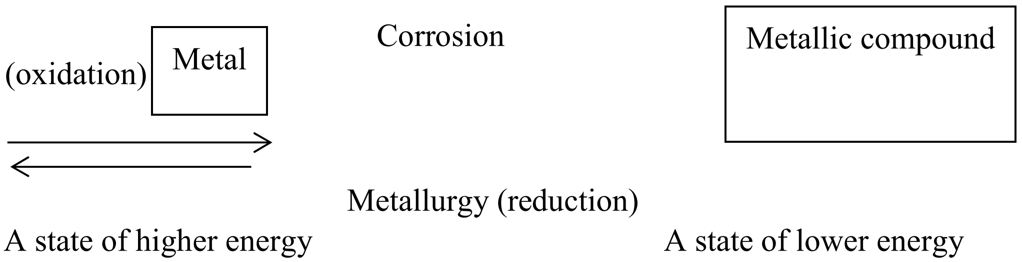
# MODULE 4: CORROSION

**Definition: Destruction or deterioration or disintegration of a metal by chemical or electrochemical reaction with its environment is called corrosion.**



**Type of environment:**

The environment could be of any type such as atmosphere, water, sea water, acids, steam gases, soils, liquid metals etc.

**Examples of corrosion:**

1. The most familiar examples of corrosion are rusting of iron when exposed to the atmospheric conditions. During this a layer of reddish scale & powder of oxide ($Fe_3O_4$) is formed & the iron becomes weak.
2. Another example is formation of green film of basic carbonate [$CuCO_3$ + $Cu(OH)_2$] the surface of copper when exposed to moist air containing $CO_2$.

**Basic requirement for corrosion:**

**For corrosion to proceed there must be an anode, a cathode and an electrolyte.**

## □□*Atmospheric corrosion (Dry or Direct chemical corrosion)*

**Definition:**

The surface of metals is directly attacked by the atmospheric gases such as $O_2$, $CO_2$, $H_2S$, halogens of the medium & gets coated with corresponding compounds like oxides, carbonates, sulphides, etc. Such type of corrosion which is brought about by the atmospheric conditions is called atmospheric corrosion or direct corrosion.

**There are three main type of chemical corrosion.**

a) **Corrosion due to oxygen.**

b) **Corrosion due to other gases** ─ **Hydrogen**, **Chlorine**

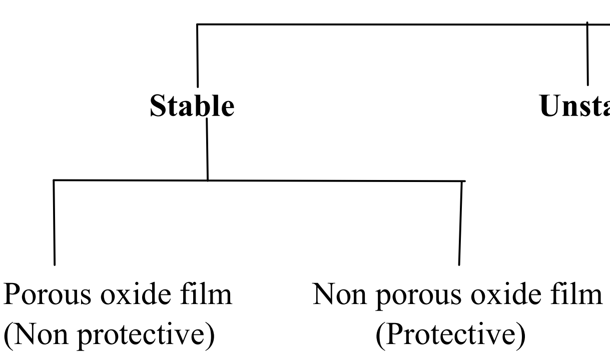
c) **Liquid metal corrosion.**

**a)Corrosion due to oxygen ( Oxidation corrosion) :-**

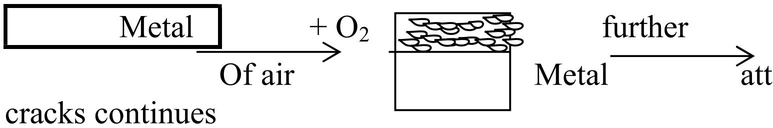
Oxygen present in the medium directly attacks the metal surface at low or high temperature.

$$2M + O_2 \longrightarrow 2MO \quad \{Metal + O_2 + Metal\ Oxide\}$$

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



**1) Stable Oxide film:**
A stable oxide film consists of fine grains in its structure & it can get adhered tightly to the metal surface.



attack through pores / cracks continues

Fig: - Porous Oxide layer

is of two types
- Porous oxide film (Non protective) It
- Non porous oxide film (Protective)

The protective & non protective nature of the oxide layer depends mainly upon the "pilling Bedworth Rule".

**Pilling Bedworth rule:**
**According to this rule, an oxide is protective or non porous if, the volume of oxide (film) is at least as great as the volume of metal from which it is formed.**

**If the volume of oxide is less than the volume of metal from which it is formed, it will be nonprotective as it cannot prevent the diffusion/access of oxygen to the fresh metal surface below.**

E.g: <u>Porous oxide film.</u>
Alkali metals such as Li, Na, K or alkaline earth metal such as Ca, Mg react with oxygen, forming oxide such as $Na_2O$, $K_2O$, CaO, MgO etc.

E.g: <u>Non- Porous oxide film.</u> Metals like Al, Cr etc. form this oxide such as $Al_2O_3$, $Cr_2O_3$ etc. **2) Unstable Oxide film: -** Where the oxide film formed is unstable & it decomposes back into metal & oxygen.

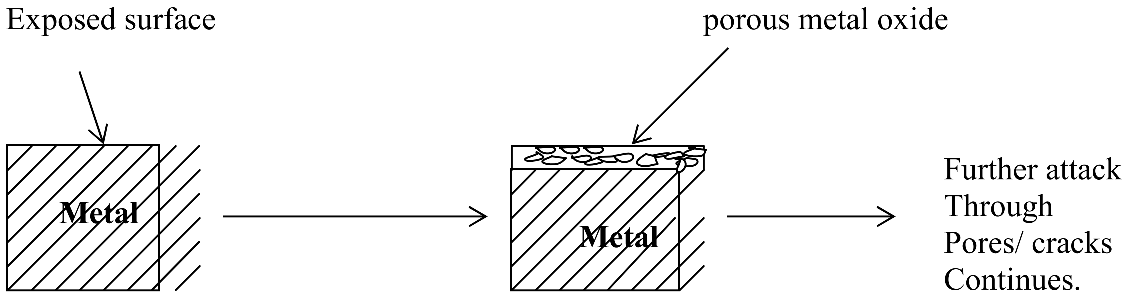
$$\text{Metal + Oxygen} \longrightarrow \text{Metal oxide} \rightleftarrows \text{Metal + Oxygen}$$

unstable

e.g. Oxides of metals like Gold, Silver, and Platinum etc. Hence metal forming unstable oxide film does not get covered.

**3) Volatile oxide film:-**

When the oxide film formed is volatile it vaporizes as soon as it is formed, the underlying metal surface is exposed for further attack of oxygen & thus causes continue & excessive corrosion. e.g. Molybdenum metal form its oxide $MoO_3$, which is volatile



Porous oxide layer

e.g. Molybdenum metal form its oxide $MoO_3$, which is volatile.

**b) Corrosion due to other gases:**

Among the other dry gases which cause corrosion on metals are $F_2$, $Cl_2$, $H_2S$, $SO_2$ etc. The extent of corrosion depends upon the chemical affinity between the metal & gas involved. The rate of further corrosion depends upon the volume of the corrosion film & volume of the metal. e.g.

$$2Ag + Cl_2 \longrightarrow 2AgCl$$

$$Sn + 2Cl_2 \longrightarrow SnCl_4$$

Here the film of silver chloride is protective (non porous), hence the rate of further corrosion reduces while that of stannic chloride is volatile in nature, hence rate of corrosion is enhanced.

**i) Corrosion by hydrogen (hydrogen embrittlement):**

This attacks the metals like Fe as

$$Fe + H_2S \longrightarrow FeS + 2H \text{ (atomic hydrogen).}$$

The atomic hydrogen thus formed, penetrates the voids in metal by diffusion & gets accumulated there & recombines to form molecules hydrogen.

$$H + H \longrightarrow H_2 \text{ (Molecular hydrogen)}$$

The molecule hydrogen is trapped in voids & as in concentration increases, it causes blisters & fissures in the metal, considerably lowering the strength & ductility of the metal. This is known as **hydrogen embrittlement**.

**ii)** **Hydrogen attack**: At high temperature hydrogen attack is due to diffusion of atomic hydrogen into metal. But atomic hydrogen is formed by the thermal dissociation of the molecule hydrogen.

$$H_2 \xrightarrow{\text{heat}} H + H \text{ (Thermal dissociation)}$$

The atomic hydrogen is chemically very active at high temperature & readily combines with C, S, O and N usually present in small amount in metals. e.g. atomic hydrogen readily combines with C in steel at high temperature with the formation of high pressure methane gas ($CH_4$) which causes intergranular cracking fissuring or blistering in the metal.

$$C + 4H \longrightarrow CH_4\uparrow$$

This is known as **decarburization**& is considerably reduces the strength of steel & causes brittleness.

**C) Liquids metal corrosion: (Corrosion due to other liquids)**
If any liquid metal comes in contact with solid metal, a chemical action occur thereby dissolving solid metal into liquid metal or liquid metal penetrates the solid metal. By both the actions the solid metals get weakened & become brittle. Such type of corrosion has been found to occur in devices used for nuclear power.
e.g: 1) liquid metal mercury dissolves some of the metals , forming amalgams, thereby corroding them.
2) A coolent (Na metal) leads to corrosion of cadmium in nuclear reactor.

## ***2. Immersed corrosion. (Wet or Electro chemical corrosion) (Electrochemical Theory)***

This type of corrosion occurs: I) when a conducting liquid is in contact with a single metal. II) when two dissimilar metals/ alloys are either immersed or partially dipped in a solution.

