

# **Module -1**

## **Principles of Spectroscopy**

### **Introduction**

Spectroscopy is that branch of science which deals with the determination of a substance of a compound through the interaction of electromagnetic radiation with the matter.

Spectroscopy deals with the production, measurement, and interpretation of spectra arising from the interaction of electromagnetic radiation with matter. There are many different spectroscopic methods available for solving a wide range of analytical problems. The methods differ with respect to the species to be analyzed (such as molecular or atomic spectroscopy), the type of radiation-matter interaction to be monitored (such as absorption, emission, or diffraction), and the region of the electromagnetic spectrum used in the analysis. Spectroscopic methods are very informative and widely used for both quantitative and qualitative analyses. Spectroscopic methods based on the absorption or emission of radiation in the ultraviolet (UV), visible (Vis), infrared (IR), and radio (nuclear magnetic resonance, NMR) frequency ranges are most commonly encountered in traditional food analysis laboratories. Each of these methods is distinct in that it monitors different types of molecular or atomic transitions

### **Electromagnetic radiation**

The flow of energy at the universal speed of light through free space or through a material medium in the form of the electric and magnetic fields that make up electromagnetic waves such as radio waves, visible light, and gamma rays. In such a wave, time-varying electric and magnetic fields are mutually linked with each other at right angles and perpendicular to the direction of motion. An electromagnetic wave is characterized by its intensity and the frequency  $\nu$  of the time variation of the electric and magnetic fields.

### **Nature of the interaction**

The types of spectroscopy also can be distinguished by the nature of the interaction between the energy and the material. These interactions include:

- Absorption spectroscopy: Absorption occurs when energy from the radiative source is absorbed by the material. Absorption is often determined by measuring the fraction of energy transmitted through the material, with absorption decreasing the transmitted portion.
- Emission spectroscopy: Emission indicates that radiative energy is released by the material. A material's blackbody spectrum is a spontaneous emission spectrum determined by its temperature. This feature can be measured in the infrared by instruments such as the atmospheric emitted radiance interferometer. Emission can also be induced by other sources of energy such as , flames, sparks electric arcs or electromagnetic radiation in the case of fluorescence.

### **Atomic spectroscopy**

Atomic absorption spectroscopy and atomic emission spectroscopy involve visible and ultraviolet light. These absorptions and emissions, often referred to as atomic spectral lines, are due to electronic transitions of outer shell electrons as they rise and fall from one electron orbit to another. Atoms also have distinct x-ray spectra that are attributable to the excitation of inner shell electrons to excited states.

Atoms of different elements have distinct spectra and therefore atomic spectroscopy allows for the identification and quantitation of a sample's elemental composition. After inventing the spectroscope, Robert Bunsen and Gustav Kirchhoff discovered new elements by observing their emission spectra. Atomic absorption lines are observed in the solar spectrum and referred to as Fraunhofer lines after their discoverer. A comprehensive explanation of the hydrogen spectrum was an early success of quantum mechanics and explained the Lamb shift observed in the hydrogen spectrum, which further led to the development of quantum electrodynamics.

Modern implementations of atomic spectroscopy for studying visible and ultraviolet transitions include flame emission spectroscopy, inductively coupled plasma atomic emission spectroscopy, glow discharge spectroscopy, microwave induced plasma spectroscopy, and spark or arc emission spectroscopy. Techniques for studying x-ray spectra include X-ray spectroscopy and X-ray fluorescence.

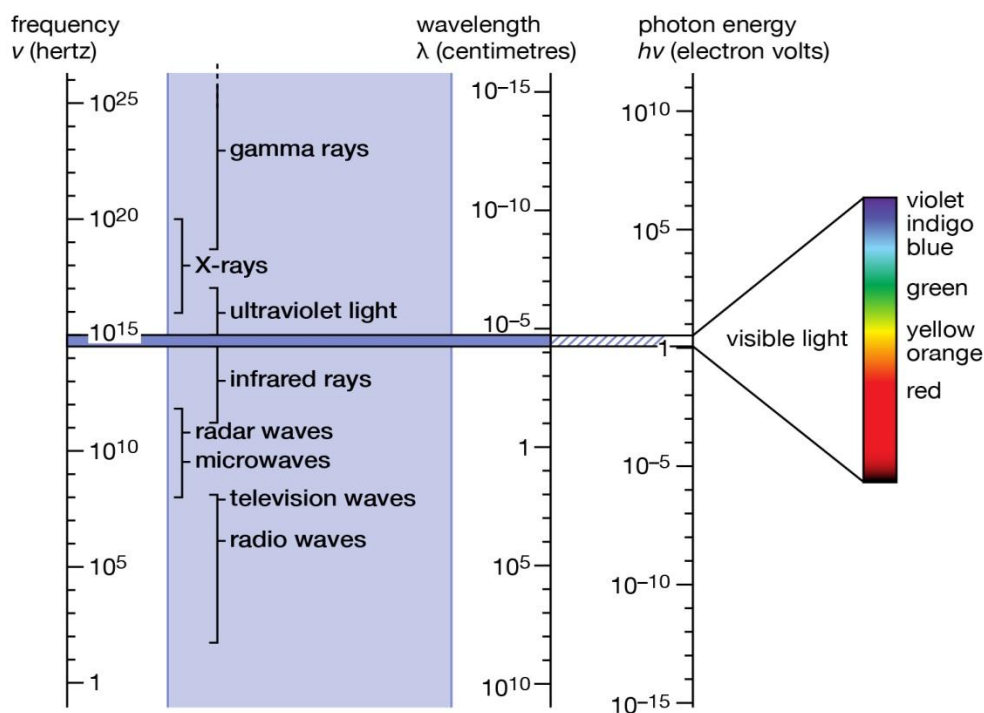
## **Molecular Spectroscopy**

The combination of atoms into molecules leads to the creation of unique types of energetic states and therefore unique spectra of the transitions between these states. Molecular spectra can be obtained due to electron spin states (electron paramagnetic resonance), molecular rotations, molecular vibration, and electronic states. Rotations are collective motions of the atomic nuclei and typically lead to spectra in the microwave and millimeter-wave spectral regions. Rotational spectroscopy and microwave spectroscopy are synonymous. Vibrations are relative motions of the atomic nuclei and are studied by both infrared and Raman spectroscopy. Electronic excitations are studied using visible and ultraviolet spectroscopy as well as fluorescence spectroscopy.

## **Selection Rule**

A **selection rule** describes how the probability of transitioning from one level to another cannot be **zero**. It has two sub-pieces: a **gross selection rule** and a **specific selection rule**. A gross selection rule illustrates characteristic requirements for atoms or molecules to display a spectrum of a given kind, such as an IR spectroscopy or a microwave spectroscopy. Once the atom or molecules follow the gross selection rule, the specific selection rule must be applied to the atom or molecules to determine whether a certain transition in quantum number may happen or not.

## Table of relation between electro-magnetic radiation



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### Types of spectroscopy

#### UV / VISIBLE SPECTROSCOPY

Absorption of light in the UV/Visible part of the spectrum (210 – 900 nm). • The transitions that result in the absorption of electromagnetic radiation in this region of the spectrum are transitions between electronic energy levels. • Generally, the most probable transition is from highest occupied molecular orbital (HOMO) to lowest occupied molecular orbital (LUMO).

#### Infrared spectroscopy

(**IR spectroscopy**) is the **spectroscopy** that deals with the **infrared** region of the electromagnetic spectrum, that is light with a longer wavelength and lower frequency than visible light. It covers a range of techniques, mostly based on absorption **spectroscopy**.

#### Nuclear magnetic resonance spectroscopy

It is most commonly known as **NMR spectroscopy** or magnetic resonance **spectroscopy** (MRS), is a **spectroscopic** technique to observe local magnetic fields around atomic nuclei. ... **NMR spectra** are unique, well-resolved, analytically tractable and often highly predictable for small molecules.

## Module 2

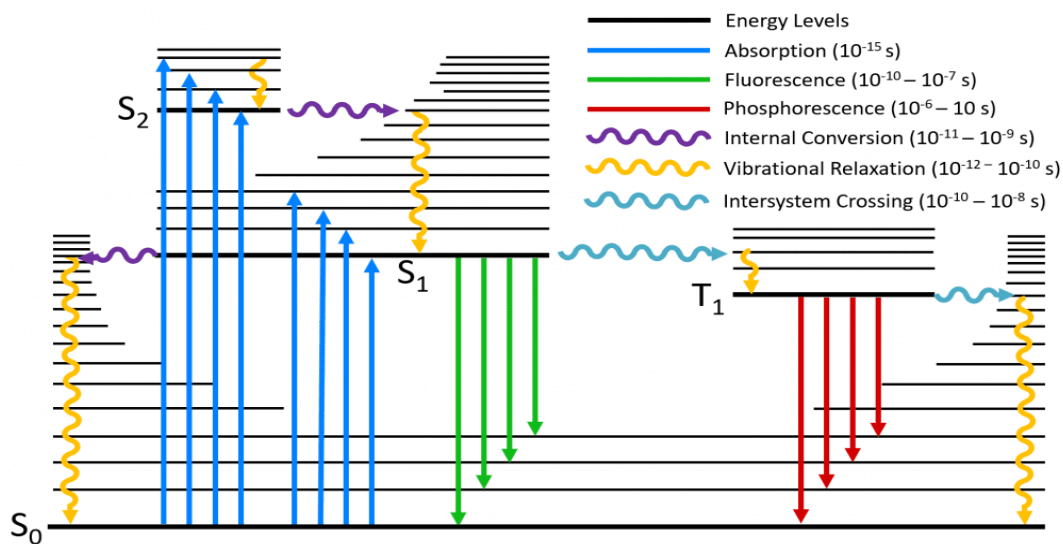
### Applications of Spectroscopy

#### **Emission spectroscopy**

Light consists of electromagnetic radiation of different wavelengths. Therefore, when the elements or their compounds are heated either on a flame or by an electric arc they emit energy in the form of light. Analysis of this light, with the help of a spectroscope gives us a discontinuous spectrum. A spectroscope or a spectrometer is an instrument which is used for separating the components of light, which have different wavelengths. The spectrum appears in a series of lines called the line spectrum. This line spectrum is called an atomic spectrum when it originates from an atom in elemental form. Each element has a different atomic spectrum. The production of line spectra by the atoms of an element indicate that an atom can radiate only a certain amount of energy. This leads to the conclusion that bound electrons cannot have just any amount of energy but only a certain amount of energy.

The emission spectrum can be used to determine the composition of a material, since it is different for each element of the periodic table. One example is astronomical spectroscopy: identifying the composition of stars by analyzing the received light. The emission spectrum characteristics of some elements are plainly visible to the naked eye when these elements are heated. For example, when platinum wire is dipped into a strontium nitrate solution and then inserted into a flame, the strontium atoms emit a red color. Similarly, when copper is inserted into a flame, the flame becomes green. These definite characteristics allow elements to be identified by their atomic emission spectrum. Not all emitted lights are perceptible to the naked eye, as the spectrum also includes ultraviolet rays and infrared lighting. An emission is formed when an excited gas is viewed directly through a spectroscope.

#### **Jablonski Diagram**



**Emission spectroscopy** is a spectroscopic technique which examines the wavelengths of photons emitted by atoms or molecules during their transition from an excited state to a lower energy state. Each element emits a characteristic set of discrete wavelengths according to

its electronic structure, and by observing these wavelengths the elemental composition of the sample can be determined. Emission spectroscopy developed in the late 19th century and efforts in theoretical explanation of atomic emission spectra eventually led to quantum mechanics.

There are many ways in which atoms can be brought to an excited state. Interaction with electromagnetic radiation is used in fluorescence spectroscopy, protons or other heavier particles in Particle-Induced X-ray Emission and electrons or X-ray photons in Energy-dispersive X-ray spectroscopy or X-ray fluorescence. The simplest method is to heat the sample to a high temperature, after which the excitations are produced by collisions between the sample atoms. This method is used in flame emission spectroscopy, and it was also the method used by Anders Jonas Ångström when he discovered the phenomenon of discrete emission lines in the 1850s. Although the emission lines are caused by a transition between quantized energy states and may at first look very sharp, they do have a finite width, i.e. they are composed of more than one wavelength of light. This spectral line broadening has many different causes.

Emission spectroscopy is often referred to as **optical emission spectroscopy** because of the light nature of what is being emitted.

### **Experimental technique in flame emission spectroscopy**

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The solution containing the relevant substance to be analyzed is drawn into the burner and dispersed into the flame as a fine spray. The solvent evaporates first, leaving finely divided solid particles which move to the hottest region of the flame where gaseous atoms and ions are produced. Here electrons are excited as described above. It is common for a monochromator to be used to allow for easy detection.

On a simple level, flame emission spectroscopy can be observed using just a flame and samples of metal salts. This method of qualitative analysis is called a flame test. For example, sodium salts placed in the flame will glow yellow from sodium ions, while strontium (used in road flares) ions color it red. Copper wire will create a blue colored flame, however in the presence of chloride gives green (molecular contribution by CuCl).

### **Emission coefficient**

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Emission coefficient is a coefficient in the power output per unit time of an electromagnetic source, a calculated value in physics. The emission coefficient of a gas varies with the wavelength of the light. It has units of  $\text{ms}^{-3}\text{sr}^{-1}$ . It is also used as a measure of environmental emissions (by mass) per MWh of electricity generated.

