\% \text{ of sulphur in coal} = \frac{32 \times \text{Weight of BaSO}_4 \text{ ppt.} \times 100}{233 \times \text{Weight of coal}}$$

Significance :

Sulphur present in metallurgical coal is harmful for use in metallurgy as it transfers to the metal and adversely affects the properties of metal. Oxidation products of sulphur (SO₂ and SO₃) especially formed in presence of moisture, have corrosive effect on the equipment and also cause atmospheric pollution. Hence the presence of sulphur in coal is undesirable.

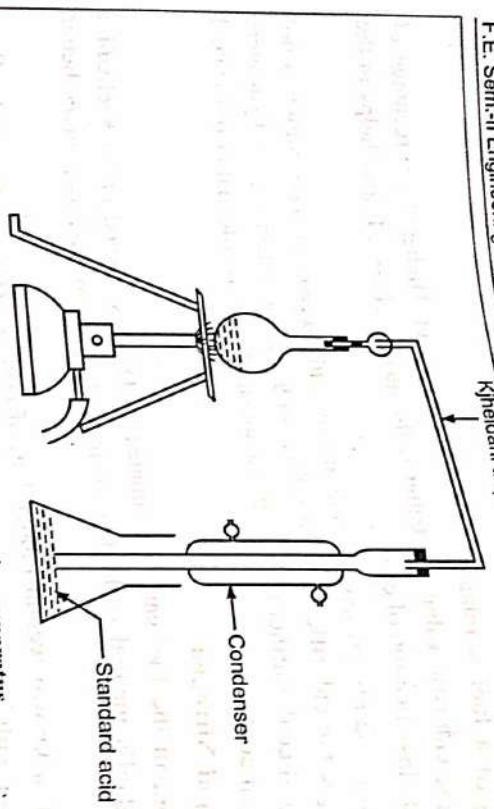


Fig. 6.3 : Ammonia distillation apparatus

The round bottom flask is heated when sodium hydroxide reacts with ammonium sulphate to produce ammonia gas which is absorbed in a 50 ml of N/10 H₂SO₄ containing two drops of methyl red which gives pink colour to acid. Heating is continued until the ammonia is completely evolved and absorbed in sulphuric acid. This stage is indicated by the light pink colour of the acid. Ammonia reacts with excess acid and the unreacted acid is back titrated with N/10 NaOH until the light pink colour is completely discharged. A blank determination is carried out without using the sample.



Calculations :

Let weight of coal taken = W g

Volume of N/10 NaOH required for blank reading = y ml

Volume of N/10 NaOH required = x ml

Volume of N/10 acid reacted with ammonia = (y - x) ml

Volume of N/10 ammonia = (y - x) ml

1000 ml of 1 N ammonia solution = 17 g of NH₃

∴ 1000 ml of 1 N ammonia solution = 14 g of Nitrogen

1000 ml of 0.1 N ammonia solution = 1.4 g of Nitrogen

$$(y-x) \text{ ml of 0.1 N ammonia solution} = \frac{(y-x) \times 1.4}{1000} \text{ g of Nitrogen}$$

$$W \text{ g of coal contains} = \frac{1.4(y-x)}{1000} \text{ g of Nitrogen}$$

NUMERICALS ON ULTIMATE ANALYSIS:

1. 0.5 g of coal sample was burnt completely in Bomb calorimeter. The ash formed

was extracted with acid and the extract obtained was treated with BaCl_2 solution to get BaSO_4 precipitate. The weight of dry precipitate was 0.04 g. Calculate the % of sulphur in the coal sample.

Solution :

$$\text{Weight of coal sample} = 0.5 \text{ g}$$

$$\text{Weight of BaSO}_4 \text{ ppt.} = 0.04 \text{ g}$$

$$\% \text{ of sulphur} = \frac{\text{Weight of BaSO}_4 \text{ ppt.} \times 32 \times 100}{\text{Weight of coal} \times 233}$$

$$= \frac{0.04 \times 32 \times 100}{0.5 \times 233}$$

$$= \frac{128}{116.7}$$

$$= 1.09$$

Ans. : % of sulphur = 1.09

2.

By Kjeldahl's method, 1.5 g of coal sample 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 of nitrogen.

Solution :

$$\text{Volume of } 0.1 \text{ N H}_2\text{SO}_4 = \text{Volume of } 0.1 \text{ N NaOH}$$

$$\text{Volume of acid taken} = 50 \text{ ml}$$

$$\text{Volume of excess acid} = 35 \text{ ml}$$

$$\therefore \text{Volume of acid used} = (50 - 35)$$

$$= 15 \text{ ml of } 0.1 \text{ N H}_2\text{SO}_4$$

$$\% \text{ of nitrogen} = \frac{\text{Volume of acid used} \times \text{Normality} \times 1.4}{\text{Weight of coal taken}}$$

$$= \frac{15 \times 0.1 \times 1.4}{1.5} = 1.4$$

Ans. : % of nitrogen = 1.4

3.

0.2 g of coal is accurately weighed and is burnt in a combustion apparatus. The gaseous products of combustion are absorbed in potash bulb and calcium

tubes of known weight. The increase in weight of calcium chloride tubes are 0.64 g and hydrogen in the coal sample, 0.06 g respectively. Calculate the % of carbon and hydrogen in the coal sample.

Solution :

$$\text{Increase in weight of KOH tube} = 0.64 \text{ g}$$

$$\% \text{ of C} = \frac{\text{Increase in weight of KOH tube} \times 12 \times 100}{\text{Weight of coal taken} \times 44}$$

$$= \frac{0.64 \times 12 \times 100}{0.2 \times 44}$$

$$= \frac{768}{88}$$

$$= 87.27\%$$

$$\text{(ii) Increase in weight of CaCl}_2 \text{ tube} = 0.06 \text{ g}$$

$$\% \text{ of hydrogen} = \frac{\text{Increase in weight of CaCl}_2 \text{ tube} \times 2 \times 100}{\text{Weight of coal sample} \times 18}$$

$$= \frac{0.06 \times 2 \times 100}{0.2 \times 18}$$

$$= \frac{12}{3.6}$$

$$= 3.3$$

Ans. : % of carbon = 87.27
% of hydrogen = 3.33

4.

1.5 g of coal sample was taken for C and H estimation by combustion method. The increase on weight 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.

[Dec. 2008, Dec. 2011]

Solution :

$$\text{(i) Increase in weight of KOH tube} = 4.88 \text{ g}$$

$$\% \text{ of C} = \frac{\text{Increase in weight of KOH tube} \times 12 \times 100}{\text{Weight of coal taken} \times 44}$$

$$= \frac{4.88 \times 12 \times 100}{1.5 \times 44}$$

$$= \frac{5856}{66}$$

$$= 88.72\%$$

(ii) Increase in weight of CaCl_2 tube = 1.25 g

$$\% \text{ of hydrogen} = \frac{\text{Increase in weight of } \text{CaCl}_2 \text{ tube} \times 2 \times 100}{\text{Weight of coal sample} \times 18}$$

$$= \frac{1.25 \times 2 \times 100}{1.5 \times 18}$$

$$= \frac{250}{27}$$

$$= 9.25\%$$

Ans. : % of carbon = 88.72
% of hydrogen = 9.25

5. 1.95 g of coal sample was taken for nitrogen estimation by Kjeldahl method. The ammonia liberated required 9.5 ml of 0.4 N H_2SO_4 for neutralization. The same sample weighing 1.5 g in Bomb calorimeter experiment produced 0.35 g of BaSO_4 . Calculate percentage of N and S.

Solution :

(i) Volume of acid used = 9.5 ml of 0.4N H_2SO_4

$$\text{Weight of coal sample} = 1.95 \text{ g}$$

$$\% \text{ of nitrogen} = \frac{\text{Volume of acid used} \times \text{Normality} \times 1.4}{\text{Weight of coal taken}}$$

$$= \frac{9.5 \times 0.4 \times 1.4}{1.95}$$

$$= 2.72\%$$

Ans. : % of nitrogen = 2.72

[Dec. 2008, May 2011]

(ii) Weight of coal sample = 2.3 g
Weight of BaSO_4 ppt. = 0.35 g

$$\% \text{ of sulphur} = \frac{\text{Weight of } \text{BaSO}_4 \text{ ppt.} \times 32 \times 100}{\text{Weight of coal} \times 233}$$

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

$$= \frac{1120}{535.9} = 2.089\%$$

Ans. : % of sulphur = 2.089

7. 2.3 g of coal sample was taken for nitrogen estimation by Kjeldahl method. The ammonia liberated required 12.5 ml of 0.5 N H_2SO_4 for neutralization. The same sample in Bomb calorimeter experiment produced 0.64 g of BaSO_4 . Calculate percentage of N and S.

Solution :

(i) Volume of acid used = 12.5 ml of 0.5N H_2SO_4

$$\text{Weight of coal sample} = 2.3 \text{ g}$$

$$\% \text{ of nitrogen} = \frac{\text{Volume of acid used} \times \text{Normality} \times 1.4}{\text{Weight of coal taken}}$$

$$= \frac{12.5 \times 0.5 \times 1.4}{2.3}$$

$$= 3.204\%$$

Ans. : % of sulphur = 3.204

6. 3 g of coal was heated in Kjeldahl's flask and 40 ml of 0.5 N H_2SO_4 . After absorption, the excess acid required was absorbed in 0.5 N KOH for neutralization. 2.3 g of coal sample was taken for nitrogen estimation. The same sample in Bomb calorimeter experiment produced 0.35 g of BaSO_4 . Calculate the % of N and S in the sample.

Solution : The analysis gave

(i) Volume of acid taken = 40 ml of 0.5 N H_2SO_4

$$\text{Volume of acid used} = (40 - 18.5)$$

$$= 21.5 \text{ ml of } 0.5 \text{ N } \text{H}_2\text{SO}_4$$

$$\% \text{ of nitrogen} = \frac{\text{Volume of acid used} \times \text{Normality} \times 1.4}{3} = 5.016\%$$

Ans. : % of nitrogen = 5.016

[May 2009]

Fuels And Combustion

(ii) Weight of coal sample = 2.3 g
 Weight of BaSO₄ ppt. = 0.64 g
 % of sulphur = $\frac{\text{Weight of BaSO}_4 \text{ ppt.} \times 32 \times 100}{\text{Weight of coal} \times 233}$

$$\begin{aligned} &= \frac{0.64 \times 32 \times 100}{2.3 \times 233} \\ &= \frac{2048}{535.9} \\ &= 3.82\% \end{aligned}$$

Ans. : % of sulphur = 3.82

8. 0.5 g of coal sample was burnt in Bomb calorimeter experiment produced 0.06 g of BaSO₄. Calculate percentage of S. [May 2010]

Solution :

$$\text{Weight of coal sample} = 0.5 \text{ g}$$

$$\text{Weight of BaSO}_4 \text{ ppt.} = 0.06 \text{ g}$$

$$\begin{aligned} \text{\% of sulphur} &= \frac{\text{Weight of BaSO}_4 \text{ ppt.} \times 32 \times 100}{\text{Weight of coal} \times 233} \\ &= \frac{0.06 \times 32 \times 100}{0.5 \times 233} \end{aligned}$$

$$\begin{aligned} &= \frac{192}{116.5} \\ &= 1.648\% \end{aligned}$$

Ans. : % of sulphur = 1.648

9. 3.2 g of coal was heated in Kjeldahl's flask and NH₃ evolved was absorbed in 40 ml of 0.5 N H₂SO₄. After absorption, the excess acid required 16 ml of 0.5 N KOH for neutralization. 2.5 g of coal sample in quantitative analysis gave 0.42 g BaSO₄. Calculate the % of N and S in the sample. [Dec. 2010]

Solution :

(i) Volume of acid taken = 40 ml of 0.5 N H₂SO₄
 Volume of excess acid = 16 ml

$$\therefore \text{Volume of acid used} = (40 - 16)$$

$$\begin{aligned} &= 24 \text{ ml of } 0.5 \text{ N H}_2\text{SO}_4 \\ &= 24 \text{ ml of } 0.5 \text{ N H}_2\text{SO}_4 \end{aligned}$$

(ii) Weight of coal sample = 2.3 g
 Weight of BaSO₄ ppt. = 0.64 g
 % of sulphur = $\frac{\text{Weight of BaSO}_4 \text{ ppt.} \times 32 \times 100}{\text{Weight of coal} \times 233}$

$$\begin{aligned} &= \frac{0.64 \times 32 \times 100}{2.3 \times 233} \\ &= \frac{2048}{535.9} \\ &= 3.82\% \end{aligned}$$

Ans. : % of nitrogen = 5.25

$$\begin{aligned} \text{Weight of coal sample} &= 2.5 \text{ g} \\ \text{Weight of BaSO}_4 \text{ ppt.} &= 0.42 \text{ g} \\ \text{\% of sulphur} &= \frac{\text{Weight of BaSO}_4 \text{ ppt.} \times 32 \times 100}{\text{Weight of coal} \times 233} \\ &= \frac{0.42 \times 32 \times 100}{2.5 \times 233} \end{aligned}$$

Ans. : % of sulphur = 2.30

10. 1 g of coal sample was used for determination of N by Kjeldahl's method. The ammonia evolved was passed into 50 ml of 0.1 N H₂SO₄. The excess acid required 42 ml of 0.1 N NaOH for neutralization. Calculate % of N. [May 2012]

Solution :

$$\text{Volume of acid taken} = 50 \text{ ml of } 0.1 \text{ N H}_2\text{SO}_4$$

$$\text{Volume of excess acid} = 42 \text{ ml}$$

$$\therefore \text{Volume of acid used} = (50 - 42)$$

$$= 8 \text{ ml of } 0.1 \text{ N H}_2\text{SO}_4$$

$$\begin{aligned} \text{\% of nitrogen} &= \frac{\text{Volume of acid used} \times \text{Normality} \times 1.4}{\text{Weight of coal taken}} \\ &= \frac{8 \times 0.1 \times 1.4}{1} = 1.12\% \end{aligned}$$

Ans. : % of nitrogen = 1.12

Volume of nitrogen = $\frac{\text{Volume of acid used} \times \text{Normality} \times 1.4}{\text{Weight of coal taken}}$
 Fuels And Combustion

11. By Kjeldahl's method, 3.5 g of coal sample was analyzed. The ammonia evolved was absorbed in 50 ml of 0.1 N H₂SO₄. After absorption, the excess H₂SO₄ required 15 ml of 0.1 N NaOH for neutralization. Calculate the percentage of nitrogen. [Dec. 2012]

Solution :

$$\text{Volume of } 0.1 \text{ N H}_2\text{SO}_4 = \text{Volume of } 0.1 \text{ N NaOH}$$

$$= \frac{1344}{349.5} = 3.845$$

Volume of acid taken = 50 ml

Volume of acid used = 15 ml

Volume of excess acid = $(50 - 15)$

Volume of acid used = 35 ml of 0.1 N H_2SO_4

\therefore Volume of acid used $= \frac{\text{Volume of acid used} \times \text{Normality} \times 1.4}{\text{Weight of coal taken}}$

$$\% \text{ of nitrogen} = \frac{35 \times 0.1 \times 1.4}{3.5}$$

$$= 1.4$$

Ans. : % of nitrogen = 1.4

12. A coal sample was subjected to ultimate analysis. 0.6 g of coal on combustion produces 0.05 g BaSO_4 . Calculate percentage of sulphur in coal sample.
- [May 2013]

Solution :

Weight of coal sample = 0.6 g

Weight of BaSO_4 ppt. = 0.05 g

$$\% \text{ of sulphur} = \frac{\text{Weight of BaSO}_4 \text{ ppt.} \times 32 \times 100}{\text{Weight of coal} \times 233}$$

$$= \frac{0.05 \times 32 \times 100}{0.6 \times 233}$$

$$= \frac{160}{139.8}$$

$$= 1.14$$

Ans. : % of sulphur = 1.14

13. A coal sample was subjected to ultimate analysis. 1.5 g of coal on combustion produces 0.42 g BaSO_4 . Calculate percentage of sulphur in coal sample.
- [Dec. 2013]

Solution :

Weight of coal sample = 1.5 g

Weight of BaSO_4 ppt. = 0.42 g

$$\% \text{ of sulphur} = \frac{\text{Weight of BaSO}_4 \text{ ppt.} \times 32 \times 100}{\text{Weight of coal} \times 233}$$

- Ans. : % of sulphur = 3.845**

14. A coal sample was subjected to ultimate analysis. 1.5 g of coal on combustion produces 0.24 g BaSO_4 . Calculate percentage of sulphur in coal sample.
- [May 2014]

Solution : Weight of coal sample = 1.5 g

Weight of BaSO_4 ppt. = 0.24 g

$$\% \text{ of sulphur} = \frac{\text{Weight of BaSO}_4 \text{ ppt.} \times 32 \times 100}{\text{Weight of coal} \times 233}$$

$$= \frac{0.24 \times 32 \times 100}{1.5 \times 233}$$

$$= \frac{768}{349.5}$$

$$= 2.197$$

Ans. : % of sulphur = 2.197

15. 2.5 g of coal sample was taken for nitrogen estimation by Kjeldahl method. The ammonia liberated required 12.7 ml of 0.5 N H_2SO_4 for neutralization. Using Bomb calorimeter 1.5 g of coal sample produced 0.28 g of BaSO_4 . Calculate percentage of N and S.
- [November 2014]

Solution :

i) Weight of acid used = 12.7 ml of 0.5N H_2SO_4

Weight of coal sample = 2.5 g

$$\% \text{ of nitrogen} = \frac{\text{Volume of acid used} \times \text{Normality} \times 1.4}{\text{Weight of coal taken}}$$

$$= \frac{12.7 \times 0.5 \times 1.4}{2.5}$$

Ans. : % of nitrogen = 3.56

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6.39

- (i) Weight of coal sample = 1.5 g
 Weight of BaSO₄ ppt. = 0.28 g

$$\text{Weight of BaSO}_4 \text{ ppt.} \times 32 \times 100$$

$$\text{Weight of coal} \times 233$$

$$\begin{aligned}\% \text{ of sulphur} &= \frac{\text{Weight of BaSO}_4 \text{ ppt.} \times 32 \times 100}{\text{Weight of coal} \times 233} \\ &= \frac{0.28 \times 32 \times 100}{1.5 \times 233} \\ &= \frac{896}{349.5} \\ &= 2.56\%\end{aligned}$$

$\therefore \% \text{ of Carbon} = 71.27\%$ and $\% \text{ of Hydrogen} = 9.25\%$

Ans. : % of sulphur = 2.56

16. A coal sample was subjected to a ultimate analysis. 1.6 g of coal on combustion in a bomb calorimeter gave 0.47 g of BaSO₄. Calculate % of sulphur in the sample.

$$\begin{aligned}\text{Weight of coal sample} &= 1.6 \text{ g} \\ \text{Weight of BaSO}_4 \text{ ppt.} &= 0.47 \text{ g}\end{aligned}$$

$$\% \text{ of Sulphur} = \frac{\text{Weight of BaSO}_4 \text{ ppt.} \times 32 \times 100}{\text{Weight of coal} \times 233}$$

$$\% \text{ of Sulphur} = \frac{0.47 \times 32 \times 100}{1.6 \times 233}$$

$$\% \text{ of Sulphur} = 4.03\%$$

Ans. : % of sulphur = 4.03

17. 1.5g of coal sample was burnt in a combustion apparatus. The products of combustion were collected in previously weighed KOH bulb and CaCl₂ tube. The increase in weights of KOH bulb and CaCl₂ tube were found to be 3.92g and 1.25g respectively. Calculate the percentage of Carbon and Hydrogen in the coal sample.

Solution:

$$(i) \text{ Increase in weight of KOH tube} = 3.92 \text{ g}$$

$$\% \text{ of Carbon} = \frac{\text{Increase in weight of KOH tube} \times 12 \times 100}{\text{Weight of coal taken} \times 44}$$

$$\begin{aligned}&= \frac{3.92 \times 12 \times 100}{1.5 \times 44} \\ &= \frac{4704}{66} = 71.27\%\end{aligned}$$

Ans. : % of sulphur = 2.746

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6.40

- (ii) Increase in weight of CaCl₂ tube = 1.25 g

$$\% \text{ of Hydrogen} = \frac{\text{Increase in weight of CaCl}_2 \text{ tube} \times 2 \times 100}{\text{Weight of coal sample} \times 18}$$

$$\begin{aligned}&= \frac{1.25 \times 2 \times 100}{1.5 \times 18} \\ &= \frac{250}{27} = 9.25\%\end{aligned}$$

Ans. : % of Carbon = 71.27
 % of Hydrogen = 9.25

16. 1.5 g of coal sample was analysed for nitrogen content by Kjeldahl's method. The liberated ammonia required 14 ml of 0.1 N H₂SO₄ solution for neutralization. In a separate experiment using Bomb Calorimeter, 1.5 g of the same sample gave 0.3 g of BaSO₄. Calculate the percentage of Nitrogen and Sulphur in the sample.

Solution:

$$\text{Volume of acid used} = 14 \text{ ml of } 0.1 \text{ N H}_2\text{SO}_4$$

$$\% \text{ of nitrogen} = \frac{\text{Volume of acid used} \times \text{Normality} \times 1.4}{\text{Weight of coal taken}}$$

$$\begin{aligned}\text{Weight of coal sample} &= 1.5 \text{ g} \\ \% \text{ of nitrogen} &= \frac{14 \times 0.1 \times 1.4}{1.5} \\ &= 1.31\%\end{aligned}$$

Ans. : % of nitrogen = 1.31

- (ii) Weight of coal sample = 1.5 g
 Weight of BaSO₄ ppt. = 0.3 g

$$\% \text{ of sulphur} = \frac{\text{Weight of BaSO}_4 \text{ ppt.} \times 32 \times 100}{\text{Weight of coal} \times 233}$$

$$\begin{aligned}\text{Weight of coal sample} &= 1.5 \text{ g} \\ \text{Weight of BaSO}_4 \text{ ppt.} &= 0.3 \text{ g}\end{aligned}$$

$$\% \text{ of sulphur} = \frac{0.3 \times 32 \times 100}{1.5 \times 233}$$

$$= \frac{960}{349.5}$$

$$= 2.746\%$$

Ans. : % of sulphur = 2.746

19. A coal sample was subjected to ultimate analysis. 2.45 g of coal on combustion in a Bomb Calorimeter gave 0.67 g of BaSO_4 . Calculate the percentage of Sulphur.

Solution:

$$\text{Weight of coal sample} = 2.45 \text{ g}$$

$$\text{Weight of BaSO}_4 \text{ ppt.} = 0.67 \text{ g}$$

$$\% \text{ of sulphur} = \frac{\text{Weight of BaSO}_4 \text{ ppt.} \times 32 \times 100}{\text{Weight of coal} \times 233}$$

$$= \frac{0.67 \times 32 \times 100}{2.45 \times 233}$$

$$= \frac{2144}{570.85}$$

$$= 3.755\%$$

Ans. : % of sulphur = 3.755

20. 0.5 gm of coal sample was burnt in Bomb Calorimeter produced 0.06 gm of BaSO_4 . Calculate percentage of Sulphur.

Solution:

$$\text{Weight of coal sample} = 0.5 \text{ g}$$

$$\text{Weight of BaSO}_4 \text{ ppt.} = 0.06 \text{ g}$$

$$\% \text{ of sulphur} = \frac{\text{Weight of BaSO}_4 \text{ ppt.} \times 32 \times 100}{\text{Weight of coal} \times 233}$$

$$= \frac{0.06 \times 32 \times 100}{0.5 \times 233}$$

$$= \frac{192}{116.5}$$

$$= 1.648\%$$

Ans. : % of sulphur = 1.648

21. 1.56 gm of Coal Sample was kjeldahlised and ammonia gas evolved was absorbed in 50ml of 0.1N H_2SO_4 . After absorption the excess acid required 6.25 ml of 0.1N NaOH for exact neutralization. Calculate the % of Nitrogen in the Coal Sample.

Solution :

$$\text{Volume of } 0.1 \text{ N H}_2\text{SO}_4 = \text{Volume of } 0.1 \text{ N NaOH}$$

$$\text{Volume of acid taken} = 50 \text{ ml}$$

$$\begin{aligned} \text{Volume of excess acid} &= 6.25 \text{ ml} \\ \text{Volume of acid used} &= (50 - 6.25) \\ &= 43.75 \text{ ml of } 0.1 \text{ N H}_2\text{SO}_4 \end{aligned}$$

$$\% \text{ of nitrogen} = \frac{\text{Weight of acid used} \times \text{Normality} \times 1.4}{1.56}$$

$$\begin{aligned} \text{Ans. : } \% \text{ of nitrogen} &= 0.606 \\ &= \frac{6.75 \times 0.1 \times 1.4}{1.56} \\ &= 0.606 \end{aligned}$$

1.95 gm of coal sample was taken for nitrogen estimation by Kjeldhal's method. Calculate percentage of Nitrogen in the coal sample.

[Dec 2017]

$$\begin{aligned} \text{Weight of acid used} &= 9.5 \text{ ml of } 0.4 \text{ N H}_2\text{SO}_4 \\ \text{Weight of coal sample} &= 1.95 \text{ g} \\ \% \text{ of nitrogen} &= \frac{\text{Volume of acid used} \times \text{Normality} \times 1.4}{\text{Weight of coal taken}} \\ &= \frac{9.5 \times 0.4 \times 1.4}{1.95} \\ &= 2.72\% \end{aligned}$$

Ans. : % of nitrogen = 2.72

21. 0.5 gm of Coal Sample was burnt in Bomb Calorimeter produced 0.06 gm of BaSO_4 . Calculate the % of Sulphur.

Solution :

$$\text{Weight of coal sample} = 0.5 \text{ g}$$

$$\text{Weight of BaSO}_4 \text{ ppt.} = 0.06 \text{ g}$$

$$\% \text{ of sulphur} = \frac{\text{Weight of BaSO}_4 \text{ ppt.} \times 32 \times 100}{\text{Weight of coal} \times 233}$$

$$= \frac{0.06 \times 32 \times 100}{0.5 \times 233}$$

$$= \frac{192}{116.5}$$

$$= 1.648\%$$

Ans. : % of sulphur = 1.648

$$\% \text{ of nitrogen} = \frac{\text{Weight of acid used} \times \text{Normality} \times 1.4}{1.56}$$

$$\begin{aligned} \text{Ans. : } \% \text{ of nitrogen} &= 0.606 \\ &= \frac{6.75 \times 0.1 \times 1.4}{1.56} \\ &= 0.606 \end{aligned}$$

[May 2018]

(24) 1.4 g of coal sample on combustion gave 0.3 g of BaSO_4 precipitate. Calculate the % of Sulphur in the sample.

Solution :

$$\text{Weight of coal sample} = 1.4 \text{ g}$$

$$\text{Weight of BaSO}_4 \text{ ppt.} = 0.3 \text{ g}$$

$$\% \text{ of sulphur} = \frac{\text{Weight of BaSO}_4 \text{ ppt.} \times 32 \times 100}{\text{Weight of coal} \times 233}$$

$$= \frac{0.3 \times 32 \times 100}{1.4 \times 233}$$

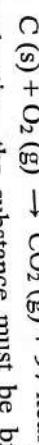
$$= \frac{960}{326.2}$$

$$= 2.942\%$$

Ans. : % of sulphur = 2.942

6.7 COMBUSTION

Combustion is an exothermic chemical reaction, which is accompanied by development of heat and light at a rapid rate, so that temperature rises considerably. For example, combustion of carbon in oxygen.



For proper combustion, the substance must be brought to its kindling or ignition temperature which may be defined as "the minimum temperature at which the substance ignites and burns without further addition of heat from outside".

Calculation of Air Quantities:

To find the amount of oxygen and hence the amount of air required for the combustion of a unit quantity of a fuel, it is necessary to apply the following elementary principles :

(1) Substances always combine in definite proportions and these proportions are determined by the molecular masses of the substances involved and the products formed. In order to know the amount of oxygen required for combustion of an element or a gas, we must know the combustion reaction.

For example, when carbon combines with oxygen to form carbon dioxide.

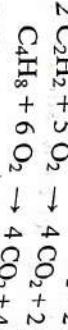
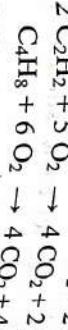
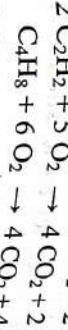
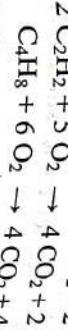
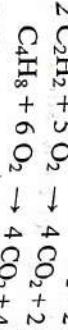
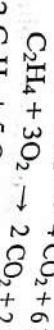
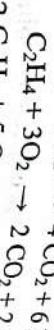
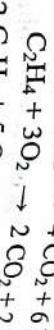
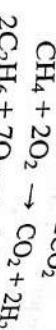
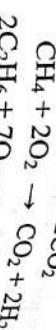
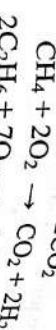


Mass proportion	12	32	44
Volume proportion	1 vol	1 vol	1 vol

Thus 12 parts by weight of carbon required 32 parts by weight of oxygen and 44 parts by weight of carbon dioxide produced by 12 parts by weight of carbon.

Or volume carbon requires one volume of oxygen and one volume carbon dioxide produced by 1 volume of carbon.

The most commonly involved combustion reactions may be written as follows:



Nitrogen, ash and carbon dioxide, if any, present in the fuel or air are incombustible gasses and hence they do not take oxygen during combustion reaction. The total amount

of oxygen required by the fuel can be given by sum of the amounts of oxygen required by individual constituent present in the fuel and these calculations are shown below:

- (a) **Combustion of carbon :**

Combustion of carbon is expressed by equation



12 kg of carbon requires for complete combustion 32 kg of oxygen.

∴ C kg of carbon requires for complete combustion = $\frac{\text{C} \times 32}{12} = 2.67 \text{ C kg of oxygen.}$

∴ Quantity of oxygen required for C kg of carbon = 2.67 C kg

- (b) **Combustion of hydrogen :**

Combustion of hydrogen is expressed by equation



4 kg hydrogen requires for complete combustion 32 kg of oxygen

∴ H kg hydrogen requires for complete combustion 8H kg of oxygen

- (c) **Combustion of sulphur :**

Combustion of sulphur is expressed by equation



32 kg sulphur requires for complete combustion 32 kg of oxygen.

\therefore S kg of sulphur requires for complete combustion S kg of oxygen.

Thus the quantity of oxygen required for complete combustion of 1 kg of fuel can be given by,

$$(2.67 C + 8H + S) \text{ kg}$$

(2) But some quantity of oxygen required for complete combustion of 1 kg of fuel can be minimum corrected quantity of oxygen required for complete combustion of 1 kg of fuel given by,

$$(2.67 C + 8H + S - O) \text{ kg}$$

(3) Air contains 23% oxygen by weight and 21% oxygen by volume

From the above total quantity of air required for combustion of 1 kg of fuel can be calculated.

23 kg oxygen is present in 100 kg of air

$$\therefore (2.67 C + 8H + S - O) \text{ kg} \text{ is present in } (2.67 C + 8H + S - O) \times \frac{100}{23} \text{ kg}$$

(4) Further it should be noted that weight can be converted into volume in the following ways:

At N.T.P. (i.e. at 0°C and 760 mm pressure), 22.4 litre of any gas will weigh one gram molecule i.e. its molecular weight in grams. For example, 22.4 litres of CO_2 at N.T.P. will weigh 44 g of CO_2 (44 being the molecular weight of CO_2)

OR

$$22.4 \text{ m}^3 \text{ of } \text{CO}_2 = 44 \text{ kg of } \text{CO}_2$$

(5) The average molecular weight of air is taken as 28.97.

(6) For calculating the quantity of air required for combustion following formulae can be applied.

$$\text{Weight of air needed} = \left\{ \frac{32C}{12} + \frac{16H}{2} + \frac{32S}{32} - O \right\} \times 100$$

(O' is oxygen present in fuel)

Volume of air required = (Number of moles of air) \times 22.4 litres at N.T.P.

$$= \frac{\text{Weight of air needed in g}}{28.94} \times 22.4 \text{ litres at N.T.P.}$$

(7) The mass of any gas can be converted to its volume at certain temperature and pressure by using the gas equation

$$PV = nRT$$

Where P = Pressure of gas in atmosphere

V = Volume of gas in litres

Ques. 2 A liquid fuel has C = 80%, H = 12%, O₂ = 8%. Find the minimum quantity of air needed for complete combustion of 1 kg of the above liquid fuel.

Solution :

Let us find the weight of each constituent per kg of fuel

Constituent	% by weight	Weight of each pr kg of fuel
C	80	80/100 = 0.8
H	12	12/100 = 0.12
O ₂	8	8/100 = 0.08

Quantity of air needed for combustion of 1 kg of fuel = $\frac{100}{23} (2.67 C + 8H + S - O) \text{ kg}$

$$= \frac{100}{23} [2.67 \times 0.8 + 8 \times 0.12 + 0 - 0.08] \text{ kg}$$

$$= \frac{100}{23} [2.136 + 0.96 - 0.08] \text{ kg}$$

$$= \frac{100}{23} [3.016] \text{ kg}$$

$$= 13.113 \text{ kg}$$

Ans. : Quantity of air needed = 13.113 kg

2. A coal sample was found to contain the following constituents : C = 81%, O = 7%, S = 1%, H = 6%, N = 1% ash = 4%. Calculate the minimum amount of air required for complete combustion of 1 kg of coal.

Solution :

Constituent	% by weight	Weight of each pr kg of fuel
C	81	81/100 = 0.81
O	7	7/100 = 0.07
S	1	1/100 = 0.01
H	6	6/100 = 0.06
N	1	Do not contribute

$$\text{Amount of air required} = \frac{100}{23} (2.67 \text{ C} + 8\text{H} + \text{S} - \text{O}) \text{ kg}$$

$$\begin{aligned} &= \frac{100}{23} [2.67 \times 0.81 + 8 \times 0.06 + 0.01 - 0.07] \text{ kg} \\ &= \frac{100}{23} [2.163 + 0.48 + 0.01 - 0.07] \text{ kg} \\ &= \frac{100}{23} [2.583] \text{ kg} \\ &= 11.23 \text{ kg} \end{aligned}$$

Ans. : Quantity of air needed = 11.23 kg

3. Calculate the quantity of air by weight and volume for combustion of 2 kg of carbon.

Solution :

Quantity of air needed for combustion of 1 kg of fuel = $\frac{100}{23} (2.67 \text{ C} + 8\text{H} + \text{S} - \text{O}) \text{ kg}$

Here % of carbon is 100, as no other element is present

$$\therefore \text{Weight of carbon per kg} = 100/100 = 1.$$

$$= \frac{100}{23} (2.67 \times 1)$$

$$= 11.60 \text{ kg}$$

$$\therefore \text{For } 2 \text{ kg of air} = 11.6 \times 2 = 23.2 \text{ kg.}$$

Now, 28.949 kg of air occupies 22.4 m³ of air

$$\therefore 23.2 \text{ kg of air will occupy} = \frac{23.2 \times 22.4}{28.949} \text{ m}^3 \text{ of air}$$

$$= 17.95 \text{ m}^3$$

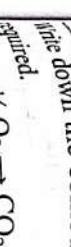
Ans. : Amount of air required for combustion of 2 kg C = 23.2 kg

Volume of air required for combustion of 2 kg C = 17.95 m³

- Calculate the volume of air required for combustion of 2 kg of fuel with following composition. CO = complete combustion of fuel, CO₂ = remaining. Fuels And Combustion
- Fuel = 6%, C₂H₄ = 4%, C₂H₄ = 1%, CH₄ = 8%, N₂ = 3%, N₂ = 50%.
- Solution :**

Constituent	% by weight	Weight of each pr kg of fuel
CO	46	Weight of each pr kg of fuel
C ₂ H ₄	1	0.46
CH ₄	8	0.01
N ₂	3	0.08
H ₂	6	Do not contribute
CO ₂	Remaining	0.6

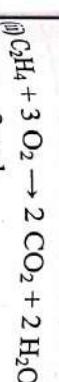
Write down the combustion reactions for each constituent to calculate amount of oxygen required.