**Definition:**

The corrosion which is brought about through ionic reaction in presence of moisture or solution as a conducting medium is called electrochemical corrosion or immersed corrosion as it occurs where they are immersed in the solution.

**Essential are:-**

i) The formation of anodic & cathodic part ii)
Presence of a conducting medium. iii)
Corrosion of anodic part only.
iv) Cathodic reaction can take place in two ways, I) By $H_2$ evolution II) By $O_2$ absorption v)
Formation of corrosion product between anode and cathode.

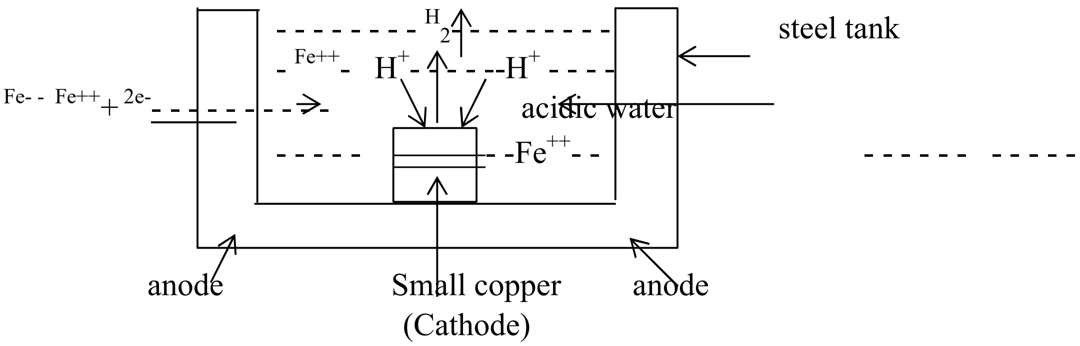
**Mechanism of electrochemical corrosion**

**i) Evolution of Hydrogen :-**

- This type of corrosion will take place if the medium is acidic.

E.g. A steel tank containing acidic industrial waste and a small piece of copper scrap in contact with the steel.

**Hydrogen Evolution Mechanism**



- Iron from steel forms Anode and undergo oxidation as follows, Anodic reaction: $Fe \rightarrow Fe^{2+} + 2e^-$ (oxidation)
- $Fe^{2+}$ is released in acidic water and electrons travel from anode to cathode.
- At cathode hydrogen ion from the acidic undergo reduction as follows,

Cathodic reaction: $2H^+ + 2e^- \rightarrow H_2 \uparrow$ ( reduction)

- In hydrogen evolution type of corrosion *cathode are small* areas &*anodes are usually large* areas, hence extent of corrosion is less.

**ii) Absorption of Oxygen:**

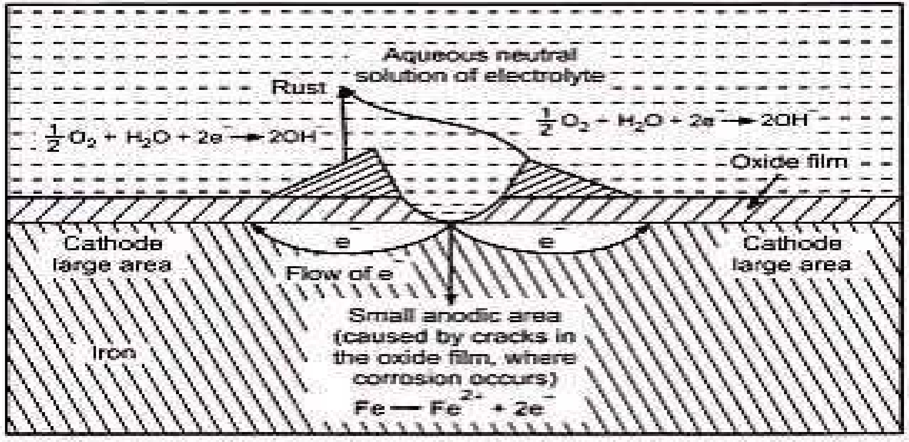


**Fig. 1.7 : Mechanism of wet-corrosion by oxygen absorption**

- This type of corrosion will take place if the medium contains oxygen.
- E.g. rusting of iron.
- The surface of iron is generally coated with a thin film of iron oxide. However if this iron oxide film develops some cracks, anodic areas are created on the surface of the exposed iron metal while the rest metal surface forms the cathode & neutral aqueous solution like NaCl acts as an electrolyte.
- At anode iron undergoes oxidation as follows,

  Anodic reaction: $Fe \rightarrow Fe^{+2} + 2e^-$ ( oxidation)
- $Fe^{2+}$ is released in aqueous medium and electrons travel from anode to cathode. Dissolved oxygen from electrolyte undergoes reduction as follows.

  Cathodic reaction: $H_2O + 1/2O_2 + 2e^- \rightarrow 2(OH)^-$ (Reduction)

- The $Fe^{+2}$ ions at anode & $OH^-$ ions at cathode combine to form compound

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

  If enough oxygen is present, ferrous hydroxide is easily oxidized to ferric hydroxide

  $2\ Fe(OH)_2 + 1/2\ O_2 + H_2O \rightarrow 2Fe(OH)_3\downarrow$

  Yellow Rust
- If supply oxygen is limited the corrosion product is black anhydrous magnetite ($Fe_3O_4$)
- Here the *anodic area is smaller* than the cathodic area thus the rate of corrosion is faster as large cathodic areas demand more electrons and small anodic areas undergo corrosion to greater extent.

**Distinguish between Atmospheric corrosion and electrochemical corrosion**.

| **Atmospheric corrosion/chemical corrosion** | | **Electrochemical corrosion** | |
|---|---|---|---|
| **1** | It occurs in dry condition. | **1** | It occurs in presence of aqueous solution or electrolyte. |
| **2** | It involves the direct chemical attack on the metal by environment. | **2** | It occurs through large number of galvanic cells. |

| | | | |
|---|---|---|---|
| **3** | It can be explained by absorption mechanism. | **3** | It can be explained by electrochemical reaction mechanism. |
| **4** | Corrosion products accumulate at the same spot where corrosion starts. Hence, further corrosion is prevented. | **4** | Corrosion products accumulate at the cathodic area. Hence, further corrosion occurs. |
| **5** | It is a slow process. | **5** | It is a rapid process. |
| **6** | It occurs on both homogenous and heterogeneous surfaces. | **6** | It occurs on heterogeneous surfaces. |
| **7** | Corrosion is uniform. | **6** | Corrosion is not uniform. |

## Different Types of corrosion

**1. Galvanic Corrosion (Bimetallic corrosion):- Definition:**

When two metallic materials (dissimilar metals) are electrically connected and exposed to an electrolyte, the metal occupying higher position in electrochemical/galvanic series undergoes corrosion, is called ‘galvanic corrosion’. **Explanation:**

When two dissimilar metals as Zn & Cu are electrically connected & exposed to electrolyte. Zinc which is higher in electrochemical series forms the anode & undergoes corrosion (attacked & get dissolved) while copper which is lower in electrochemical series acts as the cathode and is protected from corrosion. **This type of corrosion is known as galvanic corrosion. It is wet or electrochemical corrosion.**

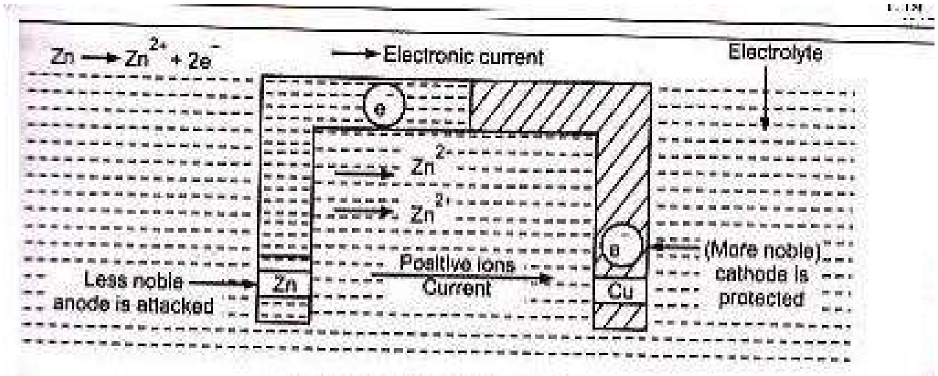


Fig. 1.10 : Galvanic corrosion

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

**Examples**:

1. Copper sheet joined by iron nails.

□□Steel screw in marine brass hardware.

**Role of metallic impurities in Galvanic Corrosion:**

- The metal in pure state corrodes to a very small extent. But when the metal contains metallic impurities, the degree of corrosion is very high.

- The corrosion of metals in presence of other metallic impurity depends upon their position in electrochemical series. The metal which is anodic will get corroded while cathodic metal will remain unaffected.
- E.g: If a plate of zinc is placed in dilute acid solution, it will not corrode, while if zinc contains iron as impurity, zinc corrodes to larger extents, since iron is cathodic to zinc. Thus presence of cathodic impurities increases the rate of corrosion of metals. If the metal contains more active metal as an impurity (anodic), then the corrosion of the metal can be prevented.