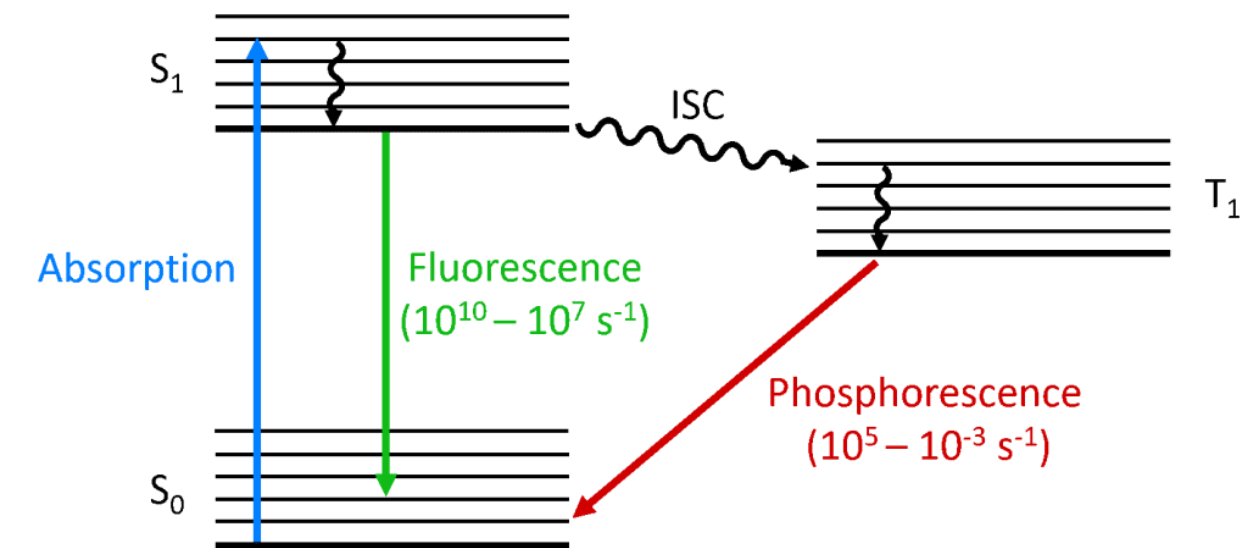
### **Spontaneous emission**

A warm body emitting photons has a monochromatic emission coefficient relating to its temperature and total power radiation. This is sometimes called the second Einstein coefficient, and can be deduced from quantum mechanical theory.

### **Introduction to Fluorescence and Phosphorescence**

Luminescence is the emission of photons from electronically excited states. Fluorescence and phosphorescence are two types of luminescence which differ in the nature of the ground and excited states. A molecule may be excited from a singlet ground state to a singlet excited state by the absorption of radiation in the UV or visible region of the spectrum. Electronic excitation is accompanied by excitation to a higher vibrational energy level. The excited molecules may rapidly lose vibrational energy by collisions with neighbouring molecules. Fluorescence is the emission of light at a longer wavelength than the incident radiation as the molecule returns from a singlet excited state to a singlet ground state after the loss of vibrational energy (Figure 7.1).

Phosphorescence is the emission of light at a longer wavelength than the incident radiation as a molecule returns from an excited electronic state to a ground electronic state of different spin multiplicity, generally a triplet excited state returning to a singlet ground state.



### Application of Fluorescence

Fluorescence spectroscopy seems to be promising diagnostic technique with fast and rapid diagnosis ability. Studies indicate high sensitivity and specificity rate which makes Fluorescence spectroscopy an ideal diagnostic tool for medical microbiology field. But, there is need for further studies and clinical trials to validate this new diagnostic technique.

At present, Fluorescence spectroscopy is being applied in medical microbiology field for various purposes. There are many studies which indicate that Fluorescence spectroscopy is promising diagnostic technique with high sensitivity and specificity for microorganisms associated diseases diagnosis with the help of spectroscopic fingerprints. Also, Fluorescence spectroscopy and Fluorescence correlation spectroscopy (FCS) may be applied to understand various pathophysiological steps of various microorganisms

Fluorescence spectroscopy is a type of electromagnetic spectroscopy which analyzes fluorescence from a sample. The sample is excited by using a beam of light which results in emission of light of a lower energy resulting in an emission spectrum which is used to interpret results. Fluorescence correlation spectroscopy (FCS), a technique basically used for spatial and temporal analysis of molecular interactions of extremely low concentrated biomolecules in solution. FCS measures both the average number of molecules in the detection volume and the diffusion time of the molecules through the open detection volume. As the diffusion speed is directly correlated with the molecular mass and shape of the fluorescent molecule, it is possible to study the complex formation between a small fluorescent labeled and a big unlabelled molecule.

## **MODULE 3**

### **CONCEPT OF ELECTROCHEMISTRY**

**Electrochemistry** deals with the relationship between electrical energy and chemical energy and their inter conversion into one another.

**Electrochemical changes** can occur in (i) Electrochemical cell (ii) Concentration cell and (iii) Electrolytic cell

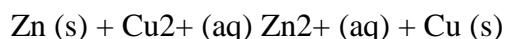
**(i) Electrolytic cell:** Device in which electrical energy is converted to chemical energy through electrolysis. For Ex. Electrolysis of NaCl produces Na metal and Cl<sub>2</sub> gas.

**(ii) Electrochemical cells/Galvanic cells:** Device in which chemical energy is converted to electrical energy. For Ex. Daniel cell

**(iii) Concentration cell:** Device in which electrical energy is produced due to the difference in concentration of the same substance in the two half cells.

### **ELECTROCHEMICAL CELLS/GALVANIC CELLS**

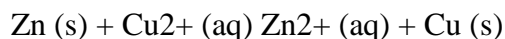
A Device, in which chemical energy is converted into electrical energy is known as Electrochemical cell or Galvanic cell.. The conversion is due to redox reactions taking place in the cell. For Ex. Daniel cell



The oxidation and reduction occur in separate containers called as half cells and because the redox reaction taking place, electricity is produced. The resulting cell has voltage of 1.1 V.

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### **Important points**

1. The metallic rods are called as electrodes (anode and cathode).
2. Salt bridge is used for maintaining electrical neutrality and completing the circuit.
3. The concentration of Zn<sup>2+</sup> ions increases while that of Cu<sup>2+</sup> ions decreases.
4. Zn rod loses its weight while Cu gets deposited on cathode.
5. In electrochemical cells, oxidation occurs on anode while reduction on cathode .
6. The flow of electrons is from anode to cathode while that of electric current is reverse of it.

### **Representation of a Cell**

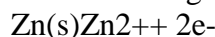
(Anode half-cell) (Salt Bridge) (Cathode half-cell)

Metal / Electrolyte or its cation (with conc.) // Electrolyte or its cation (with conc.) / Metal

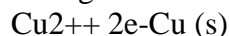


**Electrode Potential:** The electrical potential difference set up between the metal and its solution of 1 M concentration at 25 °C is called as electrode potential. It is of two types:

**1. Oxidation Potential:** It is the measure of the tendency of a metallic electrode to lose electrons or to get oxidised. For e.g.



**2. Reduction Potential:** It is the measure of the tendency of a metallic electrode to gain electrons or to get reduced. For e.g.



Thus oxidation potential is the reverse of reduction potential. For e.g.

If reduction potential of Zn = -0.76 V

Oxidation potential of Zn will be = +0.76 V

NOTE: The half-cell reactions are always written as reduction half reactions and their potentials are represented as reduction potentials.

The electrode potential depends upon:

1. The nature of the metal and its ions
2. Concentration of the ions in the solution and
3. Temperature

### **EMF/Cell Potential of a Cell**

The difference between the electrode potentials of the two electrodes constituting an electrochemical cell is known as electromotive force (EMF) or cell potential of a cell. This acts as a driving force for the cell reaction, expressed as volts.

EMF = Reduction potential of cathode – Reduction potential of Anode or

$E_{\text{cell}} = E(\text{cathode}) - E(\text{anode})$  or

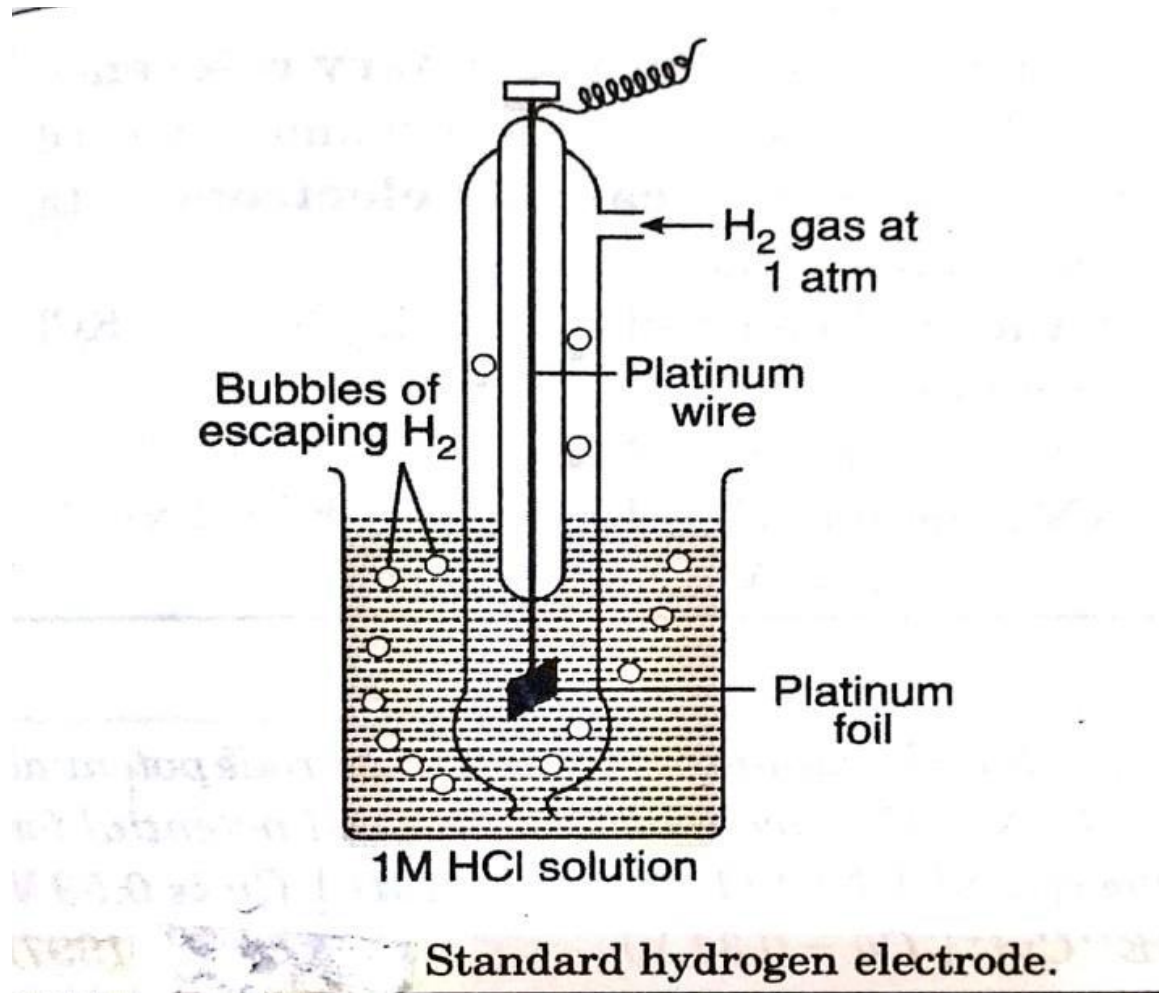
$E_{\text{cell}} = E(\text{right}) - E(\text{left})$

**Measurement of Electrode Potential:** As it is impossible to measure absolute value of single electrode potential neither oxidation nor reduction takes place independently, the electrode potential is measured with the help of a reference electrode. For this purpose Standard Hydrogen Electrode (SHE) can be used.

**Standard Hydrogen Electrode (SHE):** It consists of a platinum wire or foil coated with platinum black dipped in 1 M solution of  $\text{H}^+$  ions. Hydrogen gas at 1 atm pressure is continuously passed through it at 298 K.

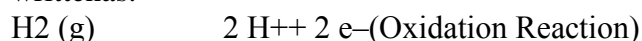
The SHE can act as a cathode or an anode depending upon the nature of another electrode to which it is connected. Thus SHE is also known as **reversible electrode**.





**SHE is represented as:**  $\text{Pt}, \text{H}_2 (1\text{atm}) / \text{H}^+ (1\text{M})$

In a cell when the standard hydrogen electrode acts **as anode**, the electrode reaction can be written as:



When the standard hydrogen electrode acts **as cathode**, the electrode reaction can be written as:

$$2\text{H}^{++} + 2\text{e}^- \rightarrow \text{H}_2 (\text{g}) \text{ (Reduction Reaction)}$$

The electrode potential of SHE is zero. The electrode potential of any electrode can be determined by connecting its half-cell with SHE.

➤ When E.P. of a metal electrode is determined with respect to SHE, it is called as Standard Electrode Potential ( $E^0$ ).

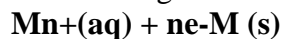
➤ The electrode at which reduction occurs with respect to SHE has +ve reduction potential while the electrode at which oxidation occurs with respect to SHE has -ve reduction potential.

### **Nernst Equation: Dependence of electrode potential and cell potential on Concentration**

If the concentration of the electrolyte solution is 1 mol/L or 1M and the temperature is 298 K (25 °C), the electrode potential of the given electrode is called **Standard Electrode Potential**

(E<sub>0</sub>). However, if the concentration of the electrolyte solution is different from 1M, the electrode potential of the electrode has different value from that of standard electrode potential, E<sub>0</sub>. This value can be calculated with the help of Nernst Equation. For this purpose, the electrode reaction is always written as reduction reaction.

Consider a general electrode reaction:



(Reactant)(Product)

Nernst Equation for this electrode:

$$E = E_0 - \frac{2.303 RT}{nF} \log \frac{[\text{M}(\text{s})]}{[\text{Mn}^{+}(\text{aq})]}$$

Where, E = Electrode Potential

E<sub>0</sub> = Standard Electrode Potential (for a 1M solution of metal ions)

F = Faraday of electricity (96500 C)

T = Temperature (K)

R = Gas Constant (8.314 JK<sup>-1</sup>mol<sup>-1</sup>)

n = No. of electrons involved in the electrode reduction reaction

[M(s)] = Molar concentration of metal

[Mn<sup>+</sup>(aq)] = Molar concentration of metal ions

At T = 298 K, Putting the value of R and F, we get:

$$E = E_0 - 0.0591n \log \frac{[\text{M}(\text{s})]}{[\text{Mn}^{+}(\text{aq})]}$$

Since, Molar concentration of pure solids is taken as unity; [M(s)] = 1

$$E = E_0 - 0.0591n \log [\text{Mn}^{+}(\text{aq})]$$

At any other temperature (T),

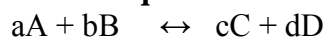
$$E = E_0 - \frac{2.303 RT}{nF} \log [\text{Mn}^{+}(\text{aq})]$$

From the above equations, it can be concluded that,

(a) E increases as [Mn<sup>+</sup>] increases.

(b) E decreases as temperature increases.