1 vol. 0.5 Vol.

i.e. 1 volume of CO requires 0.5 volume of oxygen

$$\therefore 0.46 \text{ volume of CO will require} \frac{0.46 \times 0.5}{1} = 0.23 \text{ m}^3 \text{ of oxygen}$$



1 vol. 3 vol.

i.e. 1 volume of C₂H₄ requires 3 volume of oxygen

$$\therefore 0.01 \text{ volume of C}_2\text{H}_4 \text{ will require } 0.01 \times 3 = 0.03 \text{ m}^3 \text{ of oxygen.}$$



1 vol. 2 Vol.

i.e. 1 volume of CH₄ requires 2 volume of oxygen

$$\therefore 0.08 \text{ volume of CH}_4 \text{ will require } 0.08 \times 2 = 0.16 \text{ m}^3 \text{ of oxygen.}$$



1 vol. 0.5 Vol.

i.e. 1 volume of H₂ requires 0.5 volume of oxygen

$$\therefore 0.06 \text{ volume of H}_2 \text{ requires } 0.06 \times 0.5 = 0.03 \text{ m}^3 \text{ of oxygen}$$

$$\therefore \text{Total volume of O}_2 \text{ required} = 0.23 + 0.03 + 0.16 + 0.03 = 0.45 \text{ m}^3 \text{ of oxygen}$$

Now for finding volume of air, we know that air contains 21% of oxygen. i.e. 21 m³ oxygen is present in 100 m³ of air

F.E. Sem.-II Engineering Chemistry-II
Fuels and Combustion

0.45 m^3 oxygen will be present in $\frac{0.45 \times 100}{21}$

$\therefore 0.45 \text{ m}^3$ oxygen will be present in 2.119 m^3 of air.

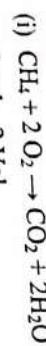
$$= 2.119 \text{ m}^3 \text{ of air.}$$

For 6 m^3 of fuel volume of air required is 12.714 m^3

Ans. : Volume of air required for complete combustion of 1 m^3 of gaseous fuel, which possess by volume $\text{CH}_4 = 35\%$, $\text{C}_2\text{H}_4 = 4\%$, $\text{CO} = 10\%$, $\text{H}_2 = 45\%$, $\text{N}_2 = 2\%$, water vapour = 4% .

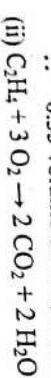
Solution :	% by weight	Weight of each pr kg of fuel
Constituent		
CH_4	35	0.35
C_2H_4	04	0.04
CO	10	0.1
H_2	45	0.45
N_2	02	-
Water vapour	04	-

Combustion reactions :



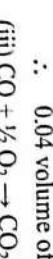
i.e. 1 volume of CH_4 requires 2 volume of oxygen

$$\therefore 0.35 \text{ volume of } \text{CH}_4 \text{ will require } 0.35 \times 2 = 0.70 \text{ m}^3 \text{ of oxygen.}$$



i.e. 1 volume of C_2H_4 requires 3 volume of oxygen

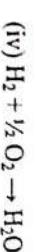
$$\therefore 0.04 \text{ volume of } \text{C}_2\text{H}_4 \text{ will require } 0.04 \times 3 = 0.12 \text{ m}^3 \text{ of oxygen.}$$



1 vol. 0.5 Vol.

i.e. 1 volume of CO requires 0.5 volume of oxygen

$$\therefore 0.1 \text{ volume of } \text{CO} \text{ will require } \frac{0.1 \times 0.5}{1} = 0.05 \text{ m}^3 \text{ of oxygen.}$$



1 vol. 0.5 Vol.

i.e. 1 volume of H_2 requires 0.5 volume of oxygen

F.E. Sem.-II Applied Chemistry-II
Fuels And Combustion

$0.45 \text{ volume of } \text{H}_2 \text{ requires } 0.45 \times 0.5 = 0.225 \text{ m}^3 \text{ of oxygen}$

$\therefore \text{Total volume of } \text{O}_2 \text{ required} = 0.7 + 0.12 + 0.05 + 0.225$

$$= 1.095 \text{ m}^3 \text{ of oxygen}$$

Air contains 21% of oxygen.

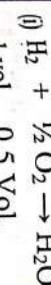
i.e. 21 m^3 oxygen is present in 100 m^3 of air

$$\therefore 1.095 \text{ m}^3 \text{ oxygen will be present in } \frac{1.095 \times 100}{21}$$

Ans. : Volume of air required for 1 m^3 of fuel is 5.214 m^3

Solution :	% by weight	Weight of each pr kg of fuel
Constituent		
H_2	10	1.0
CH_4	15	0.15
C_2H_6	25	0.25
N_2	05	Do not contribute
CO	20	0.2
CO_2	20	-
O_2	05	0.05

Combustion reactions :



1 vol. 0.5 Vol.

i.e. 1 volume of H_2 requires 0.5 volume of oxygen

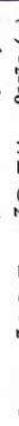
$$\therefore 0.1 \text{ volume of } \text{H}_2 \text{ requires } 0.1 \times 0.5 = 0.05 \text{ m}^3 \text{ of oxygen.}$$



1 vol. 2 Vol.

i.e. 1 volume of CH_4 requires 2 volume of oxygen

$$\therefore 0.15 \text{ volume of } \text{CH}_4 \text{ will require } 0.15 \times 2 = 0.3 \text{ m}^3 \text{ of oxygen.}$$

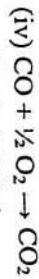


1 vol. 3.5 vol.

i.e. 1 volume of C_2H_6 requires 3.5 volume of oxygen

$$\therefore 0.25 \text{ volume of } \text{C}_2\text{H}_6 \text{ will require } 0.25 \times 3.5 = 0.875 \text{ m}^3 \text{ of oxygen.}$$

6.51



1 vol. 0.5 Vol.

i.e. 1 volume of CO requires 0.5 volume of oxygen

∴ 0.2 volume of CO will require $\frac{0.2 \times 0.5}{1} = 0.1 \text{ m}^3$ of oxygenCO₂ and N₂ are non combustible.∴ Volume of oxygen required = $0.05 + 0.3 + 0.875 + 0.5$

$$= 1.725 \text{ m}^3$$

But 0.05 m³ of oxygen is already present in the fuel.∴ Actual volume of oxygen required = $1.725 - 0.05$

$$= 1.675 \text{ m}^3$$

For 8 m³ of the fuel = 8×1.675

$$= 13.4 \text{ m}^3$$
 of oxygen.

To find volume of air :

21 m³ of oxygen is present in 100 m³ of air.∴ 13.4 m³ of oxygen will be present in $\frac{13.4}{21} \times 100$

$$= 63.80 \text{ m}^3$$
 of air.

Ans. : Volume of oxygen required for combustion of gas = 13.4 m³.Volume of air required for combustion of gas = 63.8 m³.

7. Calculate volume of air containing 20% oxygen by volume at 27°C and 760 mm pressure which will be required for complete combustion of 2 kg of fuel containing C = 70%, H = 25%, ash = 5%.

Solution :

Constituent	% by weight	Weight of each per kg
C	70	0.75
H	25	0.25

- (i) Calculation of weight of O
- ₂

Weight of oxygen required per kg of fuel = $[2.67 \text{ C} + 8\text{H} + \text{S} - \text{O}] \text{ kg}$

$$= [2.67 \times 0.75 + 8 \times 0.25]$$

$$= 2.0025 + 2$$

$$= 4.0025 \text{ kg.}$$

Weight of oxygen required for 2 kg of fuel = 2×4.0025

$$= 8.005 \text{ kg of oxygen.}$$

(ii) Calculation of volume occupies 22.4 m³ of oxygen at S.T.P.

$$= \frac{8.005}{32} \times 22.4$$

Calculation of volume of O₂ at given temperature, P₁ and T₁ are the

$$\frac{P_0 V_0}{T_0} = \frac{P_1 V_1}{T_1}$$

Where P₀, V₀ and T₀ are standard pressure, volume and temperature.Given pressure and temperature, P₁ and T₁ are the

$$\frac{760 \times 5.6}{273} = \frac{760 \times V_1}{300}$$

$$V_1 = \frac{300 \times 5.6}{273}$$

$$= 6.157 \text{ m}^3$$
 of oxygen.

(iii) Calculation of volume of air at 27°C and 760 mm. It is given that, air contains 20% oxygen by volume

20 m³ of oxygen is present in 100 m³ of air.

$$\therefore 6.157 \text{ m}^3 \text{ of oxygen will be present in } \frac{6.157 \times 100}{20}$$

$$= 30.785 \text{ m}^3 \text{ of oxygen}$$

Ans. : Volume of air required for complete combustion of 2 kg of fuel = 30.785 m³ at given temperature and pressure.

8. A gas has the following composition by volume H₂ = 20%, CH₄ = 5%, CO = 25%, CO₂ = 10%, O₂ = 6%, N₂ = 34%. If 20% excess air is used, find the weight of air supplied per m³ of gas.

Constituent	% by weight	Weight of each pr kg of fuel
H ₂	20	0.2
CH ₄	05	0.05
CO	25	0.25
CO ₂	10	Non-combustible
O ₂	06	0.06
N ₂	34	Non-combustible

F.I.E., Sem.-I Engineering Chemistry-IICombustion reactions :

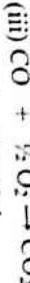
1 vol.

0.5 Vol.

i.e. 1 volume of H_2 requires 0.5 volume of oxygeni.e. 1 volume of H_2 requires $0.2 \times 0.5 = 0.1 \text{ m}^3$ of oxygen.

1 vol.

2 Vol.

i.e. 1 volume of CH_4 requires 2 volume of oxygeni.e. 1 volume of CH_4 requires $0.05 \times 2 = 0.1 \text{ m}^3$ of oxygen.

1 vol.

0.5 Vol.

i.e. 1 volume of CO requires 0.5 volume of oxygeni.e. 1 volume of CO will require $\frac{0.25 \times 0.5}{1} = 0.125 \text{ m}^3$ of oxygen0.25 volume of CO will require 1 m^3 of oxygenTotal volume of air required = $0.1 + 0.1 + 0.125 - 0.06 = 0.265 \text{ m}^3$ of oxygen

It is given that air contains 21% oxygen by volume.

21 m^3 of oxygen will be present in $\frac{0.265 \times 100}{21} = 1.262 \text{ m}^3$.

But 20% excess air is used

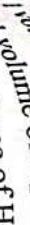
$$\therefore \text{Volume of air} = \frac{20}{100} \times 1.262 = 0.252 \text{ m}^3.$$

$$\therefore \text{Total volume of air supplied} = 1.262 + 0.252 = 1.514 \text{ m}^3.$$

Ans. : Total volume of air supplied = 1.514 m^3 .9. A gaseous fuel has the following composition by volume : $\text{H}_2 = 30\%$, $\text{CH}_4 = 40\%$, $\text{C}_2\text{H}_6 = 10\%$, $\text{CO} = 10\%$, $\text{N}_2 = 5\%$. Calculate volume of air required if 20% excess air is used for complete combustion assuming air contains 20% oxygen by volume.

Solution :

Constituent	% by volume	Volume of each per m^3
H_2	30	0.3
CH_4	40	0.4
C_2H_6	10	0.1
CO	10	0.1
N_2	5	-

F.I.E., Sem.-II Applied Chemistry-IIPiston reactions :

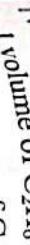
1 vol.

0.5 Vol.

i.e. 1 volume of H_2 requires 0.5 volume of oxygeni.e. 1 volume of H_2 requires $0.5 \times 0.3 = 0.15 \text{ m}^3$ of oxygen.

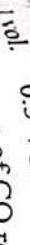
1 vol.

2 Vol.

i.e. 1 volume of CH_4 requires 2 volume of oxygeni.e. 1 volume of CH_4 requires $0.4 \times 2 = 0.8 \text{ m}^3$ of oxygen.

1 vol.

3.5 vol.

i.e. 1 volume of C_2H_6 will require 0.1 \times 3.5 = 0.35 m^3 of oxygen.

1 vol.

0.5 Vol.

i.e. 1 volume of CO requires 0.5 volume of oxygeni.e. 1 volume of CO will require $\frac{0.1 \times 0.5}{1} = 0.05 \text{ m}^3$ of oxygenTotal volume of air required = $0.15 + 0.8 + 0.35 + 0.05$ = 1.35 m^3 of oxygen

It is given that air contains 20% oxygen by volume.

i.e. 20 m^3 of oxygen will corresponds to 100 m^3 of air.

$$\therefore 1.35 \text{ m}^3 \text{ of oxygen will correspond to } \frac{1.35}{20} \times 100$$

$$= 6.75 \text{ m}^3 \text{ of air.}$$

Ans. : Theoretical requirement of air for complete combustion is 6.75 m^3 .

Actually 20% excess air is used,

$$\therefore \text{Actual air used} = 6.75 + \frac{20}{100} \times 6.75$$

$$= 6.75 + 1.35 = 8.1 \text{ m}^3.$$

Ans. : Total volume of air required for complete combustion = 8.1 m^3

10. The percentage composition by mass of a sample of coal is as follows :

 $\text{C} = 75\%$, $\text{H} = 10\%$, $\text{O} = 10\%$, $\text{S} = 1\%$, $\text{N} = 2\%$, rest is ash.Calculate (a) amount of air required for complete combustion of 1 kg of fuel.
b) G.C.V and N.C.V.

F.E. Sem.-II Engineering Chemistry-II

Ans. : weight of carbon = 100.
Weight per kg = $100/100 = 1$.

Quantity of air needed for = $\frac{100}{23} [2.67 \times C]$

Constituent	% by weight	Weight of each pr kg of fuel
C	75	0.75
H	10	0.1
O	10	0.1
S	01	0.01

$$\text{Amount of air required} = \frac{100}{23} (2.67 C + 8H + S - O) \text{ kg}$$

$$\begin{aligned} &= \frac{100}{23} [2.67 \times 0.75 + 8 \times 0.1 + 0.01 - 0.1] \text{ kg} \\ &= \frac{100}{23} [2.0025 + 0.8 + 0.01 - 0.1] \text{ kg} \\ &= \frac{100}{23} [2.7125] \text{ kg} \\ &= 11.793 \text{ kg} \end{aligned}$$

To find gross and net calorific value, using Dulong's formula,

$$\text{G.C.V.} = \frac{1}{100} [8080 C + 34500 (H - \frac{O}{8}) + 2240 S] \text{ kcal/kg}$$

$$\begin{aligned} &= \frac{1}{100} [8080 \times 75 + 34500 (10 - \frac{10}{8}) + 2240 \times 1] \\ &= \frac{1}{100} [606000 + 301875 + 2240] \\ &= 9101.15 \text{ kcal/kg} \end{aligned}$$

A coal sample contains C = 65%, H = 15%, O = 10%, S = 4%, ash = 4% and N = 2%. Calculate the minimum amount of air needed for complete combustion of 2 kg of coal.

Constituent	% by weight	Weight of each pr kg of fuel
C	65	0.65
H	15	0.15
O	10	0.1
S	04	0.04
Ash	04	-
N	02	-

Ans. : i) Amount of air required for combustion = 11.793 m³.

- ii) G.C.V. = 9101.15 kcal/kg
- iii) N.C.V. = 8572.85 kcal/kg

11. Combustion of 5 kg of carbon is carried out using air containing oxygen = 20%, and nitrogen = 80% by volume. Calculate quantity of air by weight and volume needed for complete combustion.

$$\begin{aligned}
 &= \frac{100}{23} [1.7355 + 1.2 + 0.04 - 0.1] \text{ kg} \\
 &= \frac{100}{23} [2.8755] \text{ kg} \\
 &= 12.502 \text{ kg}
 \end{aligned}$$

Weight of air needed for combustion of 2 kg of fuel = 2×12.502

$$= 25.004 \text{ kg.}$$

Ans. : Weight of air needed for combustion of 2 kg of fuel = 25.004 kg

- 13. Calculate the weight and volume of air required for complete combustion of coal with following composition C = 85%, H = 10%, O = 5%.**

Solution :

Constituent	% by weight	Weight of each pr kg of fuel
C	85	0.85
H	10	0.1
O	05	0.05

$$(i) \text{ Amount of air required} = \frac{100}{23} (2.67C + 8H + S - O) \text{ kg}$$

$$= \frac{100}{23} [2.67 \times 0.85 + 8 \times 0.1 - 0.05] \text{ kg}$$

$$\text{Gross calorific value of coal} = \frac{100}{23} [2.2695 + 0.8 - 0.05] \text{ kg}$$

$$= \frac{100}{23} [3.0195] \text{ kg}$$

$$= 13.128 \text{ kg}$$

\therefore Air required for 5 kg of coal = 13.128×5

$$= 65.641 \text{ kg.}$$

(ii) Molecular weight of air = 28.94 g

\therefore 28.94 kg of air occupies 22.4 m^3 of air

$$58.04 \text{ kg of air will occupy } \frac{65.64}{28.94} \times 22.4$$

$$= 50.79 \text{ m}^3.$$

Ans. i) Weight of air required = 65.641 kg

ii) Volume of air required = 50.79 m³ of air

Fuels And Combustion
Analysis of a sample of coal gave the following information, C = 80%, H = 6%, O = 8%, ash = 3.5%. Calculate the minimum quantity of air required for complete combustion of 1 kg of the above coal.

Solution :

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

$$= \frac{1}{100} [646400 + 172500 + 5600]$$

$$\text{L.C.V.} = \text{H.C.V.} - 0.09H \times 587$$

$$= 8245 - 0.09 \times 6 \times 587$$

$$= 7928.02 \text{ kcal/kg.}$$

$$\text{Amount of air required} = \frac{100}{23} (2.67C + 8H + S - O) \text{ kg}$$

$$= \frac{100}{23} [2.67 \times 0.8 + 8 \times 0.06 + 0.025 - 0.08] \text{ kg}$$

$$= \frac{100}{23} [2.136 + 0.48 + 0.025 - 0.08] \text{ kg}$$

$$= 11.134 \text{ kg}$$

Ans. : H.C.V. = 8245 kcal/kg.

L.C.V. = 7928.02 kcal/kg.

Amount of air required = 11.134 kg.

Calculate the weight and volume of air needed for complete combustion of 1 kg of coal containing C = 54%, H = 6.5%, O = 3%, N = 1.8%, moisture = 17.3%, ash = 17.4%. (Given molecular weight of air = 28.949)

Solution :

Constituent	% by weight	Weight of each pr kg of fuel
C	54	0.54
H	6.5	0.065
O	3.0	0.03
N	1.8	0.018

F.E. Sem.-II Engineering Chemistry-II
 (i) Amount of air required = $\frac{100}{23} (2.67C + 8H + S - O) \text{ kg}$
 = $\frac{100}{23} [2.67 \times 0.54 + 8 \times 0.065 - 0.03] \text{ kg}$
 = $\frac{100}{23} [1.44 + 0.52 - 0.03] \text{ kg}$
 = $\frac{100}{23} [1.93] \text{ kg}$
 = 8.39 kg

Volume of air needed for 1 kg coal = Number of moles of air $\times 22.4$

$$\begin{aligned} &= \frac{8.39}{28.94} \times 22.4 \\ &= 6.49 \text{ m}^3. \end{aligned}$$

Ans. : Weight of air needed = 8.39 kg
 Volume of air needed = 6.49 m³

16. Calculate the weight of air needed for complete combustion of 5 Kg of coal containing C = 80%, H = 15%, O = remaining.

Solution :

Constituent	% by weight	Weight of each pr kg of fuel
C	80	0.8
H	15	0.15
O	05	0.05
S	0.5	-

(i) Amount of air required = $\frac{100}{23} (2.67C + 8H + S - O) \text{ kg}$
 = $\frac{100}{23} [2.67 \times 0.8 + 8 \times 0.15 - 0.05] \text{ kg}$
 = $\frac{100}{23} [2.136 + 1.2 - 0.05] \text{ kg}$
 = $\frac{100}{23} [3.286] \text{ kg}$
 = 14.286 kg

Amount of air needed for combustion of 5 kg of coal = 5×14.286
 = 71.434 kg.

Ans. : Weight of air required for combustion of 5 kg of coal = 71.434 kg.

Constituent	% by weight	Weight of each pr kg of fuel
C	88	Weight of each pr kg of fuel
H	3.5	0.88
O	5.0	0.035
N	1.0	0.05
S	0.5	-

Minimum amount of oxygen = $[2.67C + 8H + S - O] \text{ kg}$
 = $[2.67 \times 0.88 + 8 \times 0.035 + 0.05 - 0.05] \text{ kg}$
 = 2.349 + 0.28

$$= 2.629 \text{ kg.}$$

Minimum amount of oxygen for 2 kg fuel = 2×2.629
 = 5.258 kg

Weight of air needed for combustion of 2 kg of coal = $\frac{100}{23} \times 5.258$
 = 22.86 kg.

$$\text{Moles of oxygen} = \frac{\text{Weight of oxygen}}{\text{Molecular weight of oxygen}}$$

$$= \frac{5.258}{32}$$

$$\text{PV} = nRT$$

$$V = \frac{nRT}{P}$$

$$= \frac{0.164 \times 0.082 \times 300}{1}$$

$$= 4.04 \text{ litres.}$$

$$\text{Moles of air} = \frac{\text{Weight of air}}{\text{Molecular weight}}$$

$$\text{CO}_2 = V \cdot \frac{P}{RT} = 2 \cdot \frac{0.082}{22.86} = \frac{22.86}{28.94} \text{ mol. of CO}_2 \text{ produced per litre of air}$$

$$= 0.789$$

$$\text{Volume of air at } 27^\circ\text{C and 1 atmospheric pressure} = \frac{nRT}{P}$$

$$= \frac{0.789 \times 0.082 \times 300}{1}$$

$$= 19.43 \text{ litres.}$$

Ans. : Minimum amount of oxygen = 5.258 kg.
Minimum amount of air = 22.86 kg
Volume of oxygen = 4.04 litres.

- 18. A coal sample C = 70%, H = 10%, O = 0.05%, S = 3%, ash = 6.5% and N = 2%. Calculate the minimum amount of air needed for complete combustion of 1 kg of coal.**

Solution :
Amount of air required = $\frac{100}{23} [2.67 \text{ C} + 8\text{H} + \text{S} - \text{O}] \text{ kg}$

$$= \frac{100}{23} [2.67 \times 0.7 + 8 \times 0.13 + 0.04 - 0.02] \text{ kg}$$

$$= 11.97 \text{ kg}$$

Ans. : Weight of air needed for combustion of 1 kg of fuel = 11.97 kg.

Constituent	% by weight	Weight of each pr kg of fuel
C	70	0.7
H	10	0.1
O	05	0.05
N	02	-
S	03	0.03
Ash	6.5	-

(i) Minimum amount of oxygen = $\frac{100}{23} [2.67 \text{ C} + 8\text{H} + \text{S} - \text{O}] \text{ kg}$

$$= \frac{100}{23} [2.67 \times 0.7 + 8 \times 0.1 + 0.03 - 0.05] \text{ kg}$$

$$= \frac{100}{23} [1.869 + 0.8 + 0.03 - 0.05]$$

$$= \frac{100}{23} \times 2.649$$

$$= 11.517 \text{ kg.}$$

Ans. : Weight of air needed for combustion of 1 kg of fuel = 11.517 kg.

- 19. A coal sample contains C = 65%, H = 13%, O = 6%, S = 4%, N = 2%. Calculate the minimum amount of air needed for complete combustion of 1 kg of coal.**

Solution :
Amount of air required = $\frac{100}{23} (2.67 \text{ C} + 8\text{H} + \text{S} - \text{O}) \text{ kg}$

$$= \frac{100}{23} [2.67 \times 0.84 + 8 \times 0.06 + 0.01 - 0.08] \text{ kg}$$

$$= \frac{100}{23} [2.2428 + 0.48 - 0.07] \text{ kg}$$

[May 2008]

C_2H_6 + 3.5 vol.

$$\begin{aligned} &= \frac{100}{23} [2.7628] \text{ kg} \\ &= 11.533 \text{ kg} \end{aligned}$$

Weight needed for combustion of 2kg of the fuel = 2×11.533
= 23.066 kg

(ii) Molecular weight of air = 28.949 g

∴ 28.949 kg of air occupies 22.4 m^3 of air

$$\begin{aligned} \therefore 23.066 \text{ kg of air occupies } &= \frac{23.066}{28.949} \times 22.4 \text{ m}^3 \text{ of air} \\ &= 17.847 \text{ m}^3 \text{ of air.} \end{aligned}$$

Ans. : Amount of air required for 2 kg of fuel = 23.066 kg
Volume of air required per kg of fuel = 17.847 m^3

21. The composition of gas was found to be $H_2 = 10\%$, $CH_4 = 16\%$, $C_2H_6 = 20\%$, $N_2 = 6\%$, $CO = 22\%$, $CO_2 = 18\%$, $O_2 = 8\%$. Calculate the volume of air required for complete combustion of 1 m^3 of this gas.

Solution :

Constituent	% by weight	Weight of each pr kg of fuel
H_2	10	0.1
CH_4	16	0.16
C_2H_6	20	0.2
N_2	06	Do not contribute
CO	22	0.22
CO_2	18	Do not contribute
O_2	08	0.08

$$\begin{aligned} \therefore 1.1 \text{ m}^3 \text{ of oxygen will be present in } &\frac{1.1}{21} \times 100 \\ &= 5.24 \text{ m}^3 \text{ of air.} \end{aligned}$$

Ans. : Volume of air required for combustion of gas = 5.24 m^3 .

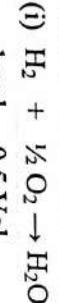
A coal sample contains $C = 75\%$, $H = 12\%$, $O = 6\%$, $S = 4\%$. Calculate the minimum amount of air by volume and weight required for complete combustion of 5 kg of fuel.

[Dec. 2009]

Solution :

Constituent	% by weight	Weight of each pr kg of fuel
C	75	0.75
H	12	0.12
O	06	0.06
S	04	0.04

Combustion reactions :



1 vol. 0.5 Vol.

i.e. 1 volume of H_2 requires 0.5 volume of oxygen

∴ 0.1 volume of H_2 requires $0.1 \times 0.5 = 0.05 \text{ m}^3$ of oxygen.



1 vol. 2 Vol.

i.e. 1 volume of CH_4 requires 2 volume of oxygen

∴ 0.16 volume of CH_4 will require $0.16 \times 2 = 0.32 \text{ m}^3$ of oxygen.

1 volume of C_2H_6 requires 3.5 volume of oxygen
∴ 1 volume of C_2H_6 will require $0.2 \times 3.5 = 0.7 \text{ m}^3$ of oxygen
 $\therefore C_2H_6 + \frac{7}{2} O_2 \rightarrow CO_2$
∴ 0.5 Vol.

1 volume of CO requires 0.5 volume of oxygen
∴ 1 volume of CO will require $0.22 \times 0.5 = 0.11 \text{ m}^3$ of oxygen
∴ N_2 and O_2 are non combustible.
Volume of oxygen required = $0.05 + 0.32 + 0.7 + 0.11$
= 1.18 m^3 .

But 0.08 m^3 of oxygen is already present in the fuel.
Actual volume of oxygen required = $1.18 - 0.08$
= 1.1 m^3 .

To find volume of air :

1 m^3 of oxygen is present in 100 m^3 of air.

$$\begin{aligned} \therefore 1.1 \text{ m}^3 \text{ of oxygen will be present in } &\frac{1.1}{21} \times 100 \\ &= 5.24 \text{ m}^3 \text{ of air.} \end{aligned}$$

Ans. : Volume of air required for combustion of gas = 5.24 m^3 .

A coal sample contains $C = 75\%$, $H = 12\%$, $O = 6\%$, $S = 4\%$. Calculate the minimum amount of air by volume and weight required for complete combustion of 5 kg of fuel.

[Dec. 2009]

Solution :

Constituent	% by weight	Weight of each pr kg of fuel
C	75	0.75
H	12	0.12
O	06	0.06
S	04	0.04

Ans. : Volume of air required for combustion of gas = 5.24 m^3 .

A coal sample contains $C = 75\%$, $H = 12\%$, $O = 6\%$, $S = 4\%$. Calculate the minimum amount of air by volume and weight required for complete combustion of 5 kg of fuel.

[Dec. 2009]

Solution :

$$\begin{aligned} \text{Weight of each pr kg of fuel} &= \frac{100}{23} (2.67C + 8H + S - O) \text{ kg} \\ &= \frac{100}{23} [2.67 \times 0.75 + 8 \times 0.12 + 0.04 - 0.06] \text{ kg} \\ &= \frac{100}{23} [2.0025 + 0.96 + 0.04 - 0.06] \text{ kg} \end{aligned}$$

$$= \frac{100}{23} [2.9425] \text{ kg}$$

$$= 12.793 \text{ kg}$$

∴ Amount of air required for 5 kg of fuel = 5×12.793

$$= 63.963 \text{ kg}$$

(ii) Molecular weight of air = 28.949 g

∴ 28.949 kg of air occupies 22.4 m^3 of air

$$\therefore 63.963 \text{ kg of air occupies } = \frac{63.963}{28.949} \times 22.4 \text{ m}^3 \text{ of air}$$

$$= 49.51 \text{ m}^3 \text{ of air.}$$

Ans. : Amount of air required for 5 kg of fuel = 63.963 kg

Volume of air required for 5 kg of fuel = 49.51 m^3

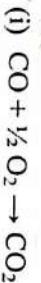
23. Calculate the volume of air required for complete combustion of 1 m^3 of gaseous fuel with following composition. $\text{CO} = 5\%$, $\text{C}_2\text{H}_4 = 10\%$, $\text{CH}_4 = 40\%$, $\text{N}_2 = 2.5\%$, $\text{H}_2 = 35\%$, $\text{CO}_2 = 2\%$, $\text{O}_2 = 2.5\%$.

[Dec. 2009]

Solution :

Constituent	% by weight	Weight of each pr kg of fuel
CO	5	0.05
C_2H_4	10	0.1
CH ₄	40	0.4
N ₂	2.5	Do not contribute
H ₂	35	0.35
CO ₂	2	Do not contribute
O ₂	2.5	0.025

Write down the combustion reactions for each constituent to calculate amount of oxygen required.



1 vol. 0.5 Vol.

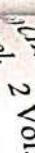
i.e. 1 volume of CO requires 0.5 volume of oxygen



1 vol. 3 vol.

i.e. 1 volume of C_2H_4 requires 3 volume of oxygen

∴ 0.1 volume of C_2H_4 will require $0.1 \times 3 = 0.3 \text{ m}^3$ of oxygen.



A coal sample was found to contain the following constituents : C = 81%, O = 8%, S = 1%, H = 5%, N = 1%, ash = 4%. Calculate the minimum amount of air required for complete combustion of 2kg of coal.

[May 2010]

Constituent	% by weight	Weight of each pr kg of fuel
C	81	0.81
O	8	0.08
S	1	0.01
H	5	0.05
N	1	Do not contribute

Ans. : Volume of air required for 1 m^3 of fuel is 13.57 m^3 .
Now for finding volume of air, we know that air contains 21% of oxygen.
i.e. 21 m^3 oxygen is present in 100 m^3 of air
∴ Total volume of O_2 required = $0.025 + 0.3 + 0.8 + 1.75 - 0.025$
= 2.85 m^3 of oxygen
∴ 2.85 m^3 oxygen will be present in $\frac{2.85 \times 100}{21}$
= 13.57 m^3 of air.

Ans. : Volume of air required for 1 m^3 of fuel is 13.57 m^3 .

A coal sample was found to contain the following constituents : C = 81%, O = 8%, S = 1%, H = 5%, N = 1%, ash = 4%. Calculate the minimum amount of air required for complete combustion of 2kg of coal.

[May 2010]

$$\text{Amount of air required} = \frac{100}{23} (2.67 \text{ C} + 8\text{H} + \text{S} - \text{O}) \text{ kg}$$

$$= \frac{100}{23} [2.67 \times 0.81 + 8 \times 0.05 + 0.01 - 0.08] \text{ kg}$$

$$= \frac{100}{23} [2.163 + 0.4 + 0.01 - 0.08] \text{ kg}$$

$$= \frac{100}{23} [2.503] \text{ kg}$$

$$= 10.882 \text{ kg}$$

\therefore Amount of air required for 2 kg of coal = $2 \times 10.882 \text{ kg}$

$$= 21.76 \text{ kg}$$

Ans.: Amount of air needed for 2 kg of coal = 21.76 kg

25. A gas has the following composition by volume H₂ = 20%, CH₄ = 6%, CO = 22%, CO₂ = 4%, O₂ = 4%, N₂ = 44%. Find volume of air required per m³ for combustion of this gas.

Solution :

Constituent	% by weight	Weight of each per kg of fuel
H ₂	20	0.2
CH ₄	06	0.06
CO	22	0.22
CO ₂	04	Non-combustible
O ₂	04	0.04
N ₂	.44	Non-combustible

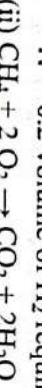
Combustion reactions :



$$1 \text{ vol. } 0.5 \text{ Vol.}$$

i.e. 1 volume of H₂ requires 0.5 volume of oxygen

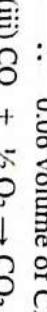
\therefore 0.2 volume of H₂ requires $0.2 \times 0.5 = 0.1 \text{ m}^3$ of oxygen.



$$1 \text{ vol. } 2 \text{ Vol.}$$

i.e. 1 volume of CH₄ requires 2 volume of oxygen

\therefore 0.06 volume of CH₄ will require $0.06 \times 2 = 0.12 \text{ m}^3$ of oxygen.



$$1 \text{ vol. } 0.5 \text{ Vol.}$$

i.e. 1 volume of CO requires 0.5 volume of oxygen

\therefore 0.22 volume of CO will require $0.22 \times 0.5 = 0.11 \text{ m}^3$ of oxygen

Total volume of oxygen required = $0.1 + 0.12 + 0.11 - 0.04$

$$= 0.29 \text{ m}^3 \text{ of oxygen}$$

Calculation of volume of air required

It is given that air contains 21% oxygen by volume.

\therefore 1 m^3 of oxygen will be present in $\frac{0.29 \times 100}{21}$ m³.

$$= 1.38 \text{ m}^3$$

Ans.: Volume of air supplied = 1.38 m³.

A coal sample contains C = 85%, H = 5%, O = 5%, S = 2% and Ash = 3%. Calculate the minimum amount of air by volume and weight required for complete combustion of 2 kg of fuel.

[Dec. 2010]

Constituent	% by weight	Weight of each per kg of fuel
C	85	
H	05	0.85
O	05	0.05
S	02	0.02

$$\text{Amount of air required} = \frac{100}{23} (2.67 \text{ C} + 8\text{H} + \text{S} - 0) \text{ kg}$$

$$= \frac{100}{23} [2.67 \times 0.85 + 8 \times 0.05 + 0.02 - 0.05] \text{ kg}$$

$$= 11.47 \text{ kg}$$

= 22.94 kg

Molecular weight of air = 28.949 g

\therefore 28.949 kg of air occupies 22.4 m³ of air

\therefore 22.94 kg of air occupies $\frac{22.94}{28.949} \times 22.4 \text{ m}^3$ of air

$$= 17.75 \text{ m}^3 \text{ of air.}$$

Ans.: Amount of air required for 2 kg of fuel = 22.94 kg

Volume of air required for 2 kg of fuel = 17.75 m³

Q. 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 the ash. Molecular weight of air = 28.949 g.

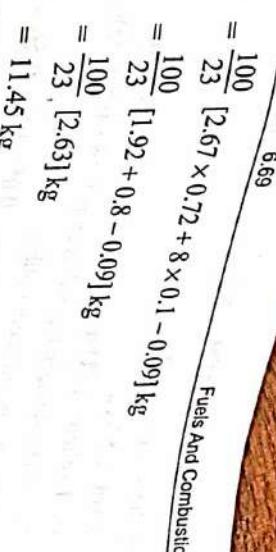
[May 2011]

Solution :

Constituent	% by weight	Weight of each pr kg of fuel
C	65	0.65
H	04	0.04
O	07	0.07
N	03	-
Moisture	15	-

- (i) Amount of air required = $\frac{100}{23} (2.67 \text{ C} + 8\text{H} + \text{S} - \text{O}) \text{ kg}$

$$= \frac{100}{23} [2.67 \times 0.72 + 8 \times 0.1 - 0.09] \text{ kg}$$



Ans. : Weight of air required for combustion of 1 kg of coal = 11.45 kg.

- (ii) Molecular weight of gas was found to be H₂ = 10%, CH₄ = 20%, C₂H₆ = 16%, N = 6%, CO = 18%, CO₂ = 22%, O₂ = 8%. Calculate the volume of air required for complete combustion of 1 m³ of this gas.