**2. Concentration cell corrosion (Differential aeration corrosion.)**

- This type of corrosion occurs when one single metal is exposed to different concentration of electrolyte or air.
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- **Differential aeration:** It is the most important type of concentration cell corrosion which occurs when one part of a metal is exposed to a different air concentration from the other part of the metal.
- As a result, difference in the potential takes place between differently aerated areas. It has been found experimentally that **poor oxygenated (poorly aerated) parts of metals are anodic and highly oxygenated (highly aerated) parts of metal are cathodic**.
- Example:

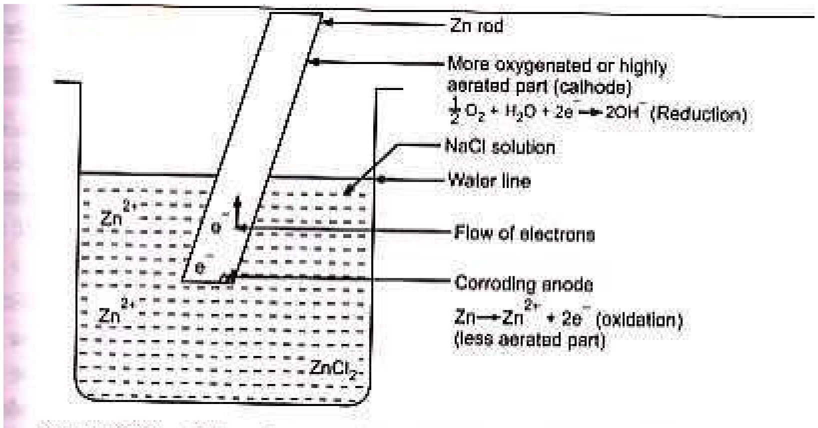

**Fig. 1.8 : Differential aeration corrosion of a metal immersed partially in solution**

- If a piece of metal say Zinc is partially immersed in dilute solution of a salt NaCl & the solution is not mixed properly, the parts above & closely adjacent to the water line are most strongly aerated because of the easy access of oxygen to this area & hence become cathodic.
- On the other hand, parts immersed to greater depth have less access of oxygen & so they are poorly aerated i.e. they show a smaller oxygen concentration & thus become anodic.
- As a result difference of potential is created which is responsible for the flow of current between two differently aerated areas of same metal Zinc.
- Zinc will dissolve at the anodic area & oxygen will take up electrons at the cathodic area to form hydroxyl ions.
- The reactions involved are as follows,

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

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

- The circuit is completed by migration of ions, through the electrolyte & flow of electrons through the metal from anode to cathode.

**Pitting corrosion:**

- Pits are holes or cavities that are developed on the metal surface when the protective oxide film breaks.
- Around such pits, small anodic and cathodic areas are formed. Due to this corrosion is accelerated in localized area known as pitting corrosion.
- Pits may also be formed due to surface roughness, scratches, sliding under the load, action of some chemicals etc.
- When such pits are covered by a drop of water or impurity (dust, dirt, scale), anodic and cathodic areas are formed. The part under the drop of water acts as an anode as it is poorly oxygenated, while the remaining portion of the surface forms cathode.
- Eg. Iron rod under drop of water/ dust/ sand/ scale.

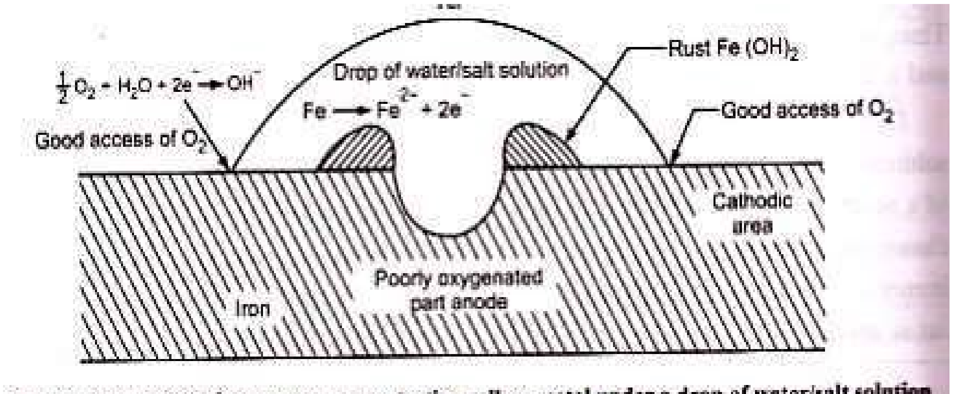

**Fig. 1.9 : Formation of an oxygen concentration cell on metal under a drop of water/salt solution**

- At anode iron undergoes oxidation as follows,

  Anodic reaction: $Fe \rightarrow Fe^{+2} + 2e^-$ ( oxidation)
- $Fe^{2+}$ is released in aqueous medium and electrons travel from anode to cathode. Dissolved oxygen from electrolyte undergoes reduction as follows.

  Cathodic reaction: $H_2O + 1/2O_2 + 2e^- \rightarrow 2(OH)^-$ (Reduction)

- The $Fe^{+2}$ ions at anode & $OH^-$ ions at cathode combine to form compound

  $Fe^{++} + 2\,OH^- \rightarrow Fe(OH)_2$ (brown rust)

  If enough oxygen is present, ferrous hydroxide is easily oxidized to ferric hydroxide

  $2\,Fe(OH)_2 + 1/2\,O_2 + H_2O \rightarrow 2Fe(OH)_3\downarrow$

  Yellow Rust
- If supply oxygen is limited the corrosion product is black anhydrous magnetite ($Fe_3O_4$)

**Waterline corrosion:**

- It is observed in a steel tank containing stagnant(unmoving) water for a long time.
- The area above the waterline is highly oxygenated, hence behaves as cathode. While the area just below the water meniscus is poorly oxygenated hence behaves as an anode.

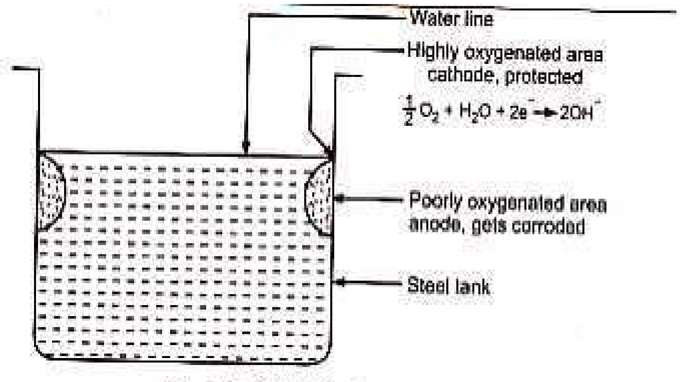

Fig. 1.12 : Waterline Corrosion

- Maximum corrosion of the part just below the waterline takes place as follows:
- At anode iron undergoes oxidation as follows,

Anodic reaction: $Fe \rightarrow Fe^{+2} + 2e^-$ ( oxidation)

- $Fe^{2+}$ is released in aqueous medium and electrons travel from anode to cathode. Dissolved oxygen from electrolyte undergoes reduction as follows.

Cathodic reaction: $H_2O + 1/2O_2 + 2e^- \rightarrow 2(OH)^-$ (Reduction)

- The $Fe^{+2}$ ions at anode & $OH^-$ ions at cathode combine to form compound

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Yellow Rust

- If supply oxygen is limited the corrosion product is black anhydrous magnetite ($Fe_3O_4$)
- The rust is deposited at waterline hence the corrosion is called **waterline corrosion**.
- This corrosion is a serious problem of ocean going ships which can be prevented by painting the sides of ships by special antifouling paint.

### 3. Intergranular Corrosion

- Smaller subunit of an alloy or metal is called as **grains.**

- Each grain consists of all the constituents of the alloy.
- All the grains of a given metal/alloy have identical arrangement of atoms.
- This type of corrosion occurs along the grain boundaries where the material is sensitive to corrosion attack (anodic) as compare to that at the centre in particular corrosion medium. .

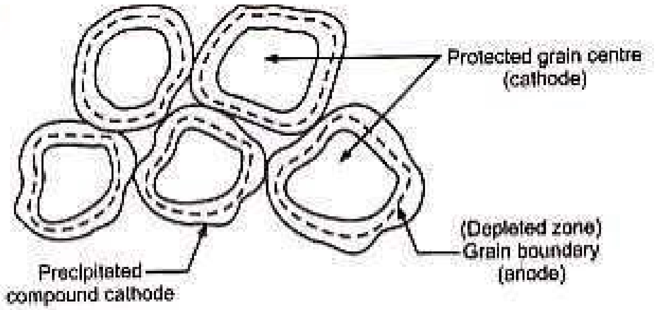


Fig. 1.14 : Intergranular corrosion

- Example: During welding of stainless steel (which is the alloys of iron, chromium, carbon)
- Chromium Carbide gets precipitated at the grain boundaries.

$$\mathbf{Cr + C \rightarrow CrC}$$

- Thus the concentration of chromium at the grain boundary decreases therefore becomes more anodic to the grain centre & also to the precipitated chromium carbide.
- Hence corrosion takes place at grain boundary.
- The grain boundary corrosion is a microscopic attack without any apparent external signs.
- Hence in most of the cases without any pre warning sudden failure of material occurs as cohesion between the grains is lost during corrosion.
- This type of corrosion can be avoided or controlled to a greater extent by proper heat treatment during the formation of an alloy material followed by rapid cooling to avoid the precipitation of a compound of alloying elements (like CrC) which normally takes place with slow cooling.
- It can also be avoided by using steels with less carbon content or by inclusion of titanium.
- Hence by taking precaution during manufacture of alloy intergranular corrosion can be avoided.