**Nernst Equation for a Cell:** Nernst equation can also be applied to any cell reaction such as:



$$E_{\text{cell}} = E_0_{\text{cell}} - \frac{2.303 RT}{nF} \log \frac{[\text{C}]^c [\text{D}]^d}{[\text{A}]^a [\text{B}]^b}$$

Thus Nernst equation is applicable for the determination of e.m.f. of a cell.

## TYPES OF ELECTROCHEMICAL CELLS

1. Electrolytic cell

2. Galvanic cell or voltaic cell (Electro-chemical cell)

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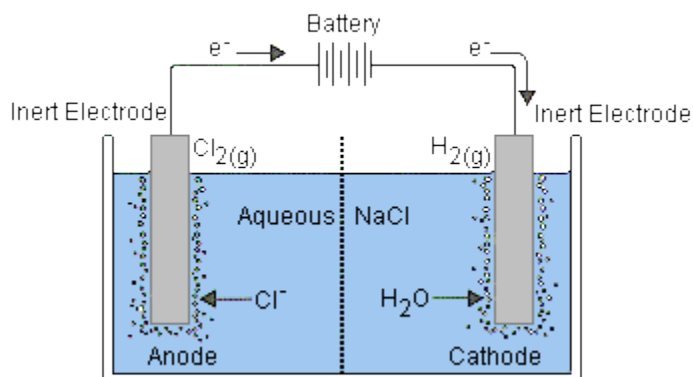
### Electrolytic cell

An **electrolytic cell** is an electrochemical cell that drives a non-spontaneous redox reaction through the application of electrical energy. They are often used to decompose chemical compounds, in a process called electrolysis—the Greek word lysis means *to break up*.

Important examples of electrolysis are the decomposition of water into hydrogen and oxygen, and bauxite into aluminium and other chemicals. Electroplating (e.g. of copper, silver, nickel or chromium) is done using an electrolytic cell. Electrolysis is a technique that uses a direct electric current (DC).

An electrolytic cell has three component parts: an electrolyte and two electrodes (a cathode and an anode). The electrolyte is usually a solution of water or other solvents in which ions are

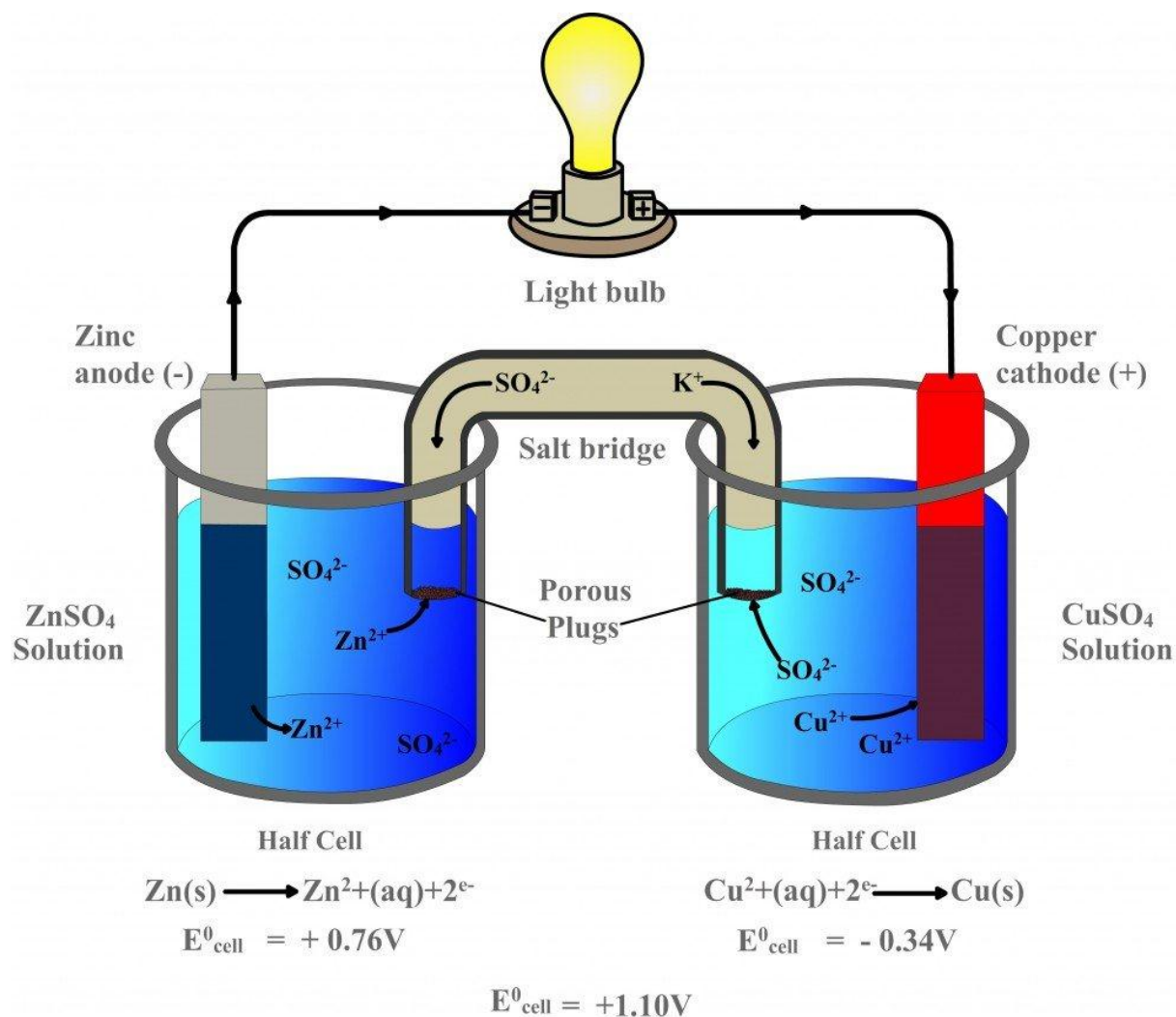
dissolved. Molten salts such as sodium chloride are also electrolytes. When driven by an external voltage applied to the electrodes, the ions in the electrolyte are attracted to an electrode with the opposite charge, where charge-transferring (also called faradaic or redox) reactions can take place. Only with an external electrical potential (i.e. voltage) of correct polarity and sufficient magnitude can an electrolytic cell decompose a normally stable, or inert chemical compound in the solution. The electrical energy provided can produce a chemical reaction which would not occur spontaneously otherwise



### **Galvanic cell or voltaic cell**

A galvanic cell, or voltaic cell, named after Luigi Galvani, or Alessandro Volta respectively, is an electrochemical cell that derives electrical energy from spontaneous redox reactions taking place within the cell. It generally consists of two different metals connected by a salt bridge, or individual half-cells separated by a porous membrane.

Volta was the inventor of the voltaic pile, the first electrical battery. In common usage, the word "battery" has come to include a single galvanic cell, but a battery properly consists of multiple cells.



## Electrochemical Series

By measuring the potentials of various electrodes versus standard hydrogen electrode (SHE), a series of standard electrode potentials has been established.

When the electrodes (metals and non-metals) in contact with their ions are arranged on the basis of the values of their standard reduction potentials or standard oxidation potentials, the resulting series is called the **electrochemical** or **electromotive** or **activity series** of the elements.

By international convention, the standard potentials of electrodes are tabulated for reduction half reactions, indicating the tendencies of the electrodes to behave as cathodes towards SHE.

Electrodes with positive  $E^{\circ}$  values for reduction half reactions do in fact act as cathodes versus SHE, while those with negative  $E^{\circ}$  values of reduction half reactions behave instead as anodes versus SHE. The electrochemical series is shown in the following table.

**Standard Aqueous Electrode Potentials at 25°C 'The Electrochemical Series'**

nt	Electrode Reaction (Reduction)	Standard Electrode Reduction potential
Li	$\text{Li}^+ + \text{e}^- \rightarrow \text{Li}$	-3.05
K	$\text{K}^+ + \text{e}^- \rightarrow \text{K}$	-2.925
Ca	$\text{Ca}^{2+} + 2\text{e}^- \rightarrow \text{Ca}$	-2.87
Na	$\text{Na}^+ + \text{e}^- \rightarrow \text{Na}$	-2.714
Mg	$\text{Mg}^{2+} + 2\text{e}^- \rightarrow \text{Mg}$	-2.37
Al	$\text{Al}^{3+} + 3\text{e}^- \rightarrow \text{Al}$	-1.66
Zn	$\text{Zn}^{2+} + 2\text{e}^- \rightarrow \text{Zn}$	-0.7628
Cr	$\text{Cr}^{3+} + 3\text{e}^- \rightarrow \text{Cr}$	-0.74
Fe	$\text{Fe}^{2+} + 2\text{e}^- \rightarrow \text{Fe}$	-0.44
Cd	$\text{Cd}^{2+} + 2\text{e}^- \rightarrow \text{Cd}$	-0.403
Ni	$\text{Ni}^{2+} + 2\text{e}^- \rightarrow \text{Ni}$	-0.25
Sn	$\text{Sn}^{2+} + 2\text{e}^- \rightarrow \text{Sn}$	-0.14
H <sub>2</sub>	$2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$	0.00
Cu	$\text{Cu}^{2+} + 2\text{e}^- \rightarrow \text{Cu}$	+0.337
I <sub>2</sub>	$\text{I}_2 + 2\text{e}^- \rightarrow 2\text{I}^-$	+0.535
Ag	$\text{Ag}^+ + \text{e}^- \rightarrow \text{Ag}$	+0.799
Hg	$\text{Hg}^{2+} + 2\text{e}^- \rightarrow \text{Hg}$	+0.885
Br <sub>2</sub>	$\text{Br}_2 + 2\text{e}^- \rightarrow 2\text{Br}^-$	+1.08
Cl <sub>2</sub>	$\text{Cl}_2 + 2\text{e}^- \rightarrow 2\text{Cl}^-$	+1.36
Au	$\text{Au}^{3+} + 3\text{e}^- \rightarrow \text{Au}$	+1.50
F <sub>2</sub>	$\text{F}_2 + 2\text{e}^- \rightarrow 2\text{F}^-$	+2.87

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

For example, standard reduction potential of zinc is -0.76 volt.

When zinc electrode is joined with SHE, it acts as anode (-ve electrode) i.e., oxidation occurs on this electrode. Similarly, the +ve sign of standard reduction potential indicates that the electrode when joined with SHE acts as cathode and reduction occurs on this electrode.

### **Characteristics of Electrochemical Series**

- The substances which are stronger reducing agents than hydrogen are placed above hydrogen in the series and have negative values of standard reduction potentials.
- All those substances which have positive values of reduction potentials and placed below hydrogen in the series are weaker reducing agents than hydrogen.
- The substances which are stronger oxidising agents than  $H^+$  ion are placed below hydrogen in the series.
- The metals on the top (having high negative values of standard reduction potentials) have the tendency to lose electrons readily. These are active metals.
- The activity of metals decreases from top to bottom.
- The non-metals on the bottom (having high positive values of standard reduction potentials) have the tendency to accept electrons readily. These are active non-metals.
- The activity of non-metals increases from top to bottom.

### **Numerical on Nernst equation**

**1. The standard electrode potential of zinc ions is 0.76V. What will be the potential of a 2M solution at 300K?**

Solution:

The Nernst equation for the given conditions can be written as follows;

$$E_{M^{n+}/M} = E^\circ - [(2.303RT)/nF] \times \log 1/[M^{n+}]$$

Here,

- $E^\circ = 0.76V$
- $n = 2$
- $F = 96500 \text{ C/mole}$
- $[M^{n+}] = 2 \text{ M}$
- $R = 8.314 \text{ J/K mole}$
- $T = 300 \text{ K}$

Substituting the given values in Nernst equation we get,

$$\begin{aligned} E_{Zn^{2+}/Zn} &= 0.76 - [(2.303 \times 8.314 \times 300)/(2 \times 96500)] \times \log 1/2 = 0.76 - [0.0298 \times (-0.301)] \\ &= 0.76 + 0.009 = \mathbf{0.769V} \end{aligned}$$

Therefore, the potential of a 2M solution at 300K is 0.769V.

## **MODULE 4**

### **CORROSION**

**Definition:** The loss of metals/alloys or their useful properties by their chemical or electrochemical interaction with its environment is known as corrosion. Corrosion is the reverse process of metallurgy.

**Cause of Corrosion:** For e.g., rusting of iron, tarnishing and blackening of silver articles and dulling of brass etc. when they are exposed to atmospheric conditions.

In nature, most of the metals exist in combined state as their compounds called ores or minerals. These compounds represent their thermodynamically stable state. The metals are extracted from these ores after expending a lot of energy. These pure metals have a natural tendency to convert back to their natural stable states, i.e. combined state. This is the basic reason for metallic corrosion.

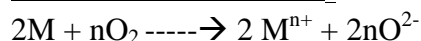
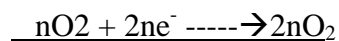
### **THEORY OF CORROSION**

1. **Dry /Direct chemical attack /Chemical or atmospheric corrosion:** This type of corrosion occurs due to direct action of atmospheric gases like  $O_2$ ,  $CO_2$ ,  $H_2S$ ,  $SO_2$ ,  $N_2$ ,  $X_2$  etc.

Three main types of chemical corrosion –

- I) Oxidation corrosion
- II) Corrosion by other gases
- III) Liquid-metal corrosion
- I) **Oxidation corrosion** – In this type the metal surface is attacked by oxygen in the atmosphere. generally metals like Li, Ca, Na, Mg etc. are attacked.

Reactions involved-



Mechanism – After formation of metal oxide it act as barrier for further corrosion but under following two cases the corrosion can continue-

- i) The metal diffuse outward
- ii) Oxygen diffuse inward

But since metal ion is smaller than oxygen ion, hence mostly first process takes place.

Nature of oxide film will effect further corrosion.

Nature of film	Extent of oxidation corrosion
Stable	Less ,protects underlying metal
Unstable	Oxidation does not occur.
Volatile	Rapid and continuous
Porous	Corrosion continues unobstructed.



- II) Corrosion by other gases –some time metal surface is attacked by gases other than oxygen such as  $\text{CO}_2$ ,  $\text{SO}_2$ ,  $\text{H}_2\text{S}$ ,  $\text{F}_2$ ,  $\text{Cl}_2$  .
- e.g. i)  $\text{Cl}_2$  on Ag. –It forms non-protective silver chloride film.
- E.g. ii)  $\text{Cl}_2$  on Sn –Forms volatile, non-protective stannic chloride film.