[Dec. 2011]

- Ans. : Weight of air required for combustion of 1 m³ of this gas = 11.45 kg.

- (i) Amount of air required = $\frac{100}{23} (2.67 \text{ C} + 8\text{H} + \text{S} - \text{O}) \text{ kg}$

$$= \frac{100}{23} [2.67 \times 0.65 + 8 \times 0.04 + 0 - 0.07] \text{ kg}$$

Constituent	% by weight	Weight of each pr kg of fuel
H ₂	10	0.1
CH ₄	20	0.2
C ₂ H ₆	16	0.16
N ₂	06	Do not contribute
CO	18	0.18
CO ₂	22	Do not contribute
O ₂	08	0.08

Ans. : Amount of air required per kg of fuel = 8.632 kg
Volume of air required per kg of fuel = 6.679 m³

28. Calculate weight of air needed for complete combustion of 1kg of coal containing C = 72%, H = 10%, O = 9%, N = 3% and remaining being ash.

[Dec. 2011]

Solution :

Constituent	% by weight	Weight of each pr kg of fuel
C	72	0.72
H	10	0.1
O	09	0.09

- (i) Amount of air required = $\frac{100}{23} (2.67 \text{ C} + 8\text{H} + \text{S} - \text{O}) \text{ kg}$

$$= \frac{100}{23} (2.67 \times 0.72 + 8 \times 0.1 - 0.09) \text{ kg}$$

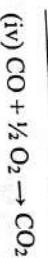
- i.e. 1 volume of CH₄ requires 2 volume of oxygen
 $\therefore 0.2 \text{ volume of CH}_4 \text{ will require } 0.2 \times 2 = 0.4 \text{ m}^3 \text{ of oxygen.}$
 $\text{C}_2\text{H}_6 + 7/2 \text{ O}_2 \rightarrow 2 \text{ CO}_2 + 3 \text{ H}_2\text{O}$
 1 vol. 3.5 vol.
 i.e. 1 volume of C₂H₆ requires 3.5 volume of oxygen
 $\therefore 0.16 \text{ volume of C}_2\text{H}_6 \text{ will require } 0.16 \times 3.5 = 0.56 \text{ m}^3 \text{ of oxygen.}$

Fuels and Combustion



F.E. Sem.-II Engineering Chemistry-II

6.70



i.e. 1 volume of CO requires 0.5 volume of oxygen
i.e. 1 volume of CO will require $0.18 \times 0.5 = 0.09 \text{ m}^3$ of oxygen

\therefore 0.18 volume of CO will require 0.18 m³ of oxygen.
 CO_2 and N_2 are non combustible.

\therefore Volume of oxygen required = $0.05 + 0.4 + 0.56 + 0.09$
= 1.1 m^3 .

But 0.08 m³ of oxygen is already present in the fuel.
Actual volume of oxygen required = $1.1 - 0.08$
= 1.02 m^3 .

To find volume of air:

21 m³ of oxygen is present in 100 m^3 of air.
 \therefore 1.02 m³ of oxygen will be present in $\frac{1.02}{21} \times 100$
= 4.85 m^3 of air.

Ans.: Volume of air required for combustion of gas = 4.85 m^3 .

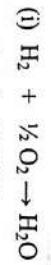
30. A gaseous fuel has the following composition by volume H = 35%, CH_4 = 45%, C_2H_6 = 6%, CO = 12% and remaining nitrogen. Calculate the minimum amount of air required at 27 °C and 760 mm Hg pressure for the complete combustion of 1 m³ of fuel.

[May 2012]

Solution :

Constituent	% by weight	Weight of each pr kg of fuel
H ₂	35	0.35
CH ₄	45	0.45
C ₂ H ₆	6	0.06
N ₂	2	Do not contribute
CO	12	0.12

Combustion reactions :



1 vol. 0.5 Vol.

i.e. 1 volume of H₂ requires 0.5 volume of oxygen

\therefore 0.35 volume of H₂ requires $0.35 \times 0.5 = 0.175 \text{ m}^3$ of oxygen.

Ans.: Volume of air required for combustion of gas = 7.03 m^3 .

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%, moisture = 15%, and remaining is ash. (Given molecular weight of air = 28.949)

[Dec. 2012]

Solution :

Constituent	% by weight	Weight of each pr kg of fuel
C	65	0.65
H	4	0.04
O	7	0.07
N	3	0.03

(i) Amount of air required = $\frac{100}{23} (2.67 C + 8H + S - O) \text{ kg}$

$$= \frac{100}{23} [2.67 \times 0.65 + 8 \times 0.04 - 0.07] \text{ kg}$$

$$= \frac{100}{23} [1.735 + 0.32 - 0.07] \text{ kg}$$

$$= \frac{100}{23} [1.985] \text{ kg} = 8.63 \text{ kg}$$

Volume of air needed for 1 kg coal = Number of moles of air $\times 22.4$

$$= \frac{8.63}{28.94} \times 22.4 = 6.68 \text{ m}^3.$$

Ans. : Weight of air needed = 8.63 kg

Volume of air needed = 6.68 m^3

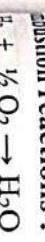
32. A coal sample contains C = 82%, H = 3%, O = 8%, S = 2%, N = 2% and Ash = 3%. Calculate the minimum amount of air by volume and weight required for complete combustion of 2 kg of fuel. (Given molecular weight of air = 28.949)

[May 2013]

Solution :

Constituent	% by weight	Weight of each pr kg of fuel
C	82	0.82
H	03	0.03
O	08	0.08
S	02	0.02

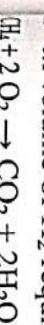
Combustion reactions :



vol. 0.5 Vol.

i.e. 1 volume of H₂ requires 0.5 volume of oxygen

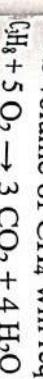
i.e. 0.1 volume of H₂ requires $0.1 \times 0.5 = 0.05 \text{ m}^3$ of oxygen.



vol. 2 Vol.

i.e. 1 volume of CH₄ requires 2 volume of oxygen

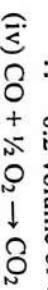
i.e. 0.3 volume of CH₄ will require $0.3 \times 2 = 0.6 \text{ m}^3$ of oxygen.



vol. 5 vol.

$$= \frac{100}{23} \left[\frac{10.3}{2.369} \right] \text{ kg}$$

- i.e. 1 volume of C_3H_8 requires 5 volume of oxygen
 $\therefore 0.2$ volume of C_3H_8 will require $0.2 \times 5 = 1 m^3$ of oxygen.



1 vol. 0.5 Vol.

i.e. 1 volume of CO requires 0.5 volume of oxygen

i.e. 0.2 volume of CO will require $0.2 \times 0.5 = 0.1 m^3$ of oxygen

CO_2 and N_2 are non combustible.

\therefore Volume of oxygen required = $0.05 + 0.6 + 1 + 0.1 = 1.75 m^3$.

$\therefore 1.75 m^3$ of oxygen will be present in $\frac{1.75}{21} \times 100$

$$= 8.33 m^3 \text{ of air.}$$

Ans. : Volume of air required for combustion of gas = $8.33 m^3$.

34. Calculate the volume and weight of air required for complete combustion of gaseous fuel, which has by volume $CH_4 = 30\%$, $C_2H_4 = 5\%$, $CO = 10\%$, $H_2 = 50\%$, $N_2 = 1\%$ $O_2 = 2\%$ & $CO_2 = 2\%$. (Molecular Weight of Air = 28.949) [Dec. 2013]

Solution :

Constituent	% by weight	Weight of each pr kg of fuel
CH_4	30	0.3
C_2H_4	05	0.05
CO	10	0.1
H_2	50	0.5
N_2	01	-
CO_2	2	-
O_2	2	0.02

Combustion reactions :



1 vol. 2 Vol.

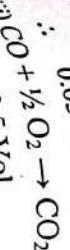
i.e. 1 volume of CH_4 requires 2 volume of oxygen

$\therefore 0.3$ volume of CH_4 will require $0.3 \times 2 = 0.6 m^3$ of oxygen.



1 vol. 3 vol.

- i.e. 1 volume of C_2H_4 requires 3 volume of oxygen
 $\therefore 0.05$ volume of C_2H_4 will require $0.05 \times 3 = 0.15 m^3$ of oxygen.



1 vol. 0.5 Vol.

i.e. 1 volume of CO requires 0.5 volume of oxygen

i.e. 0.1 volume of CO will require $\frac{0.1 \times 0.5}{1} = 0.05 m^3$ of oxygen



1 vol. 0.5 Vol.

i.e. 1 volume of H_2 requires 0.5 volume of oxygen

\therefore Total volume of O_2 required = $0.6 + 0.15 + 0.05 + 0.25 - 0.02$

$$= 1.03 m^3 \text{ of oxygen}$$

Air contains 21% of oxygen.

i.e. $21m^3$ oxygen is present in $100 m^3$ of air

$\therefore 1.03 m^3$ oxygen will be present in $= 4.9 m^3$ of air.

$22.4 m^3$ of air weighs 28.94 kg

$\therefore 4.9 m^3$ of air weighs 6.33 kg

Ans. : Volume of air required for $1 m^3$ of fuel is $4.9 m^3$

Weight of air required for $1 m^3$ of fuel is 6.33 kg

35. Calculate the volume and weight of air required for complete combustion of $1m^3$ of gaseous fuel, which has by volume $CH_4 = 30\%$, $C_2H_4 = 5\%$, $CO = 5\%$, $H_2 = 55\%$, $N_2 = 1\%$ $O_2 = 2\%$ & $CO_2 = 2\%$. (Molecular Weight of Air = 28.949) [May 2014]

Solution :

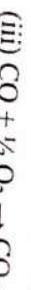
Constituent	% by weight	Weight of each pr kg of fuel
CH_4	30	0.3
C_2H_4	05	0.05
CO	10	0.1
H_2	50	0.5
N_2	01	-
CO_2	2	-
O_2	2	0.02

Combustion reactions :

1 vol. 2 Vol.

i.e. 1 volume of CH_4 requires 2 volume of oxygen∴ 0.3 volume of CH_4 will require $0.3 \times 2 = 0.6 \text{ m}^3$ of oxygen

1 vol. 3 vol.

i.e. 1 volume of C_2H_4 requires 3 volume of oxygen∴ 0.05 volume of C_2H_4 will require $0.05 \times 3 = 0.15 \text{ m}^3$ of oxygen.

1 vol. 0.5 Vol.

i.e. 1 volume of CO requires 0.5 volume of oxygen

∴ 0.05 volume of CO will require 0.025 m^3 of oxygen

1 vol. 0.5 Vol.

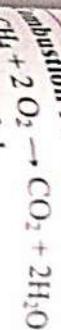
i.e. 1 volume of H_2 requires 0.5 volume of oxygen∴ 0.55 volume of H_2 requires $0.55 \times 0.5 = 0.275 \text{ m}^3$ of oxygen∴ Total volume of O_2 required = $0.6 + 0.15 + 0.025 + 0.275 - 0.02$

= 1.03 m^3 of oxygen

Air contains 21% of oxygen.

i.e. 21 m^3 oxygen is present in 100 m^3 of air∴ 1.03 m^3 oxygen will be present in $= 4.9 \text{ m}^3$ of air.22.4 m^3 of air weighs 28.94 kg∴ 4.9 m^3 of air weighs 6.33 kg**Ans. : Volume of air required for 1 m^3 of fuel is 4.9 m^3** **Weight of air required for 1 m^3 of fuel is 6.33 kg****36. A gaseous fuel has the following composition by volume: $\text{H}_2=40\%$, $\text{CH}_4=30\%$, $\text{C}_3\text{H}_8=12\%$, $\text{CO}=10\%$, $\text{CO}_2=3\%$, $\text{N}_2=3\%$, $\text{O}_2=2\%$. Calculate the volume and weight of air required for complete combustion of 1 m^3 of this fuel. (Molecular Weight of Air = 28.949)**

Constituent	% by weight	Weight of each pr kg of fuel
CH_4	30	
C_3H_8	12	
CO	10	0.3
H_2	40	0.12
N_2	3	0.1
CO_2	3	0.4
O_2	2	
		0.02

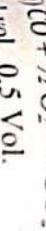
Combustion reactions :

1 vol. 2 Vol.

i.e. 1 volume of CH_4 requires 2 volume of oxygen∴ 0.3 volume of CH_4 will require $0.3 \times 2 = 0.6 \text{ m}^3$ of oxygen.

1 vol. 0.5 Vol.

i.e. 1 volume of CO requires 0.5 volume of oxygen

∴ 0.05 volume of CO will require $0.05 \times 0.5 = 0.025 \text{ m}^3$ of oxygen.

1 vol. 0.5 Vol.

i.e. 1 volume of CO requires 0.5 volume of oxygen

∴ 0.12 volume of CO will require $0.12 \times 0.5 = 0.06 \text{ m}^3$ of oxygen.

1 vol. 0.5 Vol.

i.e. 1 volume of H_2 requires 0.5 volume of oxygen∴ 0.4 volume of H_2 requires $0.4 \times 0.5 = 0.2 \text{ m}^3$ of oxygen∴ Total volume of O_2 required = $0.6 + 0.15 + 0.025 + 0.05 - 0.02$

= 1.43 m^3 of oxygen

Air contains 21% of oxygen.

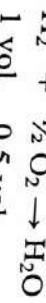
∴ 21 m^3 oxygen is present in 100 m^3 of air∴ 1.43 m^3 oxygen will be present in $= 6.809 \text{ m}^3$ of air.22.4 m^3 of air weighs 28.94 kg∴ 6.809 m^3 of air weighs 8.66 kg**Ans. : Volume of air required for 1 m^3 of fuel is 6.809 m^3** **Weight of air required for 1 m^3 of fuel is 8.66 kg**

37. A gaseous fuel has the following composition by volume.
 $\text{CH}_4 = 35\%$, $\text{C}_2\text{H}_4 = 5\%$, $\text{CO} = 15\%$, $\text{H}_2 = 40\%$, $\text{N}_2 = 1\%$, Water vapour = 4%.

Solution:

Constituent	% by weight	Weight of each pr kg of fuel
H ₂	40	0.40
CH ₄	35	0.35
C ₂ H ₄	5	0.05
N ₂	1	Do not contribute
CO	15	0.15
Water Vapour	4	Do not contribute

Combustion reactions :



1 vol. 0.5 vol.

i.e. 1 volume of H₂ requires 0.5 volume of oxygen

(ii) $\text{CH}_4 + 2\text{O}_2 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O}$

1 vol. 2 vol.

i.e. 1 volume of CH₄ requires 2 volume of oxygen

(iii) $\text{C}_2\text{H}_4 + 3\text{O}_2 \rightarrow 2\text{CO}_2 + 2\text{H}_2\text{O}$

1 vol. 3 vol.

i.e. 1 volume of C₂H₄ requires 3 volume of oxygen

(iv) $\text{CO} + \frac{1}{2}\text{O}_2 \rightarrow \text{CO}_2$

1 vol. 0.5 vol.

i.e. 1 volume of CO requires 0.5 volume of oxygen

$\therefore 0.15$ volume of CO will require $0.15 \times 0.5 = 0.075 \text{ m}^3$ of oxygen
 Water Vapour and N₂ are non-combustible.

\therefore Volume of oxygen required = $0.2 + 0.7 + 0.15 + 0.075 = 1.125 \text{ m}^3$.
 $\therefore 1.125 \text{ m}^3$ of oxygen will be present in $\frac{1.125}{21} \times 100 = 5.357 \text{ m}^3$ of air.

$$\therefore \text{Weight of air required is } = \frac{28.97 \times 5.357}{22.4} = 6.921 \text{ kg}$$

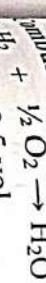
Ans. : Volume of air required for 1 m³ of fuel is 5.357 m³

Weight of air required for 1 m³ of fuel is 6.921 kg

Constituent	% by weight	Weight of each pr kg of fuel
H ₂	30	Weight of this gas, calculate the volume and weight of this gas, $\text{H}_2 = 30\%$, $\text{CH}_4 = 10\%$, $\text{C}_2\text{H}_4 = 4\%$, $\text{CO} = 46\%$, $\text{CO}_2 = 2\%$, $\text{N}_2 = 1\%$.
CH ₄	10	Weight of each pr kg of fuel
C ₂ H ₄	4	0.30
N ₂	1	0.1
CO	46	0.04
CO ₂	2	Do not contribute
O ₂	7	0.46

Constituent	% by weight	Weight of each pr kg of fuel
H ₂	30	Weight of this gas, calculate the volume and weight of this gas, $\text{H}_2 = 30\%$, $\text{CH}_4 = 10\%$, $\text{C}_2\text{H}_4 = 4\%$, $\text{CO} = 46\%$, $\text{CO}_2 = 2\%$, $\text{N}_2 = 1\%$.
CH ₄	10	Weight of each pr kg of fuel
C ₂ H ₄	4	0.30
N ₂	1	0.1
CO	46	0.04
CO ₂	2	Do not contribute
O ₂	7	0.46

Combustion reactions :



1 vol. 0.5 vol.

i.e. 1 volume of H₂ requires 0.5 volume of oxygen

(ii) $\text{CH}_4 + 2\text{O}_2 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O}$

1 vol. 2 vol.

i.e. 1 volume of CH₄ requires 2 volume of oxygen

(iii) $\text{C}_2\text{H}_4 + 3\text{O}_2 \rightarrow 2\text{CO}_2 + 2\text{H}_2\text{O}$

1 vol. 3 vol.

i.e. 1 volume of C₂H₄ requires 3 volume of oxygen

(iv) $\text{CO} + \frac{1}{2}\text{O}_2 \rightarrow \text{CO}_2$

1 vol. 0.5 vol.

i.e. 1 volume of CO requires 0.5 volume of oxygen

$\therefore 0.46$ volume of CO will require $0.46 \times 0.5 = 0.23 \text{ m}^3$ of oxygen
 Water Vapour and N₂ are non-combustible.

\therefore Volume of oxygen required = $0.15 + 0.2 + 0.12 + 0.23 - 0.07 = 0.63 \text{ m}^3$.
 $\therefore 0.63 \text{ m}^3$ of oxygen will be present in $\frac{0.63}{21} \times 100 = 3 \text{ m}^3$ of air.

$$\therefore \text{Weight of air required is } = \frac{28.94 \times 3}{22.4} = 3.875 \text{ kg}$$

Ans. : Volume of air required for 1 m³ of fuel is 3 m³

Weight of air required for 1 m³ of fuel is 3.875 kg

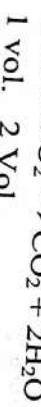
$\text{CH}_4 = 4\%$, $\text{C}_3\text{H}_8 = 4\%$, $\text{CO} = 40\%$, $\text{H}_2 = 42\%$, $\text{N}_2 = 4\%$, $\text{O}_2 = 6\%$.

Calculate volume and weight of air required for complete combustion of 1 m^3 of fuel (mol. wt. of air = 28.94).

Solution:

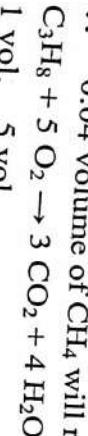
Constituent	% by weight	Weight of each pr kg of fuel
CH_4	4	0.04
C_3H_8	4	0.04
CO	40	0.4
H_2	42	0.42
N_2	4	-
O_2	6	0.06

Combustion reactions :



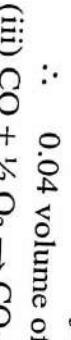
i.e. 1 volume of CH_4 requires 2 volume of oxygen

∴ 0.04 volume of CH_4 will require $0.04 \times 2 = 0.08 \text{ m}^3$ of oxygen.



1 vol. 5 vol.

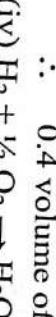
i.e. 1 volume of C_3H_8 requires 5 volume of oxygen



1 vol. 0.5 Vol.

i.e. 1 volume of CO requires 0.5 volume of oxygen

∴ 0.4 volume of CO will require 0.2 m^3 of oxygen



1 vol. 0.5 Vol.

i.e. 1 volume of H_2 requires 0.5 volume of oxygen

∴ 0.42 volume of H_2 requires $0.42 \times 0.5 = 0.21 \text{ m}^3$ of oxygen

∴ Total volume of O_2 required = $0.08 + 0.2 + 0.2 + 0.21 - 0.06$

$$= 0.63 \text{ m}^3 \text{ of oxygen}$$

Air contains 21% of oxygen.

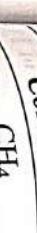
i.e. 21 m^3 oxygen is present in 100 m^3 of air

0.63 m^3 oxygen will be present in $\frac{6.3}{21} = \frac{1}{3} \text{ m}^3$ of air.

[Dec. 2016]

Constituent	% by weight	Weight of each pr kg of fuel
CH_4	30	0.3
C_3H_8	20	0.2
CO	20	0.2
H_2	25	0.25
N_2	1	0.25
CO_2	2	-
O_2	2	-

Combustion reactions :



1 vol. 2 Vol.

i.e. 1 volume of CH_4 requires 2 volume of oxygen

∴ 0.3 volume of CH_4 will require $0.3 \times 2 = 0.6 \text{ m}^3$ of oxygen.



1 vol. 5 vol.

i.e. 1 volume of C_3H_8 requires 5 volume of oxygen

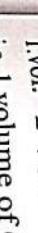
∴ 0.2 volume of C_3H_8 will require $0.2 \times 5 = 1 \text{ m}^3$ of oxygen.



1 vol. 0.5 Vol.

i.e. 1 volume of CO requires 0.5 volume of oxygen

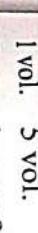
∴ 0.2 volume of CO will require 0.1 m^3 of oxygen



1 vol. 0.5 Vol.

i.e. 1 volume of H_2 requires 0.5 volume of oxygen

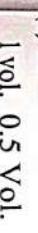
∴ 0.2 volume of H_2 requires 0.1 m^3 of oxygen



1 vol. 0.5 Vol.

i.e. 1 volume of H_2 requires 0.5 volume of oxygen

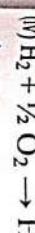
∴ 0.2 volume of H_2 requires 0.1 m^3 of oxygen



1 vol. 0.5 Vol.

i.e. 1 volume of H_2 requires 0.5 volume of oxygen

∴ 0.2 volume of H_2 requires 0.1 m^3 of oxygen



1 vol. 0.5 Vol.

i.e. 1 volume of H_2 requires 0.5 volume of oxygen

∴ 0.2 volume of H_2 requires 0.1 m^3 of oxygen



1 vol. 0.5 Vol.

$0.25 \text{ volume of } H_2 \text{ requires } 0.25 \times 0.5 = 0.125 \text{ m}^3 \text{ of oxygen}$ Total volume of O_2 required = $0.6 + 1.0 + 0.1 + 0.125 - 0.02$

$$\therefore 1.805 \text{ m}^3 \text{ of oxygen}$$

Air contains 21% of oxygen.

i.e. 21m^3 oxygen is present in 100 m^3 of air $\therefore 1.805 \text{ m}^3$ oxygen will be present in $= 8.595 \text{ m}^3$ of air. 22.4 m^3 of air weighs 28.94 kg $\therefore 8.595 \text{ m}^3$ of air weighs 11.10 kg Ans. : Volume of air required for 1 m^3 of fuel is 8.595 m^3 Weight of air required for 1 m^3 of fuel is 11.10 kg

41. Calculate the weight and volume of air needed for complete combustion of coal sample containing C=54%, H=6.5%, O=3%

(mol. wt. of air = 28.94)

Solution:

Constituent	% by weight	Weight of each pr kg of fuel
C	54	0.54
H	6.5	0.065
O	3	0.03

$$(i) \text{ Amount of air required} = \frac{100}{23} (2.67C + 8H + S - O) \text{ kg}$$

$$= \frac{100}{23} [2.67 \times 0.54 + 8 \times 0.065 - 0.03] \text{ kg}$$

$$= \frac{100}{23} [1.404 + 0.52 - 0.03] \text{ kg}$$

$$= \frac{100}{23} [1.894] \text{ kg}$$

$$= 8.235 \text{ kg}$$

$$\therefore \text{Amount of air required for } 2 \text{ kg of fuel} = 2 \times 8.235 = 16.47 \text{ kg}$$

$$(ii) \text{ Molecular weight of air} = 28.949 \text{ g}$$

$$\therefore 28.949 \text{ kg of air occupies } 22.4 \text{ m}^3 \text{ of air}$$

$$\therefore 16.47 \text{ kg of air occupies } \frac{16.47}{28.949} \times 22.4 \text{ m}^3 \text{ of air}$$

$$= 12.748 \text{ m}^3 \text{ of air.}$$

Ans. : Amount of air required for $2 \text{ kg of fuel} = 16.47 \text{ kg}$ Volume of air required for $2 \text{ kg of fuel} = 12.748 \text{ m}^3$

Calculate weight or air needed for complete combustion of coal containing C=70%, H=10%, O=10%, N=5% and ash=4%. [Dec 2017]

Constituent	% by weight	Weight of each pr kg of fuel
C	70	Weight of each pr kg of coal [Mar 2017]
O	10	$70/100 = 0.7$
H	10	$10/100 = 0.1$
N	5	$5/100 = 0.05$
Ash	-	$4/100 = 0.04$
S	1	$1/100 = 0.01$

$$\text{Amount of air required} = \frac{100}{23} (2.67C + 8H + S - O) \text{ kg}$$

$$= \frac{100}{23} [2.67 \times 0.7 + 8 \times 0.1 - 0.04] \text{ kg}$$

$$= 11.169 \text{ kg}$$

$$\text{amount of air required for } 2 \text{ kg of coal} = 2 \times 11.169$$

$$= 22.339 \text{ kg}$$

Ans. : Quantity of air needed = 22.339 kg

Calculate weight and volume of air needed for complete combustion of 1Kg of coal containing C=81%, H=5%, O=8%, N=1%, S=1% and ash=4%. [Dec 2017]

Constituent	% by weight	Weight of each pr kg of fuel
C	81	0.81
H	05	0.05
O	08	0.08
N	01	-
Ash	01	-
S	01	0.01

$$(i) \text{ Amount of air required} = \frac{100}{23} (2.67C + 8H + S - O) \text{ kg}$$

$$= \frac{100}{23} [2.67 \times 0.81 + 8 \times 0.05 + 0.01 - 0.08] \text{ kg}$$

$$= \frac{100}{23} [2.163 + 0.4 + 0.01 - 0.08] \text{ kg}$$

$\text{CO} + \frac{1}{2}\text{O}_2 \rightarrow \text{H}_2\text{O}$

$$\text{Molecular weight of CO} = \frac{100}{23} [2.493] \text{ kg}$$

$$= 10.84 \text{ kg}$$

(ii) Molecular weight of air = 28.949 g

i.e. 1 volume of air occupies 22.4 m³ of air

$$\therefore 10.84 \text{ kg of air occupies } = \frac{10.84}{28.949} \times 22.4 \text{ m}^3 \text{ of air}$$

$$= 8.39 \text{ m}^3 \text{ of air.}$$

Ans. : Amount of air required for 1 kg of fuel = 10.84 kg

Volume of air required per kg of fuel = 8.39 m³

44. A gaseous fuel contains H₂ = 50%, CH₄ = 30%, N₂ = 2%, CO = 7%, C₂H₄ = 3%, C₂H₆ = 5% and water vapour = 3%. Calculate weight and volume of air required for 2 m³ of the gas. (Mol. Wt. of air = 28.94 Kg).

Solution :

Constituent	% by volume	Volume of each pr m ³ of fuel
CH ₄	30	0.3
C ₂ H ₄	3	0.03
CO	7	0.07
H ₂	50	0.5
N ₂	2	-
C ₂ H ₆	5	0.05
Water Vapour	3	-

Combustion reactions :



1 vol. 2 Vol.

i.e. 1 volume of CH₄ requires 2 volume of oxygen

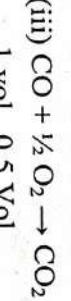
i.e. 0.3 volume of CH₄ will require $0.3 \times 2 = 0.6 \text{ m}^3$ of oxygen.



1 vol. 3 vol.

i.e. 1 volume of C₂H₄ requires 3 volume of oxygen

i.e. 0.3 volume of C₂H₄ will require $0.03 \times 3 = 0.09 \text{ m}^3$ of oxygen.



1 vol. 0.5 Vol.

$\text{CO} + \frac{1}{2}\text{O}_2 \rightarrow \text{H}_2\text{O}$

$$1 \text{ volume of CO will require } 0.5 \text{ volume of oxygen}$$

$$0.07 \text{ volume of CO will require } 0.035 \text{ m}^3 \text{ of oxygen}$$

i.e. $\frac{1}{2}\text{O}_2 \rightarrow \text{H}_2\text{O}$

i.e. 0.5 Vol.

$\text{C}_2\text{H}_6 + 3.5\text{O}_2 \rightarrow 2\text{CO}_2 + 3\text{H}_2\text{O}$

$$1 \text{ volume of C}_2\text{H}_6 \text{ requires } 3.5 \text{ volume of oxygen}$$

$$0.05 \text{ volume of C}_2\text{H}_6 \text{ requires } 0.175 \text{ m}^3 \text{ of oxygen}$$

i.e. 0.05 of C₂H₆ requires 0.175 m³ of oxygen

i.e. Total volume of O₂ required = 0.6 + 0.09 + 0.035 + 0.25 + 0.175

i.e. 1.15 m³ of oxygen

i.e. Air contains 21% of oxygen.

i.e. 21m³ oxygen is present in 100 m³ of air

i.e. 1.15 m³ oxygen will be present in = 5.47 m³ of air.

i.e. For 2 m³ of fuel, volume of air required = 10.94 m³

i.e. 22.4 m³ of air weighs 28.94 kg

i.e. 10.94 m³ of air weighs 14.13 kg

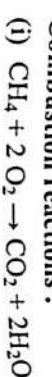
Ans. : Volume of air required for 2 m³ of fuel is 10.94 m³

i.e. Weight of air required for 2 m³ of fuel is 14.13 kg

Calculate weight and volume of air needed for complete combustion of 1m³ of gaseous fuel which possess by volume CH₄ = 35%, C₂H₄ = 5%, CO = 15%, H₂ = 40%, N₂ = 1%, Water Vapour = 4% (Mol. Wt. Of Air = 28.94)

[Dec 2018]

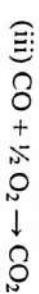
Constituent	% by weight	Weight of each pr kg of fuel
CH ₄	35	0.35
C ₂ H ₄	5	0.05
CO	15	0.15
H ₂	40	0.4
N ₂	1	-
Water Vapour	4	-

Combustion reactions:

1 vol. 2 Vol.

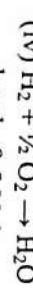
i.e. 1 volume of CH_4 requires 2 volume of oxygen $\therefore 0.35$ volume of CH_4 will require $0.35 \times 2 = 0.7 \text{ m}^3$ of oxygen.

1 vol. 3 vol.

i.e. 1 volume of C_2H_4 requires 3 volume of oxygen $\therefore 0.05$ volume of C_2H_4 will require $0.05 \times 3 = 0.15 \text{ m}^3$ of oxygen.

1 vol. 0.5 Vol.

i.e. 1 volume of CO requires 0.5 volume of oxygen

 $\therefore 0.15$ volume of CO will require 0.075 m^3 of oxygen

1 vol. 0.5 Vol.

i.e. 1 volume of H_2 requires 0.5 volume of oxygen $\therefore 0.4$ volume of H_2 requires $0.4 \times 0.5 = 0.2 \text{ m}^3$ of oxygenTotal volume of O_2 required = $0.7 + 0.15 + 0.075 + 0.2 = 1.125 \text{ m}^3$ of oxygeni.e. 2m^3 oxygen is present in 100 m^3 of air $\therefore 1.125 \text{ m}^3$ oxygen will be present in $= 5.35 \text{ m}^3$ of air. 22.4 m^3 of air weighs 28.94 kg $\therefore 5.35 \text{ m}^3$ of air weighs 6.91 kg

Ans. : Volume of air required for 1 m^3 of fuel is 5.35 m^3

Weight of air required for 1 m^3 of fuel is 6.91 kg

46. A coal sample was found to contain C=90%, O=5%, H=1%, S=0.5% and remaining being nitrogen. Calculate weight and volume of air required for complete combustion of 1 Kg of coal sample. (MW of air = 28.949) [May 2019]

Solution :

Constituent	% by weight	Weight of each pr kg of fuel
C	90	$90/100 = 0.9$
O	5	$5/100 = 0.05$
S	0.5	$0.5/100 = 0.005$
H	1	$1/100 = 0.01$
N	-	Do not contribute

6.8 LIQUID FUELS

Although the extensive use of liquid hydrocarbons for fuel is of very recent origin, the use of liquid fuels dates back to very ancient times, when vegetable and animal oils were burnt for the production of light and to some extent for heat. These oils are of little importance today, because they have been largely replaced by petroleum products. These petroleum products are very important as almost all internal combustion engines run on them. They are also used in heat generation in ovens and furnaces.

Petroleum is a natural product generated from organic material by physical and chemical processes inside the earth. It is product of decay of bodies of countless tiny sea creatures (organic material) trapped under layers of rocks. The term petroleum is made up of petra = rock and oleum = oil. The major oil fields in the world are located in Middle East (mainly Saudi Arabia, Iran, Kuwait, Iraq and Abu Dhabi) accounting for almost 56.3 percent of world reserves. Other major oil bearing countries are Russia, Mexico, U.S.A., Venezuela, Libya and Nigeria. The major oil fields in India are mainly in Assam, Gujarat and Maharashtra. Petroleum is found underneath the earth's surface at different depths varying from 500–15000 feet. Generally it is found in porous strata beneath the impervious rock floating over brine and accompanied with natural gas (mainly methane).

6.9 GASOLINE OR PETROL

Gasoline or petrol is the most important liquid fuel derived from petroleum and is obtained between 40–120°C. It is a mixture of hydrocarbons such as C_5H_{12} (pentane) to

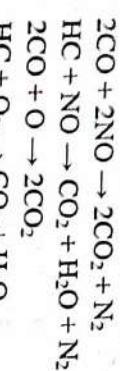
$$\begin{aligned} \text{Amount of air required} &= \frac{100}{23} (2.67 \text{ C} + 8\text{H} + \text{S} - \text{O}) \text{ kg} \\ &= \frac{100}{23} [2.67 \times 0.9 + 8 \times 0.01 + 0.005 - 0.05] \text{ kg} \\ &= \frac{100}{23} [2.403 + 0.08 + 0.005 - 0.05] \text{ kg} \\ &= \frac{100}{23} [2.438] \text{ kg} \end{aligned}$$

C_8H_{18} (octane). Its approximate composition is $C = 84\%$, $H = 15\%$, $N + S + O = 1\%$. Its calorific value is about 11,250 kcal/kg. It is highly volatile, inflammable and used as fuel for internal combustion engines of automobiles and aeroplanes.

6.9.1 Unleaded Petrol and Catalytic Converter

In leaded petrol, octane rating is increased by adding tetraethyl lead or tetramethyl lead. Combustion of such petrol leads to formation of litharge (PbO) which deposits on the inner wall of cylinder and jams the piston. It also can't be used in automobiles equipped with catalytic converter as lead present in exhaust gas poisons the catalyst. "Unleaded petrol" is one where in the enhancement of octane rating is achieved without the addition of lead compounds. This reduces undesirable lead emissions enables the use of catalytic converter. Therefore compounds like iso-octane, iso-pentane and ethyl benzene, isopropyl benzene, methyl tertiary butyl ether (MTBE) are added as an alternative method for increasing the octane number. MTBE is mostly preferred as it contains oxygen in the form of ether group, which supplies oxygen for the combustion as it petrol in internal combustion engines. This reduces the extent of peroxy compound formation.

Unleaded petrol permits the use of catalytic converter. Catalytic converter is fitted in the exhaust system after the exhaust manifold of the petrol driven vehicles. A catalytic converter contains rhodium as catalyst. When the exhaust gases flowing into the support channels come in contact with the catalyst surface, the CO and hydrocarbon of the exhaust get converted into CO_2 and H_2O . The NO_x emissions also get reduced under suitable conditions of engine operations.



6.10 KNOCKING

In an internal combustion engine (spark ignition type), a mixture of air and petrol vapour is compressed and ignited by an electric spark and the essential chemical reaction is the oxidation of hydrocarbon molecules.