**Stress Corrosion**

- Stress corrosion or stress cracking is due to the presence of stress caused by heavy working like rolling, drawing or insufficient annealing.
- This type of corrosion is the combined effect of static tensile stress and the corrosive environment like,

□□Strong caustic alkalis or nitrates (which affected mild steel)

□□Traces of ammonia (Affecting brass)

□□Marine water or $H_2S$ gas or solution of acid halides (chlorides particularly) affecting stainless steel etc.

- Stress corrosion is probably due to localized electrochemical reaction, forming local anodic & cathodic areas on the metal surface.

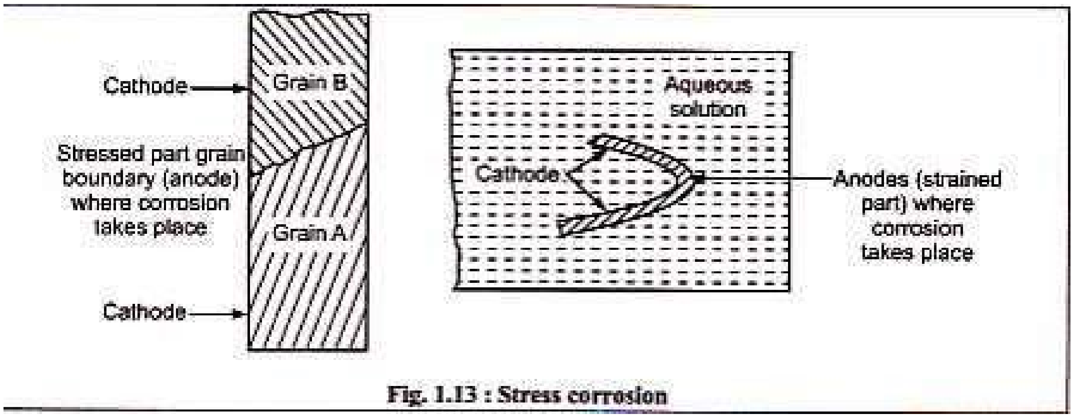


**Fig. 1.13 : Stress corrosion**

- Some typical examples of stress corrosion are,

□□**Season cracking**: It occurs in brass alloys (Cu + Zn) when exposed to ammonia (such as cartridge cases). Because Cu and Zn react with ammonia to form complex ions of $Cu(NH_3)_4{}^{+2}$ and $Zn(NH_3)_4{}^{+2}$. This causes dissolution of brass which initiates the formation of fissures that ultimately propagates which leads to formation of cracks in the presence of high tensile stress.

□□**Caustic embrittlement:** This is the most dangerous form of stress corrosion which occurs in mild steel when it is exposed to alkaline solution at high temperature as well as stress. Following reaction takes place,

$$\mathbf{Na_2CO_3 + H_2O \rightarrow NaOH + CO_2}$$

- The NaOH(caustic soda) flows into small cracks in the steel by capillary action.
- As the water evaporates the concentration of NaOH increases which reacts with Fe present in steel and corrodes it.

**Q. What is polarization of electrodes?**

- The driving force of an electrochemical corrosion is the potential difference between anode and cathode. And the corrosion rate is controlled by the current flowing in the circuit.
- Any factor that decreases the potential difference between the electrodes decreases the current flow and thereby decreases the rate of corrosion.
- The corrosion current is reduced due to back e.m.f, which is due to formation of small concentration cell. This phenomenon is called polarization.
- Polarization of the electrodes is due to concentration changes in the electrode region, overvoltage and presence of surface film.

- Therefore, polarization decreases the rate of corrosion.

## FACTORS INFLUENCING CORROSION:

### A) ***Nature of metal:***

**1)Position of metal in galvanic series(oxidation potential):-**

- The extent of corrosion depends upon the position of metal in the galvanic series.
- If the position of the metal in the galvanic series is higher, it acts as an anode and corrodes faster.
- Further, for two metals if the difference in their position in galvanic series is large faster will be the corrosion of anodic metal.
- Metals close to each other in the galvanic series show fewer tendencies to corrode when in contact with each other.

**2) Potential difference:**

Greater the difference in the electrode potential between the two metals in contact, higher is the rate of corrosion.

**3) Purity of metal (impurities):-**

- Pure metals do not undergo corrosion.
- If the metal itself contain impurity, tiny galvanic cell can be set up easily. This increases rate of corrosion.
- The effect of impurities on the rate of corrosion of Zinc can be seen from the following table.

| Metal | % purity | Corrosion rate(comparative) |
|---|---|---|
| Zn | 99.999 | 1 |
| Zn | 99.99 | 2650 |
| Zn | 99.95 | 5000 |

**4) Relative areas of cathodic & anodic parts:**

$$\text{Rate of corrosion} \quad \alpha \quad \frac{\text{Area of cathode}}{\text{Area of anode}}$$

- When two dissimilar metals are in contact, “the rate of corrosion is directly proportional to the ratio of areas of cathodic part & anodic part.

- This is because when the cathodic area is larger, demand for electrons is more. To meet this demand anodic area undergoes faster corrosion. Thus smaller the area of the anode faster is the rate of corrosion.
- E.g: steel screw (small anode) in copper plate (large cathode) gets completely corroded in corrosive environment.

**5) Nature of corrosion product (oxide film):**

- Metals form oxide film on their surface by corrosion due to oxygen.
- This film can be stable, unstable and volatile.
- The stable film can be porous or non-porous in nature.
- If the film is non-porous, the underlying metal is prevented from further corrosion since the film act as a protective covering. E.g:- Metals like Al, Cr etc. form this oxide such as $Al_2O_3$, $Cr_2O_3$ etc.
- On the other hand if the film is porous further attack of oxygen is possible. E.g:- Na, K Ca, Mg react with oxygen, forming porous oxide film such as $Na_2O$, $K_2O$, CaO, MgO etc.
- Where the oxide film formed is unstable & it decomposes back into metal & oxygen.e.g. Oxides of metals like Gold, Silver, and Platinum etc.
- If the corrosion product is volatile, it evaporates as soon as it is formed, there by leaving the underlying metal surface exposed for further attack. E.g $MoO_3$, the oxidation corrosion product of Mo is volatile.

<u>Solubility of corrosion products:</u>

- If the corrosion product is soluble in the corroding medium, then corrosion proceeds at a faster rate.

**6) Physical state of metal:-**

- The rate of corrosion is influenced by physical state of the metal (such as grain size orientation of crystals, stress etc.) For instance the smaller the grain size of the metal or alloy the grater will be the solubility & greater (as compared to the macroscopic crystals) will be its corrosion.

- The corrosion rate may also be influenced by the orientation of crystal at the metal surface e.g. the corrosion rate of copper ions was found to be different on different faces of a pure copper crystal. Moreover areas under stress, even in a pure metal tend to anodic & corrosion takes place at these areas. This is due to the fact that "atoms of a metal at the boundaries having electrode potential different than that of the atoms in the proper grain size. Consequently anode & cathode is developed.
-

The grain boundaries zone may be considered to be stressed since atoms are not at their position at lowest energy state. Similarly the electrode potential of stressed metal is lower than that of annealed metal.

**6) Over voltage:-**

Overvoltage is the difference between the actual and theoretical value of decomposition potential of the electrode.

For the evolution of hydrogen gas, this potential difference is called hydrogen overvoltage.

**Higher the overvoltage lesser is the rate of corrosion.**

E.g. If pure Zn is placed in 1N $H_2SO_4$ it undergoes corrosion at very slow rate because of the high overvoltage (about 0.7V). However if few drops of copper sulphate ($CuSO_4$) are added, the corrosion rate of Zn accelerates because some copper gets deposited on the Zn metal forming minute cathodes and over voltage drops to 0.33V. **Thus the reduction in the over voltage plays on important part in accelerating corrosion**

## ***B) Nature of the environment:-***

### 1) Temperature:

- The rate of corrosion increases with temperature, because ionization, mobility and diffusion rate of reacting ions & molecules increases.
- However solubility of gases such as $O_2$ which affect corrosion decreases with temperature so in some environment rate of corrosion is less at high temperature.

### 2) Presence of moisture: (Humidity of air)

- Atmospheric corrosion of iron is slow in dry air but increases rapidly in the presence of moisture.
- This is because moisture acts as the solvent for setting up an electrochemical corrosion cell.
- Nature of moisture source also plays an important role.

### 3) Effect of pH:

- Acidic media are generally more corrosive than alkaline & neutral media.
- In acidic media corrosion takes place by evolution of $H_2$ gas at the cathode, while in alkaline media the corrosion takes place by absorption of $O_2$, thereby forming oxide film, which gets adhered to the metal surface and further the rate of corrosion is governed by the nature of oxide film.
- E.g: Zinc is rapidly corroded even in weakly acidic solution such as carbonic acid and suffers minimum corrosion at $P^H$ 11.

### 4) Concentration of electrolytes/Formation of oxygen concentration cells:

- The rate of corrosion increases with increasing supply of oxygen or air on the most metal surface.
- Poorly oxygenated part becomes anodic where the corrosion occurs. The highly oxygenated part becomes cathodic and no corrosion occurs.
- Both anodic and cathodic areas lead to the formation of oxygen concentration cell. The reactions involved are as follows,

$$\mathbf{Fe \rightarrow Fe^{++} + 2e^{-}} \quad \textbf{(Oxidation)}$$

$$\mathbf{\tfrac{1}{2}\,O_2 + H_2O + 2e^{-} \rightarrow 2OH^{-}} \quad \textbf{(reduction)}$$

Thus formation of oxygen concentration cell promotes corrosion at anode.