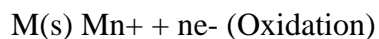
III) Liquid metal corrosion –This is due to chemical action of flowing liquid metal over the solid metal or alloy at high temperature.

## 2. Wet theory of corrosion or electrochemical corrosion

This type of corrosion takes place by:

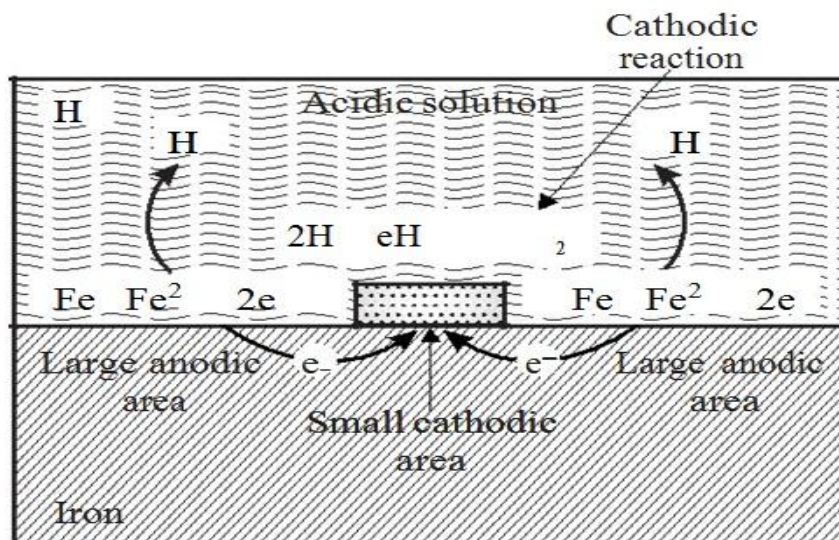
- (i) The formation of anodic and cathodic areas.
- (ii) The electrical contact between cathodic and anodic areas to enable the conduction of electrons.
- (iii) An electrolyte through which the ions can diffuse or migrate. This is usually provided by moisture.

**Mechanism:** Electrochemical corrosion involves flow of electrons between anode and cathode. The anodic reaction involves dissolution of metal liberating free electrons.



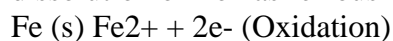
The cathodic reaction consumes electrons with either (a) evolution of hydrogen or (b) absorption of oxygen which depends on the nature of corrosive environment.

### *(a) Evolution of Hydrogen Gas*



**Fig.(a) Mechanism of electrochemical Corrosion with evolution of hydrogen**

This type of corrosion occurs **in acidic medium** e.g., considering the metal Fe, anodic reaction is dissolution of iron as ferrous ions with liberation of electrons.



The electrons released flow through the metal from anode to cathode, whereas  $\text{H}^+$  ions of acidic solution are eliminated as hydrogen gas.





The overall reaction is:  $\text{Fe (s)} + 2\text{H}^+ \text{ (aq)} \rightarrow \text{Fe}^{2+} \text{ (aq)} + \text{H}_2 \text{ (g)}$

This type of corrosion causes displacement of hydrogen ions from the solution by metal ions. All metals above hydrogen in electrochemical series have a tendency to get dissolved in acidic solution with simultaneous evolution of  $\text{H}_2$  gas. The anodes are large areas, whereas cathodes are small areas.

### (b) Absorption of oxygen

This type of corrosion takes in presence of oxygen. For example, rusting of iron **in neutral aqueous solution of electrolytes** in presence of atmospheric oxygen. Usually the surface of iron is coated with a thin film of iron oxide. If the film develops cracks, anodic areas are created on the surface. While the well metal parts act as cathodes. It shows that anodes are small areas, while the rest metallic part forms large cathodes.

At anode:  $\text{Fe (s)} \rightarrow \text{Fe}^{2+} \text{ (aq)} + 2\text{e}^-$  [Oxidation]

At cathode: The released electrons flow from anode to cathode through iron metal.

$\frac{1}{2} \text{O}_2 + \text{H}_2\text{O} + 2\text{e}^- \rightarrow 2\text{OH}^-$  [Reduction]

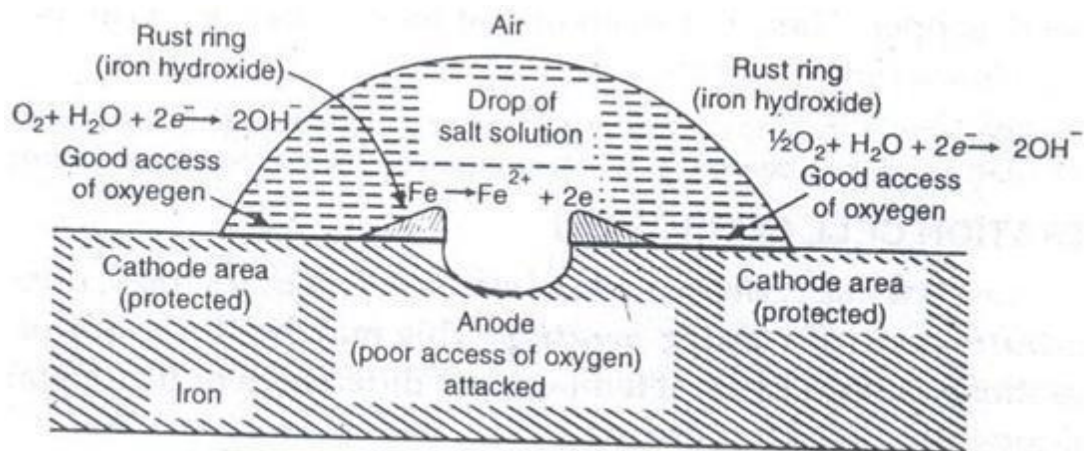
$\text{Fe}^{2+} \text{ (aq)} + 2\text{OH}^- \rightarrow \text{Fe(OH)}_2 \text{ ppt}$

(a) If oxygen is present in excess, ferrous hydroxide is easily oxidized to ferric hydroxide.

$4\text{Fe(OH)}_2 + \text{O}_2 + 2\text{H}_2\text{O} \rightarrow 4\text{Fe(OH)}_3$

The product, called yellow rust corresponds to  $\text{Fe}_2\text{O}_3 \cdot x\text{H}_2\text{O}$  (Haematite).

(b) If limited supply of oxygen is present, black magnetite (anhydrous ferrous ferric oxide;  $\text{Fe}_3\text{O}_4$ ) is formed.



Mechanism of wet corrosion by oxygen adsorption ( rusting of iron)

### Types of electro –chemical corrosion

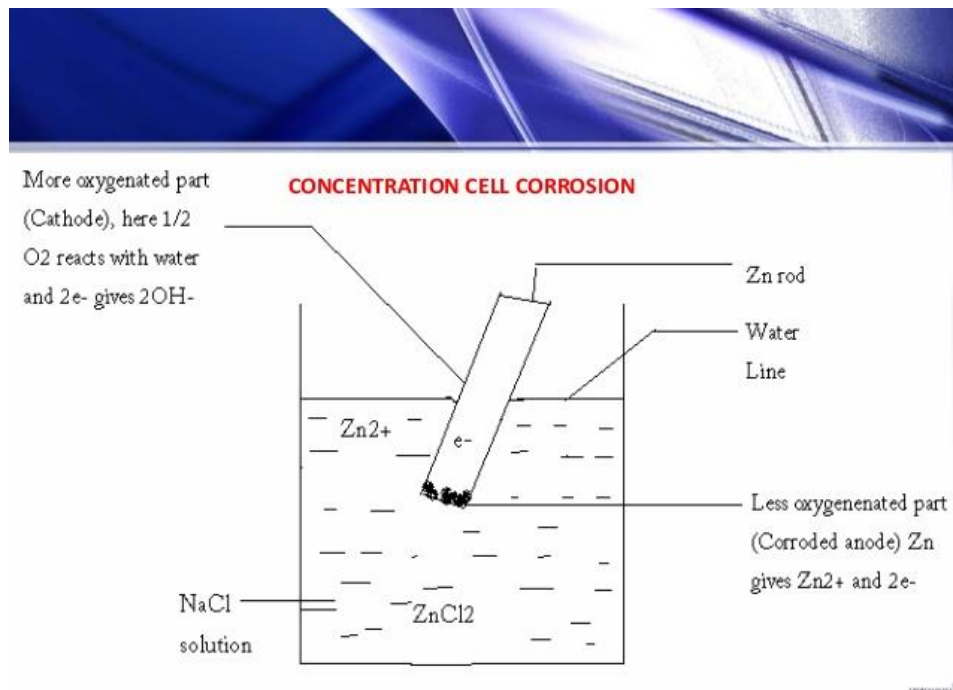
1. Concentration cell corrosion (Differential Aeration )
2. Galvanic cell corrosion. (Bimetallic corrosion).
3. Inter-granular corrosion.
4. Pitting corrosion.
5. Stress cell corrosion.
6. Waterline corrosion .
7. Under ground or soil corrosion.
8. Micro-Biological corrosion .

**NOTE (only first five type is there in syllabus .)**

## 1. Concentration cell corrosion- (Differential Aeration corrosion)

It occurs either of the two reason :

- a. Varying Concentration
- b. Varying Aeration
  - a. Varying OR Differential concentration :If metallic surface is in contact with solution of varying concentration then surface area in contact with lower concentration solution will act as anode hence, get corroded and surface area in contact with high concentration will act as cathode hence, remain protected.
  - b. Varying aeration (DIFFERENTIAL AERATION): If metallic surface is in contact with different air concentration ,then area exposed to highly oxygenated area will act as cathode hence, remain protected while, area in contact with poorly oxygenated area will act as anode hence, get corroded.



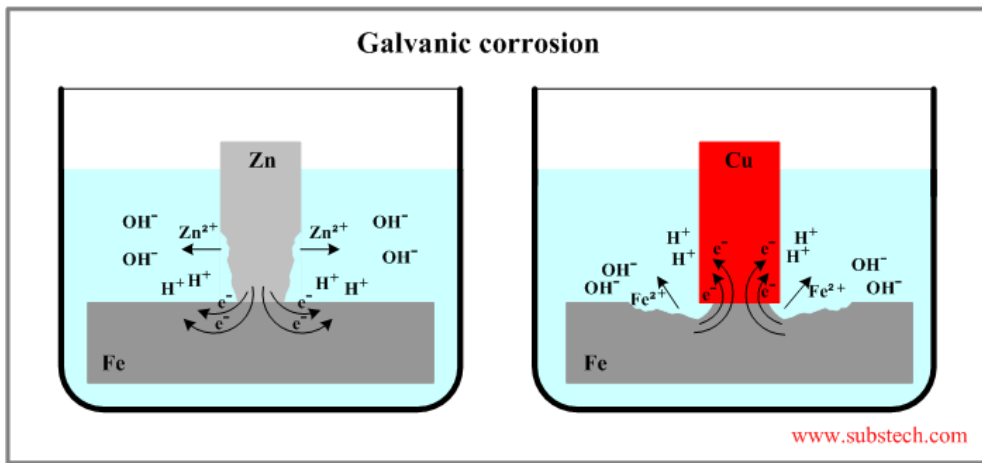
In both the cases due to potential difference between anodic and cathodic area the electron will flow from anode to cathode.

E.g. iron  $\text{Fe} \rightarrow \text{Fe}^{+2} + 2\text{e}^-$  (oxidation at anode)

$\frac{1}{2}\text{O}_2 + \text{H}_2\text{O} + 2\text{e}^- \rightarrow 2\text{OH}^-$  (Reduction reaction)

## Galvanic cell or Bimetallic corrosion

This type of corrosion occurs when two different types of metals with different electrode potentials are in contact and exposed to corrosive environment, then the metal which is at higher position than other metal in the electro-chemical series undergoes corrosion. E.g. If Zn and Cu form a galvanic cell then Zn which is higher in electro-chemical series forms an anode and is attacked whereas, Cu being lower in electro-chemical series acts as cathode and is protected.



Mechanism: In acidic solution the corrosion occurs by the hydrogen evolution process, while in a neutral or slight alkaline solution oxygen absorption occurs.

The electron current flows from the anode to cathode

At Anode:  $\text{Zn} \rightarrow \text{Zn}^{+2} + 2\text{e}^-$  (oxidation)

The cathode remains protected.

E.g. i. steel screws in a brass marine hardware

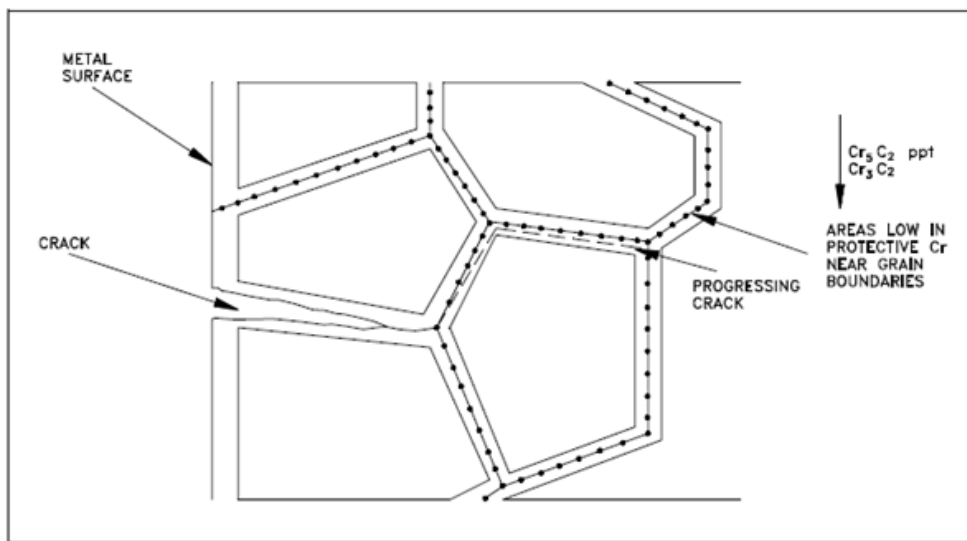
ii. Steel pipe connected to copper plumbing.