It is essential that combustion of the fuel in the cylinder of an internal combustion engine should proceed in a regular way. After the reaction is initiated by a spark, a flame should spread rapidly and smoothly through the gas mixture and expanding gas drives the piston down the cylinder. In certain circumstances, however, the rate of oxidation is so great that the mixture detonates, producing the sound called engine "knock". The rate of

Fig. 6.4 : Knocking

The diagram illustrates a cross-section of a single-cylinder internal combustion engine. The cylinder is shown with its top removed, revealing the piston at the bottom. The piston is connected via a connecting rod to a crank shaft. On the left side of the cylinder, there is an intake port leading into the cylinder. On the right side, there is an exhaust valve. A spark plug is positioned near the top of the cylinder. The engine is shown in three stages of its cycle: 1. Top Dead Centre (TDC) where the piston is at the very top of the cylinder. 2. Bottom Dead Centre (BDC) where the piston is at the very bottom of the cylinder. 3. Intermediate position where the piston is moving upwards from BDC. Arrows indicate the direction of movement for each stage. Labels include: Intake, Cylinder, Spark plug, Piston, Exhaust valve, Connecting rod, and Crank shaft.

In certain circumstances, due to compression, the fuel air mixture may get heated to a temperature higher than ignition temperature so that there is spontaneous combustion and the rate of oxidation becomes so great that the last portion of fuel air mixture gets ignited instantaneously producing an explosive violence known as knocking. It causes shock wave giving violent blow to the piston known as knocking or detonation. Knocking is defined as a sharp metallic sound produced in the internal combustion engine and results into a loss of energy. It is also defined as the rattling noise produced in an internal combustion engine.

The tendency to knock depends on (1) Fuel air ratio, (2) design of engine, (3) speed of engine, (4) shape of piston head, (5) location of spark plug and also upon the running conditions. Knocking results in the loss of efficiency of engine, causing fuel wastage and increased wear and tear of engine.

Knocking largely depends upon the type of fuel used. Tendency of gasoline to knocking depends upon the nature and structure of the hydrocarbons present in the gasoline. Petrol containing straight run paraffin knocks the most and petrol containing aromatics knocks the least. Cracked gasoline containing branched chain compounds give better performance than straight distilled gasoline. The tendency to knocking is in the following order :

Straight chain > branched chain > olefins paraffins > cyclo paraffins > aromatics

paraffins

Knocks the most

paraffins

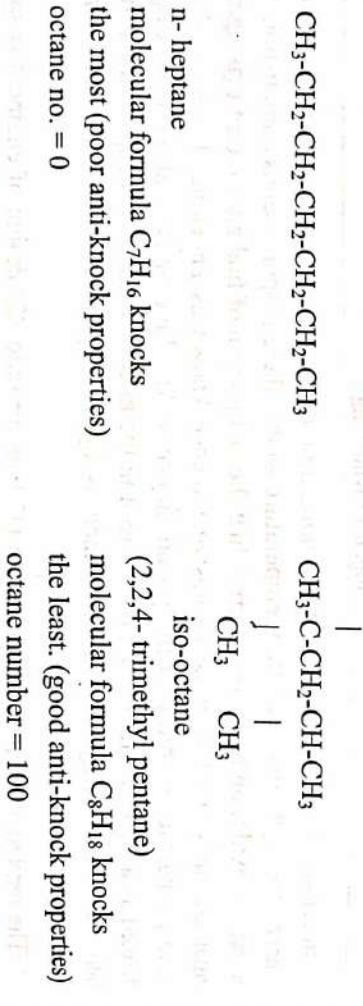
knocks the least

(low octane number)

Knocking can be prevented by using fuel of high octane value. Knocking can be minimized by adding a small amount of anti-knock compounds like tetra ethyl lead (TEL) to gasoline.

6.11 OCTANE VALUE

Octane number or octane value is an arbitrary scale which expresses commonly the knocking characteristics of a petrol. Thus the knocking quality of a petrol is measured in terms of so called octane number which was introduced by Graham Edgar in 1926. It has been found that n-heptane which knocks very badly and has poor resistance to knocking and is assigned the octane value zero. Iso-octane (2,2,4 – trimethyl pentane) which knocks the least and has good resistance to knocking and is assigned the octane value 100. Thus the octane number is defined as the percentage by volume of iso-octane in a mixture of iso-octane and n-heptane which just matches the knocking characteristics of a fuel (gasoline) under test.



Primary reference fuel is prepared, by blending these two hydrocarbons (viz. iso-octane and n-heptane) in various proportions and the knocking tendency of the gasoline sample could be determined. The gasoline sample to be tested is burnt under standard set

of conditions in a variable compression ratio engine and the critical compression ratio at which knocking occurs is determined. In the same engine under the same set of conditions and the same critical compression ratio, various blends of iso-octane and n-heptane are burnt, and the knocking produced which just matches a blend containing the percentage of iso-octane by volume is the octane number of gasoline. Thus if a sample of gasoline gives as much knocking as a mixture of 87 parts of iso-octane and 13 parts of n-heptane, then the octane number given to gasoline sample is 87.

The petrol used in aeroplanes has an octane number more than 100 and this is called aviation gasoline or aviation petrol. Now-a-days fuels with octane numbers above 100 are available. They are compared by blending iso-octane with tetraethyl lead (TEL) which greatly diminishes the tendency of knocking. The value of octane number in such cases is determined by extrapolation.

The octane no. of some common hydrocarbons are given below :

Hydrocarbons	Octane Number
Benzene	110
Toluene	104
Cyclopentane	82
Cyclohexane	77
Propene	85
Butene	80
n-propane	100
n-butane	92
n-pentane	62
n-hexane	26
n-heptane	0

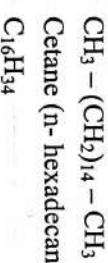
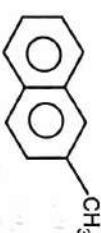
Straight-chain hydrocarbons causes severe knocking even at small critical compression ratio while the branched chain alkenes have better anti-knock properties and can be used at higher values of critical compression ratio. Even among the normal alkanes, numbers containing C_4 , C_5 have higher octane values and the octane values decrease as the carbon chain length of hydrocarbons increases. For example, in the above table, n-propane, n-butane, n-pentane, n-hexane and n-heptane has octane numbers 100, 92, 62, 26 and zero respectively. Olefins have better anti-knock properties than paraffins. Aromatic hydrocarbons and cracked gasoline have higher octane numbers and have better anti-knock properties than cycloparaffins.

The higher the octane numbers of the fuel, the higher the compression ratio at which the fuel can be used without knocking as a result greater power can be obtained from an engine and greater will be the efficiency of fuel.

Octane value of the petrol does not always correspond with the behaviour of petrol when used in automobile in normal conditions. Thus a fuel having octane number 85 may not be superior always to one with an octane number 80. This has to be actually tested in a car and rated in terms of 'performance'.

6.12 CETANE VALUE

In a diesel engine, the fuel is exploded not by a spark, but by the application of heat and pressure. Diesel engine fuels consist of longer chain hydrocarbons than internal combustion engine fuels. The knocking characteristics of diesel oil are expressed in terms of cetane number. Thus ignition quality of diesel oil is measured in terms of so called cetane number. It is desirable for a diesel fuel to ignite very quickly (without any delay) when injected into the cylinder of a compression ignition engine. The time interval between the injection and the start of combustion is called ignition delay period or ignition lag period. The combustion of fuel in a diesel engine is not instantaneous and the interval between the injection and start of ignition is called 'ignition delay' and is an important quality of the diesel fuel. In order to grade the diesel fuels, a rating called cetane rating is employed, in which cetane numbers are assigned to diesel oils. Cetane ($C_{16}H_{34}$), a saturated hydrocarbon, ignites very quickly and thus has a very short ignition lag or delay. Hence it has been given the cetane number 100 in the rating scale. On the contrary, α -methylnaphthalene ($C_{11}H_{10}$) has a very long ignition lag as compared to any diesel fuel. Hence it is given cetane number zero. Cetane number of a diesel oil is defined as the percentage by volume of cetane in a mixture of cetane and α -methylnaphthalene which just matches the knocking characteristics of diesel oil under test i.e. which has same ignition delay as the fuel under test.



Knocks the least (least ignition delay) Cetane no. 100

α -methyl naphthalene

Knocks the most

higher ignition temperature

Cetane number = 0

Ignition quality of hydrocarbon Decreases in the following order

Straight chain > cycloparaffins > olefins > branched chain hydrocarbon > aromatics

hydrocarbons: (naphthenes)

least ignition delay

(High cetane number)

high ignition delay

(low cetane number)

Among the straight chain hydrocarbons (alkanes) cetane number Decreases with Decrease in carbon chain length. The cetane number of some common compounds are given below :

Compounds (C_nH_{2n})	Cetane number
OctaDecane ($C_{16}H_{34}$)	103
Hexadecane ($C_{14}H_{30}$)	200
Tertadecane ($C_{12}H_{26}$)	96
Dodecane ($C_{10}H_{22}$)	88
Decane (C_8H_{18})	77
Heptane (C_7H_{16})	64
	56

The specific gravity of diesel fuel Decreases with increase in cetane number and the relation can be seen from the table :

Specific gravity	Cetane number
0.8	70.5
0.85	61
0.9	50
0.95	37

Oils having least ignition delay are good diesel fuels (have high cetane number) but are poor gasoline fuels (have low octane number) and vice versa. Fuel properties of diesel fuel and gasoline suggest an inverse relationship between cetane and octane numbers as illustrated as follows :

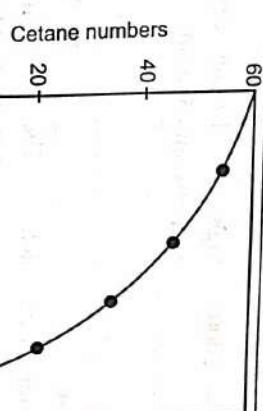


Fig. 6.5 : Graph

In petrol engines, knocking is due to sudden spontaneous combustion of last portion of the fuel, whereas knocking in the diesel engine is due to delay in combustion of the first part of the fuel.

The cetane number of diesel fuel can be increased by addition of certain compounds called dopes or ignition accelerators. The ignition accelerators added are ethyl nitrite ($C_2H_5NO_2$), ethyl nitrate ($C_2H_5NO_3$), isoamyl nitrate [$(CH_3)_2CHCH_2CH_2NO_3$] and



acetone peroxide [$CH_3C(O-O-C_2H_5)CH_3$]. Thus ignition accelerators are compounds which when added to diesel fuel, will reduce delay period. Most ignition accelerator reduce the flash point of the fuel.

Ignition accelerators are added only in small amounts (about 2%). They are not effective on diesel fuels having low cetane number. Doping is not very common in diesel oil as the use of tetrachyl lead in petrol.

Diesel engines may be classified as low, medium and high speed engines and different type of diesel oils are used for each engine. The following table shows different types of Diesel engines, their oil requirements and uses.

Types of diesel engine	Speed in r.p.m.	Diesel oil used having cetane number	Uses
Low speed	100-150	Heavy oils having cetane no. 25	Ships
Medium speed	500-1500	Medium oils having cetane no. Between 25 to 35	Tractors, locomotives etc.
High speed	1500-2000	Light oils having cetane no. Between 45 to 50	Buses, trucks etc.

Comparison :

Octane value	Cetane value
1. Octane value is an arbitrary scale which expresses the knocking characteristics of a petrol	1. The ignition quality of a diesel oil is measured in terms of cetane value
2. Octane number is defined as the percentage by volume of iso-octane in a mixture of iso-octane and n-heptane which just matches the knocking characteristics of gasoline under test.	2. Cetane number is defined as the percentage by volume of cetane in a mixture of cetane and α-methyl-naphthalene which just matches the knocking characteristics of diesel oil under test.

3. Oils having least ignition delay are poor gasoline fuels i.e. possesses low octane number.	3. Oils having least ignition delay are good diesel fuels i.e. possesses high octane number.
4. The octane number of petrol can be increased by addition of tetrachyl lead or diethyl telluride.	4. The cetane number can be increased by addition of certain additives like ethyl nitrite, ethyl nitrate etc. which are known as accelerators.
5. Petrol containing aromatics have highest octane number.	5. Diesel oils containing n-paraffins have highest cetane number.
6. Anti-knock agents are effective in petrol fuels having low octane value.	6. Anti-knock agents are not effective in petrol fuels having low cetane value.
7. Oils having high octane number has a low cetane number.	7. Oils having high cetane number has a low octane number.

6.13 ANTI-KNOCKING AGENT

The octane number of a gasoline may be increased by the addition of fuels of higher anti-knock value. To achieve this, casing-head gasoline, cracked and reformed gasoline, benzol and alcohol may be used. This process is called 'blending'. The anti-knock properties of gasoline are usually increased by adding lead tetrachyl (Tetra ethyl lead TEL) and diethyl telluride ($C_2H_5)_2Te$ and the process is called "doping." TEL is a colourless liquid with sweet odour. Its specific gravity is 1.62. It boils at 200°C with decomposition. It is highly poisonous. Gasoline containing TEL is coloured to indicate its poisonous nature. In motor spirit about 0.5 ml and in aviated fuels, about 1 to 1.5 ml of TEL is added per litre of petrol. According to the most accepted theory, TEL is converted into a cloud of finely divided lead oxide particles in the cylinder and these particles react with any hydrocarbon peroxides molecules formed, thereby slowing down the chain oxidation reaction and thus, decreasing the chances of any early detonation. However, deposit of lead oxide is harmful to the engine life. Consequently, in order to help the simultaneous elimination of lead oxide formed from the engine, a small amount of ethylene dibromide is also added to petrol. Ethylene dibromide removes lead oxide as volatile lead bromide along with the exhaust gases. The presence of sulphur compounds in petrol reduces the effectiveness of the TEL.



Ethylene dibromide

Lead bromide

Ethylene

Unfortunately, this "scavenging" of lead is not very effective in modern cars of high compression ratio during long periods of "Idling" in heavy traffic. Nowadays, it is customary to blend certain aromatic phosphates, for example, cresyl diphenyl phosphate,

with petrol. They reduce the electrical conductivity of the lead compounds deposited on the spark plug points.

6.14 POWER ALCOHOL

Ethyl alcohol is an important fuel and when it is used in an internal combustion engine, it is called power alcohol. It is not used as a prime fuel but only used as an additive to motor fuel. Blends containing up to 25% of alcohol with petrol are used. It has a calorific value of only 7000 kcal/kg but it has good anti-knocking properties. Its octane number is about 90.

Principle :

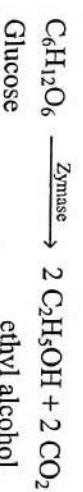
The use of biological organisms or their constituents are used for the transformation of waste input into commercial output.

Raw material generally used is wastes from sugarcane (molasses), whey, sweet sorghum, corn, barley, potatoes, raisins, banana, sugar beet etc. Micro-organisms for fermentation includes yeast, mould and bacteria. All of them produce enzymes and catalyze reaction.

In India, molasses a byproduct of sugar industry constitutes a suitable and cheap raw material for the manufacture of alcohol. Molasses is the syrup left after the separation of cane sugar (or beat sugar) crystals. It is dark coloured, syrupy mass containing about 50% to 60% sucrose and invert sugar (a mixture of glucose and fructose). The different steps involved in ethanol production are :

(a) Dilution : The molasses is diluted with water, until a concentration of 10-12% sugar is obtained in solution. A small amount of dilute sulphuric acid is added so as to adjust pH of solution to about 4.5. The acidity is maintained to favour the growth of yeast. To this solution, a small quantity of ammonium sulphate or ammonium phosphate is added, which acts as a food for the yeast cells.

(b) Alcoholic fermentation : The diluted solution is taken in big fermentation tanks and yeast is added (5% by volume of the liquid). The mixture is then allowed to stand for a few days by maintaining the temperature at about 30°C. The enzyme invertase converts sucrose into glucose and fructose. Then they are converted into ethyl alcohol by another enzyme, zymase.



The fermentation is complete in about 36 to 38 hours and carbon dioxide is the by-product formed. The fermented liquor is filtered which is called wash.

(c) Fractional distillation :

The fermented liquid contains about 18 to 20% alcohol which is fractionally distilled to get rectified spirit containing 90-95% alcohol.

This rectified spirit is digested with lime for two days and then distilled to get absolute alcohol (100% alcohol).

Advantages of alcohol blended petrol:

1. Addition of alcohol with octane value of about 90 to petrol increases the octane number of the petrol. Therefore alcohol blended petrol possesses better antiknock properties.
2. Alcohol petrol blends have lesser starting difficulties.
3. Presence of alcohol helps in absorbing traces of moisture which would otherwise enter the petrol system.

6.15 REVIEW QUESTIONS

1. What are fuels? Give complete classification of fuels with examples.

Ans. Refer Section 6.1 and 6.2.

2. What are the characteristics of good fuel?

Ans. Refer Section 6.3.

3. What is meant by calorific value of a fuel?

Ans. Refer Section 6.4.

4. Distinguish between gross and net calorific value of a fuel.

Ans. Refer Section 6.4.2 and 6.4.3.

5. Why should an ideal fuel have moderate ignition temperature?

Ans. Refer Section 6.3.

6. Explain proximate analysis of coal?

Ans. Refer Section 6.6.1.

7. Discuss the importance of ultimate analysis.

Ans. Refer Section 6.6.2.

8. Explain the significance of proximate analysis of a coal.

Ans. Refer Section 6.6.1.

9. Why a good fuel must have low ash content?

Ans. Refer Section 6.3.

10. What is the significance of volatile matter in coal?

Ans. Refer Section 6.6.1.

PRINCIPLES OF SPECTROSCOPY

SYLLABUS

- *Introduction : Principle of spectroscopy, Definition, Origin of spectrum*
- *Classification of spectroscopy – atomic and molecular, selection rules*
- *Table of relation between electromagnetic spectrum, types of spectroscopy and energy changes*

1.1 INTRODUCTION

In recent years, spectroscopy has been used extensively in the analysis/structure determination of organic compounds. The classical techniques which were successful with macro quantities of organic compounds failed when the organic compounds under investigation were available in micro or semi micro amounts. Several types of spectroscopy have been applied to the study of such organic compounds. These spectroscopic techniques possess numerous merits over the classical techniques which are as follows.

1. They take much less time.
2. They require very small amounts of the compound being studied.
3. They are generally very fast and economical in the long run.
4. They are generally non-destructive. i.e. the compounds being studied remain unchanged during spectroscopic examination and can be reused for other tests, if required.
5. They are highly reliable in establishing the identity of two compounds.
6. They give information which is recorded in the form of a permanent chart generally in an automatic or semi-automatic manner.

Electromagnetic radiation is a simple harmonic wave with the properties of a wave. It travels in a straight line unless it is refracted or reflected.

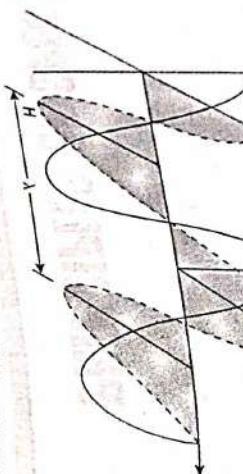


Fig. 1.1 : Electromagnetic radiation and its components

Some important characteristics of electromagnetic radiations are as follows.

- These radiations are produced by the oscillations of electric charge and magnetic field residing on this atom. The electric and magnetic components are mutually perpendicular to each other and are coplanar.
- These are characterized by their wavelength or frequencies or wave numbers.
- The energy carried by an electromagnetic radiation is directly proportional to its frequency. The emission or absorption of radiation is quantized and each quantum of radiation is called a photon.
- All types of radiations travel with the same velocity and no medium is required for their propagation. They can travel through vacuum.
- When visible light (a group of electromagnetic radiations) is passed through a prism it is split up into seven colours which correspond to definite wavelengths. This phenomenon is called as dispersion. Thus, a group of electromagnetic radiations can be split up into various components for analysis.

The energy changes within a molecule during absorption and emission of electromagnetic radiation are quantized. The energy changes in a molecule are specified using the terms of frequency, wavelength and wavenumber which are explained below.

A. Wavelength :

It is the distance between the two adjacent crests or troughs in a particular wave. It is denoted by the letter λ (lambda). It can be expressed in angstrom units (\AA°) or millimicrons (μm).

$$1 \text{\AA}^\circ = 10^{-8} \text{ cm}; \quad 1 \mu\text{m} = 10^{-7} \text{ cm}$$

Visible light constitutes waves ranging from 3800 \AA° (violet end) to 7600 \AA° (red end). Different colors of light have different values of their wavelengths. Human eye is sensitive only to this small visible range and fails to detect ultraviolet light ($\lambda < 3800 \text{ \AA}^\circ$) and infra-red radiations ($\lambda > 7600 \text{ \AA}^\circ$). Amplitude refers to the maximum height to which the wave oscillates and equals the height of the crest or depths of the troughs. It is measure of the radiant power of the radiation.

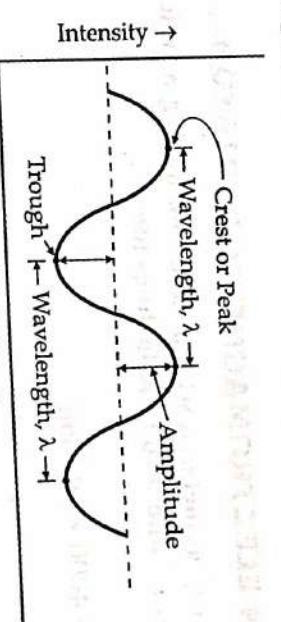


Fig. 1.2 : Illustration of wavelength and amplitude of a wave

B. Frequency :

It is defined as the number of waves which can pass through a point in one second. It is expressed as v (nu) in cycles per second or in Hertz (Hz) where $1\text{Hz} = 1$ cycle sec $^{-1}$.

$$\text{Frequency } \propto \frac{1}{\text{Wavelength}}$$

Greater the wavelength, smaller is the frequency.

$$\text{Frequency } v = \frac{c}{\lambda}$$

where c = Velocity of electromagnetic radiation

C. Wave number :

The number of waves that exist over a specific distance (unit length) is called wave number. It is expressed as \bar{v} . It is the reciprocal of wave length and is expressed per cm. It is frequently used in infra-red technique. If the wavelength of a given radiation is known, the corresponding wave number can be calculated.

$$\bar{v} = \frac{1}{\lambda}$$

D. Energy :

Energy of a wave of the particular radiation can also be calculated by the relation,

$$E = h\nu = h \cdot \frac{c}{\lambda}$$

- h = Plank's constant = 6.626×10^{-27} erg sec
 v = Frequency of radiation in cycles sec⁻¹
 c = Velocity of electromagnetic radiation
 λ = Wavelength in centimeters
- When the frequency is high, energy is higher and wavelength is smaller. When the wavelength is large, energy is lower.

NUMERICAL ON ELECTROMAGNETIC RADIATION

1. Calculate the energy associated with a radiation having wavelength 4000 Å° , Given answer in kcal mole⁻¹ and also in Kilo Jules mole⁻¹.

Solution :

$$\lambda = 4000 \text{ Å}^{\circ} = 4000 \times 10^{-8} \text{ cm}$$

$$E = h \cdot \frac{c}{\lambda}$$

$$= \frac{(6.628 \times 10^{-34}) \times (2.998 \times 10^{10})}{(4000 \times 10^{-8})}$$

$$= 4.968 \times 10^{-12} \text{ ergs}$$

$$= 4.968 \times 10^{-12} \times 6.023 \times 10^{23}$$

$$= 4.18 \times 10^{10}$$

$$= 71.6 \text{ kcal s mole}^{-1}$$

Also 1 kcal = 4,184 kJ

$$; E = 71.6 \times 4,184 = 299.5 \text{ kJ mole}^{-1}$$

Ans. : $E = 71.6 \text{ kcal s mole}^{-1}$

$$E = 299.5 \text{ kJ mole}^{-1}$$

2. The energy for a quantum of light is $4.97 \times 10^{-19} \text{ J}$. What is the wavelength and frequency of this light?

Solution :

$$E = 4.97 \times 10^{-19} \text{ J}$$

$$E = h \cdot \frac{c}{\lambda}$$

$$; \lambda = h \cdot \frac{c}{E}$$

$$= \frac{(6.62 \times 10^{-34}) \times (3 \times 10^8)}{(4.97 \times 10^{-19})}$$

$$= 3.99 \times 10^{-7} \text{ m}$$

3. Calculate the energy of green light of wavelength $535 \times 10^{-9} \text{ m}$.

Solution :

$$\lambda = 535 \times 10^{-9} \text{ m}$$

$$E = h \cdot \frac{c}{\lambda}$$

$$= \frac{(6.625 \times 10^{-34}) \times (3 \times 10^8)}{(535 \times 10^{-9})}$$

$$= 3.71 \times 10^{-19} \text{ J}$$

Ans. : $E = 3.71 \times 10^{-19} \text{ J}$

1.3 ELECTROMAGNETIC SPECTRUM

Many types of electromagnetic radiations extending from cosmic rays to radio waves are a part of an electromagnetic spectrum. It consists of an ordered organization of the different radiations according to their wavelengths and frequencies. This complete electromagnetic spectrum is shown in the Fig. 1.3.

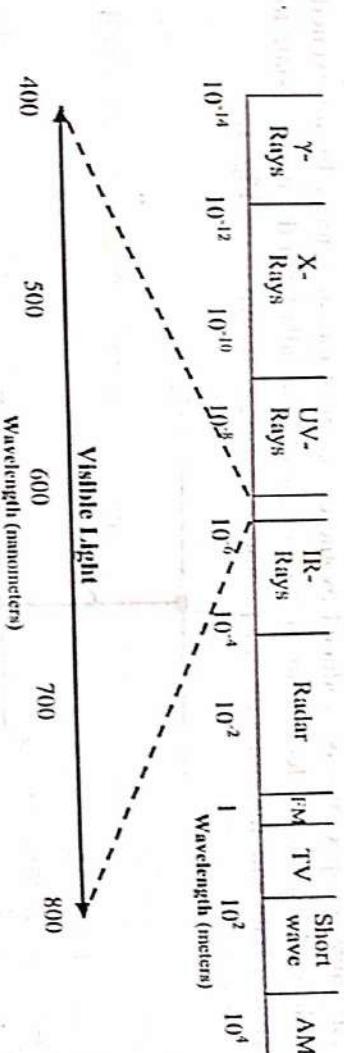


Fig. 1.3 : Various regions of electromagnetic spectrum

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The visible region is a very small part of the entire electromagnetic spectrum which range from 400 nm (Violet) to 800 nm (Red). Wavelength slightly shorter than those of visible fall into ultraviolet region.

1.4 PRINCIPLES OF SPECTROSCOPY

Spectroscopy is the analysis of the electromagnetic radiation scattered, absorbed or emitted by the molecules. It deals with the absorption of suitable radiations. Molecules are of so small dimensions that it is not possible to see them. Our knowledge of molecular structure is indirectly derived from spectroscopy.

Consider two energy levels of an atom/molecule. The energy level with lower energy is ground state energy level (E_g) and the one with higher energy is excited state energy level (E_e).

If electromagnetic radiations are passed through a substance then radiations of certain wavelengths are absorbed by the substance. The dark pattern of lines which correspond to the wavelength absorbed is called the absorption spectrum. It results when an atom or molecule undergoes a transition from lower energy level to higher one with the absorption of a photon of energy, provided this energy is equal to the energy difference between two energy levels as shown in Fig. 1.4.

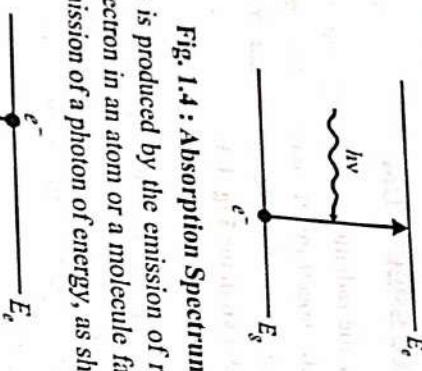


Fig. 1.4 : Absorption Spectrum

An emission spectrum is produced by the emission of radiant energy by an excited atom. It results when an electron in an atom or a molecule falls from the excited state to the ground state with the emission of a photon of energy, as shown in the Fig. 1.5.

The diagram shows a horizontal line with two points: E_g (ground state) and E_e (excited state). An upward-pointing arrow between these two levels is labeled $h\nu$, representing the energy of a photon. A wavy line above the E_e level represents the incident radiation. A downward-pointing arrow between the E_e and E_g levels is also labeled $h\nu$, representing the emitted radiation.

1.5 TYPES OF SPECTROSCOPY

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Based on the type of interaction, there are three types of spectroscopy.

(1) **Absorption spectroscopy** : Absorption spectroscopy uses the range of electromagnetic spectrum in which a substance absorbs. It is kind of spectroscopy in which absorption of radiation is observed as function of wavelength. In this, the sample is atomized and then light of particular frequency is passed through the vapour. After calibration, the amount of absorption can be related to the concentrations various metal ions through the Beer-Lambert law. This automated method is widely used to measure concentrations of ions such as sodium and calcium in blood. Other types of spectroscopy may not require sample atomization. e.g. Ultra-violet absorption spectroscopy is performed on liquid samples to detect molecular content and infrared spectroscopy is performed on liquid, semi-liquid, dried or solid samples to determine molecular information.

(2) **Emission spectroscopy** : Emission spectroscopy uses the range of electromagnetic spectra in which a substance radiates. This is the kind of spectroscopy in which emission of radiation is observed as function of wavelength. Emission spectra are of three types Line spectrum, band spectrum and continuum spectrum. Emission from excited atoms leads to sharp, well defined peak in the line spectrum. Small molecules and radicles after heating lead to emission of overlapping lines resulting into a band spectrum. Continuous spectrum is the type of spectrum observed from Sun or stars or hot solids in which radiation is distributed over all frequencies.

(3) **Scattering spectroscopy** : This spectroscopy is based on scattering phenomenon. There are two types of scattering spectroscopy, elastic and inelastic. Whenever wavelength of scattered light is same as that of incident light is called elastic scattering. Scattering where wavelength of scattered light is different from that of incident light is called inelastic scattering. One of the most useful applications of scattering spectroscopy is Raman spectroscopy. Diffraction is a special case of scattering spectroscopy. Scattering spectroscopy differs from emission spectroscopy due to the fact that the scattering process is much faster than the absorption/emission process.

1.6 SELECTION RULES

The probability of transition between two given energy levels is determined by selection rules. They specify the changes in the quantum number accompanying a particular transition. They are obtained from the quantum theory of interaction of radiation with matter.

The selection rules of the electronic transition are as follows.

- **Spin selection rule :** There should not be any change in spin orientation during the transitions. The $S \rightarrow S$, $T \rightarrow T$ transitions are allowed, but the $S \rightarrow T$, $T \rightarrow S$ are not allowed. (S stands for singlet * state of electron and T for triplet* state of electron).
- **Symmetry rule :** The product of two electric dipole vectors and the group theoretical representation of the two states are symmetric.

- **Angular momentum rule :** The change in angular momentum must be within one unit (0 or ± 1).

On the basis of selection rules, transitions can be categorized as,

- (i) **Allowed transitions:** They are spectral transitions which obey selection rules. They are stronger and more intense. They yield spectral lines with greater intensity than the forbidden ones.
- (ii) **Forbidden Transitions :** They are spectral transitions which do not obey the selection rules. They are weak and less intense. They yield spectral lines which have less intensity than the forbidden ones.

1.7 APPLICATIONS OF MOLECULAR SPECTROSCOPY

Applications of molecular spectroscopy are as follows.

- It is used in structural investigation. Electronic energy levels, bond lengths, bond angles and strength of bonds can be determined with the help of molecular spectroscopy.
- It can be used to monitor changing concentrations of reactants or products in kinetic studies.
- It helps to understand the colour in the world around us.
- Emission spectroscopy is used for the study of energetically excited reaction products.

1.8 TYPES OF MOLECULAR ENERGIES

Apart from the translational energy which is not of concern in molecular

- vibrational and electronic energies.

1.9 TYPES OF MOLECULAR SPECTROSCOPY

The different groups of frequency comprising the electromagnetic radiation lead to transition between different kinds of energy levels (nuclear, electronic, rotational...).

They differ in the way they interact with molecules and gives rise to different kinds of spectroscopy as shown in the Table 1.1.

1. **Rotational energy :**
It is associated with rotational motion of the molecule as a whole. According to the classical theory, the value of rotational energy is given by

$$E_{\text{rot}} = \frac{1}{2} I \omega^2$$

Where I = moment of inertia and ω = angular velocity of the rotating molecule.

The non-linear molecule can rotate about the three axes that pass through the center of gravity of the molecule and the axes are mutually perpendicular. These molecules have three degrees of freedom. The linear molecules have only two rotational degrees of freedom.

2. Vibrational energy :

The energy components associated with the vibration of the constituent atoms in the molecule is called vibrational energy. The energy of each vibrational level may be expressed as

$$E_{\text{vib}} = h\nu_0 \left(v + \frac{1}{2} \right); \text{ for } v = 0, 1, 2, 3, \dots$$

Where ν_0 is defined as a zero-point vibrational frequency and v represents the vibrational quantum number.

When a molecule is set into vibration, there are two types of fundamental vibrations: stretching and bending vibrations. Various stretching and bending vibrations of a bond occur at certain quantized frequencies. When radiation of that frequency is incident on the molecule, energy is absorbed and the amplitude of the vibration is increased.

3. Electronic energy :

Electronic energy is associated with the motion of electrons while considering the nuclei of atoms in a molecule as fixed points. The increase in the electronic energy of a molecule is due to the increase in the kinetic and potential energies of the electrons in the molecule.

Table 1.1 : Types of spectroscopy				
Type	Nature of Transition	Energy Range	Frequency Range	Wavelength Range
γ -ray	Nuclear	10-12 GJ/mol	30 EH-300EH	1000 pm to 10 pm
X-ray	Inner electronic	10-100 MJ/mol	30PHz-30EH	10 pm to 10 nm
UV	Outer electronic	300-1000 KJ/mol	800THz-30THz	10 nm to 380 nm
Visible	Outer electronic	100-300 KJ/mol	400THz-800THz	380 nm to 750 nm
Infrared	Vibration, Rotation	10^3 - 10^5 J/mol	300GHz-400GHz	750 nm to 1mm
Microwave	Rotation	10^1 - 10^3 J/mol	300MHz-300GHz	1 mm to 100 mm
Radiofrequency	Nuclear spin	10^{-3} - 10^1 J/mol	1-1000MHz	10 m to 1 cm

Hz, PHz, THz, GHz and MHz stand for exahertz, petahertz, terahertz, gigahertz, and megahertz respectively.

- The microwave spectroscopy :** A polar molecule like HCl has a permanent dipole moment. On rotating the molecule about its center of gravity, the positive and negative charges change places periodically. As a result of interaction between fluctuating dipole and radiation, energy may be emitted or absorbed. Rotation of polar molecule gives rise to spectrum in the microwave region.
- Infrared spectroscopy :** The quantized absorption of infrared radiation leads to vibrational transition of the molecules. The absorption bands in this region correspond to fundamental vibrational frequencies of molecules, interspersed with the substantially weaker overtones and combinations involving lower frequency fundamentals.
- The visible and ultraviolet spectroscopy :** In this region, valence electrons get excited and move from one energy level to another in the molecule. These electronic changes in the molecule causes change in the electric dipole which interacts with the electric field of the electromagnetic radiation. The interaction gives rise to the spectrum in the UV-visible region.
- Nuclear magnetic resonance (NMR) spectroscopy :** Nuclear magnetic resonance spectroscopy is concerned with the study of interaction of energy with spin-active nuclei. Spin active nuclei have permanent magnetic moments and quantized nuclear spin states. The number of spin states for a given nucleus is given by expression $(2I + 1)$, where I is the overall nuclear spin of that nucleus. Nuclear magnetic

resonance spectroscopy measures the energy necessary to bring about transitions between these energy levels by subjecting the nuclei to a powerful magnetic field and simultaneously irradiating it with a radiofrequency source.