**5) Presence of impurities in atmosphere:-**
Atmosphere in the vicinity of industrial areas contains corrosive gases like $CO_2$, $H_2S$, $SO_2$& fumes of HCl, $H_2SO_4$ etc. In presence of these gases the acidity of the liquid adjacent to the metal surface increases & its electrical conductivity also increases. This consequently results in an increase of corrosion current flowing in the local electrochemical cells on the exposed metal surfaces. Similarly in the marine atmosphere presence of sodium & other chlorides leads to increased conductivity thereby corrosion is speed up.

**6) Nature of ions :- (anions & cations)**
Chlorides ions present in the medium destroy the passive film & corrode many metal & alloys. On the contrary, some anions like silicates may form an insoluble reaction product (eg silica gel) which inhibits corrosion. Traces of cell or more noble metals accelerate the corrosion of the irons pipes carrying mine water. Many metals including iron corrode more rapidly in ammonium salts than in sodium salts of identical concentration.

**7)Conductance of the medium:-**
The conductance of the medium is of profound importance in the corrosion of underground or submerged stricture because of the corrosion current depends on this factor. Conductance of clay & mineralized soils is higher than that of dry & sandy soils. Hence stray current from power leakage will damages the metal structure buried under soils of higher conductance to a greater extent than these under dry sandy soils having higher resistance.

## Prevention & control of corrosion

The following are the methods which can be used either singly or in combination in order to protect the metals from corrosion.

- Proper selection of materials and
- Improvement of design (proper design)
- Use of inhibitors.
- Use of alloys/ Pure metal.
- Cathodic & Anodic protection
- Application of protective coating. e.g. i) Metallic coatings & ii) Organic coatings.

- **Proper selection of materials**

**<u>Proper selection of material:</u>**

Proper selection of material is the main factor for corrosion control. This can be done by taking following precaution.

1. **Avoid contact of dissimilar metals especially if the working environment is corrosive.** Example:- Joining different part to make a ship, if iron metal strips are used to join the wooden parts together & of screws used are of brass ( Cu & Zn alloys) when ship floats on marine water , localized corrosion enhanced tremendously & highly active metal starts (Zinc) acting as anode.
2. Suppose if it is unavoidable to choose two dissimilar metals, then **area of anodic metal should be larger than that of cathodic metal.**
3. If two dissimilar metals are to be selected, then metals should be chosen in such a way that **they are as close as possible in the galvanic series**.
4. When two dissimilar metals are required to be joined their **direct contact should be avoided by inserting a piece of hard plastic or rubber into the joint.** The piece acts as an insulator & current flow should be reduced & minimizes galvanic corrosion.
5. When **two dissimilar metals are used in contact the anodic metal should not be painted or coated**. Any crack lead to rapid localized corrosion.

## 2. Proper designing:

- Corrosion resistance of metal parts or machines can be improved by improving the design.
- **The design of the metal should be such that "corrosion even if it occurs is uniform & does not result in intense & localized corrosion.**
- A better design should always avoid sharp bends, corners, projected parts etc.
- As far as possible use of screws, nuts, and bolts should be avoided, rather welding can be used since welded joints do not allow the entry of gases & liquids inside, which cause corrosion.
- As far as possible metal washer should be replaced by rubber or plastic washer as they do not absorb water & do not generate galvanic couples.
- The surfaces of two joining parts should be as smooth as possible, which avoids accumulation of the corrosive liquids, suspended particle, dust, dirt. The equipment should be kept free from dust & dirt to reduce rusting due to pitting & differential aeration effect.
- Wherever possible the equipment should be supported on legs instead on large block to allow free circulation of air & prevent the formation of damp areas. Design of joints should be such that the chance of water entering inside is limited.

## 5. Cathodic & Anodic protection:

### 1) Cathodic protection:

- **The principle involved in this method is to force the metal to be protected to behave like a cathode, thereby corrosion does not occur.**
- There are two types of cathodic protections:
  - i) **Sacrificial anode method**
  - ii) **Impressed current method**

### a) Sacrificial anode method:

- In this protection method, the metallic structure to be protected is connected by a wire to a more anodic metal, so that all the corrosion is concentrated at this more active metal.
- The more active metal itself gets corroded slowly, while the parent structure is protected.
- Since the more active metal sacrifices itself, by undergoing corrosion and saving the base metal, the method is named as **Sacrificial anode** method or auxillary anode method.
- When the piece of more active metal gets corroded completely, it is simply replaced by new piece.
- Most of the common sacrificial anodes are based on the alloys of magnesium, zinc and aluminium which are placed above iron in electrochemical or galvanic series.
- Applications of this method are seen to protect cables or iron pipelines, by connecting them to Mg- block and in case of marine structures ships are protected by using Zn-plates as sacrificial anode. Even water tanks, boilers are protected by using Zn metal.

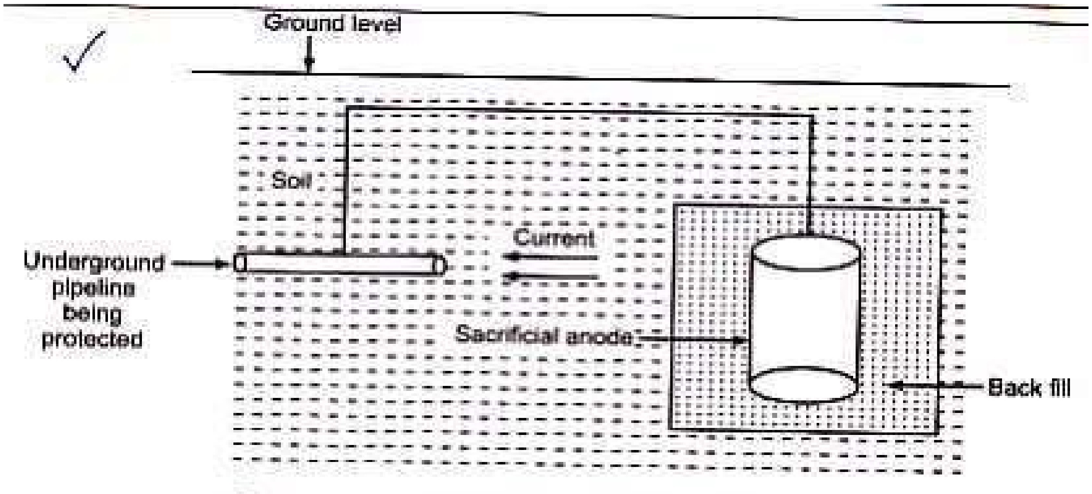


Fig. 1.21 : Galvanic protection using sacrificial anode

**b) Impressed current method:**

- During corrosion, electrons flow from anode to cathode and corrosion current flows from cathode to anode.
- In this method, an impressed current is applied in opposite direction to that of corrosion current; thereby nullify the effect of corrosion current, and converting the corroding metal from anode to cathode.
- In this method, the insoluble material (Like stainless steel, platinum, scrap iron, graphite or high silica iron) is usually kept in backfill made up of gypsum or any such material, which can help in increasing electric contact with soil.
- This insoluble material is buried underground. Usually D.C. current by using battery or dry cell is applied to it and it is then connected to the structure to be protected.

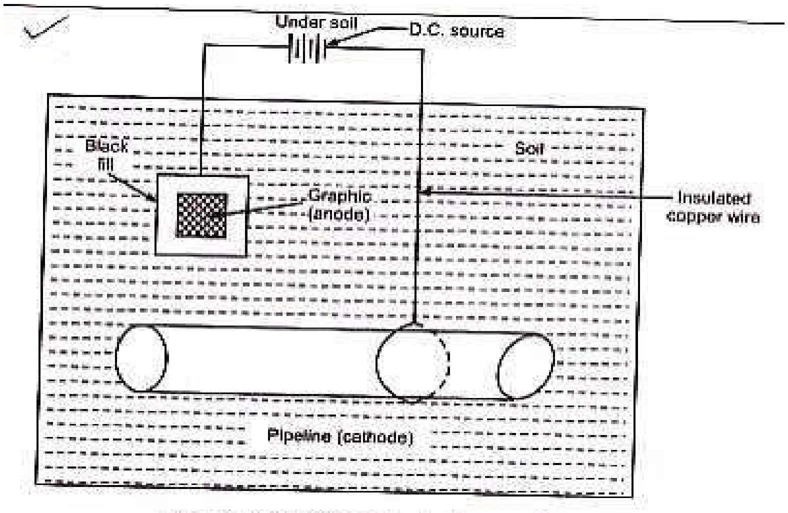


Fig. 1.23 : Corrosion control by impressed current

- As a result of impressed current, the burried material starts acting as anode and deteriorates and the structure to be protected acts as cathode.

- The burried anode has to be replaced periodically.
- This anode may be single (as in simple applications) or many anodes (as in pipe lines). **Applications:**
- This type of cathodic protection by impressed current is applied to open water box coolers, water tanks, buried water or pipelines, condensers, transmission line towers, marine piers, laid-up ships etc.

## 2) Anodic protection:

- This is another important form of corrosion control in which the anodic metal is made more anodic ( passivated) by applying current.
- In this the basic principle involved is to grow a protective oxide film on the surface of anodic metal. This phenomena is called passivity.
- This method can be used for only those metals which exhibit passivity like Fe, Cr, Al and Ti.
- Thus the principle involved is to increase the passivity of the base metal by applying current in the direction in which the metal would become more anodic.