### **Inter-granular corrosion**

This type of corrosion occurs along grain boundaries under following conditions

- I) The material is highly sensitive to corrosive attack
- II) Corrosive liquid possess a selective character of attacking only at the grain boundaries but leaving the grain centers untouched.

Inter-granular corrosion follows the path of grain boundaries and occurs on microscopic scale, without any apparent external signs of any intensive attack. Hence, sudden failure of material occurs.



The grain boundary type of corrosion is generally encountered in alloys. For example, during the welding of stainless (An alloy of Fe, C, AND Cr. ) Chromium carbide is precipitated at the grain boundaries , thereby region just adjacent to grain boundaries becomes depleted in chromium composition and is more anodic with respect to the solid solution within the grain ( which is richer in chromium ) For the same reason it is also anodic to particles of chromium carbide so precipitated.

Inter granular corrosion can be removed/ avoided by

- I) Proper heat treatment, followed by quenching to avoid the heterogeneous precipitation that usually occurs due to slow cooling.
- II) *The use of low carbon content in steel.*

### **Stress cell corrosion (Stress corrosion cracking)**

It is characterized by highly localized attack and it is combined effect of

- I) Tensile stress
  - II) Specific corrosive environment.  
The corrosive agents are highly specific and selective such as :  
E.g. a) Caustic alkalis' and strong nitrate solution for mild steel .b) Traces of  $\text{NH}_3$  for brass c) Acid chloride solution for stainless steel.
1. Corrosion of metals is also influenced by some physical differences like internal stresses in the metals .
  2. Such difference results during manufacturing, fabrication and heat treatment.
  3. Metal components are subjected to unevenly distributed stresses during their manufacturing process. The electrode potential thus varies from one point to another.
  4. Area under great stress act as anode while area not under stress act as cathode.
  5. Treatment of metals and alloys such as cold working or quenching, ending and pressing introduces uneven stress and lead to corrosion.

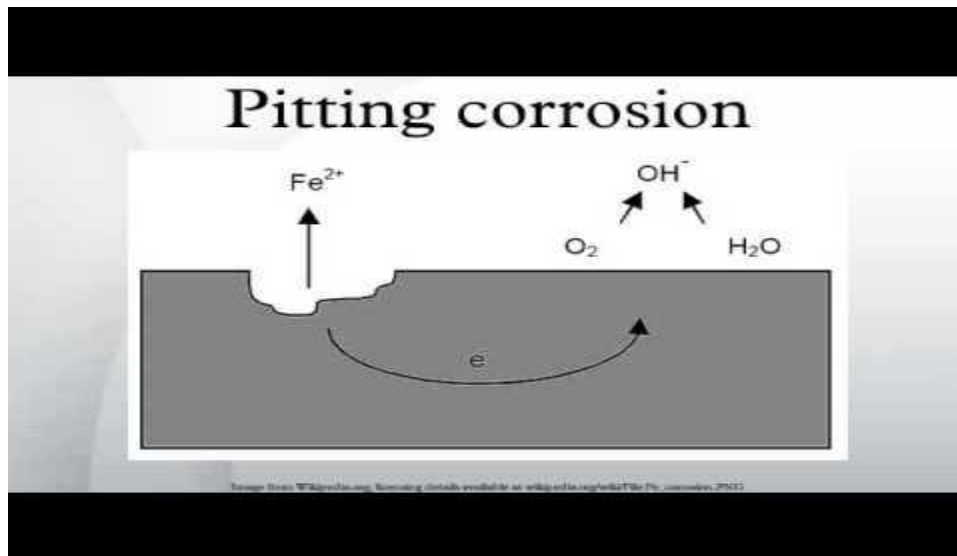
6. Corrosion takes place to minimize the stress .Most of the time it ends in breaking of the component in to pieces.

E.g. Season cracking: It is the stress corrosion of Cu alloy mainly brasses. Pure Cu is immune to stress corrosion, but presence of small amount of alloying element (like P, As, Zn , So, Al ) result in marked sensitivity.

Alpha brass which when highly stressed undergo inter-granular cracking in a atmosphere containing traces of ammonia or Amines .The attack occurs along the grain boundaries which become more anodic with respect to the grain themselves. Both Cu and Zn are electrochemically very active in  $\text{NH}_3$  solution and start to dissolve and initiating in fissures, which propagates resulting in formation of crack.

## **PITTING CORROSION**

**Pitting corrosion**, or **pitting**, is a form of extremely localized corrosion that leads to the creation of small holes in the metal. The driving power for pitting corrosion is the de passivation of a small area, which becomes anodic while an unknown but potentially vast area becomes cathodic, leading to very localized galvanic corrosion. The corrosion penetrates the mass of the metal, with a limited diffusion of ions. The mechanism of pitting corrosion is probably the same as crevice corrosion.



The more conventional explanation for pitting corrosion is that it is an autocatalytic process. Metal oxidation results in localized acidity that is maintained by the spatial separation of the cathodic and anodic half-reactions, which creates a potential gradient and electromigration of aggressive anions into the pit. For example, when a metal is present in an oxygenated NaCl electrolyte, the pit acts as anode and the metal surface acts as cathode. The localized production of positive metal ions in the pit gives a local excess of positive charge which attracts the negative chlorine ions from the electrolyte to produce charge neutrality. The pit contains a high concentration of MCl molecules which react with water to produce HCl, the metal hydroxide, and  $\text{H}^+$  ions, accelerating the corrosion process. In the pit, the oxygen concentration is essentially zero and all of the cathodic oxygen reactions take place on the metal surface outside the pit. The pit is anodic and the locus of rapid dissolution of the metal.<sup>[2]</sup> The metal corrosion initiation is autocatalytic in nature however its propagation is not. This kind of corrosion is extremely insidious, as it causes little loss of material with the small effect on its surface, while it damages the deep structures of the metal. The pits on the surface are often obscured by corrosion products. Pitting can be initiated by a small

Surface defect, being a scratch or a local change in composition, or a damage to the protective coating. Polished surfaces display higher resistance to pitting.

## **Factors Affecting Corrosion**

Corrosion of metal prominently depends on:

(i) Nature of metal (ii) Nature of environment

### **(i) Nature of Metal:**

**(a) Relative areas of Anodic to Cathodic parts:** Small anodic area and large cathodic area gives rise to an intense localized corrosion. This is because the demand for electrons by large cathodic areas can be met by smaller anodic areas by undergoing corrosion more rapidly. For e.g. Steel rivets in Cu sheets

**(b) Impurities:** Impurities present in metal enhance the rate of corrosion by forming minute electrochemical cells under suitable environmental conditions and the anodic parts undergo corrosion.

**(c) Position in Galvanic Series:** The metal or alloys which are placed at higher position in the series are more reactive, thus undergoes corrosion. The greater the potential difference between the two metals coupled together, the greater is the rate of corrosion.

**(d) Nature of Oxide film:** All metals get covered by a very thin film of oxide. Greater the specific volume ratio of oxide film, lesser is the rate of corrosion. [Specific volume ratio is the ratio of volume of metal oxide to that of metal.]

**(e) Volatility of corrosion product:** When the corrosion product is volatile, it volatilizes as soon as it is formed, thus exposing the underlying metal surface for further attack. Hence in such a case, corrosion goes on increasing with time.

**(f) Solubility of corrosion product:** If the corrosion product is soluble in corroding medium, corrosion becomes faster while if it is insoluble, it forms insoluble product which functions as a physical barrier and suppresses the rate of corrosion.

### **ii) Nature of Environment**

**(a) Effect of Temperature:** Increase in temperature increases the rate of corrosion as well as rate of diffusion.

**(b) Effect of pH:** Corrosion is more in acidic media ( $\text{pH} < 7$ ) than in alkaline media ( $\text{pH} > 7$ ) and neutral media ( $\text{pH} = 7$ ).

**(c) Effect of Corroding medium:** Higher the conductance of the corroding medium, more is the rate of corrosion.

**(d) Effect of Concentration of oxygen:** The rate of corrosion increases in presence of oxygen through differential aeration. The region where concentration of  $\text{O}_2$  is less becomes anodic and suffers corrosion.

**(e) Humidity:** It acts as a very good solvent for oxygen and form electrochemical cell. This rapidly increases the rate of corrosion.

**(f) Presence of impurities in atmospheres:** Atmosphere in the vicinity of the industrial area contains corrosive gases like  $\text{CO}_2$ ,  $\text{SO}_2$ , Fumes of  $\text{HCl}$ ,  $\text{H}_2\text{SO}_4$  etc which increases rate of corrosion due to their acidic nature.

## **Corrosion control methods (Prevention from Corrosion)**

The corrosion control methods are as follows:

1. Proper selection and designing

2. Modification in Properties of Metal
3. Modification of Environment:
4. Protective Coatings
5. Cathodic Protection

### **Proper selection and designing**

- Avoid sharp bends and corners in the flowing systems to reduce impingement
- Avoid galvanic coupling either by using **insulating gasket** between them or by selecting pair of metals which are **closer to each other in galvanic series**.
- Proper drainage of fluid.
- Avoid crevices in structures.
- Avoid small anodic area and large cathodic area.
- Coat the entire structure
- Increase the wall thickness of the structure.

### **Cathodic Protection**

In this method, the corroding metal is forced to behave like a cathode. There are two types of cathodic protection methods:

#### **(a) Sacrificial Anodic Protection (By Appropriate Galvanic Coupling)**

In this method, the metallic structure which is to be protected from corrosion is connected to a more anodic metal by a wire so that the entire corrosion is concentrated on this more active metal. The more active metal loses electrons and gets corroded and this metal is called sacrificial anode. Thus, the structure remains protected as it acts as a cathode. Metals commonly employed as sacrificial anode are Mg, Zn, Al and their alloys. For e.g.  $E^0$  for Mg = -2.36 V, while for Al = -1.66 V. Therefore Mg acts as sacrificial anode for Al.

#### **Applications:**

- Important applications of sacrificial anodic method include protection of buried pipe lines and underground cables from soil corrosion.
- Protection of ships and boats hulls from marine corrosion.
- Prevention of rusting water by inserting Mg sheets or rods into domestic water boilers or tanks.

#### **(b) Impressed current cathodic protection**

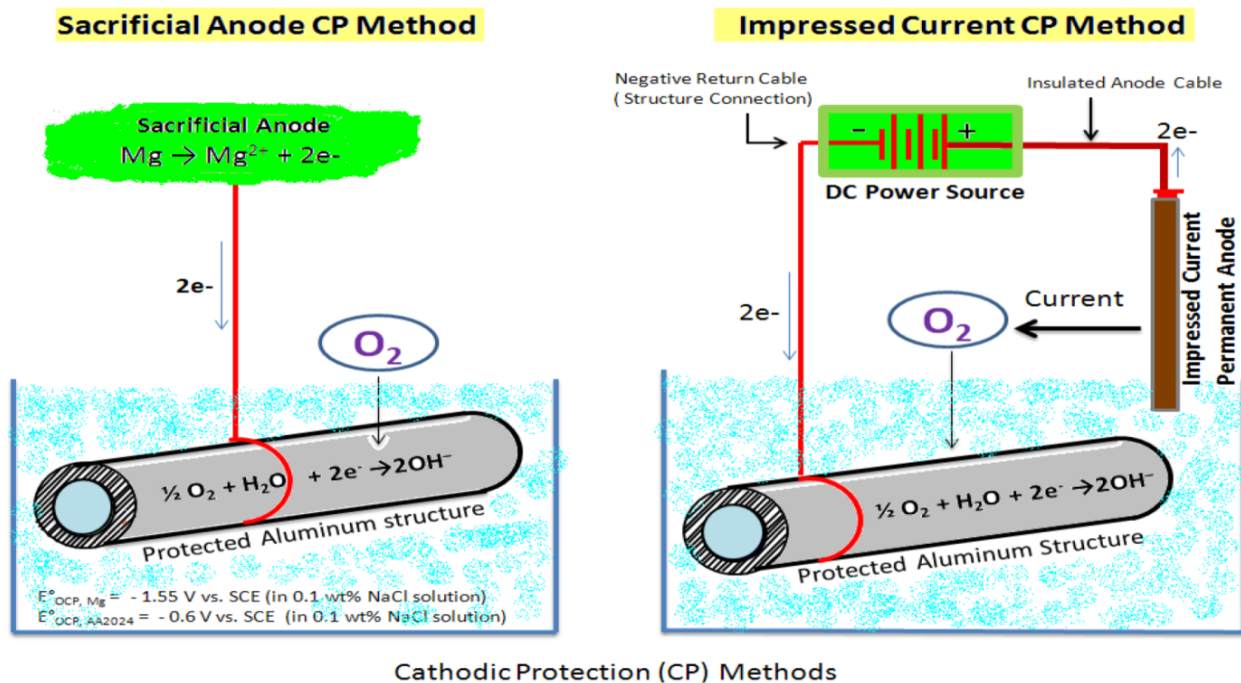
An impressed current is applied to convert the corroding metal from anode to cathode. The applied current is in opposite direction to nullify the corrosion current. Usually the Impressed current cathodic protection requires impressed current derived from a DC source (like battery or rectifier) and an insoluble anode (like graphite, high silica iron, stainless steel or platinum). The anode is buried in the soil or placed in a backfill (composed of graphite or gypsum etc.) so as to increase the electrical contact with the surrounding soil.

In impressed current cathodic protection, electrons are supplied from an external source, so that the object itself becomes cathodic and not oxidized.

**Application:** This type of cathodic protection has been applied to water coolers, water tanks, buried oil and water pipes, transmission towers etc. This type of protection is employed when

- Long term protection is needed
- Large structures are to be protected
- There is a cheap source of electrical power.

This method has advantage over sacrificial anodic protection as (i) It can be controlled from outside, (ii) No anode has to be replaced.