1.10 REVIEW QUESTIONS

- What are the advantages of spectroscopic techniques over the classical techniques?
Ans. Refer Section 1.1.
- Explain the terms wavelength, wavenumber, frequency and energy.
Ans. Refer Section 1.2.
- Calculate the energy associated with a radiation having wavelength 5000 Å.
Ans. 3.973×10^{-12} ergs.
- The energy for a quantum of light is 3.82×10^{-19} J. What is the wavelength and frequency of this light?
Ans. $\lambda = 5.199 \times 10^{-7}$ m, $\nu = 5.77 \times 10^{14}$ Hz.
- Calculate the energy of a light of wavelength 343×10^{-9} m.
Ans. $E = 5.79 \times 10^{-19}$ J.
- Write an informative note on types of spectroscopy.
Ans. Refer Section 1.5.
- Explain in short absorption spectroscopy.
Ans. Refer Section 1.5.
- Write a short note on (i) Emission Spectroscopy (ii) Scattering Spectroscopy.
Ans. Refer Section 1.6.
- Give the characteristics of electromagnetic radiation.
Ans. Refer Section 1.2.
- Write an informative note on selection rules.
Ans. Refer Section 1.6.
- Explain the different types of molecular spectroscopy.
Ans. Refer Section 1.9.
- Explain the different types of molecular energies.
Ans. Refer Section 1.8.
- Write a note on electromagnetic spectrum.
Ans. Refer Section 1.3.

APPLICATIONS OF SPECTROSCOPY

SYLLABUS

- Emission spectroscopy- Principle, Instrumentation and applications (Flame Photometry)
- Introduction to fluorescence and phosphorescence, Jablonski diagram, application of fluorescence in medicine only.

2.1 INTRODUCTION OF FLAME PHOTOMETRY

Flame photometry is an emission spectroscopic method. In this method, a flame is used as the excitation source and an electronic photodetector is used as the measuring device. It is a sensitive method for quantitative analysis of alkali and alkaline earth metals.

2.2 THEORY OF FLAME PHOTOMETRY

Principle:

Characteristic colour imparted to the flame by the emission of radiation from the alkali metals excited in flame is the basis of flame photometry.

Theory:

If a solution containing metallic salt is introduced into a flame, a vapour containing the atom of the metal is formed. Some of these gaseous atoms may be excited to a higher energy level. When they return to the ground state, the excited atoms emit radiation characteristic of the element. The emitted radiation is passed through a monochromator and the spectrum is registered by a photodetector. The intensity of the emitted radiation is proportional to the concentration of the element. This forms the basis of quantitative analysis. The stages involved are shown in the Fig. 2.1.

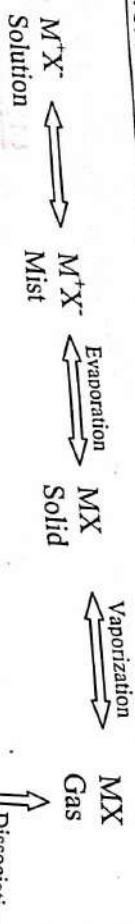


Fig. 2.1 : Stages involved in flame photometry

2.3 INSTRUMENTATION OF FLAME PHOTOMETRY

The essential components of Flame photometer are,

1. Pressure regulators and flow meters for the fuel and oxidant gases :

Whenever the flame photometer is operated, a constant thermal environment and uniform spray should be maintained. The gas pressure and gas flows should be maintained at the same level. The fuel to be used is usually contained in a cylinder under pressure. The oxidant, air may be directly used from a compressor. A diaphragm pressure regulatory valve is used to obtain a constant flow.

2. Nebulizer and burner assembly :

This system converts salt in the solution to atomic vapour. Nebulizer produces a mist or aerosol of the test solution by drawing the solution through a capillary tube using a jet of air at high pressure. The fuel, air and the solution (aerosol) are passed through channels to an opening on which the flame is produced. A burner is used as the flame source to provide the energy for excitation of electrons. The flame is maintained at a constant temperature. The flame temperature depends on the proportion of oxidant and fuel. Generally, oxidants such as air, oxygen or nitrous oxide are used. A propane-air flame is used for metals which easily get converted into atomic vapour state. In case of high temperature requirements, acetylene-air or acetylene-nitrous oxide mixtures are used.

3. Optical system :

The function of the optical system is to select a given line in the emission spectrum and isolate it from the rest. It comprises of three parts.

Convex mirror : It transmits the emitted light and focuses it to the lens.

Convex lens : It helps to focus the emitted light on to a point called slit.

Colour filters : After passing through the slit, colour filters isolate the wavelength of interest from rest of the irrelevant emissions. Filters are sufficient when a simple spectrum is obtained in the visible region as in the case of alkali metals.

A prism or a grating monochromator may also be used for more accurate results.

4. Detectors :

It detects the intensity of emitted radiations which are then converted into electric signals. Many filter flame photometers use photovoltaic cell for detecting the radiation characteristic of the test metal. A photomultiplier is the best detector in the range of 200-750 nm. A red-sensitive phototube should be used, for longer wavelength.

5. Amplifier and readout system :

Output from the photodetector is amplified and measured on a digital readout system. A schematic diagram of flame photometry is shown in the Fig. 2.2.

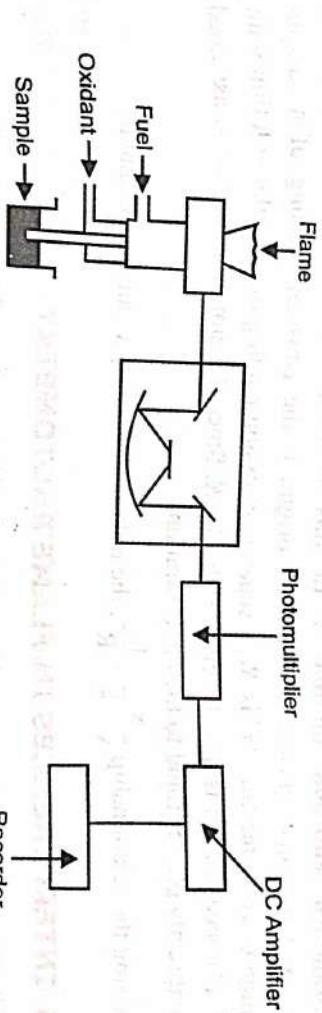


Fig. 2.2 : Schematic diagram of a flame photometer

2.4 WORKING OF FLAME PHOTOMETER

- The sample solution is dried where sample particles are dehydrated using flame (desolvation).
- The solvent is evaporated completely from the sample solution leaving behind solid particles (vaporization).
- The solid particles are introduced in the flame, leading to the formation of gaseous molecules which undergo thermal dissociation and finally form gaseous atoms or ions (atomization).
- These atoms or ions at the ground state absorb energy from the flame and are excited to a higher energy state (excitation).
- These unstable atoms or ions return to the ground state by emitting photons of characteristic wavelength (emission).

- These radiations are focused on monochromator where it selects only the radiations characteristic of the sample.
- Selected radiation is allowed to fall on a photocell, and its output is measured by a galvanometer.
- Concentration of unknown solution can be found out either by 'calibration curve method' or 'standard addition method'.

Two types of methods are used for quantitative estimation in flame photometry.

- Calibration curve method :** In this method, a calibration curve of 'emission intensity v/s concentration' of the element is drawn. The emission intensity is expressed in arbitrary units. This curve is linear over a small concentration range. Once the intensity of emission for a solution is known, its concentration can be found out from the calibration curve.

Standard addition method : In this method, the 'emission intensity v/s concentration' curve passes through the origin. If the emission reading of a sample solution of concentration 'x' is R_x , a separate emission reading of a similar solution with 'x + k' concentration is also taken. Let this be R. Since the emission reading is assumed to be directly proportional to the concentration,

Using the relationship $\frac{x}{x+k} = \frac{R_x}{R}$, the unknown quantity x can be calculated.

2.6 INTERFERENCES IN FLAME PHOTOMETRY

The major factors known to interfere in the determination of concentration of a given element are as follows.

Spectral Interference : This type of interference is caused due to some other elements present in the sample emitting radiations with nearly the same wavelength as the element whose concentration is being measured. For example, europium is found to interfere in the estimation of copper and mercury in the estimation of cobalt. By improving the resolution of the instrument, the spectral interference can be minimized.

Chemical Interference : The chemical compounds such as oxides and hydroxides formed in the flame decrease the population of free metal atoms, thereby decreasing the effective concentration of free metal ions. Since many compounds dissociate at higher temperatures, this problem can be minimized, by using as hotter flames as practicable. For example, the presence of phosphates interferes in the estimation of calcium.

2.7 APPLICATIONS OF FLAME PHOTOMETRY

- It is primarily used for the analysis of those elements which have an easily excited flame spectrum of sufficient intensity for detection of photocell. For example, for the analysis of sodium, potassium, calcium and lithium.
- It is extensively used in the analysis of biological fluids and tissues.
- It is used in agriculture field for the analysis of water, soil and plant products.
- The flame test analysis of soil sample helps in choosing an appropriate fertilizer for soil cultivation.

- It is used in medical field for the testing of urine and blood samples.
- It is used in industries for the detection of elements in fuel, glass, cement, metallurgical samples etc.
- It is used for analysis of soft drinks, fruit juices and alcoholic beverages.

2.8 ADVANTAGES & DISADVANTAGES OF FLAME PHOTOMETRY

Advantages :

1. It is very easy and simple analytical technique.
2. It has low operating cost and maintenance cost.
3. It is reliable and convenient technique for the determination of alkali and alkaline earth metals.
4. It is sensitive to wide range of concentration, parts per million (ppm) to parts per billion (ppb).

Disadvantages:

1. It cannot be used for measurement of metals in solution.
2. It cannot be used to analyze the solutions with higher concentrations.
3. It cannot be used to detect non-metals such as carbon and halides.
4. It cannot be used for the analysis of those metals which have tendency for incomplete vaporization.
5. A standard solution with known concentration is required to analyze the emission results.

2.9 JABLONSKI DIAGRAM

Aleksander Jablonski in 1935 suggested the famous diagram, which makes it possible to explain both the kinetics and spectra of fluorescence and phosphorescence.

Once a molecule has absorbed the energy in the form of electromagnetic radiations it goes to higher energy level (excited state) from ground state. The electron of the absorbing molecule may jump from S_0 (singlet ground state) to S_1 or S_2 or S_3 (singlet excited state) depending upon the energy of light photon absorbed. For each singlet excited state (S_1 , S_2 , S_3), there is a corresponding triplet excited state (T_1 , T_2 , T_3). The activated molecule returns to the ground state by dissipating its energy through the following processes.

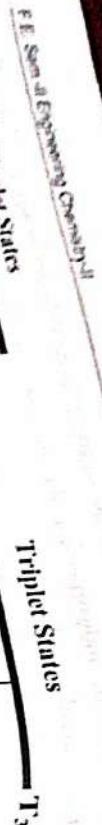


Fig. 2.3 : Jablonski Diagram

Near-radioactive transitions : These transitions are from the higher excited state (S_2 , S_1 , or T_1 , T_2) to the first excited state (S_1 or T_1) which doesn't involve emission of any radiation. This happens through any of the following processes.

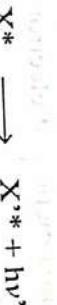
- Internal conversion (IC) :** In this process, the energy of the activated molecule is dissipated through molecular collisions in the form of heat. It occurs in less than 10^{-14} s.
- Intersystem crossing (ISC) :** In this process, the energy of the activated molecule is dissipated through transitions between states of different spins (for example S_2 to T_1 or S_1 to T_1). Such transitions are spectroscopically forbidden. But they do occur at slow rate.
- Vibrational relaxation :** It is the most common transition experienced by the excited molecule with other particles, with which energy (in the form of vibrations and rotations) can be transferred through collisions.

Radiative transition : In these transitions, the activated molecule returns from the singlet excited state (S_1) and triplet excited state (T_1) to the singlet ground state (S_0) which involves the emission of radiation. There are two types of radiative transitions.

- Fluorescence :** When a molecule in the (S_1) state returns to the ground state (S_0), emission of radiation occurs in about 10^{-8} s. This process is known as fluorescence.
- Phosphorescence :** When a molecule in the (T_1) state returns to the ground state (S_0), emission of radiation occurs at a slow rate. This process is known as phosphorescence. Such transitions are spectroscopically forbidden, and hence, its life time is much longer (10^{-3} s or more). It can occur only when the intersystem crossing (T_1 to S_0) does not happen rapidly.

2.10 INTRODUCTION TO FLUORESCENCE

The process in which certain substances when exposed to light radiation of short wavelength (high frequency) emit light of different frequencies compared to that of incident radiation is called fluorescence. It stops when the incident radiation is cut-off. The decay period is very short. When the light is absorbed by a fluorescent substance, the excited state of an atom emits light radiations in several transitions. The emitted light has different frequency for each transition.



Where X^{**} denotes the energy state between X and X^* . The incident and emitted radiation frequencies are different. Fluorescence is a secondary effect that results from the primary process of absorption of a quantum of light by the substance. The emitted radiations are of greater wavelengths than the exciting radiations. After absorbing the light radiations, the electrons are raised to higher energy levels and then they return to the original level in steps. These jumps possess lesser energy than the original jump. Thus the emitted light has lower frequency than the light absorbed.

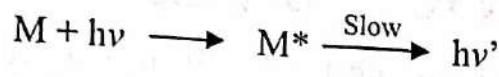
The substance which exhibits fluorescence is called fluorescent substance. They are chemical compounds which spontaneously give an illuminating effect influenced by visible or ultraviolet light, that is, when substances absorb incident light. They are typically non-volatile organic compounds. Some of the examples of fluorescent substances are petroleum, chlorophyll, uranium, calcium fluoride, biphenyl, naphthalene vapours of iodine, sodium and mercury. It is generally, seen in solid substances.

2.11 INTRODUCTION TO PHOSPHORESCENCE

The process in which, many substances when exposed to light radiation of short wavelength (high frequency) continue to emit light for some time (10^{-4} to few seconds).

even after the incident light is cut off is called phosphorescence. Depending on the material, temperature and other factors, the afterglow may last from fraction of seconds to hours, or even days. Phosphorescence is mainly caused by ultraviolet and visible light.

When a molecule absorbs high energy radiation, it gets excited to higher energy states, and starts emitting light energy of longer wavelength while returning to the ground state. During the process of return, the excited molecule passes from one series of electronic states to another and gets trapped. It then emits light which persists even after the source of light is removed. Therefore, phosphorescence is also called as **delayed fluorescence**.



The substance which exhibits phosphorescence is called phosphorescent substance. They are generally solid substances. Some of the examples of phosphorescent substances are zinc sulphide, calcium sulphide, barium sulphide and strontium sulphide.

Comparison :

Fluorescence	Phosphorescence
It is the absorption of energy by atoms or molecules followed by immediate emission of light or electromagnetic radiation.	It is the absorption of energy by atoms or molecules followed by delayed emission of electromagnetic radiation.
The emission of radiation or light suddenly stops on removal of source of excitation.	The emission of radiation remains for some time even after the removal of source of excitation.
The excited atom has comparatively short life time before its transition to low energy state.	The excited atom has comparatively long life time before its transition to low energy state.
The emitted photon has lower energy than the absorbed photon and emission occurs at a longer wavelength than the incident light.	The emitted photon has lower energy than the absorbed photon and emission occurs at a longer wavelength than the fluorescence.
Fluorescent materials give an immediate flash or afterglow on excitation.	Phosphorescent appear to glow in the dark because of slow emission of light over time.
It is the radiation emitted in a transition between states of same multiplicity.	It is the radiation emitted in a transition between states of different multiplicity.
For example, calcium fluoride, sodium, iodine and mercury vapours.	For example, zinc sulphide, calcium sulphide, barium sulphide and strontium sulphide

2.12 APPLICATIONS OF FLUORESCENCE IN MEDICINES

Fluorescence has proven to be a versatile tool for a vast number of applications. It is a powerful technique for studying molecular interactions in analytical chemistry, biochemistry, cell biology, physiology, nephrology, cardiology, photo chemistry and environmental sciences. Some of the major applications in the field of medicine are discussed below.

1. **Laser induced fluorescence spectroscopy of human tissues for cancer diagnosis :** Laser induced fluorescence is used to diagnose cancer. A drug (haematoporphyrin derivative HpD) is systematically administered so that it is selectively retained by a tumor. When photo excited with light of appropriate wavelength, the drug localized in the tumor fluoresces. This fluorescence is used for detection and imaging of the tumor.
2. **Photodynamic therapy of tumor :** Photo excitation leads to colonization of the triplet state. The molecule in the excited triplet state can directly react with the biomolecules or lead to generation of singlet oxygen that is harmful to the host tissue. The resulting destruction of the host tissue is exploited for photodynamic therapy of tumor.
3. **Detection of glucose :** Glucose is a key constituent of plant and animal carbohydrates in a biological system. Blood glucose levels are an indicator of human health conditions. Abnormal amount of glucose gives significant information of many diseases such as diabetes or hypoglycemia. In recent years, bio-molecule-stabilized Au nanoclusters are used for sensitive and selective detection of glucose.

2.13 REVIEW QUESTIONS

1. Explain the theory of Flame photometry.

Ans. Refer Section 2.2.

2. Explain the instrumentation in flame photometer.

Ans. Refer Section 2.3.

3. Write an informative note on working of flame photometer.

Ans. Refer Section 2.4.

4. Give the applications of flame photometry.

Ans. Refer Section 2.7.

5. What are the advantages and disadvantages of the flame photometry?

Ans. Refer Section 2.8.

6. Write a note on fluorescence.

Ans. Refer Section 2.10.

GREEN CHEMISTRY AND SYNTHESIS OF DRUGS

SYLLABUS

- Introduction – Definition, significance
 - Twelve Principles of Green chemistry
 - Conventional and green synthesis of Adipic acid, Indigo, Carbaryl, Ibuprofen, Benzimidazole, Benzyl alcohol
 - Atom economy and their numericals
 - Green fuel- Biodiesel
-

5.1 INTRODUCTION

Green chemistry, also called sustainable chemistry, is a chemical philosophy encouraging the design of products and processes that reduce, recycle or eliminate the use and generation of hazardous substances by finding creative ways to minimize the human and environmental impact without stifling scientific progress. Whereas environmental chemistry is the chemistry of the natural environment, and of pollutant chemicals in nature, green chemistry seeks to reduce and prevent pollution at its source. In 1990 the Pollution Prevention Act was passed in the United States. This act helped in dealing with pollution in an original and innovative way.

Any ideal chemical synthesis should be simple, safe, efficient and environment friendly. In practice, it is impossible to achieve all these attributes simultaneously. In fact it is a challenge for chemists and engineers to identify environment friendly reactions pathways that optimize the balance of all the desirable attributes.

Chemical synthesis which takes into account environmental considerations in the selection of reactants and reaction conditions is growing in importance as both industrial

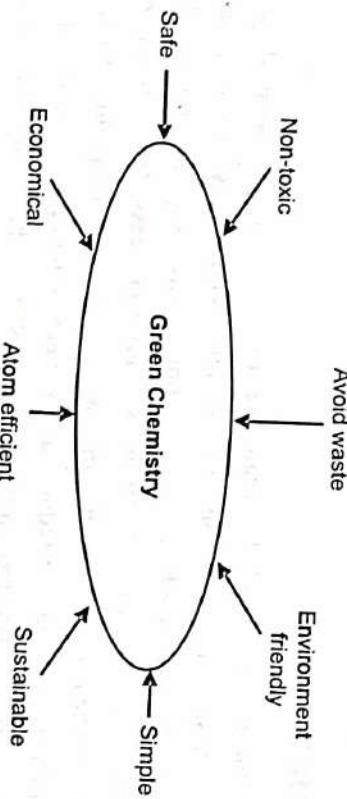
and academic researchers become aware of the environmental and economic advantages of an environmentally benign or "green" approach. The principles of a green approach are not covered in traditional chemistry courses, perhaps contributing to its slow growth as an area of academic research.

Finding creative ways to reduce hazard and waste has been the goal of many academic labs across the world. In recent history, the trend has been toward "microscale" methods; using smaller quantities of reactants to minimize the impact.

In contrast, green chemistry focuses on using less toxic reactants in the first place, thus reducing the need to use microscale methods. Students in a green chemistry lab can use quantities more typical of an industrial setting than their counterparts in a microscale lab.

As a chemical philosophy, green chemistry derives from organic chemistry, inorganic chemistry, biochemistry, analytical chemistry, even physical chemistry. However, the philosophy of green chemistry tends to focus on industrial applications. The focus is on minimizing the hazard and maximizing the efficiency of any chemical choice. Bioengineering is also seen as a promising technique for achieving green chemistry goals. It is distinct from environmental chemistry which focuses on chemical phenomena in the environment.

In a broad sense, green chemistry includes any chemical process or technology that improves the environment and thus our quality of life.



5.2 BASIC PRINCIPLES OF GREEN CHEMISTRY

Paul Anastas, then of the United States Environmental Protection Agency, and John C. Warner developed twelve principles of green chemistry, which help to explain what the definition means in practice. The principles cover such concepts as:

- Design the processes to maximize the amount of raw material that ends up in the product;

• Use of safe, environment-benign substances, including solvents, whenever possible;

• Design energy efficient processes;

• Do not create waste or the best form of disposal.

The basic principles of Green Chemistry are as follows:

1. Prevent waste : It is better to design chemical syntheses to prevent waste rather than leaving no waste to treat or clean up after it is formed.

In most of the cases, the cost involved in the treatment and disposal of wastes adds to the overall cost of the production. The unreacted starting materials also form part of the waste. The waste if discharged in the atmosphere, sea or land causes pollution and also requires expenditure for cleaning up.

2. Design safer chemicals and products : Fully effective chemical products should be designed with little or no toxicity.

It is very important that the synthesized chemical (dyes, paints, cosmetics, pharmaceuticals) should be safe to use. For example, a drug thalidomide was used for reducing the effects of nausea and vomiting during pregnancy. As the children born to women taking thalidomide suffered birth defects, the use of this drug was banned. Later strict regulations were passed for testing all new drugs. Now it is possible to design and produce safer chemicals with the help of advanced technology.

3. Design less hazardous chemical syntheses : Wherever practicable chemical syntheses should be designed to use and generate substances with little or no toxicity to humans and the environment.

One of the most important principle of green chemistry is to prevent or at least minimize the formation of hazardous product which may be toxic and/or environmentally harmful. In case hazardous products are formed, their effects on the workers must be minimized by the use of protective clothing etc.

The starting material selected should be least toxic e.g. use of carcinogenic compounds such as benzene, pyridine should be avoided. The reactions in which intermediates or reagents are toxic should not be followed.

4. Use renewable feedstock: Raw materials and feedstock should be renewable rather than depleting whenever technically and economically practicable.

The starting materials can be obtained from renewable or non-renewable materials. The materials obtained from agricultural or biological processes are referred to as renewable materials. Depleting feedstock are made from fossil fuels (petroleum, natural gas, or coal) or are mined.

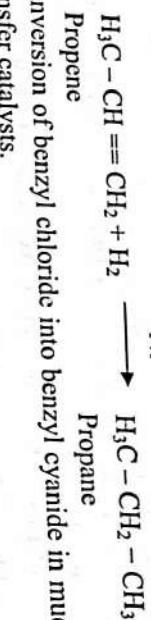
5. Use catalysts, not stoichiometric reagents: Minimize waste by using catalytic reactions.

Catalysts are used in small amounts and can carry out a single reaction many times. They are preferable to stoichiometric reagents, which are used in excess and work only

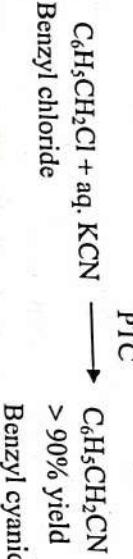
Once. Catalysts are selective in their action. By using catalyst both starting material utilization is enhanced and formation of waste is reduced. In stoichiometric processes product obtained is one mole for every mole of the reagent used. However a catalyst will carry out thousands of transformations before being exhausted. Catalytic reactions are faster and require less energy.

Some of the applications of the use of catalyst are as follows :

- Hydrogenation of olefins in presence of nickel catalyst gives much better yields.



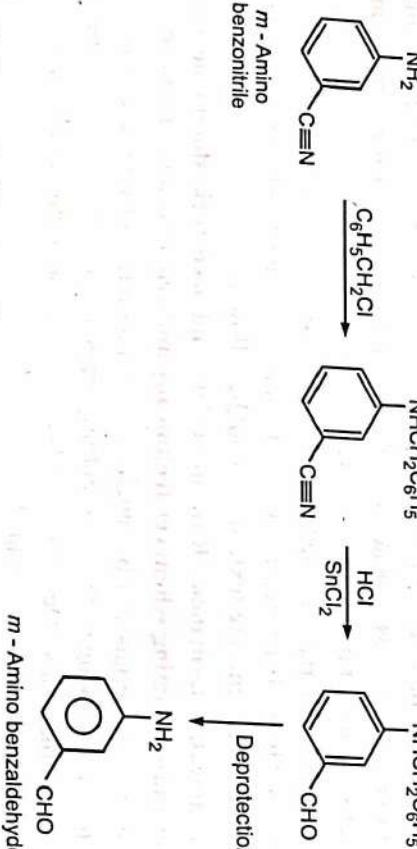
- Conversion of benzyl chloride into benzyl cyanide in much better yields using phase transfer catalysts.



Benzyl cyanide
> 90% yield

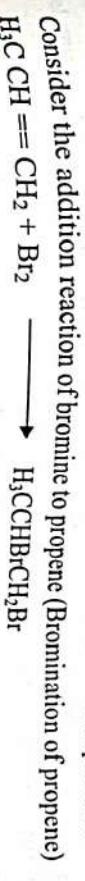
6. Avoid chemical derivatives : Avoid using blocking or protecting groups or any temporary modifications if possible.

A commonly used technique in organic synthesis is the use of protecting or blocking group. A typical example of this type of transformation is the protection of amine by reacting it with benzyl chloride. After the reaction is complete amino group can be regenerated as shown in the following reaction.



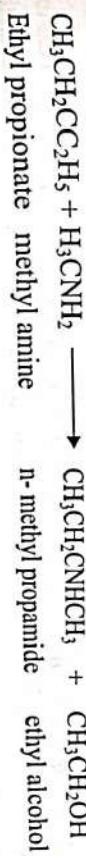
- Maximize atom economy:** Design syntheses so that the final product contains the maximum proportion of the starting materials.
- The percentage yield for any reaction is calculated by
- $$\% \text{ yield} = \frac{\text{Actual yield of the product}}{\text{Theoretical yield of the product}} \times 100$$
- From the calculations it is clear that if one mole of a starting material produces one mole of the product, the yield is 100%. Such a synthesis even though is 100% is not considered to be a green synthesis as it may generate significant amount of waste or byproducts which is not visible in the above calculation.
- A reaction or a synthesis is considered to be green if there is maximum incorporation of the starting materials or reagents in the final product. The percentage atom utilization, which is determined by the following equation.

$$\% \text{ atom utilization} = \frac{\text{MW of desired product}}{\text{MW of desired product} + \text{MW of waste products}} \times 100$$



In the above reaction all the elements of the reactants are incorporated into the final product. So this reaction is 100% atom economical reaction.

Consider the substitution reaction of ethyl propionate with methyl amine.



In the above reaction the leaving group (OC_2H_5) and one hydrogen atom of the amine is not incorporated in the product. This reaction is not 100% atom economical reaction.

- The use of auxiliary substances (solvents, separation agents, etc.) should be made unnecessary whenever possible and, when used, innocuous.

A number of solvents like methylene chloride, chloroform, carbon tetrachloride, benzene and other aromatic hydrocarbons which are suspected human carcinogens have been used in many reactions due to their excellent solvent properties. The solvent selected for a particular reaction should not cause any environmental pollution and health hazard.

Derivatization of this type is common in the synthesis of fine chemicals, pharmaceuticals, pesticides and certain dyes. Benzyl chloride needs to be handled with care and then regenerated as waste. In this procedure as the protecting group is not incorporated into the final product, the reaction becomes less atom economical.

For example, chlorofluoro carbons (CFC) which have been used as cleaning agents, blowing agents and as refrigerants are found to be responsible for depleting the ozone layer having disastrous effect on human survival. 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.

As far as possible the pathway for the reaction should be such that there is no need for separation or purification.

9. Increase energy efficiency : Energy requirements of chemical processes should be recognized for their environmental and economic impacts.

In any chemical synthesis the requirement of energy should be kept to a minimum. The reactions in which the reaction mixture has to be heated to reflux for completing the reaction, the time required for completion of the reaction should be minimum, so that less amount of energy is required. Even the use of a catalyst lowers the requirement of energy of a reaction. If the final product obtained is impure, purification is carried out by distillation, recrystallisation or ultrafiltration. As it requires energy, the process should be designed in such a way that there is no need for separation or purification.

10. Design chemicals and products to degrade after use: Design chemical products to break down to innocuous substances after use so that they do not accumulate in the environment.

The problem of non-biodegradability is generally associated with pesticides, plastics and other organic molecules. Most of the pesticides are organo-halogen based compounds which generally tend to bioaccumulate in plants and animals. For example, the pesticide DDT.

The chemical with functional group which are susceptible to hydrolysis, photolysis have been used to ensure that products will undergo biodegradation. Care should be taken that the biodegradation products should not be toxic.

11. Analyze in real time to prevent pollution: Include in-process real-time monitoring and control during syntheses to minimize or eliminate the formation of hazardous substances.

Analytical methodologies and technology have been developed to allow the prevention and minimization of the generation of hazardous substances in chemical processes. Using various techniques, a chemical process can be monitored for generation of hazardous by products and side reactions. These procedures can prevent any accident which may occur in chemical plants.

12. Minimize the potential for accidents: Design chemicals and their forms (solid, liquid, or gas) to minimize the potential for chemical accidents including explosions, fires, and releases to the environment.

At times it is possible to increase accident potential in an attempt to minimize the generation of waste in order to prevent pollution. An attempt of recycling the solvents from a process usually increases the potential for a chemical accident.

BASIC IDEAS IN THE FIELD OF GREEN CHEMISTRY RESEARCH

The major research efforts in green chemistry may be broadly classified into the four areas which are inter-related and overlapping. They are as follows :

- (1) Alternative feedstock or starting materials.
- (2) Alternative reagents or transformations.
- (3) Alternative reaction conditions.
- (4) Alternative final products or target molecules.

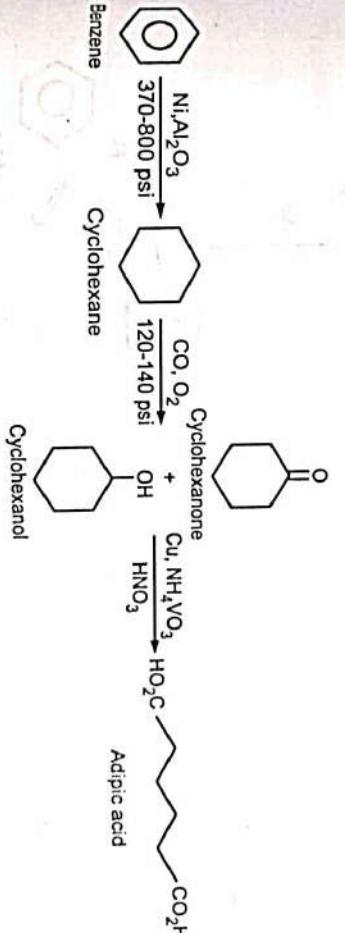
The intensity of the risk to human health and environment can be reduced by utilizing environmentally benign feedstocks. Different methods can be adopted as –

- (i) The amount of starting material used for the reaction can be reduced.
- (ii) By carrying out the structural modifications, intrinsic toxicity of starting material can be reduced.
- (iii) The starting material used for that particular reaction can be replaced.

Following examples are the economically viable solutions that are offered by Green Chemistry.

(A) SYNTHESIS OF ADIPIC ACID : For the manufacture of adipic acid, catechol and hydroquinone, initially the substrate used was benzene which is carcinogenic. The continuous use of benzene affects the human health.

The traditional synthetic pathway for the manufacture of adipic acid is given below.

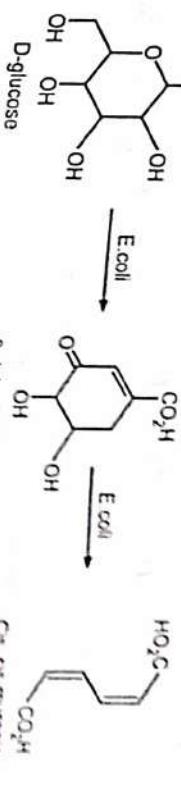


In the new synthetic pathway, traditionally used benzene is substituted by a new substrate glucose, a renewable feed stock. Being a non toxic substance glucose is absolutely safe to use as a substrate.

The alternative greener pathway is given below.

5.8

Green Chemistry and Synthesis of Drugs



(B) SYNTHESIS OF INDIGO :

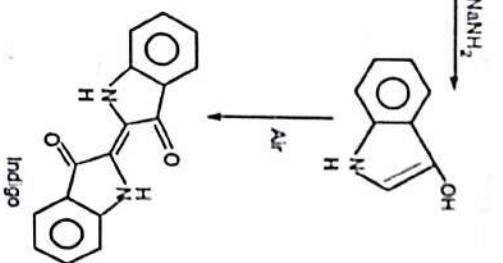
Indigo is the dye which is used to colour blue.

This conventional route makes use of aniline as a starting material.

(1) Use of highly toxic aniline.

(2) Generation of considerable amount of waste salts, thereby causing disposal problems.

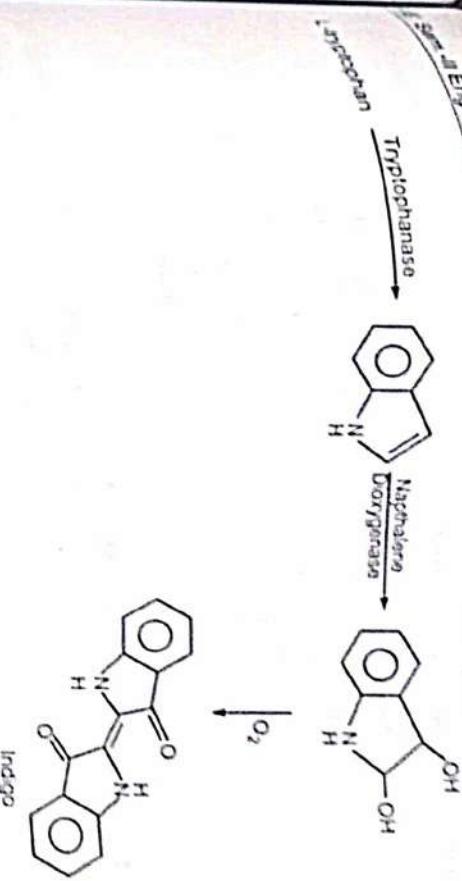
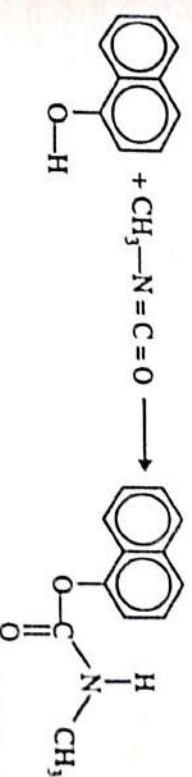
The conventional route for the production of indigo using hazardous aniline is given below.



(C) SYNTHESIS OF CARBARYL : The Union Carbide was manufacturing a pesticide called carbaryl (1-naphthyl-methyl carbamate). The traditional method involved 1-naphthol and methylisocyanate as reactants. Methylisocyanate is highly hazardous.

An alternative reaction pathway is suggested to minimize the use of hazardous materials. In this method 1-naphthol and phosgene are used as reactants to produce 1-naphthyl chloroformate. It is then treated with methyl amine to give carbaryl. This alternative process eliminates the formation of methylisocyanate which is highly hazardous.

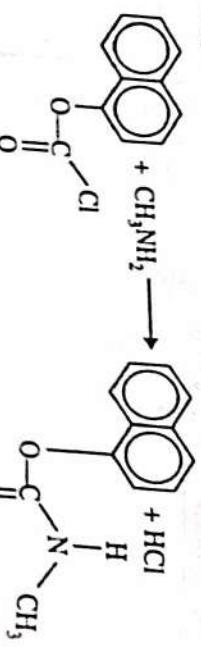
Traditional Synthesis of Carbaryl



The greener route makes use of the reaction in which the side chain of tryptophan is removed enzymatically to give indole. It can be dehydroxylated enzymatically and its oxidized with oxygen to indigo.