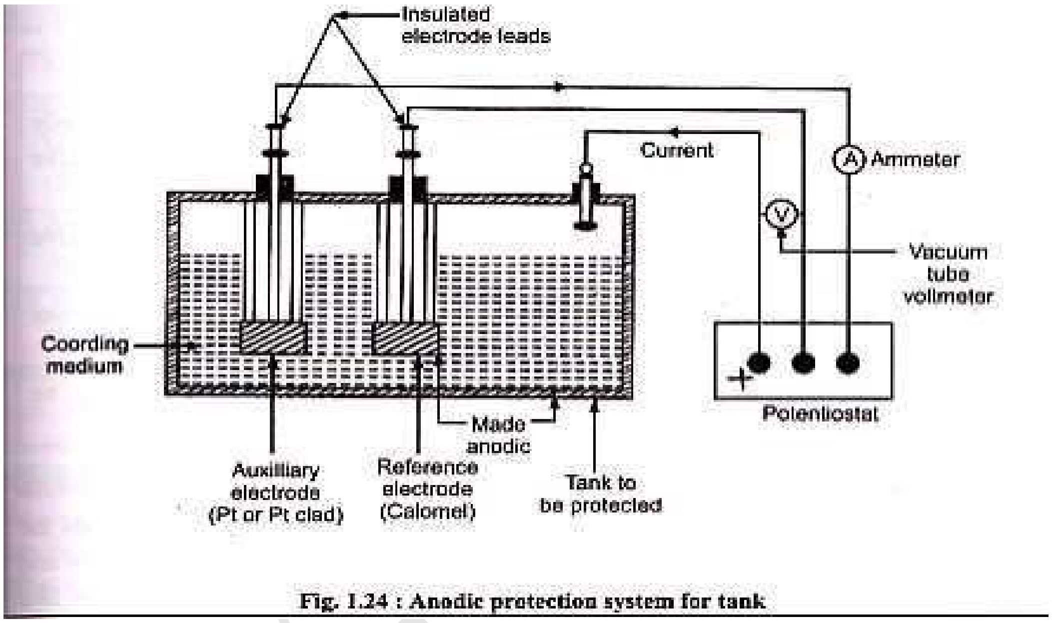


Fig. 1.24 : Anodic protection system for tank

The schematic arrangement for anodic protection is as shown in the fig.

To protect structure anodically, a device called ‘potentiostat’ is used. Potentiostat is a device to maintain the metal at constant potential with respect to the reference electrode. A potentiostat has three terminals, one is connected to the structure that is to be protected, and the other connected to platinum electrode and the third to a reference calomel electrode. The metal specimen to be protected is kept in a suitable oxidizing atmosphere and acts as a working electrode (anode). The potentiostat maintains a constant potential between the specimen to be protected and the reference electrode. Due to the constant potential, meta to be protected is passivated(covered with a thin protective film).

**Advantages of anodic protection:**

1) Low operating cost
2) Applicability to wide range of corroding environment.
3) Ability to protect complex structures.
4) Needs few auxiliary or sacrificial electrodes.

**Disadvantages of anodic protection:**

1) Suitable for only those metals and alloys, which show passivity.
2) High installation cost requiring a potentiostat, reference electrode and auxiliary electrode. 3) If the system goes out of control, high corrosion rate may occur..

**Distinguish between cathodic and anodic protection**.

| **Cathodic Protection** | | **Anodic Protection** | |
|---|---|---|---|
| 1 | This method is applicable to all metals. | 1 | This method is applicable to only those metals which show passivity. |
| 2 | Useful for weak or moderate environments | 2 | More aggressive corrosive environments can be handled. |
| 3 | Lower installation costs but higher operating cost. | 3 | Higher installation costs but lower operating costs. |
| 4 | Applied current cannot give any indication of corrosion. | 4 | Applied current gives an indication of corrosion rate. |

**6. Application of protective coating.**

In order to protect the metal from corrosion effects, it is possible to cover their surface in various ways.

The main types of protective coatings may be classified as
1) Metallic coatings and, metallic cladding
2) Non-metallic coatings
3) Organic coatings

**1) Metallic coatings:**

Metallic coatings can be divided into anodic and Cathodic coatings. **The metal to be protected is called the base metal; whereas the metal used for protection is called the 'coating metal'.**

**a. Anodic coating (coating with more active metal)**

- For example coating of zinc on steel.
- If any cracks, pores or breaks occur in such anodic coatings, a galvanic cell is formed between the coating metal and the exposed part of base metal.
- Zinc, being anodic to iron forms anode and will dissolve.

- The iron being Cathodic is protected.
- Thus, no attack on iron occurs until practically all the zinc first corroded in the vicinity of exposed iron parts. Hence, zinc coating protects iron "sacrificially".

**□□Cathodic coatings:**

- For example coating of tin on steel.
- If any cracks, pores or breaks occur in such Cathodic coatings, a galvanic cell is formed between the coating metal and the exposed part of base metal.
- Iron , being anodic to tin forms anode and undergoes corrosion.
- The tin being Cathodic is protected.
- Thus, if such coatings are broken or punctured much more damage can be done to a base metal .

**Methods of applications of metal coatings:**

The protective metallic coating can be made by the following methods:
1) Hot dipping - a) Galvanizing b) Tinning
2) Metal spraying
3) Sherardising 4) Electroplating 5) Metal cladding.

**□)Hot dipping A)**
**Galvanizing:**
It is a process of coating the base metal, like iron or steel, with appropriate thickness of zinc coating, to prevent the base metal from corrosion. Zinc being more electropositive than iron, in electrochemical series, becomes anode, Fe forms cathode and remains unaffected, thus it is prevented from undergoing corrosion. The method is used for coating iron or steel sheets, wires, tubes etc. for the purpose.

**Process:**

- The process of galvanizing involves initial cleaning of base metal articles by pickling it in the solution of dilute sulphuric acid at 60 to $90^{o}C$ for 10 to 20 minutes to remove any adherent scale, rust and any other impurities. It is then thoroughly washed with water and dried.
- It is then dipped in the bath of molten zinc maintained at $425\text{-}430^{o}C$.
- The surface of the bath is kept covered with a flux of ammonium chloride to prevent any oxidation. On taking out the sheet, it is found to be covered with zinc.
- To make the coating more uniform it is next passed through a pair of hot rollers, which removes any excess deposit.

- Finally the sheet is annealed at a temperature of $650^0C$ and then cooled slowly to room temperature to improve its machinability (see fig. below)

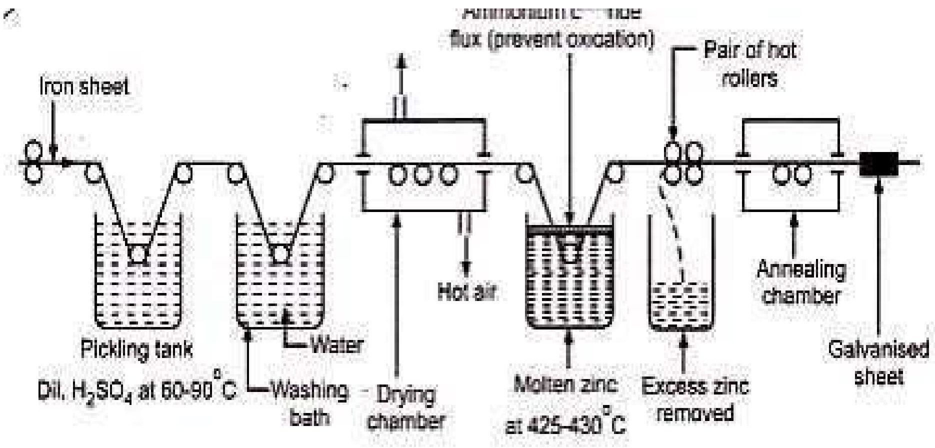


Fig. 1.29 : Galvanizing of steel sheet

**Applications:**
The process of galvanizing is commonly used for coating the iron or steel sheets, tubes, pipes, screws, nuts, bolts and wires for protection against corrosion.

**Advantages:**
Zinc offers better protection against corrosion because even if any cracks are developed over the film of deposit, at a later stage, zinc being more reactive than iron or steel, undergoes corrosion keeping the base metal article unaffected.

**Disadvantages:**
Galvanized zinc coated utensils or containers can not be used for preparing or storing food stuffs, particularly those which are acidic in nature. This is because zinc dissolves to form poisonous zinc compounds which are injurious to human health.

**B) Tinning:**
It is similar to that of galvanizing i.e. it is also a process of hot dipping. Tinning is a process of converting iron or steel articles with a thin coating of tin, to preventing it rusting.