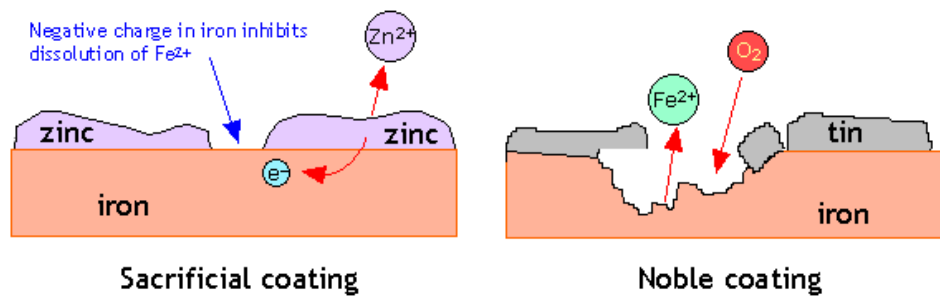


**Metallic coatings** : Surface coatings made up of metals are known as metallic coatings

It is of two types: 1

- a. Anodic coatings
  - b. Cathodic coatings
- a. Anodic coatings: These are done by coating with metals which are anodic to the base metal ( i.e. metal to protected) e.g. coating of Zn ,Al, and Cd on steel /iron are anodic coating because F/ steel is present below these metals in galvanic series hence it will act as cathode.if any crack ,pores or discontinuities occurs in such anodic coating ,coating which is acting as anode gets corroded and base metal which act as cathode remains protected.
  - b. Cathodic coating: Are obtained by coating a more noble metal (i.e. having higher electrode potential ) than the base metal .coating act as cathode with respect to base metal .





*e.g. Sn*

on Fe – Sn act as cathode and Fe as anode. If any crack ,pores, break or discontinuities occur s then base metal will lead to corrosion since it will anode. Hence, this type of coating is effecting only for completely continuous and break free coating.

### Distinguish between Anodic and Cathodic coating

#### Anodic coating

1. Protects the underlying metal Sacrificially.
2. Electrode potential of the coating Metal is lower than the base metal.
3. If any discontinuity occurs in the coating the base metal is not corroded until all the coating metal is destroyed.
4. E.g. Zn on Fe

#### Cathodic coating

1. Protects the base metal due to its Noble character .
2. Electrode potential of coating metal Is higher than the base metal.
3. If any discontinuity occurs in the coating the corrosion of the base metal Is speeded up.
4. E.g. Sn on Fe

### Methods of imparting metallic coatings

- a. *Galvanizing –E.g. Zn on steel*
- b. *Tinning – E.g. Tin on iron*

### DISTINGUISH BETWEEN GALVANIZING AND TINNING

#### Galvanizing

1. *Coating of zinc on iron or steel for Prevention of corrosion is called Galvanizing.*
2. *Zinc, being higher in electro-chemical Series,protects sacrificially.*
3. *Zinc is higher in position than iron ,*

#### Tinning

1. *Coating of tin on steel ,to prevent it from corrosion is called Tinning.*
2. *Tin is lower in electrochemical series and Protects iron from corrosion because of its noble and corrosion resistant nature.*

*Hence become anodic ,thus it provides Anodic coating to iron.*

- 4. In galvanic articles zinc protects the Underlying iron by sacrificial action If the coating is broken at some places.*
- 5. Zinc react with food acids forming Highly toxic compounds .thus Galvanized containers cannot be used For storing acidic food stuffs.*

- 3. Tin is lower in position than iron ,becomes Cathode and hence provide cathodic to iron.*

- 4. In tin coated article tin protects underlying Iron , as long as coating is perfect. Any break in coating causes rapid and severe corrosion of iron.*
- 5. Since tin is non-toxic and does not produce Poisonous compounds ,tin coated containers And utensils can be used for storing any food stuffs*

## MODULE 5

### Green Chemistry

#### Principles of green chemistry

1. Prevention of waste / byproducts.
2. Maximize atom economy.
3. Non-hazardous chemical.
4. Designing of safer chemicals.
5. Energy efficiency: Energy requirement for any synthesis should be minimum.
6. Auxiliary substances : selecting the most appropriate solvent.
7. Renewable feed stock.
8. Use of protecting group or chemical derivatives should be avoided whenever possible.
9. Use of catalysts should be preferred wherever possible.
10. Products obtained should be bio-degradable .
11. Accident prevention.
12. New analytical techniques to control hazardous compounds.

1. Prevention of waste /byproducts:

Green chemistry involved to design chemical synthesis in such a way that the process involves pathway to give products , leaving no waste to treat or clean up i.e prevention is better than cure. Hence it will avoid:

- i. Dumping problem and related soil,water and air pollution.
- ii. Compulsion to have waste treatment and disposal units attaches to manufacturing plants.
- iii. Cost on waste treatment or disposal.

2. Maximize atom economy :

- i. The design of the synthesis of the product should be such that all the chemicals or materials used in the process is converted into the required product to the maximum extent.
- ii. The process involving formation of undesired products along with desired products along with desired products should be replaced by new process in which most of the starting materials gets converted into required product.
- iii. This green process is economical and it maximize atom economy.

$$\% \text{ Atom economy} = \frac{\text{molecular weight of product} \times 100}{\text{Total molecular weight of reactants}}$$

e.g. preparation of maleic anhydride :

Maleic anhydride can be prepared by oxidation of benzene, butane or butane

### 3. Non- hazardous chemical synthesis :

- i. The synthetic method should be designed wherever possible to use and generate substances having little or no toxicity to human health and the environment.
- ii. The starting material selected should be least toxic .Thus e.g. pyridine or b-naphthyl amine being known to be carcinogenic should be avoided as starting material.
- iii. The reactions in which intermediates or reagents or products are toxic ,should not be followed .Instead alternative pathway should be used for synthesis. E.g. MIC leakage in Bhopal in 1984 , is an intermediate in manufacturing of agricultural pesticides and it is highly poisonous.

### 4. Design safer chemicals and products:

The chemical products should be designed to preserve the efficiency of desired function while reducing toxicity.e.g. 1. Before medical formulations are to be put in market ,they are put first on trail to check their toxic effects on humans. If found to be toxic then alternatives are prepared keeping in mind the function of the medicine but toxicity is reduced.. e.g. 2 Biological pesticides are more to be use compare to synthetical like DDT , Gamaxene etc. which are found to be toxic to humans.

### 5. Energy efficiency:

- i. The aim of green chemistry is to increase energy efficiency.
- ii. The energy requirements of chemical processes should be minimized considering their environmental and economic impacts.the synthetic methods should be carried out at ambient temperature and pressure wherever possible .
- iii. This can be achieved by use of catalyst and by stopping the use of fossil /gaseous fuels which releases solid or gaseous pollutants.
- iv. The energy efficiency of process can be increased by :
  - a. Proper heat transfer and
  - b. *Minimal wastage of energy during the process.*

e.g. 1. Microwave radiations and ultra sound , are used in the processes requiring very less energy .

e.g.2. many chemicals are produced by fermentation process where energy requirements is low and also the products are less harmful.

### 6. Auxiliary substances(use safer solvents and reaction conditions):

- i. The use of auxiliary substance like solvents ,separating agents etc. should be made unnecessary wherever possible and harmless if used.i.e the solvent selected for a particular reaction should not cause any environmental pollution and health hazard. E.g. 1. For drycleaning the fabrics, the toxic solvents like per chloro-ethylene should be replaced by liquid CO<sub>2</sub> e.2. solvents such as acetone ,benzene ,ether being highly inflammable should be avoided .

ii. A better method is to carry out reactions in the solid phase .since, major problem with many liquid phase solvents is their volatility that may damage human health and the environment.

iv. Also immobilized solvent i.e. Binding the solvent to polymer can be used to avoid hazards.

#### 7. Use renewable feed stock :

The starting material i.e. feed stock should be renewable wherever technically and economically feasible .It means that the starting materials which can be obtained from agricultural or biological products are referred to as renewable starting materials. depleting feed stock i.e. fossil fuels should be replaced by renewable feed stock wherever possible. for e.g. A new method is developed to prepare adipic acid from glucose obtained from corn starch or cellulose .This is green process because it replaces benzene as starting material for production of same product. Since, benzene is carcinogenic.

#### 8. Avoid chemical derivatives :

- i. During synthesis unnecessary derivatisation such as blocking or protecting groups or any temporary modifications should be avoided if possible.
- ii. The use of derivatives increases the steps of process, additional reagents are required ,more waste products are generated.
- iii. To avoid these effects, alternative reagents are to be used which are more selective.

#### 9. Use of catalyst should be preferred wherever possible:

Advantages:

- i. Use of catalyst minimizes the waste produced .
- ii. Catalyst are used in small amounts and can carry out a single reaction many times .
- iii. They are preferable to stoichiometric reagents ,which are used in excess and work only once.
- iv. Catalytic reactions are faster and hence require less energy .
- v. Non- toxic recoverable catalysts and bio-catalyst can be used.

#### 10. Products obtained should be bio- degradable.:

Chemical products should be designed such that they break down to harmless substances after use so that they do not accumulate in the environment.

e.g.1. DDT when used as pesticides ,its residue remain in soil for many years causing pollution .The alternative to this is biological insecticides.

e.g.2. The packaging material such as plastic or polystyrene are non-biodegradable and cause solid waste .The alternative to this the bio-degradable plastics containing cellulose and the packing pellets made up of starch are used.

#### 11. New analytical techniques /methods:(Analyze in real time to prevent pollution):

New analytical processes have to be developed to allow on-line monitoring and control prior to the formation of hazardous substances.

e.g. Preparation of ethylene glycol in which if reaction conditions are not monitored perfectly ,toxic substances are produced at higher temperature.

## 12. Accident prevention :

The hazards posed by toxicity ,explosions , fire, chemical release etc. must be looked into and the manufacturing plants should be so designed to eliminate the possibility of accidents during operation.

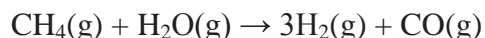
The use of safer chemicals ,minimizing temperature ,pressure and using catalysts helps in minimizing the potential of accidents.

### Atom economy

No atoms are gained or lost in a chemical reaction. However, some atoms in the reactants may not end up in the desired product. They instead form other products, and so are regarded as by-products.

For example, hydrogen can be manufactured by reacting methane with steam:

methane + steam  $\rightarrow$  hydrogen + carbon monoxide



In this reaction, carbon and oxygen atoms in the reactants do not form the useful product. Carbon monoxide is a waste gas.

The atom economy of a reaction is a measure of the amount of starting materials that end up as useful products. It is important for sustainable development and for economic reasons to use reactions with high atom economy.

### Calculating percentage atom economy

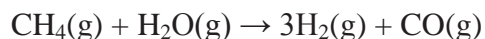
The percentage atom economy of a reaction is calculated using this equation:

$$\text{atom economy} = \frac{\text{total } M_r \text{ of the desired product}}{\text{total } M_r \text{ of all reactants}} \times 100$$

The highest possible value of atom economy is 100%, when all the reactant atoms end up in the desired product. If the atom economy is 50%, for example, then half the reactant atoms end up in the desired product or products.

### **Worked example**

Hydrogen can be manufactured by reacting methane with steam:



Calculate the atom economy for the reaction. ( $A_r$  of H = 1,  $A_r$  of C = 12,  $A_r$  of O = 16)

$$M_r \text{ of } \text{CH}_4 = 12 + (4 \times 1) = 16$$

$$M_r \text{ of H}_2\text{O} = (2 \times 1) + 16 = 18$$

total  $M_r$  of reactants =  $16 + 18 = 34$

$$A_r \text{ of } H_2 = (2 \times 1) = 2$$

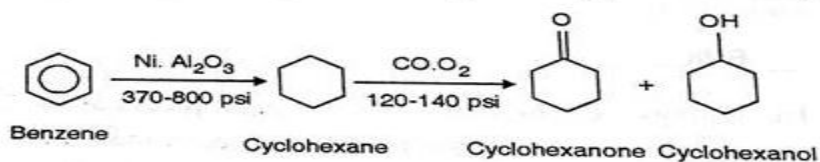
total  $M_r$  of desired product =  $3 \times 2 = 6$  (there are three  $H_2$  in the balanced equation)

$$\text{atom economy} = \frac{\text{total } M_r \text{ of the desired product}}{\text{total } M_r \text{ of all reactants}} \times 100$$

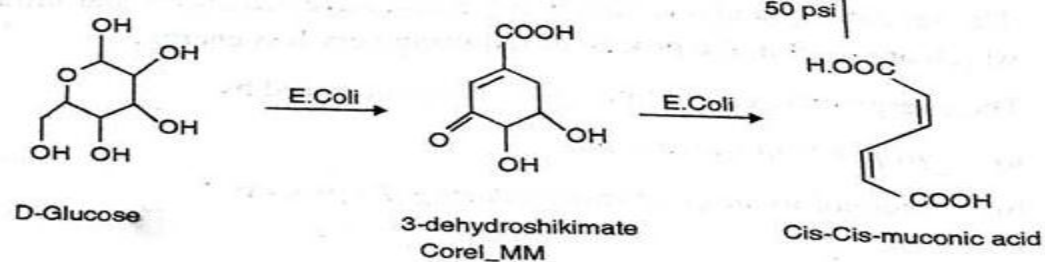
$$\text{atom economy} = \frac{6}{34} \times 100$$

atom economy = 17.6% (to 3 significant figures)

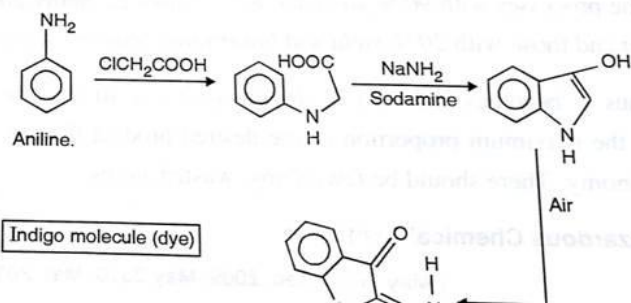
**(A) Traditional pathway : Using Benzene (Carcinogenic solvent)**



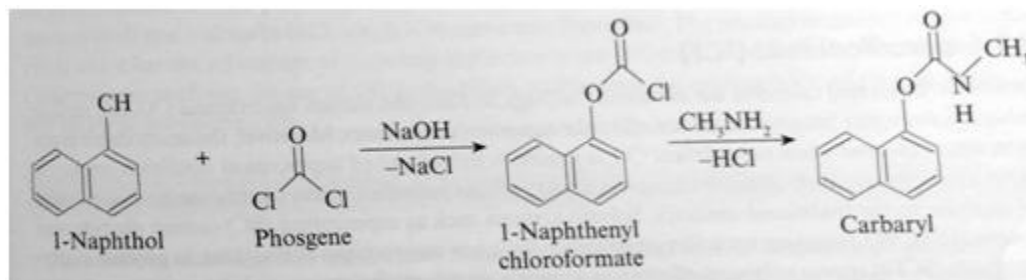
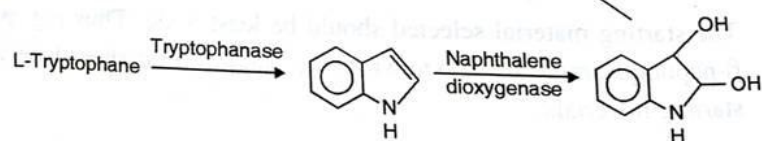
**B) Greener pathway :**  
**Using glucose (absolutely safe)**