The conventional route makes use of the reaction in which the side chain of tryptophan is removed enzymatically to give indole. It can be dehydroxylated enzymatically and its oxidized with oxygen to indigo.

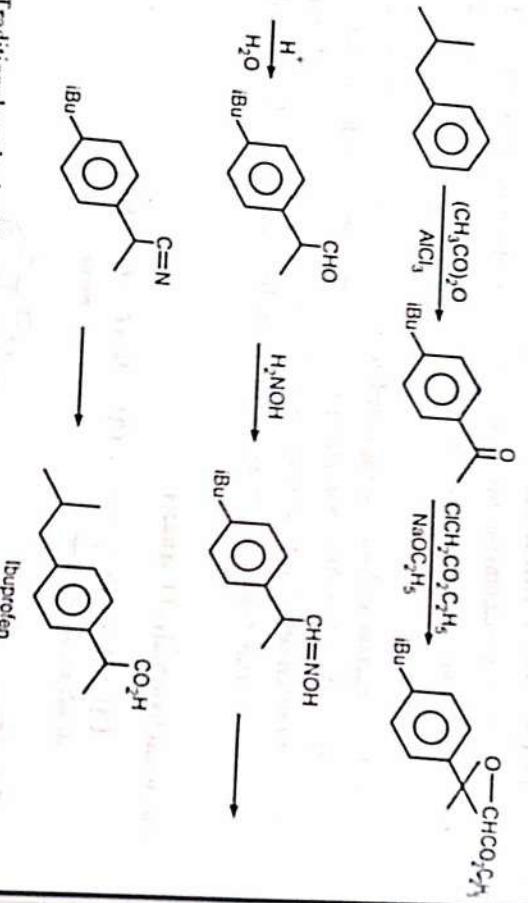
Alternate Synthesis of Carbaryl



(D) SYNTHESIS OF IBUPROFEN:

In the traditional pathway, ibuprofen is synthesized from isobutyl benzene. In a greener pathway, it is synthesized from the same substrate, but with recoverable acid as a catalyst and with minimum use of reagents.

Traditional synthesis of Ibuprofen

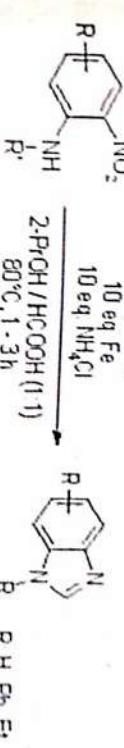


Alternative method with Atom Economy 77%.

(E) SYNTHESIS OF BENZIMIDAZOLE:

Benzimidazole is a heterocyclic aromatic organic compound consisting of fusion of benzene and imidazole. They are bioactive. Many of the anthelmintic drugs belong to the benzimidazole class of compounds. Benzimidazole fungicides are available in the market. They act by binding to the fungal microtubules and stop hyphal growth. It also resists nuclear division. Several dyes are derived from benzimidazole.

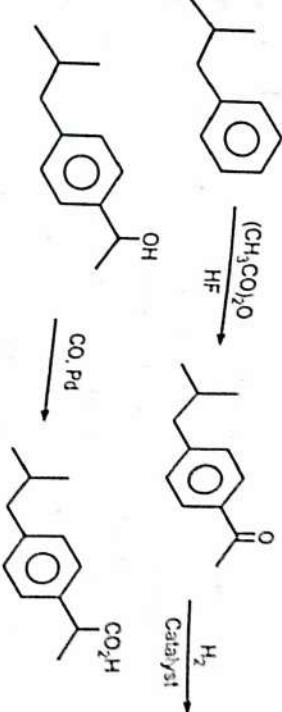
Traditional synthesis of Benzimidazole



Aromatic and heteroaromatic 2-nitroamines can be converted into bicyclic 2H-benzimidazoles. This synthesis employs formic acid, iron powder, and NH₄Cl as additives to reduce the nitro group, and effects the imidazole cyclization. This synthesis affords high-yield within one to two hours.

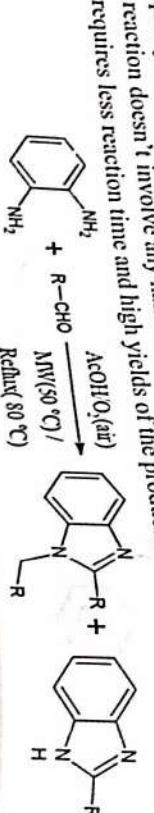
Green Synthesis of Benzimidazole:

- The benzimidazole ring system can be synthesized through a carbon-nitrogen cross-coupling reaction in the presence of K₂CO₃ in water at 100 °C for 30h. The intermolecular cyclization of N-(2-iodoaryl) benzamidine provides benzimidazole derivatives in moderate to high yields. The procedure occurs exclusively in water and doesn't require the use of any additional reagent/catalyst. The methodology is highly valuable from both environmental and economic points of view.



F.E. Sem.-II Engineering Chemistry-II
5.12
The green route occurs exclusively in water, and there is no need of any reagent or catalyst.

(ii) The benzimidazoles can also be synthesized by condensation of phenylenediamine with aldehydes promoted by acetic acid under microwave. This reaction doesn't involve any hazardous solvent. It is a mild and eco-friendly synthesis. It requires less reaction time and high yields of the products.



5.4 ATOM ECONOMY

Reaction efficiency and product selectivity are the important goals of any synthetic design. However, after achieving hundred percent selectivity to the desired product, a substantial quantity of waste can be regenerated if the synthetic transformation is not "atom economical". The concept of Atom Economy as developed by Barry Trost is a consideration of "how much of the atoms in the reactants end up in the final synthesis is, in which all of the atoms in the reactants are incorporated into the final product. In theory this reaction would not produce any waste byproducts. Atom economy indicates the intrinsic efficiency of the desired transformation.

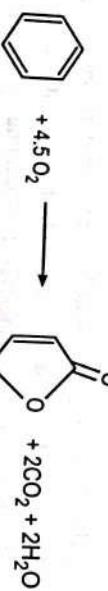
Atom Economy may be defined as the ratio of formula weight of target molecule to the formula weight all the starting materials and the reagents.

$$\text{Atom Economy} = \frac{\text{FW of atoms utilized}}{\text{FW of the reactants used in the reaction}} \times 100$$

NUMERICALS BASED ON ATOM ECONOMY:

1. Calculate percentage economy for the following reaction:

Synthesis of Maleic Anhydride by oxidation of benzene [May 08, 10, Dec. 2012]



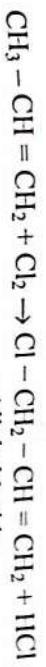
$$\text{Ans. \% Atom Economy} = 67.69\%$$

1. Calculate percentage economy for the following reaction:
Synthesis of Maleic Anhydride by oxidation of butane. [May 2009, Dec. 2000]



MW=78 MW=144 MW=98

1. Calculate the % Atom economy for the following reaction with respect to Allyl Chloride. [Dec. 2008, 2011, 2014, 2017, 2018, May 2019]



MW=42 MW=71 MW=76.5

$$\% \text{Atom Economy} = \frac{\text{MW of product}}{\text{Total MW of reactant}} \times 100$$

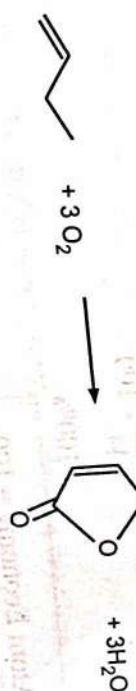
$$= \frac{76.5}{42+71} \times 100$$

$$= \frac{76.5}{113} \times 100$$

$$= 67.69\%$$

$$\text{Ans. \% Atom Economy} = 67.69\%$$

1. Calculate percentage economy for the following reaction:
Synthesis of Maleic Anhydride by oxidation of butane. [May 2009, Dec. 2000]



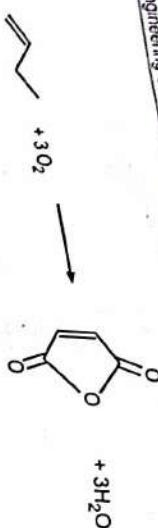
$$\% \text{Atom Economy} = \frac{\text{MW of product}}{\text{Total MW of reactant}} \times 100$$

$$= \frac{98}{78 + 144} \times 100$$

$$= \frac{98}{222} \times 100$$

$$= 44.1\%$$

$$\boxed{\text{Ans. \% Atom Economy} = 44.1}$$

Solution :

MW=56

MW=96

MW=98

$$\% \text{Atom Economy} = \frac{\text{MW of product}}{\text{Total MW of reactant}} \times 100$$

$$= \frac{98}{56 + 96} \times 100$$

$$= \frac{98}{152} \times 100$$

$$= 64.5\%$$

Ans. % Atom Economy = 64.5

4. Calculate the % Atom economy for the following reaction.**Solution :**

(i)



MW=42

MW=2

MW=44

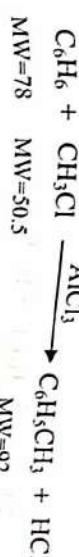
$$\% \text{Atom Economy} = \frac{\text{MW of product}}{\text{Total MW of reactant}} \times 100$$

$$= \frac{44}{42+2} \times 100$$

$$= \frac{44}{44} \times 100$$

$$= 100\%$$

Ans. % Atom Economy = 100



MW=78

MW=50.5

MW=92

$$\% \text{Atom Economy} = \frac{\text{MW of product}}{\text{Total MW of reactant}} \times 100$$

$$= \frac{92}{78 + 50.5} \times 100$$

$$= \frac{92}{128.5} \times 100$$

$$= 71.59\%$$

Ans. % Atom Economy = 71.59

5. Calculate the % Atom Economy for the following reaction with respect to acetanilide.**[May 2011]**

Acetanilide

Solution :

MW=93

MW=102

MW=135

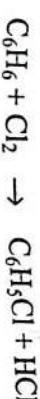
$$\% \text{Atom Economy} = \frac{\text{MW of product}}{\text{Total MW of reactant}} \times 100$$

$$= \frac{135}{93 + 102} \times 100$$

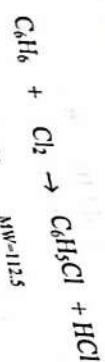
$$= \frac{135}{195} \times 100$$

$$= 69.23\%$$

Ans. % Atom Economy = 69.23

6. Calculate the % Atom Economy for the following reaction.**[May 2013]**

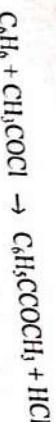
$$= \frac{57}{130} \times 100 = 43.84\%$$

Solution :

$$\% \text{ Atom Economy} = \frac{\text{MW of product}}{\text{Total MW of reactant}} \times 100$$

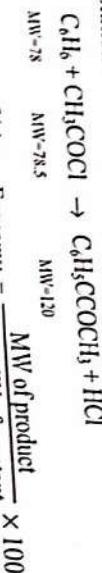
$$= \frac{112.5}{78+71} \times 100$$

$$= 75.5\%$$

Ans. % Atom Economy = 75.5**7. Calculate the % Atom Economy for the following reaction.****[Dec. 2013, 2016, May 2018]**

$$\% \text{ Atom Economy} = \frac{\text{MW of product}}{\text{Total MW of reactant}} \times 100$$

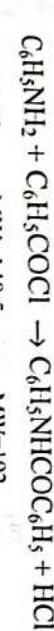
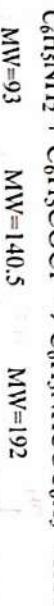
$$= \frac{132}{106+44} \times 100 = 88\%$$

Ans. % Atom Economy = 88**Solution :**

$$\% \text{ Atom Economy} = \frac{\text{MW of product}}{\text{Total MW of reactant}} \times 100$$

$$= \frac{120}{78+78.5} \times 100$$

$$= 76.67\%$$

Ans. % Atom Economy = 76.67**8. Calculate the % Atom Economy for the following reaction.****[May 2015, 2017]****10. Calculate the % Atom Economy for the following reaction wr.t. Benzanilide.****[May 2016]****Solution:**

$$\% \text{ Atom Economy} = \frac{\text{MW of product}}{\text{Total MW of reactant}} \times 100$$

$$= \frac{192}{93+140.5} \times 100$$

$$= \frac{192}{233.5} \times 100$$

$$= 82.23\%$$

Ans. % Atom Economy = 82.23

$$\% \text{ Atom Economy} = \frac{\text{MW of product}}{\text{Total MW of reactant}} \times 100$$

$$= \frac{57}{31+99} \times 100$$

5.5 INDUSTRIAL APPLICATIONS OF GREEN CHEMISTRY

Now-a-days the green chemistry is finding wider applications in the industrial processes as explained below :

[I] Green Fuel – Biodiesel :

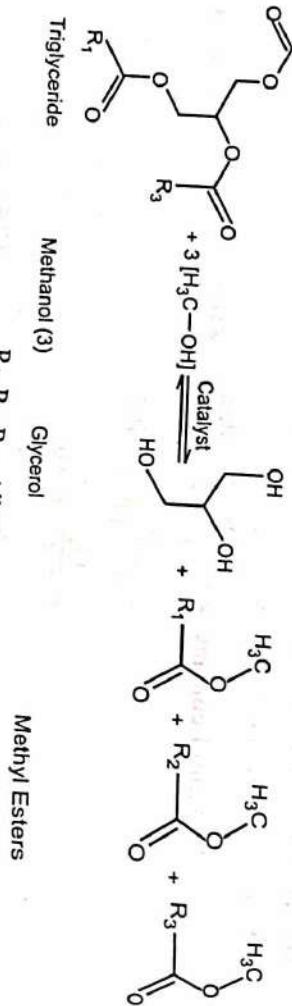
The conventional hydrocarbon based diesel fuels are fast depleting therefore there is need for alternative diesel fuels fulfilling the criteria of easy availability, economic viability, technical feasibility and environmental compatibility. On the basis of this, biodiesel derived from vegetable oils, petrocrops, cola, agricultural wastes are considered as alternative diesel fuels.

Bio-diesel is derived from vegetable oil which comprise of 90 - 98% triglycerides with small quantities of mono and diglycerides, free fatty acids, phospholipids, carotenes, sulphur compounds etc. Triglycerides are esters of long chain fatty acids such as stearic acid, palmitic acid, oleic acid, linoleic acid and linolenic acid.

Biodiesel Synthesis

Biodiesel can be obtained from various vegetable oils like soyabean oil, palm oil, groundnut oil, cotton seed oil, mustard oil, sunflower oil etc. and also from animal fats. It is obtained by transesterification of vegetable oil or animal fats with methyl alcohol using sodium metal or sodium methoxide as catalyst. Transesterification is the process of converting one ester to another ester.

Vegetable oil or fat is first filtered and then heated at 110°C with stirring to remove any water from it. Sodium methoxide and methanol is then added to it. The mixture is then heated for half an hour with stirring. The reaction mixture is then cooled and mixed with sufficient amount of water. The glycerol and soap gets dissolved in the water phase. Water insoluble phase (Biodiesel) is separated and antioxidant is added to it to avoid oxidation and polymerization.



The product is given the name 'Biodiesel' as it is obtained from biological products and it is biodegradable material or green fuel.

Advantages of Biodiesel

It is prepared from renewable resources.

It is biodegradable and non-toxic.

The exhaust gas emission (for example, CO, unburnt, hydrocarbons, particulate matter etc.) is lesser as compared to the conventional diesel fuel. Since the organic carbon present in biodiesel is photosynthetic in origin, it does not contribute to the rise in the level of environmental CO₂ and the consequent global warming.

It is free from sulphur and aromatics.

It is safer to handle and easy to manufacture.

It's cetane number is 46 to 52.

Like any other fuel, it can also be used as a heating fuel in domestic and commercial boilers.

[ii] Green solvents :

During the manufacture, processing, formulation and use of chemical products, a variety of associated substances such as the solvents used in reaction media, create the major problem of environmental pollution. The volatile organic solvents have their toxic contributions to air and water pollution. Hence, the R&D in green chemistry reaction conditions is focussed on alternative solvents.

Supercritical fluids, aqueous solvents, polymerized solvents, ionic liquids, solventless systems may be considered as substitutes for the traditional solvents.

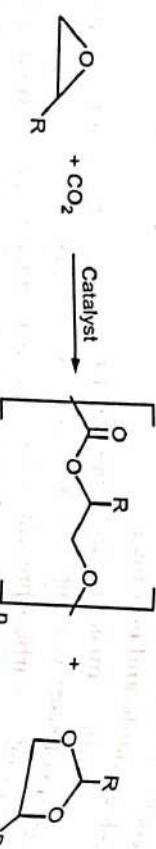
Super critical fluid (SCF) systems : Super critical fluids such as supercritical carbon dioxide and supercritical CO₂/ H₂O mixtures are under investigation for use. Supercritical CO₂ is a fluid state of carbon dioxide above its critical temperature 31.10°C and critical pressure 72.9 bar. It has following characteristics.

- It is readily available and naturally abundant.
- It is chemically stable.
- It is non-toxic, non-flammable and inexpensive.
- It is easily recyclable.

As the solubility of most of the solutes changes near the critical point, they can be recovered from the solvent (super critical CO₂) by reducing the pressure to below the critical point. Supercritical CO₂ application is found in de-caffeinating coffee (where methylene chloride is replaced by supercritical CO₂), which strictly depend upon the physical solvating properties of this solvent. High molecular weight hydrocarbons are not highly soluble in supercritical CO₂. In this case, surfactant is added to supercritical CO₂ which generates a micelle phase in which these insoluble materials can be suspended.

For example,

Catalytic copolymerization of CO₂ with epoxides :



Thus, the polymerization reaction producing high molecular weight materials carried out in a surfactant supercritical CO₂ system.

When free-radical halogenations in SCF are compared with standard brominating reactions of alkylated aromatics it was found that the yields and selectivities of the reactions of SCFs are superior to those conducted in conventional solvent systems.

After studying asymmetric catalytic reductions in supercritical CO₂, it was found the selectivities achieved are superior to those obtained in conventional solvents. In the production of Teflon instead of trichloro trifluoroethane, supercritical CO₂ can be used. In nano-electronics, supercritical CO₂ can replace ultra high purity CO₂ because it does not affect nanometric structures.

5.6 REVIEW QUESTIONS

1. What is green chemistry?

Ans. Refer Section 5.1.

2. What are the principles of green chemistry?

Ans. Refer Section 5.2.

3. Write informative notes on

(i) Supercritical carbon dioxide

Ans. Atom Economy.

4. Discuss the industrial applications of Green Chemistry.

Ans. Refer Section 5.5.

5. Explain the basic idea in the field of green chemistry research with the example of

(i) Adipic acid, (ii) Indigo, (iii) Ibuprofene, (iv) Carbaryl.

Ans. Refer Section 5.3.

6. Explain any two principles of green chemistry with examples.

Ans. Refer Section 5.2.

7. What is biodiesel?

Ans. Refer Section 5.5.

5.7 UNIVERSITY QUESTIONS

May 2008

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8. Explain the method to obtain biodiesel from vegetable oil.

9. Give advantages of biodiesel.

Ans. Refer Section 5.5.

Green Chemistry and Synthesis of Drugs

Ans. % Atom economy = 44.1.

5. What is biodiesel? Explain the method to obtain biodiesel from vegetable oil.

Give advantages of biodiesel.

Ans. Refer Section 5.5.

4. Calculate % Atom economy for the formation of maleic anhydride reaction. [3M]
 Ans. Refer Section 5.5.
 (2M)



Dec. 2008
 Ans. % Atom Economy = 67.69%.

1. Calculate the % Atom economy for the following reaction with respect to Allyl Chloride. [3M]
- CH₃ – CH = CH₂ + Cl₂ → Cl – CH₂ – CH = CH₂ + HCl
 Allyl chloride

Ans. % Atom Economy = 67.69%.

2. Giving conventional and green chemistry route of production of Adipic acid, highlight the green chemistry principles addressed in this case. [5M]
- Ans. Refer Section 5.3.

CHAPTER 4

CORROSION

SYLLABUS

- Definition, Mechanism 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 Corrosion - Galvanic cell corrosion, Concentration cell corrosion (differential aeration principle), Pitting corrosion, Intergranular corrosion, Stress corrosion
- Factors affecting the rate of corrosion- (i) Nature of metal, (ii) Nature of corroding environment
- Methods of corrosion control- (I) Material selection and proper designing, (II) Cathodic protection - i) Sacrificial anodic protection, ii) Impressed current method, (III) Metallic coatings- only Cathodic coating (tinning) and anodic coatings (Galvanising)

4.1 INTRODUCTION

Most materials experience some type of interaction with a large number of diverse environments, as a result they deteriorate. Deterioration is continuously taking place. It costs enormous wastage of money each year in maintenance and repair. Deteriorative mechanisms are different for three types of materials. In metals there is actual material loss either by dissolution or by formation of non-metallic scale or film. Ceramic materials are relatively resistant to deterioration, which usually occurs at elevated temperature or in extreme environment. In polymers degradation occurs.

Corrosion is a general term applied to the deterioration of a metal as a result of its reaction with its immediate environment consisting of either gaseous or liquid substances. It may also be defined as the gradual eating away or disintegration or deterioration of a metal by chemical or electrochemical reaction with its environment. Corrosion is an important factor in any chemical process plant. It makes all the difference between a trouble-free operation and a costly shut down.

green film of basic carbonate [$\text{CuCO}_3 + \text{Cu(OH)}_2$] on the surface of copper, when exposed to moist air containing carbon dioxide.

All metals and alloys are susceptible to corrosion. No single material may be suitable for all applications. For instance, gold has excellent resistance to corrosion under atmospheric conditions but it gets readily corroded in the atmosphere but it does not corrode at ambient temperature. On the other hand, iron gets rusted in the atmosphere but it does not corrode in mercury. Thus, several methods to effectively control and minimize corrosion because further, there are several methods to effectively control and minimize corrosion because secret of effective engineering lies in controlling rather than preventing corrosion.

4.2 CAUSE OF CORROSION

It is generally easier to understand why corrosion occurs than how. Most of the metals (with the exception of noble metals such as Au, Pt, etc.) exist in nature in combined forms as their oxides, carbonates, sulphides, chlorides and silicates. These compounds represent their thermodynamically stable state. During the extraction processes, these compounds are reduced to their metallic states from their ores after expending a lot of energy. Consequently, isolated pure metals can be regarded in excited state (a higher energy state) than their corresponding ores and they have a natural tendency to revert back to combined state (or lower energy state). Hence, when metals are put into use in various forms, they are exposed to environment (such as dry gases moisture, liquids etc.), the exposed metal surfaces begin to decay (i.e., conversion into more stable metal compounds) more or less rapidly, when they come in contact with gaseous and/or liquid environment. In other words, destruction or deterioration of the metal starts at the surface. This type of metallic destruction may be due to direct chemical attack (by environment) or electrochemical attack.

Thus corrosion can be defined as any process of deterioration (or destruction) and consequent loss of a solid metallic material, through an unwanted chemical or electrochemical attack by its environment, starting at its surface, or it can be considered as a process "reverse of extraction of metals."

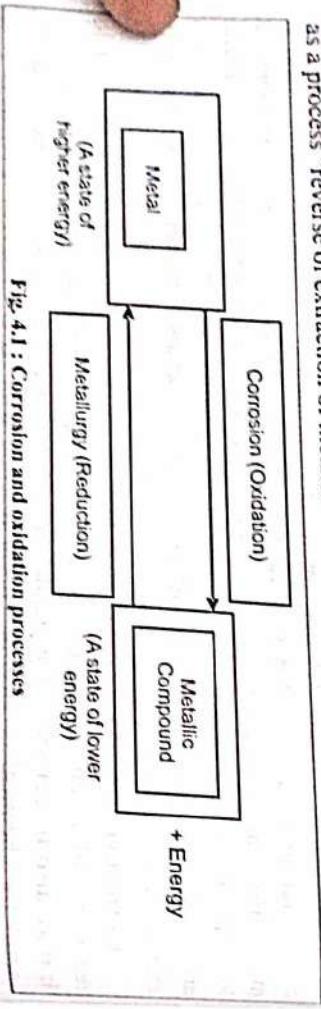


Fig. 4.1 : Corrosion and oxidation processes

The most familiar example of corrosion which everybody knows is rusting of iron when exposed to the atmospheric conditions. Another common example is formation of

4.3 THEORIES OF CORROSION

Corrosion processes are usually classified broadly on the basis of the following factors :

- Nature of corrodent :** Corrosion can be classified as 'dry' or 'wet'. Dry corrosion usually involves reaction with gases at high temperature, wet corrosion occurs in presence of water or a conducting liquid.
- Mechanism of corrosion :** This may involve direct chemical attack or indirect electrochemical attack.
- Appearance of corroded metal :** Corrosion may be either uniform or it is localized and only small areas are attacked.

4.3.1 DRY OR CHEMICAL OR ATMOSPHERIC CORROSION

The corrosion occurring through chemical reaction of gases such as oxygen, halogens, hydrogen sulphide, nitrogen and sulphur dioxide with metal or alloy surface is called as dry corrosion. This type of corrosion forms solid layer of corrosion products of different kinds. If the layer formed is very thin (less than 300\AA) it is called 'film' and if it exceeds this value it is called 'scale'. The extent of corrosion of metal due to attack of atmospheric gases depends on the chemical affinity between gas and metal as well as on the ability of metal to form a protective film and temperature.

Thus the surface of metals which is directly attacked by atmospheric gases forms a layer of compounds like oxides, sulphides, carbonates etc. Such a type of corrosion which is brought about by atmospheric conditions is called atmospheric corrosion. 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 :

- Corrosion due to oxygen – leading to formation of oxides.
- Corrosion due to other gases – leading to formation of other compounds.
- Corrosion due to other corrosive liquids – such as other molten metals.

(A) Corrosion Due to Oxygen :

This type of corrosion occurs due to attack of atmospheric oxygen on metal surface either at low or high temperatures, usually in the absence of moisture forming metal oxide as

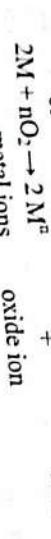
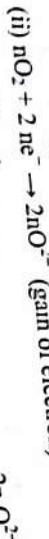


Normally, more active metals get corroded faster than less active metals. For example, alkali metals and alkaline earth metals (Li, Na, Ca, Mg, Be etc.) get oxidized

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4.4
The nature and stability of oxide film depends on temperature, humidity and other atmospheric conditions. The extent of the corrosion depends upon the type of the oxide film. It can be classified as follows.

even at low temperatures as compared to other metals which are less active. Practically almost all metals (except Ag, Au and Pt) are oxidized at high temperatures.

Following reactions take place during oxidation corrosion.



Mechanism : Surface of the metal is oxidized to form metal oxide scale which forms a barrier for further oxidation. Under such circumstances, oxidation is continuous under following two cases :

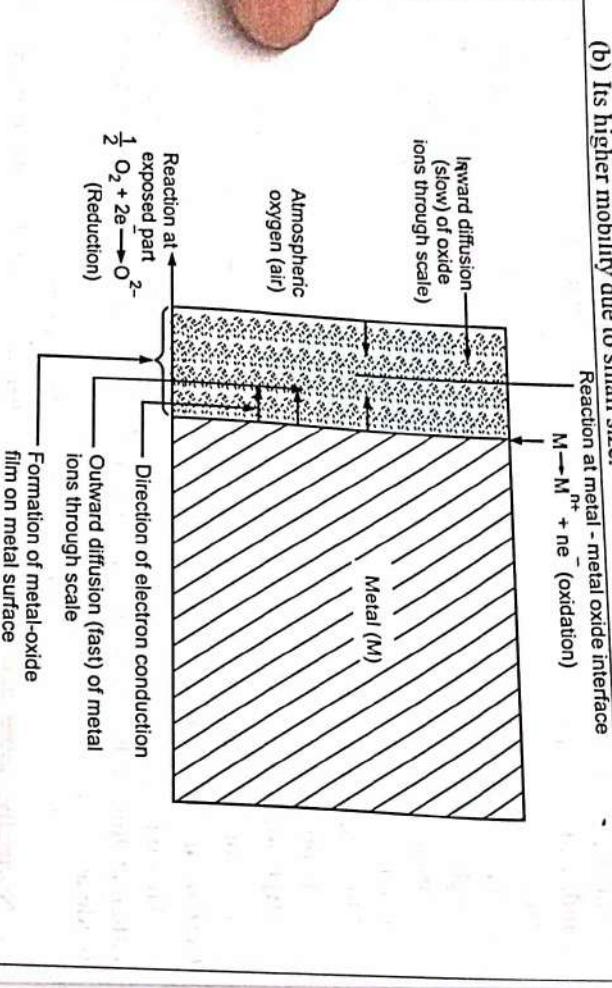
(i) The metal diffuses outwards through the scale to the surface.

(ii) Oxygen diffuses inwards through the scale to the underlying metal.

Although both of the above transfer occurs (Fig. 4.2) the outward diffusion of metal occurs mostly for two reasons :

(a) Metal ion is appreciably smaller than oxygen ion.

(b) Its higher mobility due to small size.



The nature and stability of oxide film depends on temperature, humidity and other atmospheric conditions. The extent of the corrosion depends upon the type of the oxide film. It can be classified as follows.

- (a) Stable oxide film (i) Porous. (ii) Non-porous.
- (b) Unstable oxide film.
- (c) Volatile oxide film.

Pilling – Bedworth Rule :

According to it "an oxide is protective or non-porous, if the volume of the oxide is at least as great as the volume of the metal from which it is formed." On the other hand, "if the volume of the oxide is less than the volume of the metal, the oxide layer is porous (or non-continuous) and hence non-protective because it cannot prevent the access of oxygen to the fresh metal surface below."

(a) Stable oxide film : If the oxide film formed is stable, it acts as a protective coating to the metal surface. In stable oxide film, the film layer is tightly adhered to the metal and it is impervious in nature i.e. does not allow oxygen to reach the underlying metal, thereby reducing rate of further corrosion. But extent of further corrosion depends upon the type of stable film formed.

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 the reacted metal. Thus, oxide layer is not able to cover the entire surface of the metal block. Consequently, the oxide layer faces stress and strains, thereby developing cracks and pores in its structure. Porous oxide scale permits free access of oxygen to the underlying metal surface. (through cracks and pores) for fresh action and thus, corrosion continues non-stop.

On the other hand, if the oxide film formed is non-porous in nature, the rate of corrosion reduces considerably and in most of the cases corrosion of the metal stops. The metals like aluminium, chromium, copper, lead, tin etc. forms 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. 4.2 : Oxidation corrosion of metals

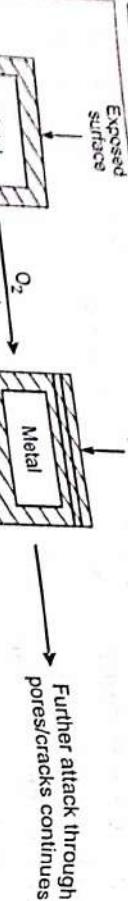
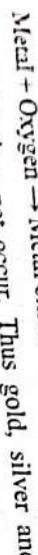


Fig. 4.3 : Porous oxide layer

(b) **Unstable oxide film** : If the oxide film formed is unstable, it decomposes on the

metal surfaces forming back the metal and oxygen.



Metal + Oxygen \rightarrow Metal + oxygen
Thus oxidation corrosion does not occur. Thus gold, silver and platinum do not

undergo oxidation corrosion.

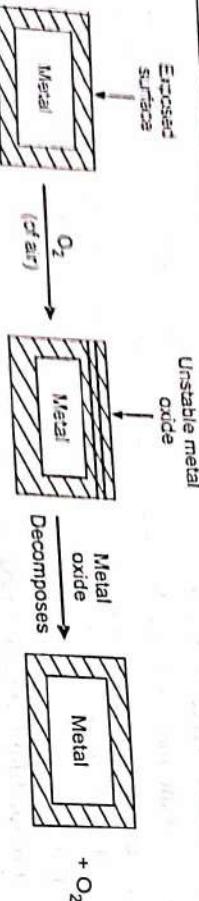


Fig. 4.4 : Unstable oxide layer

(c) **Volatile oxide film** : If the oxide film formed is volatile, the oxide layer volatilize as soon as it is formed and hence the underlying metal surface is exposed for further attack. In such case, corrosion is rapid and continuous as in case of molybdenum because MoO_3 (molybdenum oxide) is volatile. Thus, corrosion continues till the metal is available.

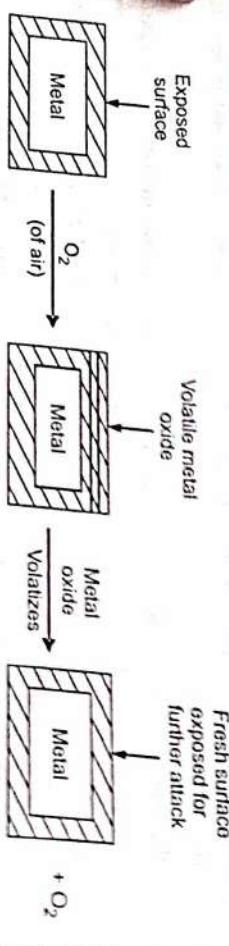


Fig. 4.5 : Volatile oxide layer

(B) Corrosion Due to Other Gases :

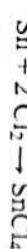
Gases like carbon dioxide, sulphur dioxide, nitrogen oxides, chlorine, and fluorine under dry conditions corrode metals. The degree of corrosion depends upon chemical

affinity of metal and the above gases. The degree of attack depends on the formation of protective or non-protective films on the metal surface.

If the film formed is protective or non-porous the intensity or extent of attack decreases as the film formed protects the metal from further attack. In case of silver, due to action of chlorine, silver chloride film is formed. It protects the metal from further corrosion.



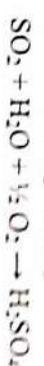
But chlorine when attacks tin, stanic chloride being volatile, is easily volatilized as soon as it is formed. Thus more and more metal gets corroded due to chlorine attack.



In an industrial atmosphere, all types of contaminants by sulphur in the form of sulphur dioxide and hydrogen sulphides are corrosive. In petroleum industry, hydrogen sulphide at high temperature corrodes steel.



The burning of fossil fuels generate large amount of sulphur dioxide. Primary cause of atmospheric corrosion is the dry deposition of sulphur dioxide on metallic surface. In presence of oxygen and moisture, sulphur dioxide is oxidized to sulphuric and sulphurous acid which are highly corrosive to metallic equipments.



(C) Liquid Metal Corrosion

This type of corrosion is due to chemical action of flowing liquid metal at high temperatures on solid metal or alloy. Such corrosion occur in devices used for nuclear power.

The corrosion reaction involves either (i) dissolution of a solid metal by a liquid metal or (ii) internal penetration of the liquid metal into the solid metal. Both these modes of corrosion cause weakening of the solid metal.

4.3.2 WET CORROSION OR ELECTROCHEMICAL 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 the metal. This gives rise to corrosion which proceeds by electrochemical principles. In fact wet corrosion is more common than dry corrosion.

Wet corrosion also known as immersed corrosion occurs under the following conditions :

- When a conducting liquid is in contact with the metal.
- When two different metals or alloys are partially or completely immersed in a solution.

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According to electrochemical theory, the chemically non uniform surfaces of metals behave like small electric arcs in aqueous solution is an electrochemical phenomenon which involves flow of electron current between anodic and cathodic areas.

Thus corrosion of metal as corresponding metal ions with the anodic reaction always occurs at anode. On the other hand, the liberation of electrons, evolved in the anodic reaction, with evolution of oxygen, depending upon the nature of corrosive environment. Usually, cathodic reactions do not affect cathode as it can't be further reduced. So at cathodic part, dissolved constituents in the conducting medium accepts the electrons to form some ions (like OH^- , O_2^-). The metallic ions (at anodic part) and non metallic ions (at cathode part) diffuse towards each other and form a corrosion product.



At anode

M^{n+} → Dissolves in solution

Forms compound such as oxide.

Thus we may sum up that electrochemical corrosion involves (i) the formation of anodic and cathodic areas or parts in contact with each other. (ii) Presence of a conducting medium. (iii) Corrosion of anodic areas only and (iv) formation of corrosion product somewhere between anodic and cathodic areas.

Mechanism of wet corrosion :

Wet corrosion of metal occurs by mechanism essentially electrochemical in nature. It is associated with flow of electron current between anodic and cathodic areas. At anode metal dissolves forming corresponding positive ions and electrons.