**Process:**

- The article to be coated is first cleaned by pickling in dilute sulphuric acid for the removal of rust and any other impurities (if any) followed by through washing with water.
- Then the article is dipped in the bath of molten zinc chloride flux which helps molten metal to get adhered to the base metal.
- The article is next dipped in molten tin. And finally after passing through a layer of palm oil (which prevents oxidation) the steel sheet comes out which is found to be coated with a layer of tin
- It is then passed through a pair of hot rollers to make the deposit more uniform and to remove any excess deposit. (see fig. below)

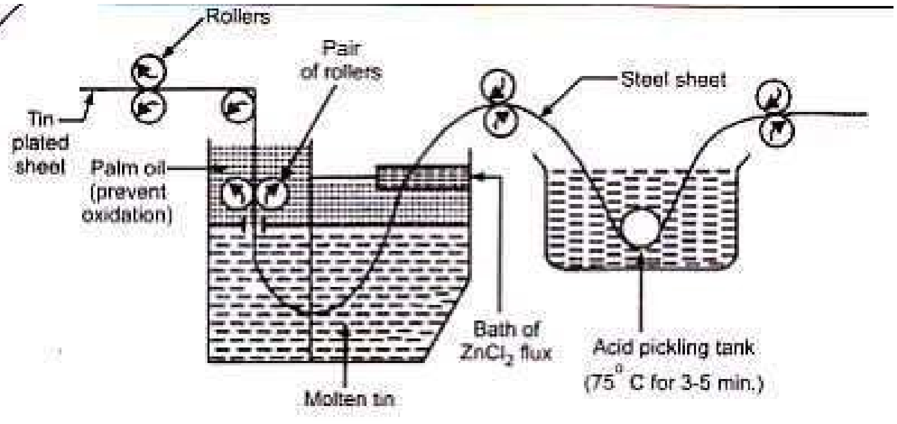


Fig. 1.30 : Tinning of steel sheet

**Applications:**

1. Tin coated sheets are used for making trunks, boxes, for containers of petroleum products etc.
2. Copper wires are tinned to facilitate soldering.
3. Copper wire is usually tinned first to protect it from the attack of rubber insulation.
4. The tinned copper sheets are used for cooking utensils, refrigeration equipment and copper tubes used in refrigerators.

**Advantages:**

- Tin coated containers can be used for preparing and storing food stuffs, chemicals etc., as tin do not form any poisonous products with such acidic materials.
- Tin forms a better protective coating than that of zinc.

**Disadvantages:**

1. Tin only provides a mechanical protection against corrosion. It acts as a cathode to more active metal like iron and so. If any cracks are developed in the protective layer, then more rapid corrosion takes places the underlying exposed metal becomes anode.

**Distinguish between galvanizing and tinning:**

| **Galvanizing** | | **Tinning** | |
|---|---|---|---|
| 1 | It is the process of coating iron or steel sheets with a thin coat of zinc by hot dipping to prevent them from rusting | 1 | It is a process of coating steel sheets with a thon layer of tin to prevent them from corrosion. |

|  |  |  |  |
|---|---|---|---|
| 2 | Zinc metal protects iron as it is more anodic to iron. | 2 | Tin protects the base metal as it is less electropositive than iron. It is more resistant to chemical attack. |
| 3 | Zinc continues to protect the metal by galvanic action, even if the coating is broken. | 3 | In tinning, tin protects the metal till the coating is perfect. A break in coating causes rapid corrosion. |
| 4 | Galvanized container cannot be used for storing acidic food stuffs, as acids react with zinc to form poisonous compounds. | 4 | Tin containers can be used for storing acidic food stuffs as tin does not form any poisonous products. |

# MODULE 3: CONCEPT OF ELECTROCHEMISTRY

## Q.1) What is elctrochemistry?

The branch of chemistry that deals with the chemical changes produced by electricity and the production of electricity by chemical changes is called Electrochemistry.

## Q.2) Define Anode and Cathode.

**Anode:** It is defined as an electrode at which oxidation occurs as electrons are lost by some species.
**Cathode**: it is defined as an electrode at which reduction occurs as electrons are gained by some species.

## Q.3) Explain electrochemical cell.

1) In electrochemical cell, electrochemical reactions are studied. In this cell, two electronic conductors dip into an electrolyte. The electronic conductor is metal or carbon rod. The electrolyte is in the form of pure liquid or aqueous solution.
2) The electrochemical reactions are redox reactions and involve electron transfer from one species to other. At one electrode, oxidation occurs and at other electrode, reduction occurs. The sum of these oxidation and reduction half reactions is the net cell reaction.

## Q.4) What are different types of cells?

There are two types of cells which are as follows:

### 1) Electrolytic cells:

An electrochemical cell in which a non-spontaneous redox reaction is forced to occur by passing a direct current from an external source into the solution is called an electrolytic cell. These cells involve conversion of electrical energy into chemical energy. They are used for decomposition of water into hydrogen and oxygen,metal plating, purification of metals.

### 2) Voltaic or Galvanic cells:

An electrochemical cell in which a spontaneous chemical reaction produces electricity is called voltaic cell or Galvanic cell. These cells involve conversion of chemical energy into electrical energy. Ex: Dry cell, Fuel cell,etc.

### a) Concentration cell:

A concentration cell is an electrochemical device that generates electrical energy when two same metal is in contact with solution of ions at different concentration. **b) Fuel cell:**

A fuel cell is an electrochemical cell which converts chemical energy of a conventional fuel and oxygen into electrical energy.

**Q.5) Define Electrolysis**

It is defined as the process in which an electric current is used to bring about a chemical reaction or a process in which electrical energy is converted into chemical energy.

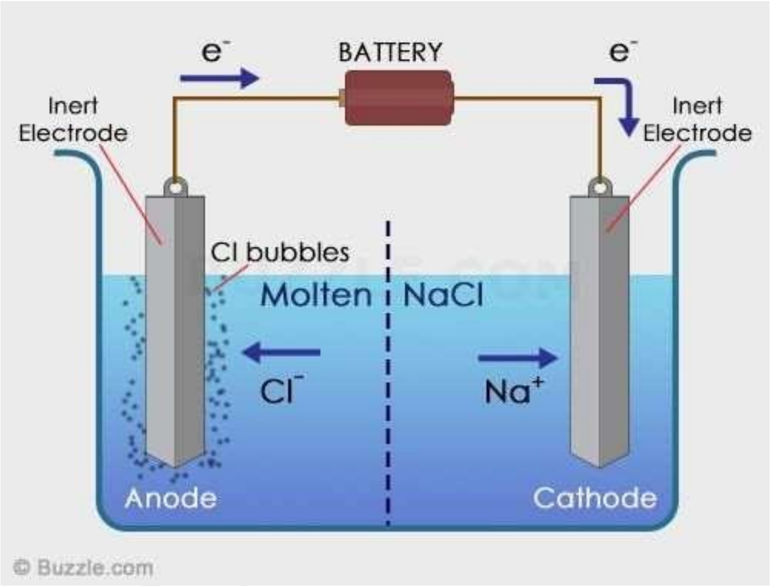
**Q. 6) Describe the electrolysis of molten sodium chloride using inert electrodes or Explain the construction and working of electrolytic cell.**

**Principle**:- In this process, there is conversion of electrical energy into chemical energy.

**Construction**:-

1. Fused NaCl is placed in a container.
2. Two graphite electrodes are dip in Fused NaCl and other end is connected to the battery.
3. Cathode is connected to the negative terminal of battery. Anode is connected to the positive terminal of battery.

**Diagram:-**



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**Working:-**

1. When the current is flowing, battery takes electron from anode and transfer them to the cathode.
2. Fused NaCl contains $Na^+$ and $Cl^-$ ions. When current is flowing is flowing Cathode attracts $Na^+$ ions and anode attracts $Cl^-$ ions.
3. As these particles are charged, their motion constitutes an electric current.

**Reaction at cathodes**

$Na^+(l) + e^- \longrightarrow Na(s)$

**Reaction at Anode**

$2Cl^- (l) \Rightarrow Cl_2(g) + 2e^-$

Net cell reactions

$2Na^{+}(l)$ ++ $2Cl^{-}$ (l) $\longrightarrow$ $2Na(s) + Cl_2(g)$

Result Of electrolysis

1. A pale green Cl2 gas is released at Anode.
2. A molten Silvery-white Na forms at Cathode.

**Q.7 Explain the construction and working of Galvanic Cell or (Daniel cell).**

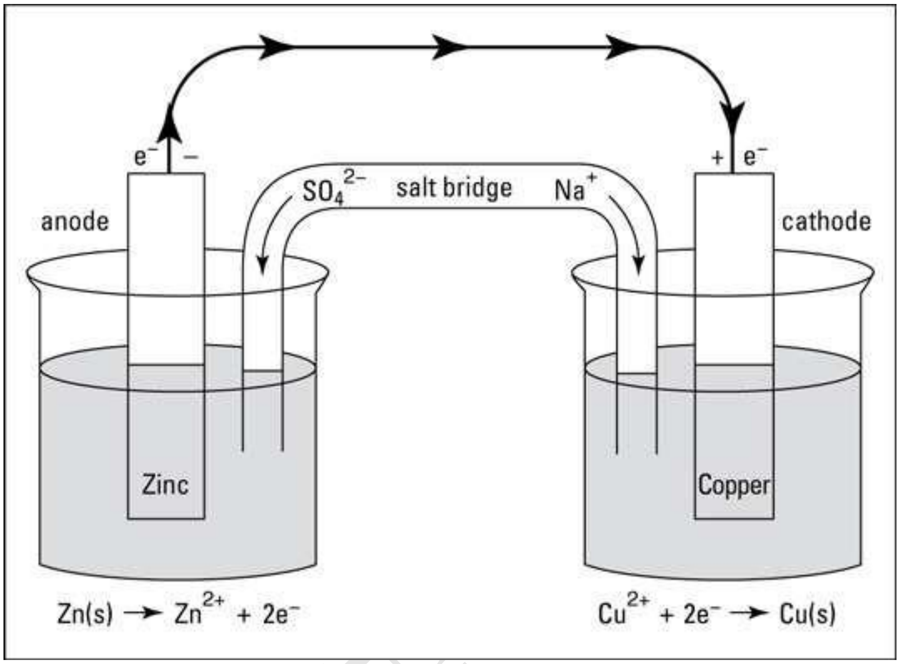
**Principle**

Daniel cell is primary galvanic cell, which is used to convert chemical energy into electrical energy.