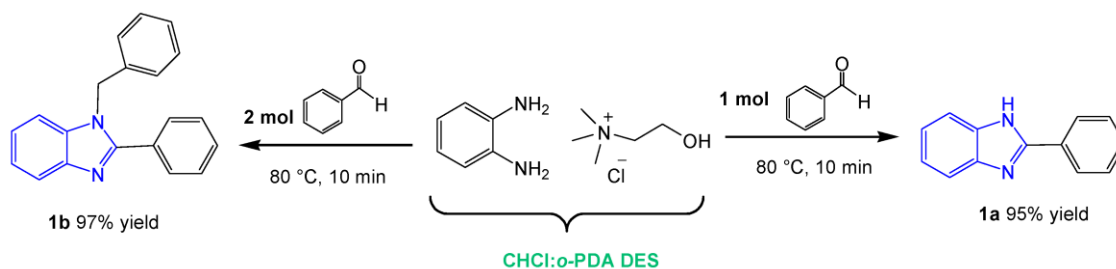
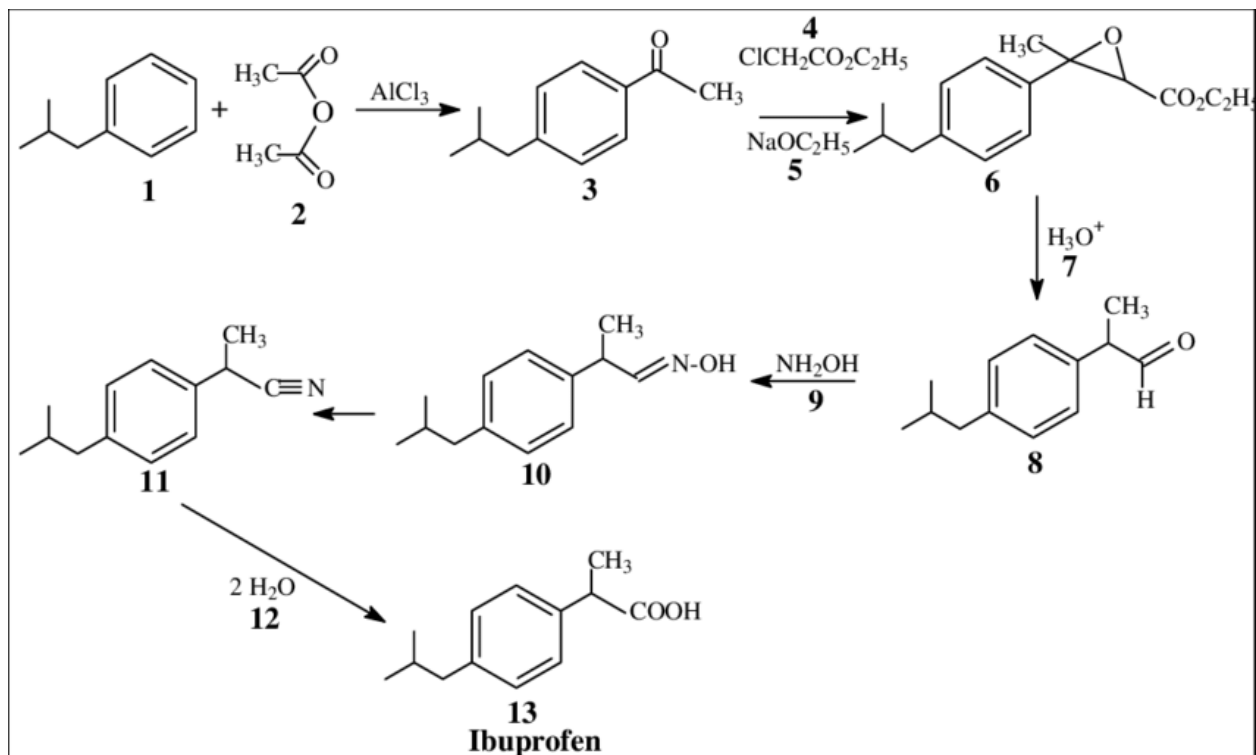
**(A) Conventional Route using hazardous Aniline**



**(B) Greener Route : Using enzyme**



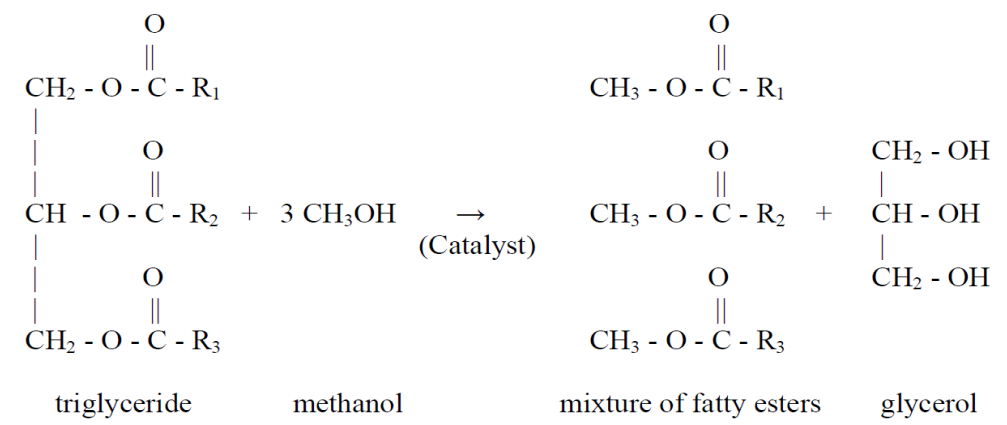




**BIO-DIESEL:** It is an alternative diesel fuel derived either from vegetable oils, petrocrops, cola, agricultural wastes etc.

Synthesis of Bio-Diesel from vegetable oil: Bio-Diesel is obtained from vegetable oil by a process known as trans-esterification or alcoholysis. During this process alcohol from an ester is displaced by another alcohol.

Eg. Trans esterification reaction of triglycerides present in vegetable oils using methanol-



Triglycerides can be readily trans-esterified batch-wise at atmospheric pressure and at temperature of about 60-70 °C with an excess of methanol in presence of alkaline catalyst. After the reaction is complete, the mixture is allowed to settle and the lower glycerin layer is drawn off. The upper layer of the methyl esters is washed and purified further. The unreacted /excess methanol is recovered and recycled.

Advantages of Bio- diesel:

1). It is prepared from renewable resources 2.) Bio-diesel is biodegradable and non- toxic 3.) The exhaust gas emission is lesser as compared to the conventional diesel fuel. 4.) Since it is of photo synthetic origin it has no harm for environment.

## **MODULE 6**

### **Fuels and Combustion**

Fuel is a combustible substance which during combustion gives large amount of heat that can be used economically for domestic and industrial purpose. In general fuels contain carbon as the main constituent. There are chemical fuels, nuclear fuels and fossil fuels. For e.g. Coke, charcoal, petroleum, diesel, kerosene oil etc. During combustion carbon, hydrogen etc. present in fuel react with  $O_2$  to form products like  $CO_2$ ,  $H_2O$  etc. and release heat.

### **Classification of Fuels**

These can be classified on the basis of their (i) **Occurrence** and (ii) **Physical state**

(i) On the basis of occurrence they are of two types:

**(a) Primary Fuels:** Fuels which occur in nature as such are called primary fuels or natural fuels. For e.g., wood, peat, coal, petroleum, and natural gas.

**(b) Secondary Fuels:** The fuels which are derived from the primary fuels by further chemical processing are called secondary fuels or artificial fuels.

For e.g., coke, charcoal, kerosene, coal gas, producer gas etc.

(ii) On the basis of physical state these may be classified as:

**Solid Fuels:** For e.g., Wood, coke, charcoal etc.

**Liquid Fuels:** For e.g. Crude oil, petrol, diesel etc.

**Gaseous Fuels:** For e.g., Natural gas, LPG, coal gas, biogas, CNG etc.

### **Characteristics of a Good Fuel**

An ideal fuel should have the following characteristics:

- ☐ **Calorific value:** It should have high calorific value.
- ☐ **Ignition Temperature:** A good fuel should have moderate ignition temperature.
- ☐ **Moisture content:** It should be low.
- ☐ **Ash content:** It should be low.
- ☐ **Rate of combustion:** It should be moderate.
- ☐ It should be **fairly , Cheap and easily** available.
- ☐ **Free from objectionable substances:** Like smoke,  $H_2S$ ,  $CO$ ,  $SO_2$  etc.
- ☐ Low **storage cost and conveniently transportable.**

**Units of Heat:** The quantity of heat can be measured in the following units:

**(i) Calorie:** It is defined as the amount of heat required to raise the temperature of 1g of water by  $1^\circ C$  ( $14.5 - 15.5^\circ C$ ).

1 calorie = 4.184 Joules

**(ii) Kilo Calorie:** It is defined as the amount of heat required to raise the temperature of 1Kg of water by  $1^\circ C$  ( $14.5 - 15.5^\circ C$ ).

1 K cal = 1000 cal

**(iii) British Thermal Unit: (B. T. U.)** It is defined as the amount of heat required to raise the temperature of 1 pound of water through  $1^\circ F$ .

1 B.T.U. = 252 Cal = 0.252 k cal

**(IV) Centigrade Heat Unit (C.H.U):** It is defined as the amount of heat required to raise the temperature of 1 pound of water through  $1^\circ C$ .

1 Kcal = 1000 Calorie = 3.968 B.T.U. = 2.2 C.H.U.

**Calorific value:** It is defined as the total amount of heat liberated when a unit mass of a fuel is burnt completely in excess supply of oxygen. For a good fuel calorific value should be high.  
Calorific value of carbon is 32.83 KJ

### **Gross and Net Calorific Value**

Depending upon the fact whether the products of combustion are allowed to cool down at room temperature or they are allowed to escape, there are two types of calorific values:

**Gross Calorific Value or Higher Calorific Value:** It is the amount of heat evolved when a unit quantity of fuel is completely burnt in excess supply of oxygen and the products of combustion are cooled down at room temperature.

As the products of combustion are cooled down to room temperature, the steam gets condensed into water and latent heat is evolved. Thus, in the determination of gross calorific value, the latent heat also gets included in the measured heat. Therefore, gross calorific value is also called the higher calorific value.

**Net Calorific Value or Lower Calorific Value:** It is the amount of heat evolved when a unit quantity of fuel is completely burnt and the products of combustion are allowed to escape.

The water vapor does not condense and escape with hot combustion gases.

Hence, lesser amount of heat than gross calorific value is available. It is also known as lower calorific value (LCV). Thus,

$LCV = HCV - \text{Latent heat of water vapors formed during burning}$

Latent heat of steam is 587 cal/g.

We know,  $H_2 + \frac{1}{2} O_2 \rightarrow H_2O (v)$

2 g 18 g

or 1 part by wt. or 9 part by wt.

Therefore,

$LCV = HCV - \text{Weight of hydrogen present per unit mass of fuel} \times 9 \times \text{latent heat of steam}$

*HCV and LCV using Dulong's formulae.*

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

$LCV = [HCV - (0.09 H \times 587)]$

### **Numerical on GCV and NCV (HCV and LCV)**

E.G. A sample of coal has the following composition by mass, C=85%, H=7%, O=3%, N=2.1%, S=3.5% and Ash=4.4%. Calculate HCV and LCV using Dulong's formulae.

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

$$= \frac{1}{100} [8080 \times 85 + 34500 (7 - 3/8) + 2240 \times 3.5] = 9232.025 \text{ KCAL /KG.}$$

$LCV = [HCV - (0.09 H \times 587)]$

$$= 9232.025 - 0.09 \times 7 \times 587 = 8862.215 \text{ KCAL/KG.}$$

## Coal

Coal is regarded as a fossil fuel produced from the fossilized remains of plants under conditions of high temperature and pressure over millions of years. It is mainly composed of C, H, N, O and non-combustible inorganic matter. The transformation of the vegetable debris to coal takes place in two stages:

(a) **Biochemical or peat stage**: During this stage, the plant materials were attacked by various micro organisms.

(b) **Chemical stage or metamorphism**: In this stage, the peat deposits buried under sedimentary deposits lose moisture and volatile components under the effect of high temperature and pressure. The peat gets enriched in carbon whereas its oxygen content decreases. The spongy peat transforms into hard brittle coal gradually. This process involved evolution of CO<sub>2</sub> & CH<sub>4</sub>, loss of water, increase in hardness and transition from vegetation to anthracite coal which is the best quality coal.

**Classification of Coal**: When wood is converted into coal, there is gradual increase in the concentration of carbon and decrease in the percentage of oxygen & nitrogen.

S.No.	Type of Coal	Percentage Carbon	Calorific Value (Kcal/Kg)
1	Peat	57	4125-5400
2	Lignite	67	6500-7100
3	Bituminous	83	8000-8500
4	Anthracite	93	8650-8700

## Analysis of Coal

**A)PROXIMATE ANALYSIS**:It involves the following determination –

1. Moisture :About 1 gm. Of finely powdered air dried coal sample is weighed in a crucible .The crucible is placed inside an electric hot air oven, maintained at 105-110 °C for 1 hr. and then cooled in desiccator and weighed .loss in weight is moisture content.

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

Significance/importance of moisture determination-high percentage of moisture is undesirable because it reduces the calorific value and increases the transport cost. A considerable amount of heat is wasted in evaporating the moisture during combustion. Hence, the lesser the moisture content, the better the quantity of coal as a fuel

2. Volatile matter: The dried sample of coal left in the crucible (1) is then covered with a lid and placed in a muffle furnace ,maintained at 925[+- 20]°C for 7 min. Then crucible is cooled in air and then inside a desiccator and weighed again .loss in weight is volatile matter in coal sample.

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

Significance /Importance of volatile matter determination-1.High volatile matter coals give long flames, high smoke and low calorific values. Hence, lesser the volatile matter content the better is the quantity of coal. ii) Higher the volatile content larger is the combustion space required .Hence the volatile matter content of a coal influences the furnace design.iii) High volatile matter content is preferable in coal gas manufacture. iv) Low volatile matter content is preferred in manufacture of metallurgical coke.