While depending upon the nature of the corrosive environment, cathodic reactions consume electrons with either by:

- (1) Evolution of Hydrogen
- (2) Absorption of Oxygen

(1) Hydrogen evolution mechanism :

Hydrogen evolution type of corrosion of metals occur when metals are exposed to acidic environment and when the amount of dissolved oxygen is low. It is nothing but displacement of hydrogen ions from the solution by metal ions.

Consider the case of iron metal, the anodic reaction involves dissolution of iron as Fe^{2+} ion with the liberation of electrons.



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These electrons flow from anode to cathode through the metal and H^+ ions from acidic solution accept them and get reduced to hydrogen gas at cathode.

$2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2 \uparrow(\text{g})$ (reduction, at cathode)

Thus the overall reaction is



In such mechanism, metal ions dissolve in solution and hydrogen ions come out of solution in the form of gas. In general, all metals above hydrogen in the electrochemical series have a tendency of dissolving in acidic solution with the liberation of hydrogen gas. In the hydrogen evolution type of corrosion, the anodes are represented by large areas while cathodes are represented by small areas. Hence rate of corrosion is little slower.

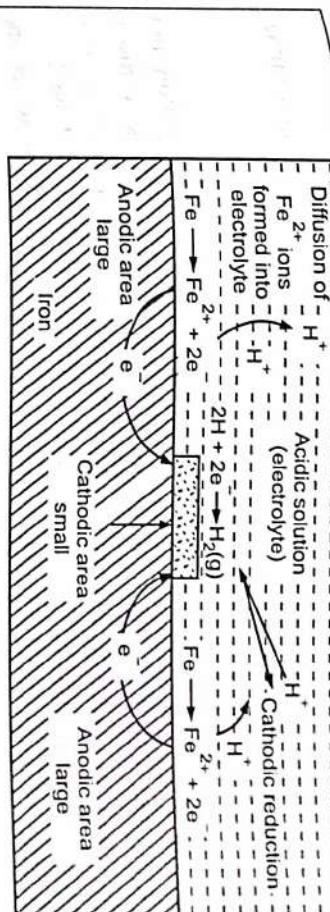


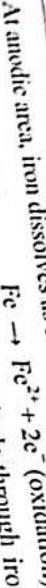
Fig. 4.6 : Mechanism of wet corrosion by hydrogen evolution

This type of corrosion occurs when industrial waste of acidic nature or small copper scrap is stored in the steel tank. Copper scrap or industrial waste becomes cathodic while steel becomes anodic and in presence of acid electrolyte a corrosion cell is formed. Steel corrodes by passing iron ions in solution as above. In galvanic corrosion i.e. when two dissimilar metals are in electrical contact with each other and are exposed to acidic environment, cathodic reaction will be hydrogen evolution process.

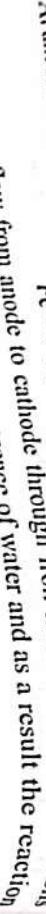
(2) Oxygen absorption mechanism :

This type of reaction mechanism occurs when dissolved oxygen is present in the electrolyte. The most important and common example of this type of corrosion is the rusting of iron. In neutral aqueous solution of electrolyte such as NaCl solution, in presence of atmospheric oxygen, iron surface is coated with a thin film of oxide. However, if this film of iron oxide develops some cracks, anodic areas are developed on the surface of the exposed iron metal while the rest metal surface forms cathode. Thus here anodic area is small while cathodic area is large. Thus, the rate of corrosion is faster, as large cathodic areas demand more electrons and small anodic areas have to undergo brisk corrosion.

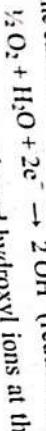
F.E. Sem.-II Engineering Chemistry-II
At anodic area, iron dissolves as ferrous ions with liberation of electrons.



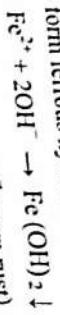
At cathodic area, iron dissolves as ferrous ions with liberation of electrons.



These electrons flow from anode to cathode through iron metal and these electrons are taken up by the dissolved oxygen at the cathode is

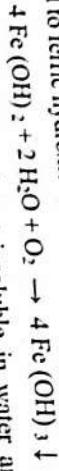


The ferrous ions at the anode and hydroxyl ions at the cathode diffuse towards each other i.e. Fe^{2+} ions diffuse towards cathode and OH^- ions diffuse towards the anode and then they combine to form ferrous hydroxide.



(brown rust)

In the presence of sufficient amount of dissolved oxygen, ferrous hydroxide is further oxidized to ferric hydroxide.



Ferric hydroxide is almost insoluble in water and precipitates out as yellow rust having composition $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$ and forms a protective layer which decreases corrosion rate. The more concentration of oxygen may lead to form protective layer on anode area If the amount of dissolved oxygen is limited, the corrosion product will be black anhydrous magnetite of composition Fe_3O_4 which is almost insoluble in water and precipitates out.

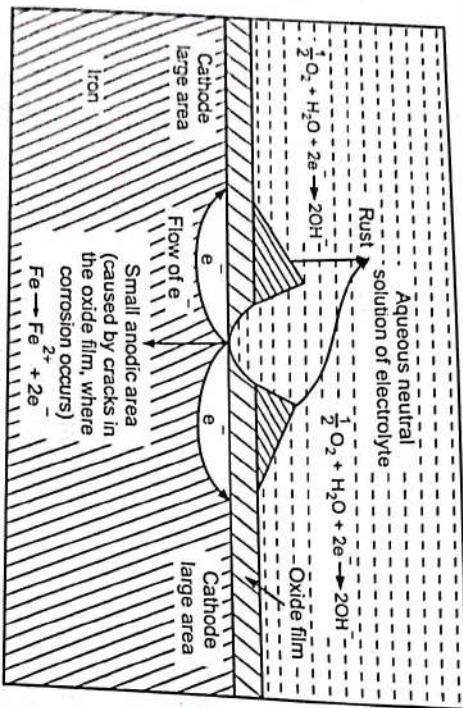


Fig. 4.7: Mechanism of wet corrosion by oxygen absorption

Note :

(i) The Fe^{2+} and OH^- diffuse from anode and cathode respectively. The smaller Fe^{2+} ions move faster than larger OH^- ions and hence combine at cathode. Hence corrosion takes place at anode but corrosion product is deposited at or near cathode.

This in turn supplies more reactants for the rust forming reaction. Evidently, presence of oxygen accelerates both corrosion and rust formation.

Thus, electrochemical corrosion involves

- (1) Formation of anodic and cathodic areas in conducting medium.
- (2) Loss of electrons i.e. oxidation at anode. Thus anode undergoes corrosion.
- (3) Gain of electrons i.e. reduction at cathode.
- (4) Formation of corrosion products.
- (5) Evolution of hydrogen in acidic medium.
- (6) Absorption of oxygen in neutral aqueous medium.
- (7) Rate of corrosion is faster in absorption of oxygen type mechanism as it provides small anodic areas when the film is broken.
- (8) Rate of corrosion is slow in H_2 evolution type as it provides large anodic areas.

Comparison :

Chemical corrosion	Electrochemical corrosion
1. It occurs in dry condition.	1. It occurs in presence of aqueous solution or electrolytes.
2. The direct chemical attack of the metal by environment.	2. It occurs through a large number of galvanic cells
3. It can be explained by absorption mechanism	3. It can be explained by electrochemical reaction
4. Corrosion products accumulate at the same spot where corrosion starts. Hence, further corrosion is prevented and it is a slow process.	4. Corrosion products generally accumulate at the cathodic area. Hence, further corrosion occurred and it is rapid process.
5. It occurs on both homogeneous and heterogeneous surfaces.	5. It occurs in heterogeneous surfaces.
6. Corrosion is uniform.	6. It is not uniform.

4.4 TYPES OF CORROSION

Different forms of corrosion are as follows :

4.4.1 Concentration Cell Corrosion

This type of corrosion is due to electrochemical attack on the metal surface, exposed to varying aeration or varying electrolyte concentration of electrolyte in contact with a metal or due to difference in aeration of air or oxygen over the metal surface. Due to this difference in aeration of air or oxygen over the metal surface, caused by local temperature or due to difference in metal-ion concentration, caused by local temperature be the result of local difference in metal-ion concentration, caused by local temperature differences or inadequate agitation or slow diffusion of metal ions produced by corrosion.

Differential aeration corrosion is the most common and important type of concentration cell corrosion. This type of corrosion occurs when one part of the metal is exposed to a different air concentration from the other part of the metal. This develops a difference in potential between differently aerated areas. It has been found experimentally that poor oxygenated parts act as anode and highly oxygenated areas act as cathode. Thus, a flow of electron from anode to cathode takes place due to differential aeration and is called differential current.

Differential aeration corrosion occurs when metals are partially immersed in a solution just below the waterline. A metal (zinc) is partially immersed in a dilute solution of a neutral salt (say NaCl) and the solution is not agitated properly. The parts above and closely adjacent to the waterline are strongly aerated and act as cathode. The parts immersed to greater depth show a smaller oxygen concentration i.e. poorly aerated and act as anode.

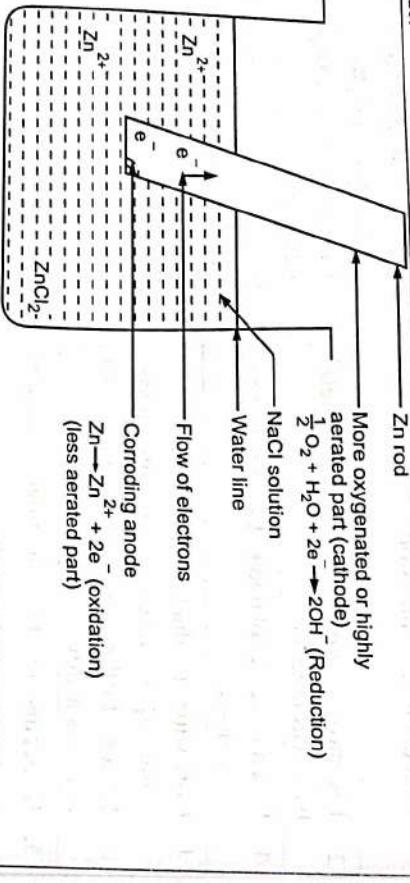
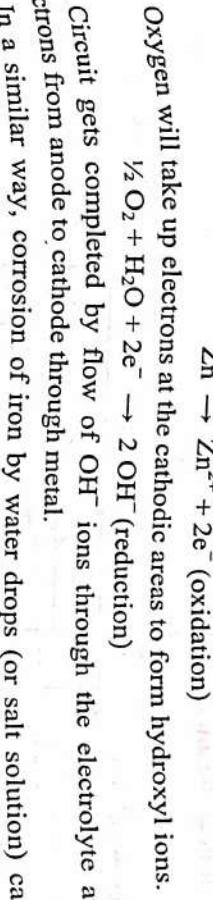


Fig. 4.8 : Differential aeration corrosion of a metal immersed partially in solution



Circuit gets completed by flow of OH^- ions through the electrolyte and flow of electrons from anode to cathode through metal.

In a similar way, corrosion of iron by water drops (or salt solution) can be easily explained. Areas covered by droplets, having no access of oxygen become anodic with respect to the other areas, which are freely exposed to air.

From the above it is clear that oxygen concentration cell increases corrosion but it occurs where the oxygen concentration is lower.

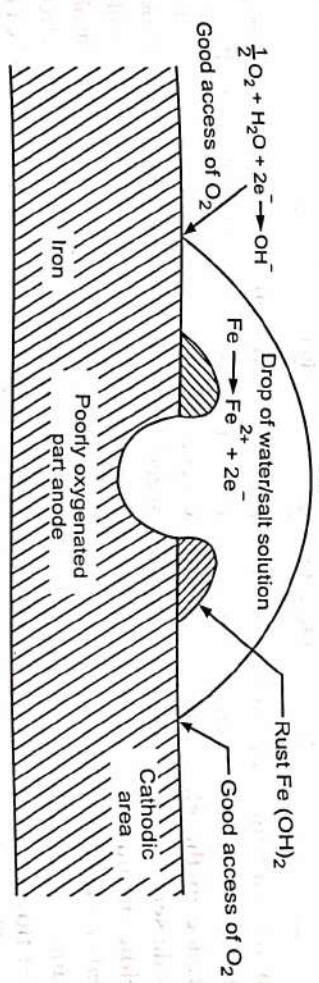


Fig. 4.9 : Formation of an oxygen concentration cell on metal under a drop of water/salt solution

4.4.2 Galvanic or Bimetallic Corrosion

It is wet type corrosion. When two dissimilar metals are in electrical contact with each other and are exposed to an electrolyte, a potential difference is created between two dissimilar metals. This potential difference produces electron flow between them. The less noble metal will dissolve and act as anode while more noble metal will act as cathode. This type of corrosion is called galvanic corrosion.

In the Fig. 4.10 two dissimilar metals, zinc and copper plates are in electrical contact with each other and are immersed into a solution of an electrolyte. The more electropositive metal zinc placed higher in electrochemical series acts as anode and is attacked and gets dissolved. Copper lower in electrochemical series acts as cathode. Zinc undergoes oxidation releasing electrons and forms metal ions. These released electrons are taken up by ions causing reduction at the cathode. The e.m.f. is generated due to

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oxidation reduction reaction causing dissolution of metal at anode causing corrosion. The oxidation reduction reaction will be more if the e.m.f. generated is large.

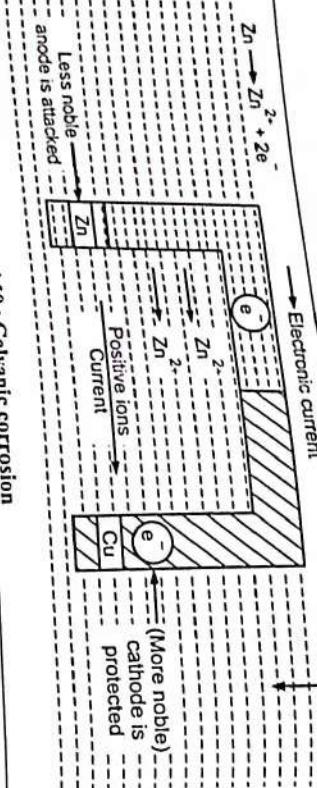


Fig. 4.10 : Galvanic corrosion

In the galvanic corrosion, cathodic metal is always protected from the corrosion attack. Then extent of corrosion depends on corrosive environment as well as the difference in the electrode potential of two contacting metals i.e. their position in the galvanic series. Further apart the metal from each other more is the intensity of corrosion.

In acidic medium the corrosion takes place by the hydrogen evolution process while in neutral or slightly alkaline solution corrosion takes place by oxygen absorption method. Galvanic corrosion depends on the relative areas of anode and cathode. The electron current flows from the anodic metal zinc which undergoes corrosion to the cathodic metal copper. Thus corrosion occurs at anodic metal while the cathodic part is protected.

The various examples of galvanic corrosion are

- (1) Lead-antimony solder around copper wire (copper being lower in series act as cathode).
- (2) Steel screws in marine hardware, made of brass (iron higher up than brass in electrochemical series gets corroded).
- (3) Steel pipe connected to copper plumbing (iron in steel higher in electrochemical series becomes anode and gets corroded).
- (4) Steel propeller shaft in bronze bearing (iron to higher up in galvanic series than bronze).

4.4.3 Pitting Corrosion

Pitting corrosion is a non-uniform corrosion and takes place by electrochemical

Pitting corrosion is extremely localized attack resulting in the formation of

cavities or holes in the metal around which the metal is relatively unattacked. Pitting may penetrate deep into the metal; it is very destructive and can ruin the metal. Pits usually grow in the direction of gravity i.e. they grow downward from horizontal surfaces.

Pitting is the result of the breakdown or cracking of the protective film on a metal at specific points. Breakdown of film may be because of mechanical factors like surface roughness, scratches, cut edges, sliding under load or because of particular type of chemical attack. Cracking of protective films form small anodic and big cathodic areas which in corrosive environment give rise to corrosive current.

Pitting corrosion may result when small particles of dust, dirt or scale are deposited on metal surfaces. The portion covered by the dust will not be well aerated compared to rest of the area. As a result, concentration cells are set up and the covered portion acts as an anode with respect to the exposed surface which acts as cathode. In the presence of moisture containing dissolved oxygen, corrosion starts underneath the impurity and forms a small shallow depression in the metal surface called pits. Once pit is formed the rate of corrosion increases because of the formation of small anodic area compared to a large cathodic area. Cathodic area induces the small anodic area to corrode faster by accepting electrons released from the anodic area resulting in the enlargement of pit. This type of corrosion is highly dangerous and cause damage and destruction of pipes, tubes and reaction vessels.

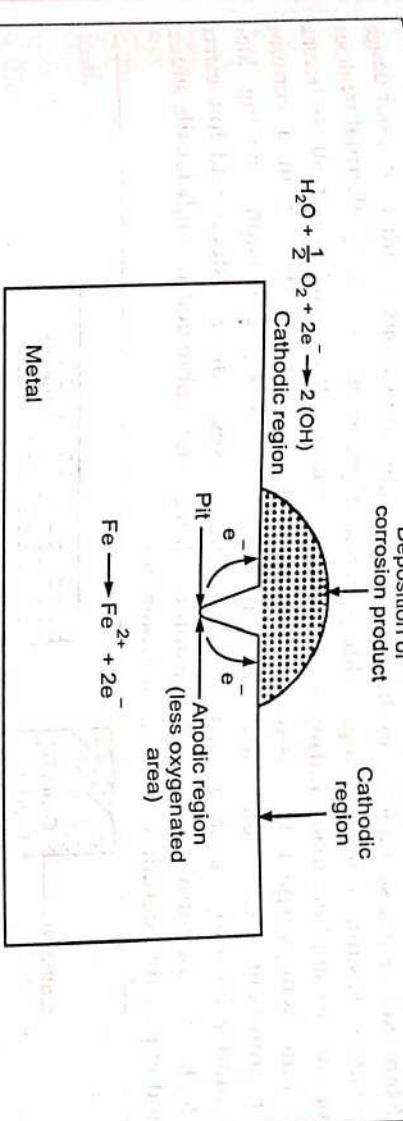


Fig. 4.11 : Pitting Corrosion

The reasons for pitting corrosion are :

- (1) Non-homogeneous metal surface.
- (2) Non-homogeneous external environment.
- (3) Films are not uniformly perfect.
- (4) Scratches or cut edges.

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4.16 Corrosion
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4.17 Corrosion

4.4.4 Stress Corrosion

Some typical examples of stress corrosion are given below :

- Local straining of metal due to non uniform finish.
- Sliding under load.
- Corrosion products may be insoluble.
- Metals which are corrosion resistant due to passive state exhibit pitting corrosion when passivity is destroyed. Thus stainless steel and aluminium show pitting in presence of chloride solution.
- A pure and homogeneous metal with a highly polished surface will be much more resistant to pitting. Surface cleanliness and selection of proper materials known to be resistant to pitting in the given environment are the usual methods to combat this problem.

4.4.4 Stress Corrosion

Stress corrosion is characterized by a highly localized attack occurring, when overall corrosion is negligible. Stress corrosion or stress cracking is the combined effect of static tensile stresses and the corrosive environment on a metal. For this type of corrosion, the corrosive agents are highly specific and selective as

- Acid chloride solution for stainless steel.
- Traces of ammonia for brass.
- Caustic alkali and strong nitrate solution for mild steel.

Stress corrosion is an important corrosion because it can occur in so many metals. Many alloys are susceptible to this type of cracking. Stress may result from poor design, riveting, residual cold working, welding, bending, pressing, quenching, thermal treatment or due to applied loads during service. In such cases, the metal under stress become anodic with respect to unstressed portion and undergoes corrosion in a corrosive environment. Pure metals are relatively immune to stress corrosion cracking. Most commercial alloys such as that of aluminium, brasses, stainless steels and low carbon steels are susceptible to stress corrosion cracking when subjected to high tensile stresses and exposed to certain corrosive environments.

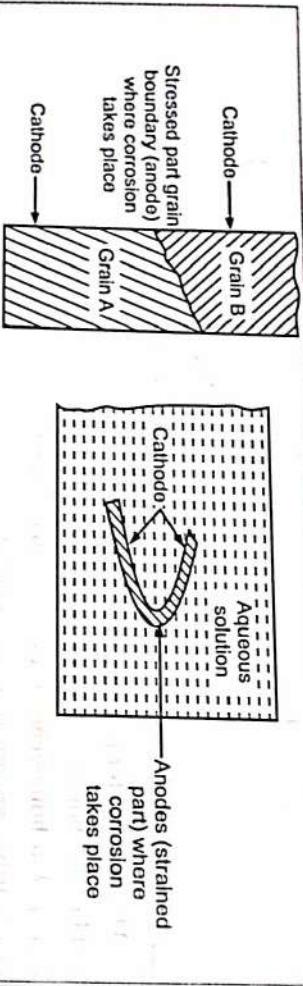


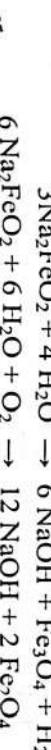
Fig. 4.12 : Stress corrosion

Some typical examples of stress corrosion are given below :

- The presence of nitrogen in iron and steel tends to make them more prone to stress corrosion cracking in some nitrate solution. But the presence of aluminium have better resistance to stress corrosion because aluminium combines with nitrogen to form aluminium nitride.
- Season cracking or stress corrosion cracking is due to the high residual stresses left in the brass (containing small amounts of alloying elements like P, As, Sb, Zn, Al, Si) as a result of cold working. These stresses make the brass more susceptible to intergranular corrosion in presence of ammonia.
- Caustic embrittlement is a very dangerous form of stress corrosion, occurring in mild steel exposed to alkaline solutions at high temperatures and stresses. Boiler water usually contains a certain proportion of sodium carbonate added for water softening. In high pressure boilers this breaks up to give sodium hydroxide and carbon dioxide which makes boiler water alkaline.



This dilute alkaline boiler water flows into the minute hair cracks and crevices (by capillary action) where water evaporates and caustic soda concentration builds up. This concentrated alkali dissolves iron as sodium ferroate in crevices, cracks where the metal is stressed and the concentration of alkali is much higher than that in the body of the liquid. The sodium ferroate (Na_2FeO_2) decomposes a short distance away from its point of formation according to the following reactions :



or $6 \text{Na}_2\text{FeO}_2 + 6 \text{H}_2\text{O} + \text{O}_2 \rightarrow 12 \text{NaOH} + 2 \text{Fe}_2\text{O}_4$

Sodium hydroxide is regenerated and magnetite (Fe_3O_4) is precipitated, thereby enhancing further dissolution of iron. The iron surrounded by the dilute NaOH (main body) is the cathodic side while the iron in contact with concentrated caustic soda (example crevices, hair cracks, rivets) is the anodic portion undergoing corrosion. Thus caustic embrittlement can be explained by considering the following electrochemical cell.

Iron/ concentrated NaOH / dilute NaOH / Iron.

The caustic embrittlement can be prevented by the addition of sodium sulphate to the boiler water or to use tannin or lignin as additives to the boiler water as these methods prevent caustic corrosion by blocking up the hair cracks and crevices.

Intergranular corrosion and stress corrosion have a very serious effect on the mechanical properties of the metal. The reduction in strength is not due to the amount of metal removed but rather to the stress concentration produced by the fine cracks. An effective control against stress corrosion is the elimination of tensile stresses from the component part.

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Stress corrosion can be minimized by
suitable treatment to relieve internal stresses.

When stainless steel assemblies are too large to be heat treated, then prevention of chromium depletion can be done in some other way. This type of corrosion can be avoided by using 18/8 stainless steel containing less than 0.03% carbon or by adding titanium to 0.08% carbon in steel.

- ### 4.4.5 Intergranular Corrosion
- (1) Suitable heat treatment.
 - (2) Removing the critical material.
 - (3) Selecting a better resistant material.
 - (4) Selecting a better composition and eliminating certain impurities.
 - (5) Adjusting the composition.

4.4.5 Intergranular Corrosion

Intergranular corrosion starts at many randomly distributed grain boundaries. When a molten metal is cast, the solidification starts at many randomly distributed nuclei. Each of them grow in a regular atomic array to form grains. The arrangement of atoms and the spacing between the grains are called grain boundaries. Such areas of mismatch between the grain centre because of grains do not match up. Such areas have high energy than the grain boundaries. Grain boundaries have high electrode potential than the grain nuclei. Each of them grow in a regular atomic array to form grains. The arrangement of atoms and the spacing between the grains are called grain boundaries. Such areas of mismatch between the grain centre because of grains do not match up. Such areas have high energy than the grain boundaries. Thus grain boundaries contain material which has high electrode potential than the grain centre. The grain boundaries called as intergranular corrosion. Fine grained metals show higher corrosion rate as compared to coarse grained metals because fine grained metals have higher potential than coarse grained metals due to a phase precipitation at the grain boundaries.

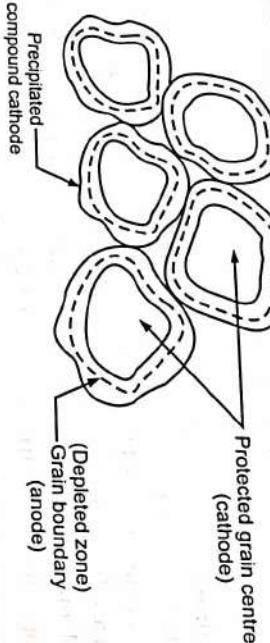


Fig. 4.13 : Intergranular corrosion

Alloys are generally more susceptible to intergranular corrosion. For example, during the welding of stainless steel (an alloy of Fe, C and Cr), chromium carbide is precipitated at the grain boundaries. It results in the formation of galvanic cells. Precipitation of chromium carbide leads to decrease in the concentration of chromium at the grain boundary area and therefore it becomes anodic. Grain centre being rich in chromium acts as cathode. As a result corrosion takes place at the grain boundaries.

Usually, corrosion in welded stainless steel is not a serious problem, since corrosion resistance can be restored by a heat treatment method which dissolves the chromium carbide precipitated during welding. However, when stainless steel assemblies are too large to be heat treated, then prevention of chromium depletion can be done in some other way. This type of corrosion can be avoided by using 18/8 stainless steel containing less than 0.03% carbon or by adding titanium to 0.08% carbon in steel.

4.5 FACTORS AFFECTING RATE OF CORROSION

Corrosion is destruction of metal through electrochemical action with the environment. The rate and extent of corrosion depends majorly on the following factors

- (1) Nature of metal.
- (2) Nature of environment.

4.5.1 Nature of Metal

(a) Position in galvanic series : According to Nernst, all metals have a tendency to pass into solution in the form of ions. But all metals will not corrode to same extent under similar conditions of environment. The extent of corrosion depends upon the position of the metal in the electrochemical series and galvanic series. More the negative value of the standard electrode potential, more the metal corrodes. For example, if zinc, copper and sodium electrodes are dipped in the solution of electrolyte, having same concentration, for same period, it is found that sodium corrodes more than zinc, copper is noble compared to them.

When two dissimilar metals are in electrical contact in presence of an electrolyte, the metal higher up in the galvanic series becomes anodic and suffers corrosion. Further, the more the two metals are apart in the galvanic series, the greater will be the difference in their oxidation potential and hence the faster will be the corrosion of the anodic metal.

(b) Over voltage : Over voltage is a polarization potential associated with the processes occurring at the electrode surface. The effect is particularly important when the product of electrolysis is a gaseous one. Thus, overvoltage is defined as the difference between the theoretical reversible electrode potential and the actual potential at which evolution of gas occurs. Overpotential of hydrogen plays very important role in corrosion process. Overpotential of hydrogen makes the metal more noble with respect to hydrogen evolution than they really are. If overpotential of hydrogen is high, rate of corrosion will be high.

For example, if pure zinc metal is placed in 1N H_2SO_4 , it undergoes corrosion forming a film and evolving hydrogen gas. The initial rate of the reaction is slow because of the high overvoltage (0.7 V) of zinc metal, which reduces the effective electrode potential to a small value. However, if a few drops of CuSO_4 are added, the corrosion rate

of zinc is accelerated, because some copper gets deposited on the zinc metal, forming tin-coated cathode. At oxygen, hydrogen overvoltage drops to 0.33 V. Hence corrosion is faster. Therefore, if overvoltage is reduced corrosion is accelerated.

(c) **Relative area of anode and cathode :** The important factor in galvanic corrosion is the area effect i.e. the ratio of cathodic to anodic area. When cathode and anode are equal, cathodic and anodic current densities are equal. Corrosion phenomenon will get accelerated. If cathode area is much larger than anode area, anodic current density will be greater; as a result corrosion of anode metal will be more.

In more easier way we can say that if the areas of cathode and anode are different, the intensity of corrosion of anode is directly proportional to the area of cathode. Thus, the corrosion is more if the area of cathode is larger than the area of anode. This is because, if the cathode area is larger than anode, the demand of electrons is more and thus more dissolution of metal at anode takes place.

Thus it can be expressed as

$$\text{Rate of corrosion} \propto \frac{\text{Cathodic area}}{\text{Anodic area}}$$

For example, steel rivets in copper plate get completely corroded in corrosive environment because the current density at smaller anodic area is much greater and the demand for electrons (by the large cathodic areas) can be met by smaller anodic area only by undergoing corrosion more briskly.

(d) **Purity of the metal :** The corrosion resistance of pure metal is usually better than that of one containing small amounts of impurities. The rate and extent of corrosion increases with the increase of the impurities. Presence of impurities accumulated on certain areas of metal are the sources of the potential difference on the metal. In corrosive environment minute galvanic cells are formed and anodic metal gets corroded.

For instance, impurities such as lead, iron or carbon in zinc lead to the formation of tiny electrochemical cells at the exposed part of the impurity and the corrosion of zinc around the impurity takes place due to 'local action'. The rate of corrosion increases with the increasing exposure to the impurities. The effect of even traces of impurities on the rate of corrosion of zinc can be seen from the following data :

Metal	% purity	Corrosion rate
Zinc	99.99	1
Zinc	99.99	2650
Zinc	99.95	5000

The impurities, present even in traces influence the rate of corrosion to a great extent. Consequently corrosion resistance of a metal may be improved by increasing its purity.

(e) **Physical state of the metal :** The rate of corrosion is influenced by physical state of the metal such as grain size, orientation of crystals, stress etc.

(i) **Grain size :** The smaller the grain size, the greater will be its solubility and hence greater will be its corrosion.

(ii) **Orientation of crystal :** Greater will be its orientation of crystals at the metal surface if the orientation of crystals at the metal surface is influenced by stress.

(iii) **Stress :** Even in a pure metal, areas under stress tend to be anodic and corrosion may be taking place at these areas. In aerated atmosphere, practically all metals get covered with an oxide film having a thickness of a few angstroms. The film may contain one or more forms of the metal oxide and its thickness depends upon the nature of the metal and the temperature. Metals such as Mg, Ca, Ba, Li, Na and K form oxides whose specific volume is lesser than that of the metal atom. Hence the oxide film formed will be porous through which oxygen can diffuse and bring about further corrosion. On the other hand, aluminum and heavy metals form oxides whose specific volume is greater than that of the metal atoms and the impervious oxide film so formed protects the metal from further oxidation, unless a crack in the film is developed.

The ratio of the volumes of the metal oxide to the metal is known as specific volume ratio. The specific volume ratios for tungsten, chromium and nickel are 3.6, 2.0 and 1.6 respectively indicating that the rate of oxidation at elevated temperature is least for tungsten. Thus, corrosion depends upon the specific volume ratio of the oxide and the metal under consideration, the thickness and conductance of the oxide film and its reaction with the environment.

(g) **Solubility and volatility of corrosion products :** The rate of corrosion is highly influenced by the following state of the corrosion product as :

(i) **Soluble corrosion product :** If the corrosion product is soluble in corroding medium corrosion of the metal will proceed faster.

(ii) **Insoluble corrosion product :** If the corrosion product formed is insoluble (e.g. many metal oxides) or if it forms another insoluble product by interaction with the medium (e.g. PbSO_4 in case of Pb in H_2SO_4 medium) it functions as a physical barrier, thereby suppressing further corrosion.

(iii) **Volatile corrosion product :** If the corrosion product is more volatile, then the metal surface is exposed for further attack i.e. corrosion rate will be more.

(h) **Passive character of metal :** Certain metals like Cr, Ni, Ag, Al and Co are passive and they exhibit much higher corrosion resistance than expected from their positions in the galvanic series, due to formation of highly protective but very thin film of

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oxide on the metal or alloy surface. The film, if broken repairs itself on re-exposure to oxidizing conditions. Thus, corrosion resistance of stainless steel is due to passivating character of chromium present in it.

4.5.2 Nature of Environment

(a) **Temperature :** As rates of all chemical reactions increase with temperature, increase in temperature increases diffusion rate of ionization and mobility of all reacting ions and molecules.

Intergranular corrosion like caustic embrittlement corrosion is less at higher temperature. Rate of corrosion of copper and mone metal is less in boiling sulphuric acid while steel pressure boilers. But in some environments corrosion is absent in boiling sulphuric acid. Dissolved oxygen is absent in boiling sulphuric acid. This corrodes more in boiling sulphuric acid. Corrosion due to differential aeration gets slowed down at higher temperatures. This is because of decreased solubility of oxygen and its faster diffusion into pits and crevices.

(b) **Humidity or moisture in air :** Humidity of the air is the deciding factor in atmospheric corrosion. Critical humidity is defined as the relative humidity above which the atmospheric corrosion rate of metal increases sharply. The value of critical humidity depends on the physical characteristics of the metal and nature of the corrosion product.

Atmospheric corrosion of iron is rather slow in dry air but increases rapidly in the presence of moisture. This is mostly due to the fact that gases and vapors present in the atmosphere furnish water to the electrolyte essential for setting up an electrochemical corrosion cell. Moreover, the oxide film on the metal surface has a tendency to absorb moisture. Hence an electrochemical cell is set up and hence corrosion rate is accelerated.

(c) **Effect of pH :** The hydrogen ion concentration of the medium is an important factor in corrosion reactions as well as corrosion control. Acidic media are generally corrosive than alkaline and neutral media. Amphoteric metals like aluminium, zinc and lead form complex ions in alkaline solution and go into solution. The corrosion rate of iron in oxygen free water is slow until the pH is below 5. But it becomes much higher in the presence of oxygen. Corrosion of metals can be reduced by increasing the pH of the attacking environment. Zinc corrodes rapidly at low as well as higher pH values, the rate being minimum at pH 11.

(d) **Presence of impurities in the atmosphere :** Atmosphere, in the vicinity of industrial areas contains corrosive gases like CO_2 , H_2S , SO_2 and fumes of HCl and H_2SO_4 which increases acidity and electrical conductivity of the liquid surrounding metal surface. This consequently, increases the corrosion current flowing in the local electrochemical cells on the exposed metal surface. Similarly in sea water, presence of sodium chloride and other salts increases conductivity of the liquid layer surrounding the metal surface, leading to increased corrosion.

(c) Presence of suspended particles in the atmosphere

In case of atmospheric corrosion, if the suspended particles are chemically active in nature like NaCl , $(\text{NH}_4)_2\text{SO}_4$; they absorb moisture and act as strong electrolyte, which in turn increase corrosion rate.

(2) If the suspended particles are chemically inactive in nature like charcoal absorb sulphur gases (SO_2 , SO_3) and moisture and slowly enhance corrosion rate.

(f) Nature of ions present:

Anions :

(1) Presence of anions like silicate may form an insoluble reaction product (silica gel) which inhibits corrosion.

(2) On the contrary, chloride ions, if present in medium destroy the protective and passive surface film and corrode metal alloy.

Cations :

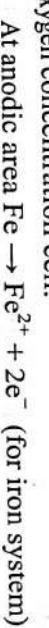
(1) Many metals corrode rapidly in the presence of ammonium (NH_4^+) salts than in sodium (Na^+) salts of same concentration.

(2) Presence of even traces of copper or any noble metal in mine waters, accelerates the corrosion of the iron pipes, used for carrying such waters.

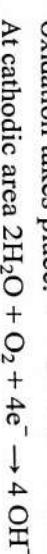
(g) **Conductance of corroding medium :** Stray current is that direct current which has leaked from an electric power circuit and flows through metallic structures in earth. The points at which stray current leaves the metallic structure, become anode where metal dissolves. In stray current corrosion, cathodes and anodes are remote from each other. If soil contains moisture and soluble salts, it will increase conductivity of soil. Increase in conductivity will increase stray current corrosion.

It is important in case of underground or submerged structures. Since conductance of dry, sandy soils is lower than that of clayey and mineralized soils, stray current (from power leakage) will produce more severe damage to the metallic structures buried under clayey and mineralized soils than those under sandy soils.

(h) **Formation of oxygen concentration cells :** The rate of corrosion increases with increasing supply of oxygen or air to the moist metal surface. Poorly oxygenated part becomes anodic where the corrosion occurs. The highly oxygenated part becomes cathodic and no corrosion occurs. Both anodic and cathodic areas lead to the formation of oxygen concentration cell.



Oxidation takes place.



The hydroxyl ions may combine with the metals. Thus oxidation concentration cell promotes corrosion at anode where oxygen concentration is lower. Waterline corrosion of buried pipeline and cables, passing through different soil types from one type of soil to another and crevice corrosion are due to differential oxygen concentration cells.

4.6 CORROSION CONTROL

Corrosion is one of the major causes of increasing maintenance cost in all industries, therefore either prevention or subsequent control of corrosion becomes all the more important. The methods of 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 single method to solve the problem.

Few methods to prevent the corrosion are discussed here, which can be summarized as :

- Design and material selection.
- Using high purity metal.
- By using metal alloys.
- Cathodic protection.
- Anodic protection.
- Application pf protective coatings
- Modification of corrosive environment.
- Use of corrosion inhibitors.

4.7 DESIGN AND MATERIAL SELECTION

It is known from experience that the selection of appropriate material for manufacturing machine parts or joining different parts in an unit helps tremendously to avoid or control the corrosion. The choice of the metal should be made not only on its cost and structure but also on its chemical properties and its environment. The design of the material should be such that corrosion if occurs be uniform and non-localized.

Some important principles of designing and selection of material are mentioned below :

- Avoid the contact of dissimilar metals in the presence of a corroding solution. If this principle is not followed then corrosion is localized on the more active metal, while the less active metal remains protected.
- Suppose it is unavoidable to choose two dissimilar metals then the anodic material should have as large area as possible whereas the cathodic metal should have as much smaller area as possible.

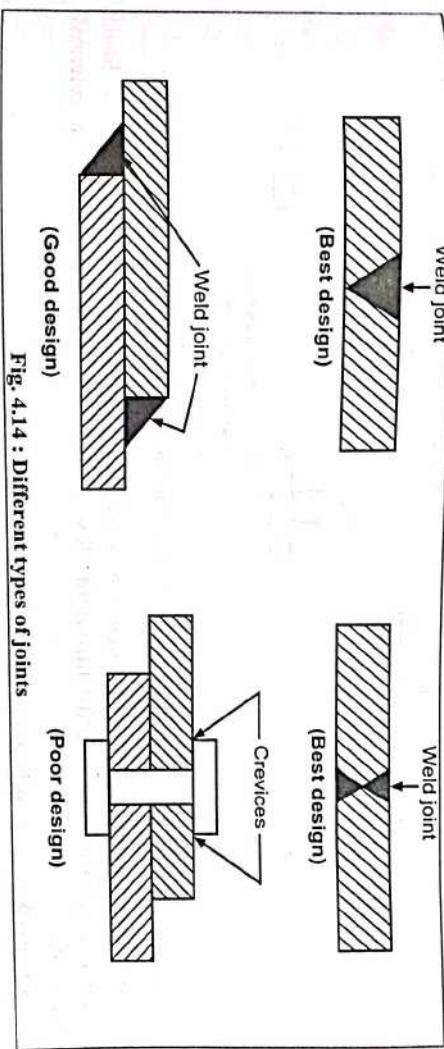


Fig. 4.14 : Different types of joints

Prevention of corrosion by design :

Proper design means the metals should keep contact with the corroding agents to a minimum and it is so designed that corrosion should be uniform, localized and less intense. The following things should be taken care of while designing :

- A proper design should avoid inhomogeneities both in the metal and in the corrosive environment. Thus a proper design should avoid the presence of the crevices between adjacent parts of the structure to avoid the formation of concentration cells. Thus the use of bolts and rivets is undesirable and these should be replaced by butt-weld.
- However when existence of crevices cannot be avoided in a given design, their harmful effects can be minimized, if the corroding medium is denied access to crevices with an impervious material or by painting.

- If two dissimilar metals are to be used, the current flow should be reduced by introducing an insulator to cut off the contact between these metals.
- If two dissimilar metals are to be selected, then metals should be chosen in such a way that they are as close as possible in the galvanic series.
- The anodic metal should not be painted or coated because any break in coating would lead to rapid localized corrosion.
- Both corrosion resistance and strength of many metals can be improved by alloying.
- Heat treatment like annealing helps to reduce internal stresses and reduce corrosion.
- Corrosion can be controlled by maintaining suitable pH.
- Wherever practicable moisture should be excluded. If moisture or electrolyte solution is present, suitable inhibitors should be employed.

(ii) The design should allow adequate cleaning and flushing of the critical parts especially those which are highly susceptible for the deposition of dirt, dust etc. Thus sharp corners and recesses should be avoided as they favour the formation of stagnant areas and accumulation of solids.

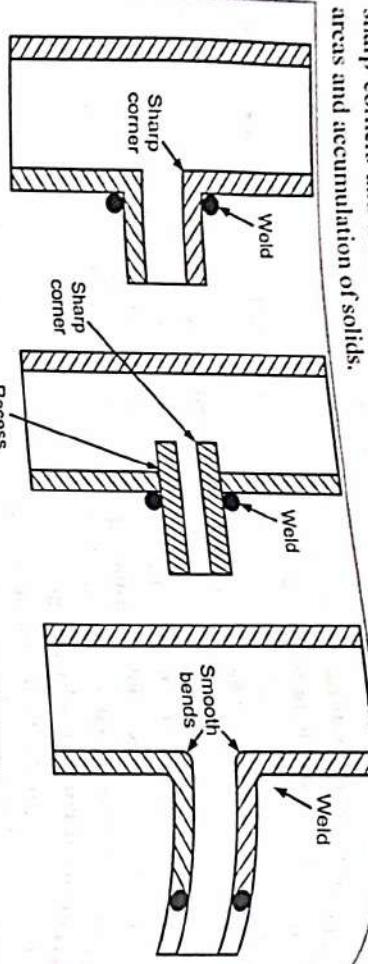


Fig. 4.15 : Effect of sharp corners and recesses on corrosion

(iii) Whenever possible, the equipment should be supported on legs to allow free circulation of air and prevent the formation of stagnant pools or damp areas.

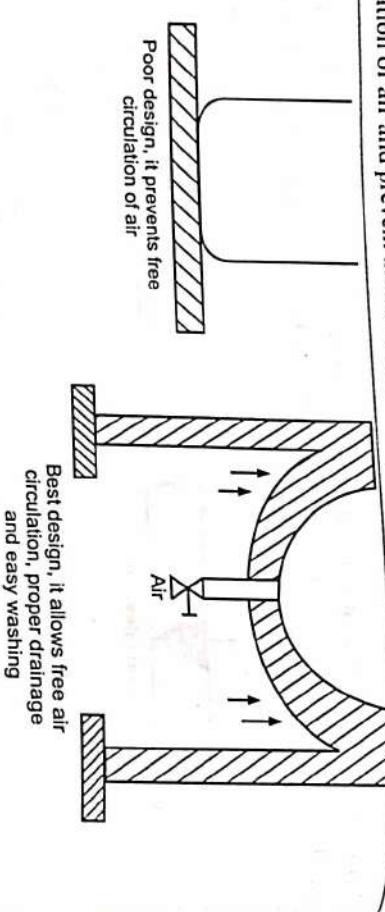


Fig. 4.16 : Prevention of corrosion by providing legs

(iv) The design should be such which allows a uniform flow of corrosive liquid because stagnant area, highly turbulent flow and high velocity can cause accelerated corrosion.

(v) Insulation avoids galvanic corrosion.



Fig. 4.17 : Protection of galvanic corrosion using insulators

(vi) Drainage affects corrosion.

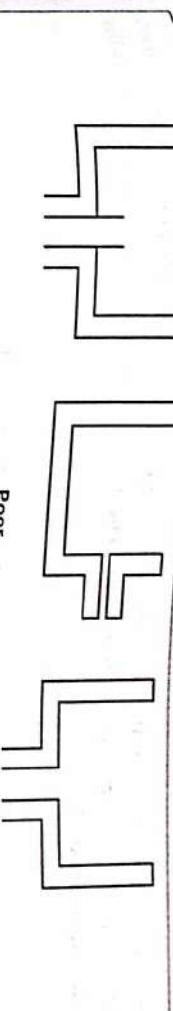


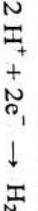
Fig. 4.18 : Drainage affects corrosion

4.8 CATHODIC PROTECTION

Humphrey Davy used cathodic protection technique on British Naval ships as early in 1824, even before, the science of electrochemistry was developed.

The principle involved in cathodic protection is to force the metal behave like a cathode and since there will not be any anodic area on the metal, corrosion does not occur.

Cathodic protection is the method of preventing metal corrosion in an electrolyte solution by supplying external current. It can be explained by considering the corrosion of metal M in acid environment. Electrochemical reactions occurring are dissolution of metal and the evolution of hydrogen gas.



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In galvanic protection from an external source to be protected, a more active metal is connected to the metal structure to be protected so that all the corrosion is concentrated at the more active metal itself gets corroded slowly protected so that all the corrosion is concentrated at the more active metal so employed is called the metal structure from the corrosion. The more active metal so employed is called 'sacrificial anode.'

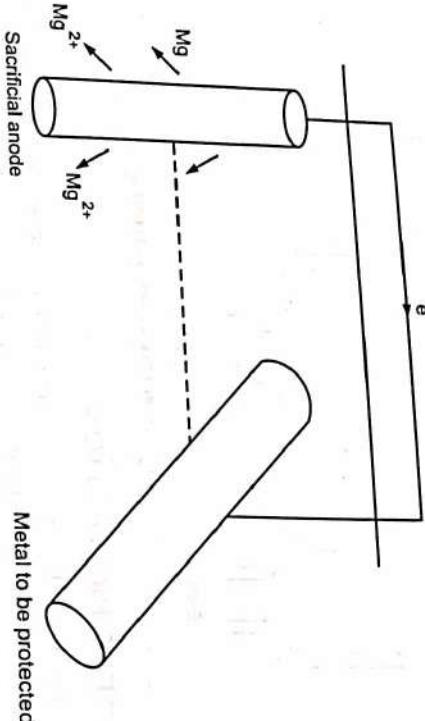


Fig. 4.19 : Cathodic protection using sacrificial anode

The corroded sacrificial anode block is replaced by a fresh one, when consumed completely.

Examples of sacrificial Anodic metal :

Metals commonly used as sacrificial anodes are magnesium, zinc, aluminium and their alloys. Magnesium has the most negative potential and can provide highest current output and hence is widely used in high resistivity electrolytes such as soils. Zinc is generally used as sacrificial anode in good electrolytes such as sea water. Aluminium

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anodes are also used but the more noble oxide films formed on them may create problems in some cases.

Cathodic protection is achieved by supplying electrons to the metal structure will support metal structure to be protected. Addition of hydrogen evolution.

metal dissolution and increase the rate of hydrogen evolution.

There are two types of cathodic protection (galvanic protection)

(i) By using galvanic or sacrificial anode (cathodic protection)

(2) By using impressed current (impressed current cathodic protection)

4.8.1 Cathodic Protection by Galvanizing Coupling

(By Sacrificial Anode)

In galvanic protection, a more active metal is connected to the metal structure to be protected so that all the corrosion is concentrated at the more active metal itself gets corroded slowly the metal structure is protected. The more active metal so employed is called while the parent structure is protected.

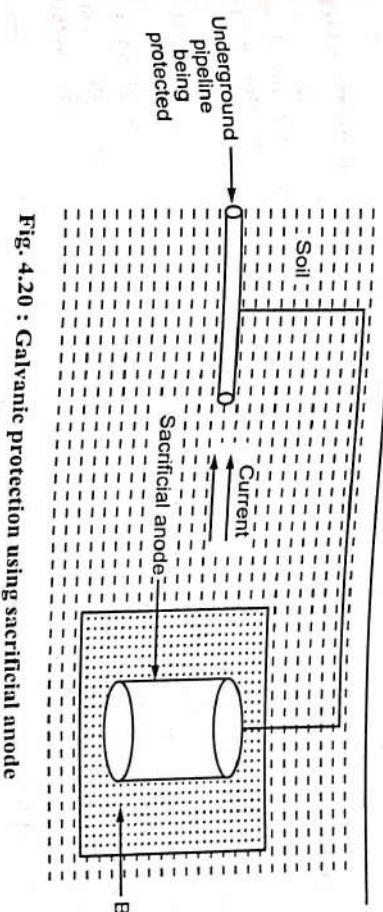


Fig. 4.20 : Galvanic protection using sacrificial anode

Galvanic protection is often preferred to impressed current techniques when current required is low and resistivity of electrolyte is low. Obviously, this is the method of choice where there is no source of electricity and when a completely underground system is desirable. This is most economical method for short term protection because the capital investment is low.

4.8.2 Impressed Current Cathodic Protection

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. 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.

Applications of impressed current cathodic protection : This type of protection has been applied to buried structures such as tanks and pipelines, transmission line towers, marined piers, laid up ships, open water box coolers etc.

Impressed current systems are particularly useful when current requirements and electrolyte resistivity are high. They are well suited for large structures and long term operation. They can be automatically controlled which reduces maintenance and operating cost.

4.9 APPLICATION OF PROTECTIVE COATING

In majority of engineering applications of metals, the corrosion factor demands the use of expensive corrosion resistant metals and alloys. High cost of various metals and fabrication problems require the use of easily available and less costly materials like steel, which is easily corroded. Hence, in order to prolong its life by protecting against the corrosive action of the environment, protective coatings are applied which include metallic, non metallic and organic coatings. To apply any type of coating it is necessary to prepare the metal surface so that the coating adheres well to the surface. The steps involved in the preparation of metal surface are

- (1) Removal of grease and other surface contamination.
- (2) Removal of oxide layer, rust and other carrier products.
- (3) Etching treatment to aid in proper adhesion to the surface.

Protective coatings function due to the interposition of a continuous physical barrier between the coated surface and its environment, under particular conditions of temperature and pressure and prevent the penetration of the environment to the base material which they protect.

Objectives of coating surfaces :

- (1) To prevent corrosion of metals.
- (2) To enhance wear and scratch resistance.
- (3) To increase hardness.
- (4) To enhance oxidation resistance.
- (5) To insulate electrically and thermally.
- (6) To impart decorative colour.

4.9.1 Metallic Coatings

Metallic coatings which are widely used for the prevention of corrosion of metals can be divided into two types :

- (1) Anodic coatings.
- (2) Cathodic coatings.

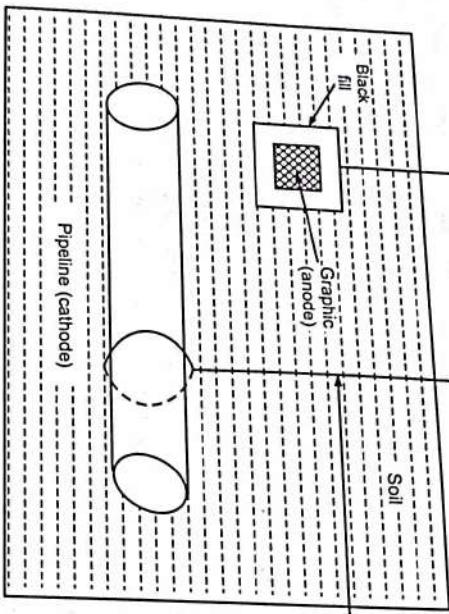


Fig. 4.22 : Corrosion control by impressed current

(1) **Anodic coatings:**

Anodic coatings are produced from coating metals which are anodic to the base metal to be protected.

For example, coating of zinc, aluminium and cadmium on steel are anodic because they are more active and their electrode potentials are lower than that of the base metal. Here, as long as coat layer is intact the corrosion of base metal is totally controlled. If any pores, breaks or discontinuities occur, a galvanic cell is formed between the coating metal and the exposed part of the base metal. In case of galvanized steel, the coating metal (being anodic) is attacked, leaving the underlying cathodic metal unattacked. Zinc dissolves anodically, whereas the iron (being cathodic) is protected. Thus, no attack on the iron occurs, until practically all the zinc has been corroded in the vicinity of the exposed iron spot. So, zinc coating protects sacrificially.

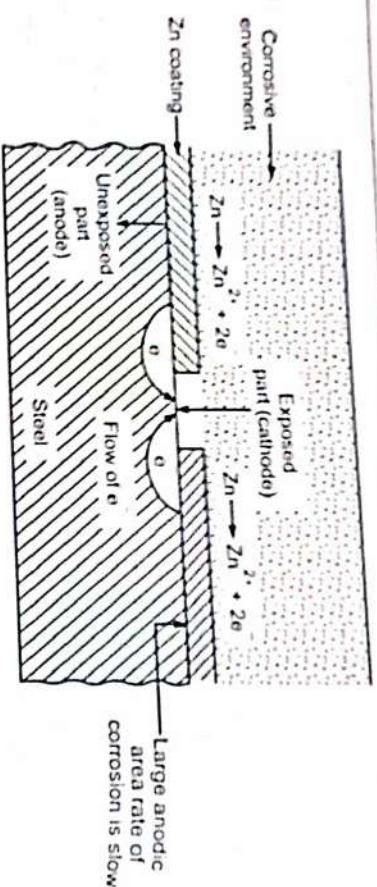


Fig. 4.23 : Functioning of anodic coating

Thus anodic coating will be good under all conditions and protect the base metal from corrosion irrespective of whether the coating is non porous or porous and continuous or discontinuous. Anodic coating takes care of corrosion but lack luster and reflectivity.

(2) **Cathodic coating:**

Cathodic coating can be obtained by application of more noble metal than the base metal. They provide effective protection to the base metal only when they are completely continuous and free from pores, breaks or discontinuities.

If such coatings are punctured much more corrosion damages can be done to the base metal than the naked metal. For example, a tin coating on a sheet of iron provides protection only as long as surface of the metal is completely covered since tin is lower

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than iron in electrochemical series. If the surface coating is punctured, the tin becomes the anode. As a result galvanic cell is set up and an intense localized corrosion occurs at small exposed part (Fig. 4.24). It results in severe pitting and perforation of the base metal, iron. Such a combination of small anode and large cathode leads to a very dangerous and severe corrosion of base metal.

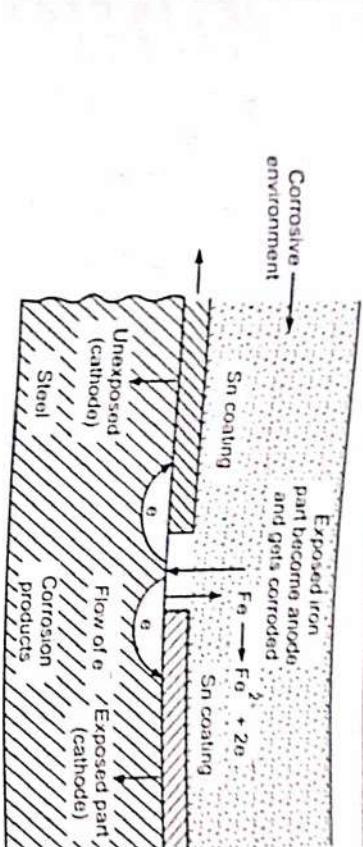


Fig. 4.24 : Functioning of cathodic coating

Comparison :

	Anodic coating	Cathodic coating
1. Protects the underlying base metal sacrificially.	1. Protects the underlying base metal due to its noble character and higher corrosion resistance.	
2. Electrode potential of coating metal is lower than that of the base metal.	2. Electrode potential of coating metal is higher than that of the base metal.	
3. If pores, breaks or discontinuities occur in such a coating, the base metal is not corroded, till all the coating metal is consumed.	3. If pores, breaks or discontinuities occur in such a coating, the corrosion of the base metal is speeded up.	
4. Coating of Zn on iron is an example.	4. Coating of tin on iron is an example.	

METHODS OF APPLICATION OF METAL COATINGS :

The following methods are generally used for applying the metallic coatings on the base metals.

- (1) Electroplating.
- (2) Metal cladding.

(3) Metal spraying.

(4) Diffusion or cementation.

(a) Coating of zinc by diffusion i.e. sheardising.

(b) Coating of aluminium by diffusion i.e. calorising.

(c) Coating of chromium by diffusion i.e. siliconising.

(d) Coating of silicon by diffusion i.e. siliconising.

(5) Hot dipping.

(a) Coating zinc on iron i.e. galvanizing.

(b) Coating tin on iron i.e. tinning.

[A] ELECTROPLATING (or Electro-deposition)

Electroplating is probably the most important and most frequently applied industrial method of producing metallic coatings. It is the process by which the coating metal deposited on the base metal by passing a direct current through an electrolytic solution containing the soluble salt of the coating metal.

made the cathode of the electrolytic cell, whereas the anode is either made of the coating metal itself or an inert material like graphite. The nature of the deposit depends upon the current density, the bath composition, temperature and presence of other additives. The film produced is quite uniform with few pin holes per unit area. The number of pin holes further decreases with increase in thickness of the deposit.

Electroplating is carried out for changing the surface properties of metals as :

- To increase the resistance to corrosion of the base metal.
- To increase resistance to wear and chemical attack.
- To improve physical appearance, hardness and surface properties.
- To increase the decorative and commercial values of the metal.

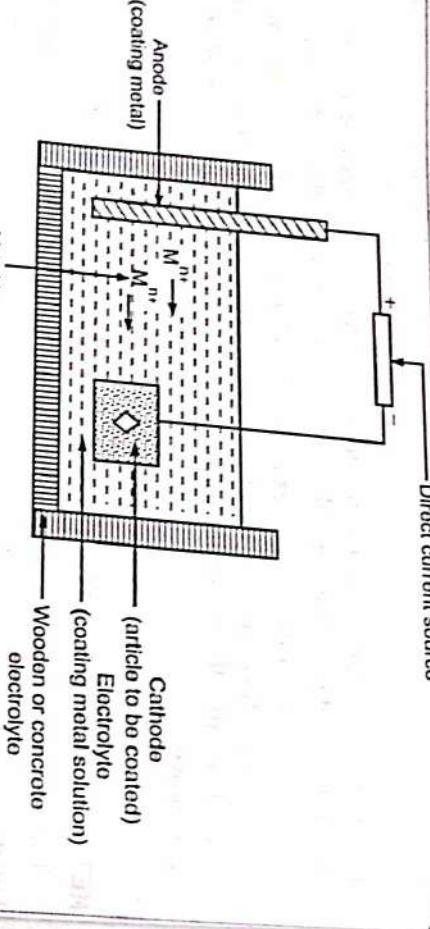


Fig. 4.25 : Electro-deposition

[B] METAL CLADDING

Metal cladding is the process by which a dense homogeneous layer of coating metal is bonded firmly and permanently to the base metal on one or both sides.

Cladding is generally done by arranging thin sheets of the coating metal and the base metal sheet in the form of a sandwich, which are then passed through rollers, under the action of heat and pressure. The choice of cladding material depends on the corrosion-resistance required for any particular environment. Almost all corrosion-resistant metals (like nickel, copper, lead, silver, platinum etc.) and alloys (like stainless steel, nickel alloys, copper alloys, lead alloys etc.) can be used as cladding materials. Among the base metal on which cladding is done are mild steel, aluminium, copper, nickel and their alloys.

'al clad' sheeting, in which a plate of duralumin in sandwiched between two layers of 99.5% pure aluminium.

[C] METAL SPRAYING

The metal surface to be coated has to be clean and rough for better adherence. The surface is, generally, roughened by sand blasting. In this method, the coating metal in molten state is sprayed on the roughened surface of the base metal using spray gun. The sprayed coatings are continuous but slightly porous. Thus a sealer oil or paint is applied on such a coating to provide a smooth surface. This method is widely used for applying coating of Cu, Pb, Ni, Sn, Al, Zn brass monel metal etc.

The advantages of the metal spraying over the processes include :

- It has larger speed of its working.
- It can be easily applied to large surfaces and irregularly shaped articles.
- It can be easily applied even to restricted areas.
- It can be applied to fabricated structure and there is no possibility of damage to the coating, during the assembly of parts.
- Thickness of coating can be controlled.
- Uniform coating can be obtained.

[D] CEMENTATION

Cementation coatings are obtained by heating the base metal in a revolving drum containing a powder of the coating metal. Coating metal diffuses into the base metal resulting in the formation of layers of alloy of varying composition. The coating thickness is controlled by varying the time of treatment and temperature. The process is suitable (for coating small articles of uneven surfaces and intricate shapes (like bolt, screw, valves, gauge tools). The coating metal must be such which can alloy with iron like zinc, lead, tin etc.

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consists in cementation of iron articles with zinc dust in a drum which is rotated slowly for 2-3 hours at a temperature of 350-370 °C. During this process, zinc diffuses into iron resulting in the formation of small articles like bolts, screws, nuts, washers etc.

Shearholding : This process is packed with zinc dust in a drum which is rotated slowly for 2-3 hours at a temperature of iron zinc alloy at the surface. The cleaned iron article has crevices or depression.

It is used for protecting small articles from atmospheric corrosion. The main advantage of shearholding is uniform coating even if the surface has crevices or depressions.

Chromizing : It is carried out using a mixture of powdered chromium (55-60%) and alumina (40-45%) at about 1300-1400 °C for 3 to 4 hours. The use of alumina prevents

coalescence of chromium particles.

Chromizing is carried out by first sand blasting the metal objects

turbo blades. Calorizing is carried out by first sand blasting the metal objects and then heating them in a tightly packed drum with a mixture of aluminium powder and ammonium chloride as a flux. Calorized steel has also been used for protecting furnace parts, screws and threaded bolts. Calorized steel has also been used for making rotors, condensers, valves etc. in petroleum refining and also in tubes of heat exchangers, radiant steam superheaters etc. for heating ferrous alloys.

[E] HOT DIPPING

In hot dipping process, the metal to be coated is immersed in a bath of molten coating metal. The molten coating metal is covered by a molten flux layer which prevents oxidation of molten coating metal and cleans the surface of the base metal. It is used for producing a coating of low melting metal such as zinc, tin, lead, aluminium etc. on iron, steel and copper which have relatively higher melting points.

Two most widely applied hot dipping processes are:

(a) **Galvanizing :** It is the process of coating iron or steel sheets with a thin coat of zinc to prevent them from rusting. Galvanizing is most widely used to protect roofing sheets, wires, pipes, nails, bolts, screws, buckets, tubes etc. from atmospheric corrosion. An important application of galvanization has been the cathodic protection of aluminium and its alloys by zinc when subjected to sea water spray and intermittent immersion in sea water.

It should be remembered that galvanized utensils should not be used for storing and cooking foods, especially acidic ones because zinc dissolves in dilute acids to form highly toxic and even poisonous compounds.

(b) **Tinning :** It is another important hot dipping process in which iron and steel articles are coated with tin.

Due to non toxic nature and resistance to atmospheric corrosion, tinning is widely used for coating steel, copper and brass sheets. They are used for manufacturing

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containers for storing foodstuffs, ghee, oils, kerosene and packing food materials. Tinned copper sheets are employed for making cooking utensils and refrigeration equipments.

Comparison :

Galvanizing	Tinning
1. A process of covering iron or steel with a thin coat of zinc to prevent it from rusting.	1. A process of covering steel with a thin coat of tin to prevent it from rusting.
2. Zinc protects the iron sacrificially, since it is more electropositive than iron and does not permit iron to pass into the outside solution.	2. Tin protects the base metal iron from corrosion due to its noble nature and higher corrosion resistance.
3. In galvanized articles, zinc continues to protect the underlying iron by galvanic cell action, even if the coating of zinc is punctured or broken at some places.	3. In tin coated articles, tin is non toxic and protects the underlying iron till the coat is perfect. Any break in coating causes rapid corrosion of iron.
4. Galvanized containers can not be used for storing acidic foodstuffs since zinc reacts with food acid forming highly toxic and poisonous zinc compounds.	4. Tin coated containers and utensils can be used for storing any food stuff, since tin is non-toxic and protects the metal from corrosion and avoids any food poisoning.

4.9.2 Organic Coating

Organic coatings are inert organic barriers (like paints, varnishes, lacquers and enamels) applied on metallic surfaces and other constructional materials for both corrosion protection and decoration. The protective value of such coating depends on (i) its chemical inertness to the corrosive environment, (ii) its good surface adhesion, (iii) its impermeability to water salts and gases as well as (iv) its proper application method.

The organic coatings may be classified as:

(A) Paints, (B) Varnishes, (C) Enamels, (D) Lacquers.

PAINTS

Paint is defined as a mechanical dispersion of mixture of one or more pigment in vehicle. It is a viscous suspension of finely divided solid pigment in a fluid medium which on drying yields an impermeable film having considerable hiding or obliterating power. The medium or vehicle consists of non-volatile film forming materials like dryir oil and resins in a suitable volatile solvents called thinners. When a paint is applied to

In case of Engineering Chemistry-II leaving behind the film forming a solid film on the surface, the thinner evaporates gradually dries into a solid film on the surface. The mixture gradually dries into a solid film on the surface. The mixture of paint on the surface. The mixture of paint with metals like lead, manganese, copper etc. are added in case of drying oil to accelerate film formation.

Driers (like metallic soaps salts of fatty acid to materials and the pigment on the surface. The commonly used driers are zinc etc.) are added in case of drying oil to accelerate film formation.

Requirements of a good paint:

- It should form a good, impervious and uniform film on the metal surface.

- It should form a good, impervious and uniform film on the metal surface.

- It should have a high covering power.

- It should have a high covering power.

- It should not crack on drying.

- It should not crack on drying.

- The film should have the required consistency for the required purpose so that it can spread on the metal surface easily.

- The film should have the required consistency for the required purpose so that it can spread on the metal surface easily.

- It should give a glossy film.

- It should give a glossy film.

- It should give a stable and decent colour on the metal surface.

- It should give a stable and decent colour on the metal surface.

- The film produced should be washable.

- The film produced should be washable.

Important constituents of paints and their functions

The important constituents of paints are as follows :

(1) **Pigment :**

It is the principal constituent of paint and provides colour to the paint.

There are three types of pigments :

(a) **Natural or mineral pigment :** It consists of minerals like clay, chalk, mica, talc, iron ores etc.

(b) **Synthetic chemical pigment :** It consists of chemicals like zinc oxide, white lead, titanium dioxide, barium sulphate etc.

(c) **Reactive pigments :** Some pigments react with drying oils or fatty acids to form soaps. E.g. red lead and zinc oxide.

The most commonly used pigments in paint are white pigments (for example, white lead, ZnO, lithophane, BaSO₄ and TiO₂). Blue pigments (for example, Prussian blue and ultramarine blue). Black pigment (for example, graphite, carbon black, lamp black). Red pigment (for example, red lead, Fe₂O₃, basic lead chromate and cadmium reds), Green pigments (for example, chromium oxide).

Functions of pigments :

- It gives opacity, strength and desired colour to paint.

- It provides an aesthetic appeal to the film.

- It protects film by reflecting harmful ultraviolet radiations.

- It provides resistance to paint against abrasion/ wear.

Characteristics of good pigments : Good pigments should be :

- opaque

- chemically inert

- non toxic

- freely mixable with film forming constituents and

- economical.

(2) **Vehicle :**

Vehicle or drying oil is a film forming constituent of paint. These are glyceryl esters of high molecular weight fatty acids present in animal and vegetable oils. The vehicle used may be drying oils (for example linseed oil, tung oil, perilla oil, dehydrated castor oil) or semi-drying oils (for example, soyabean oil, fish oil, rosin oil etc.).

Functions of vehicles :

- It holds the pigment on metal surface.

- It forms protective film by evaporation or by oxidation and polymerization of the unsaturated constituents of drying oil.

- It imparts water repellency, durability and toughness to the film.

- It improves adhesion of the film.

(3) **Thinner :**

Thinners are volatile substance which evaporates easily after application of paint. They are added to the paint to reduce consistency of the paint. The thinners commonly used are turpentine, benzene, xylol, kerosene, mineral spirits (from petroleum), methylated naphthalene etc.

Functions of thinners :

- It reduces the viscosity of paint to render it easy to handle and apply to the metal surface.

- They suspend pigments in the paint.

- They evaporate easily and help the drying of the film.

- They dissolve vehicle and the additives in the vehicle.

- They increase elasticity of paint film.

(f)

They increase the penetration of the vehicle.

(4) **Driers :**

They are oxygen carrier catalysts and helps in absorption of oxygen. Too much of drier tends to produce hard and brittle paint films. The commonly used driers are naphthenates, linoleates, borates, tungstates of metal like Pb, Co, Zn, Mn etc.

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4.41

Corrosion

Functions of drier :

(a) It acts as an oxygen carriers and accelerates drying of oil films by oxidation.

(b) It acts as a catalyst for polymerization.

(5) Fillers or extenders :

They are inert, low refractive indices materials generally of white colour. Commonly used fillers are gypsum, chalk, silica, talc, clay, asbestos, zinc oxide etc.

Functions of fillers :

(a) They serve to fill voids in film.

(b) They increase random arrangement of pigment colour.

(c) They act as carriers for the pigment without reducing the efficiency.

(d) They reduce cost of paint after drying and improve durability of the film.

(6) Plasticizers :

Plasticizers in common use are Triphenyl phosphate, Tricresyl phosphate, Tributyl phthalate, Diethyl phthalate, Dibutyl tartarate.

Functions of plasticizers :

(a) To provide elasticity.

(b) To prevent cracking of the film.

(7) Anti-skimming agent :

Anti-skimming agent are generally polyhydroxy phenols.

Functions of Anti-skimming agent :

(a) To prevent gelling and skimming of paint film.

(b) To prevent peeling of the paint after application.

The manufacture of paint essentially involves through grinding of the required amounts of the constituents in roller mills or pebble mills. The common method of application of paints are hand brushing, spraying dipping, tumbling and roller coating. Industrial spray methods make use of electrophoresis principle. A paint film may fail because of chalking, cracking, flaking or blistering.

4.10 REVIEW QUESTIONS

- What is corrosion? Discuss the corrosion due to differential aeration.
Ans. Refer Section 4.1 and 4.4.1.
- Discuss electrochemical theory of corrosion taking suitable examples with neat sketch.
Ans. Refer Section 4.3.2.

- What is corrosion? Explain the direct chemical corrosion.
Ans. Refer Section 4.1 and 4.3.1.
- What is corrosion? Explain the mechanism of electrochemical corrosion.
Ans. Refer Section 4.1 and 4.3.2.
- Discuss the corrosion caused due to the formation of concentration cells.
Ans. Refer Section 4.4.1.
- What is dry corrosion?
Ans. Refer Section 4.3.1.
- What is Pilling-Bedworth rule?
Ans. Refer Section 4.3.1.
- What is galvanic corrosion?
Ans. Refer Section 4.4.2.
- Define corrosion of metals. What are different types of corrosion? Explain the electrochemical theory of wet corrosion, giving its mechanism.
Ans. Refer Section 4.1, 4.3 and 4.3.2.
- Differentiate between chemical corrosion and electrochemical corrosion.
Ans. Refer Section 4.3.2.
- Explain rusting of iron, 'with the help of electrochemical theory of corrosion.
Ans. Refer Section 4.3.2.
- What is differential aeration corrosion?
Ans. Refer Section 4.4.1.
- How iron corrodes in neutral or alkaline solution?
Ans. Refer Section 4.3.2.
- Discuss the various factors affecting rate of corrosion.
Ans. Refer Section 4.5.
- Explain the mechanism of differential aeration. Give the example where differential aeration effect is seen.
Ans. Refer Section 4.4.1.
- Explain the effect of the following factors on the rate of corrosion :
 - Nature of corrosion product.
 - pH
 - Anodic and cathodic areas.
 - Polarization of the electrode.
Ans. Refer Section 4.5.1 and 4.5.2.
- Explain the mechanism of following types of corrosion :
 - Pitting corrosion.
 - Stress corrosion.
Ans. Refer Section 4.4.3 and 4.4.4.