3. Ash:The residual coal in the crucible in (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, cooled first in air, then in dessicator and weighed. Heating, cooling and weighing is repeated till a constant weight is obtained .The residue obtained is ash.

% of Ash=  $\frac{\text{weight of ash left}}{\text{Weight of coal taken}} \times 100$

Weight of coal taken

Significance of ash determination

- i)Ash reduce the heating value of coal
- ii) The presence of ash also increases the transportation, handling and storage cost
- iii) It also involves additional cost in ash disposal.
- iv) The % of ash determines the quality of coal. Hence, lesser the percentage of ash, better is the quality of coal.

4. Fixed carbon

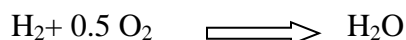
% of fixed carbon= $100 - (\text{\% of moisture} + \text{\% of volatile matter} + \text{\% of ash})$

Significance of fixed carbon

- ii)Higher the % of fixed carbon in coal greater is its calorific value
- ii) The percentage of fixed carbon helps in designing the furnace and the shape of the fire box.

## **B.ULTIMATE ANALYSIS**

1. Carbon and Hydrogen :About 1-2 gms. Of accurately weighed coal sample is burnt in a current of oxygen in a combustion apparatus .C and H of the coal are converted into  $\text{CO}_2$  and  $\text{H}_2\text{O}$  respectively. The gaseous products of combustion are absorbed respectively in KOH and  $\text{CaCl}_2$  tubes of known weights. The increase in weights of these are then determined .



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

Weight of coal sample taken x44

$$\% \text{ of H} = \frac{\text{Increase in wt. of CaCl}_2 \text{ tube} \times 2 \times 100}{\text{Wt. of coal sample taken} \times 18}$$

Wt. of coal sample taken x 18

### Significance/importance of C and H

Higher the % of C and H the better is the quality of coal and Higher is its calorific value.

2) Nitrogen: About 1 gms. Of accurately weighed powdered coal is heated with concentrated  $\text{H}_2\text{SO}_4$  along with  $\text{K}_2\text{SO}_4$  ( catalyst ) in a long necked kjeldals flask After the solution becomes clear it is treated with excess of KOH and the liberated  $\text{NH}_3$  is distilled over and absorbed in a known volume of standard acid solution . The unused acid is determined by back titration with std. NaOH solution .From the volume of acid used by  $\text{NH}_3$  liberated the % of N in a coal is calculated as follows

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

Weight of coal taken

Significance: N has no calorific value and hence its presence in coal is undesirable .Thus a good quality coal should have very little Nitrogen content.

3) Sulphur : A known weight of coal is burnt completely in bomb calorimeter in a current of oxygen . During burning S present in coal is oxidised to sulphate .Ash from bomb calorimeter is extracted with dil. HCl and acid extract is treated with  $\text{BaCl}_2$  solution to precipitate sulphate as  $\text{BaSO}_4$  .This ppt. is filtered, washed and heated to a constant weight and weighed.

$$\% \text{ of S} = \frac{\text{Weight of BaSO}_4 \times 32 \times 100}{\text{Weight of coal sample taken} \times 233}$$

Weight of coal sample taken x233

### Significance

- i) Sulphur increases the calorific value of coal
- ii) The combustion products of sulphur i.e.  $\text{SO}_2$  and  $\text{SO}_3$  have corrosion effects on equipment.
- iii) The harmful gases  $\text{SO}_2$  and  $\text{SO}_3$  will cause air pollution.
- iv) Sulphur containing coal is not suitable for the preparation of metallurgical coke as it adversely affects the properties of the metal.

4) ASH:As in proximate analysis.

### 5) Oxygen –

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

### Significance

- I. High oxygen content coals are characterized by high inherent moisture, low calorific value and low coking power.
- II. Oxygen is undesirable .Thus a good quality coal should have low % of oxygen.

## **LIQUID FUEL**

**Crude petroleum oil**: It is a dark greenish-brown viscous oil found deep in earth crust. It is composed mainly of various hydrocarbons (like straight-chain paraffin's, cyclo paraffin's, olefins and aromatics) together with small amounts of organic compounds containing oxygen, nitrogen and sulphur. Its average composition is : C=79.5% to 87.1%, H=11.5 to 14.8%, S=0.1 to 3.5%, N+O=0.1 to 0.5%

### **Classification of petroleum**

1. paraffinic-base type crude-It is mainly composed of the saturated hydrocarbons from  $\text{CH}_4$  to  $\text{C}_{35}\text{H}_{72}$  and little of naphthalene's and aromatics. The hydrocarbons from  $\text{C}_{18}$  to  $\text{C}_{35}\text{H}_{72}$  are semisolids called waxes.
2. Asphaltic-base type crude –It mainly contains cyclo paraffin's or naphthalene's with smaller amount of paraffin's and aromatic hydrocarbons
3. Mixed –base type crude- It contains both paraffinic and asphaltic hydrocarbons and are generally rich in semi-solid waxes.

### **Mining of petroleum**

It is done by drilling holes in earth's crust and sinking pipes up to the oil-bearing porous rocks. Oil usually, gushes out itself due to hydrostatic pressure of natural gas. Alternately it may be mechanically pumped up using either lift pump or air-lift pump. Air lift pump consists of two co-axial pipes, lowered into the base of oil bed. Compressed air comes out through the inner pipe.

**Knocking** : “It is defined as a sharp metallic sound produced in the internal combustion engine”. It results into loss of energy. Also defined as “The rattling noise produced in the internal combustion engine”.

Knocking is a kind of explosion due to rapid pressure rise occurring in an IC engine. In a petrol engine, a mixture of gasoline vapour and air (1:17) is used as a fuel. The air and gasoline vapours are compressed and ignited by an electric spark. The chemical reaction taking place is the oxidation of hydro-carbons. The products of oxidation reaction drives the piston down the cylinder. If the combustion proceeds in a regular way, there is no problem of knocking. But in certain circumstances, the oxidation is sudden and the mixture detonates and produces an explosive sound called “engine knock”. Which results in loss of power. It also causes mechanical damage by overheating of the cylinder parts.

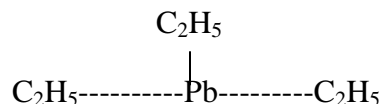
Chemical structure and knocking: i) The knocking tendency decreases with increase in the compactness of the molecules. ii) The tendency to knock decreases in the following order:



Straight chain paraffin > branched chain paraffin's > cycloparaffins > olefins > aromatics

With normal paraffin's the anti knocking properties decreases with the increase in length of the hydro carbons chain. Thus, the octane numbers of n-butane, n-pentane and n- heptanes are 90, 60, and 29 respectively.

**Anti knocking agents:** The octane number of gasoline may be increased by the addition of anti knocking agents (doping). EG. TEL Tetra ethyl lead  $(C_2H_5)_4Pb$ ; and Diethyl telluride  $(C_2H_5)_2Te$



TEL-( i). It is colorless oily liquid, with sweet odour and specific gravity 1.62 and b.p-200<sup>o</sup>.(ii) It should be handled with care to see that it does not enter the body through a bruise or cut. (iii) Gasoline containing TEL is coloured to indicate its poisonous nature .(iv) About 0.5 ml of TEL/L is added for spirit and about 1ML/L is added for aviation fuel .(v) Not more than 7ml of TEL per gallon are added to the aviation fuel.

During knocking process Hydroxyl and free radicals are produced .TEL decomposes and form lead oxide ( $PbO_2$ ) which terminates these undesired free radicals and thus chances of early detonation .The Pb and  $PbO_2$  vapours formed may contaminate the atmosphere .To avoid this ethylene bromide is added in petrol

**Octane number:** It is an arbitrary scale which expresses commonly the knocking characteristics of combustion engine petrol.

**Definition:**“The percentage of iso-octane in the mixture of iso-octane and iso-heptane which has the same knocking characteristic as the test sample under identical condition.”

It has been found that n-heptane knocks very badly and hence its antiknocking value is arbitrarily given as zero. On the other hand, iso-octane gives very little knocking and so its antiknock value has been given as 100.

Egs-

Hydro carbon	Octane number
Benzene	100+
Cyclo-hexane	77
2-methyl pentane	71
n-pentane	62
n-hexene	26

**Cetane number:** The knocking characteristic of a diesel oil are expressed in terms of cetane number .Cetane  $C_{16}H_{34}$  is a saturated hydrocarbon which has a very short ignition lag as compared to any commercial diesel fuel. Hence its cetane number is taken as 100.On the contrary , 2-methyl naphthalene(  $C_{11}H_{10}$ )has a very long ignition lag as compared to any commercial diesel oil .Hence its cetane number is taken as zero.

**Definition** :Percentage of n- Hexadecane in the mixture of n-hexadecane and 2-methyl naphthalene which has same ignition character of the diesel under test.

Ignition quality of hydrocarbon decreases in following order:

straight chain >cycloparaffins>olefins>branched chain hydrocarbons>aromatics

Cetane number of a diesel can be increased by additives such as ethyl nitrite, ethyl nitrate etc.

Compounds	Cetane number
Octa decane	200
Hexa decane	103
Tetra decane	96
Dodecane	88
Decane	77
Octane	64
Heptane	56

### **Ignition lag ( Ignition delay)**

Combustion of diesel takes place under compression and heat conditions .

Steps involved in combustion of diesel in diesel engine :

Step-1 : only air is forced in cylinder and compressed to produce 500- 700 °c .

Step 2: oil droplets are injected into the cylinder .The oil droplets absorb heat ,oil molecules get decomposed and atomization takes place .

Step3: Atomized oil chemically combines with  $O_2$  to produce more heat , expansion of combustion gases , push on the piston .

Step 2 should be as fast as possible ( i.e. 1/500 sec. for fast speed ) otherwise if there is a time lag then diesel knock is produced .This time lag is called ignition lag . The ignition lag depends upon the engine design, type of injector and mainly on chemical nature of fuel.

Note – Ignition lag notes can be included in cetane no. if weightage for cetane no. is more

### **Numerical on combustion of solid fuel or liquid fuel such as coal**

Formulae:

1.Amount of oxygen required for combustion of fuel= [2.67 C+8H+S-O] Kg

2.Amount of air required for combustion = $\frac{100[2.67C+8H+S-O]}{23}$  Kg

23

3. Volume of air required for combustion= $\frac{\text{amt of air required} \times 22.4}{28.94}$  m<sup>3</sup>

28.94(mol.wt of air)

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

Solution:

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

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

23

= $\frac{100}{23}(2.67 \times 0.8 + 8 \times 0.12 + 0 - 0.08)$  KG.

=13.113Kg.

E.g. 2 Calculate weight and volume of air needed for complete combustion of 1 kg of coal containing C=66%,H=5%,O=8%,N=2.8%,MOISTURE=14.5% and remaining is ash .( molecular weight of air=28.949 gms.) **Solution:**

Constituent	% by weight	Wt/kg of fuel
C	66	0.66
H	5	0.05
O	8	0.08
N	2.8	-----
MOISTURE	14.5	-----
ASH	-----	-----

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

= $\frac{100}{23} (2.67 \times 0.66 + 8 \times 0.05 + 0 - 0.08)$  =9.05

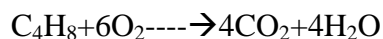
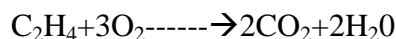
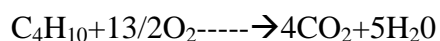
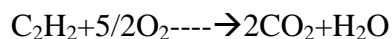
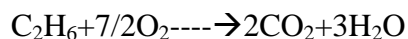
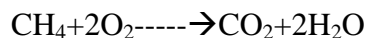
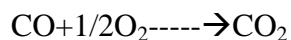
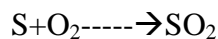
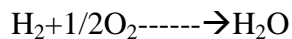
Now molecular wt. of air required is 28.949 gm .That means 28.949 kg of air occupies 22.4 m<sup>3</sup> of air.

1.05 kg of air will occupy=  $\frac{9.05 \times 22.4}{28.949}$  m<sup>3</sup> of air= 7.0026 m<sup>3</sup>

28.949

## Numerical on amount of air and oxygen required for combustion of gaseous fuel

Some important combustion reactions :

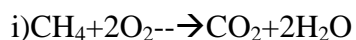


Eg.1 Calculate the volume of air required for complete combustion of 1 m<sup>3</sup> of gaseous fuel, which poses by volume CH<sub>4</sub>=35%, C<sub>2</sub>H<sub>4</sub>=4%, CO=10%, H<sub>2</sub>=45%, N<sub>2</sub>=2%, water vapour=4%.

Solution:

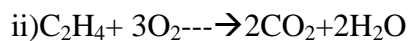
constituents	% by weight	Weight of each per kg of fuel
CH <sub>2</sub>	35	0.35
CH <sub>4</sub>	04	0.04
CO	10	0.1
H <sub>2</sub>	45	0.45
N <sub>2</sub>	02	-
WATER VAPOUR	04	-

COMBUSTION REACTIONS:



1VOL 2VOL

i.e. 1 VOLUME OF CH<sub>4</sub> requires 2 vol.of oxygen, therefore 0.35 volumes of CH<sub>4</sub> will requires 0.35x2=0.70m<sup>3</sup> of oxygen.



1VOL    3VOL

i.e. 1 VOL of  $C_2H_4$  requires 3 vol of oxygen. Therefore, 0.04 vol of  $C_2H_4$  will require  $0.04 \times 3 = 0.12m^3$  of oxygen.



1VOL    0.5VOL

i.e. 1VOL of CO requires 0.5 vol of oxygen, therefore 0.1 volume of CO will requires  $0.1 \times 0.5 = 0.05m^3$  of oxygen.



1vol    2vol

i.e. 1 vol of  $H_2$  requires 0.5 vol of oxygen, therefore 0.45 vol. of  $H_2$  requires

$$0.45 \times 0.5 = 0.225m^3$$

Total volume of  $O_2$  required  $= 0.7 + 0.12 + 0.05 + 0.225 = 1.095m^3$  of oxygen

Air contains 21% of oxygen is present in  $100m^3$  of air

Therefore,  $1.095m^3$  oxygen will be present in  $1.095/21 \times 100 = 5.214m^3$