**Construction**

1. It consist of two separate half cells.
2. One half cell is a beaker containing a strip of metallic zinc immersed in aqueous solution of zinc sulphate ($ZnSO_4$). Second half cell is a beaker containing a strip of metallic copper immersed in aqueous solution of Copper sulphate ($CuSO_4$).
3. Two electrode are connected externally by metallic wire.

**Diagram**



**Working:-**

**1. Reaction at anode**

Oxidation of Zn to $Zn^{+2}$ occurs at anode. Electrons on Zn strip are transferred from Zn to Cu electrode whereas $Zn^{+}2$ ions go into solution.

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

**2. Reaction at Cathode**

The electrons from Anode reduces $Cu^{+2}$ ions Cu metal which deposits on cathode.

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

Net Cell Reaction

$Zn(s) + Cu^{+2} \Rightarrow Zn^{+2} + Cu(s)$

**Result**

The potential of the cell is 1.1 V

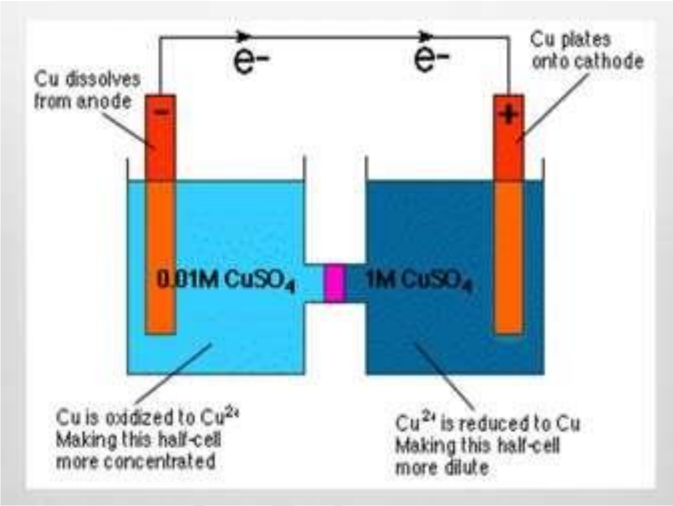
**Q.8 Explain the construction and working of Concentration cell.**

**Principle:** A concentration cell is an electrochemical device that generates electrical energy when two same metal is in contact with solution of ions at different concentration.

**Construction:**

1. It consist of two separate half cells.
2. One half cell is a beaker containing a strip of metallic copper immersed in aqueous solution of copper sulphate (concentration 0.01M). Second half cell is a beaker containing a strip of metallic copper immersed in aqueous solution of Copper sulphate (concentration 1M).
3. Two electrode are connected externally by metallic wire.

**Diagram**



**Working**

**1. As a result of difference in the concentration of solution, metal which is exposed to less concentrated solution act as anode and other metal part act as cathode**

**1. Reaction at anode**

Oxidation of Cu to $Cu^{+2}$ occurs at anode. Electrons on Cu strip are transferred Other electrode whereas $Cu^{+2}$ ions go into solution.

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

**2. Reaction at Cathode**

The electrons from Anode reduces $Cu^{+2}$ ions Cu metal which deposits on cathode.

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

**Net Cell Reaction**

$Cu(s) + Cu^{+2} \rightarrow Cu^{+2} + Cu\ (s)$

**Q.9 Explain the construction and working of fuel cell.**

## Fuel cells

- A fuel cell is an electrochemical cell which converts chemical energy of a conventional fuel and oxygen into electrical energy.
- The essentials process in fuel cell is;
  Fuel + oxygen → electricity + oxidation products.

### Hydrogen-oxygen fuel cell:

i. It contains an electrolytic solution such as 25% KOH. ii. It also has two inert porous electrode; anode and cathode both made up of material like graphite filled with Pt/Pd/Ag etc.

iii. Through the anode $H_2$ gas is bubbled. Through the cathode oxygen gas is bubbled. The reaction taking place are, At anode: $2H_2 \rightarrow 4H^+ + 4e^-$

At cathode: $O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$

Net reaction: $2H_2 + O_2 \rightarrow 2H_2O$

The only product discharged by the cell is water. iv.
The standard e.m.f of the cell is 1.23V

v. But in actual practice, e.m.f of the cell is 0.8 to 1.0V

vi. Generally number of such fuel cells are packed together in series to make a battery cell called fuel cell battery.

**Application:**

i) They are used as an auxiliary energy source in space vehicles, submarines, and other military vehicles.

ii) In space craft they are preferred due to their light weight, and by-product water which is a valuable source of fresh water for astronauts.

**Advantage over the conventional power plants:**

I) Easy to maintain.

II) They do not cause pollution.

III) As the fuel is completely consumed, it is fuel efficient.

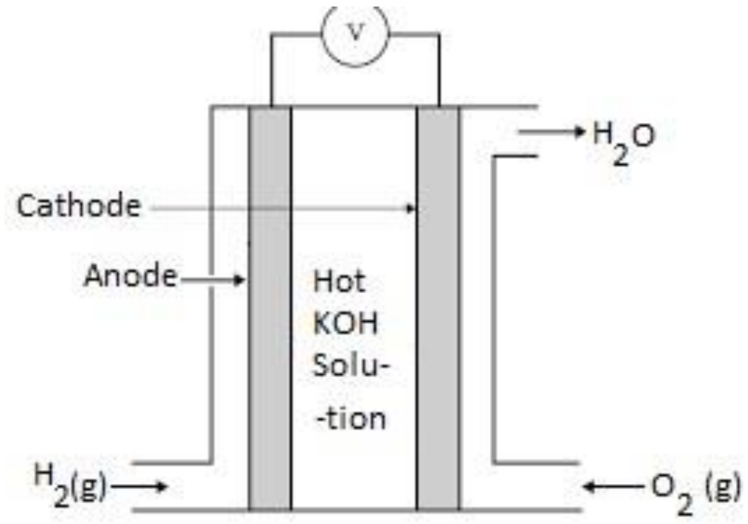
IV) They have high efficiency as it converts energy isothermally. V) Product obtained water is valuable and is of potable quality.

**Limitation:**

I) Life time of fuel cell is not accurately known.

II) Initial cost is high.
III) Pure hydrogen is costly.
IV) There is lack of infrastructure for the distribution of hydrogen.

Diagram:



**Q.10) Distinguish between Electrolytic cell and Voltaic Cell.**

| Sr no | Electrolytic cell | Voltaic Cell |
|---|---|---|
| **1** | It is used for the conversion of electrical energy into chemical energy. | It is used for the conversion of chemical energy into electrical energy |
| **2** | Electrolysis takes place. | Electricity is generated. |
| **3** | Anode requires positive charge. | Anode requires negative charge. |
| **4** | Oxidation occurs at positive electrode while reduction occurs at negative electrode | Oxidation occurs at negative electrode while reduction occurs at positive electrode |
| **5** | Both the electrodes are placed in the solution or molten electrolyte in the same container. | Two half cells are setup in different containers and are connected through salt bridge or porous partition. |
| **6** | Example: Voltameter, Electroplating, etc. | Example: Dry cell, Daniel cell, etc. |

**Q. 11) Explain the concept of electrode potential:**

1) A Galvanic cell is made up of two electrodes. One is anode(-) and other is Cathode(+). In each
2) half cell,a metal electrode dips into a solution. A potential difference between metal and solution is present at the surface of separation of metal and solution. This potential difference is called electrode potential.

2) Electrode potential is thus defined as the difference of electrical potential between metal electrodes and the solution around it under equilibrium condition.

**Q. 12) Explain the origin of electrode potential.**

1)When a metal plate is dipped into salt solution, the metal atoms have a tendency for oxidation or delectronation. They have a tendency to lose electrons and go into the solution. During process ,they leave electrons on the metal plate and try to make the metal plate negatively charged. 2) Also,the metal ions in the solution have a tendency of reduction or electronation. They have a tendency to gain electrons and deposit on the metal plate. This process makes the metal plate positively charged.

3) When equilibrium is reached, the metal plate may acquire positive charge if reduction(electronation) is faster. However the metal plate may acquire negative charge if oxidation(delectronation) is faster. Thus the charge acquired by the metal plate depends upon the rate of oxidation or reduction.

4) Charge separation results in formation of an electrical double layer at the interface between metal and solution. The charge on the solution is opposite to that of metal plate. The potential difference between metal and solution at equilibrium is known as electrode potential.

**Q. 13) Mention the factors affecting electrode potential.**

1) Nature of the element
2) Temperature
3)Concentration or activity of ions in solution.
4)Pressure in case of gas electrode.

**Q. 14) Define the terms:**

I) **Oxidation potential:-** The potential associated with an oxidation reaction at an electrode is called oxidation potential.

$$M_{(s)} \leftrightarrow M^{n+}(aq) + ne^-$$

II) **Reduction Potential:-** The potential associated with reduction reaction at an electrode is called reduction potential.

$$M^{n+}(aq) + ne^- \leftrightarrow M_{(s)}$$

III) **Cell potential or EMF (Electromotive Force ):-** It is defined as the difference of potential between the electrodes corresponding to an external flow of electrons from Anode to Cathode

$$E_{cell} = E_{oxi}\,(Anode) + E_{red}\,(Cathode)$$

### IV) Standard electrode potential

### Concept of standard electrode potential with example:

**Definition:** The potential of an electrode at 25°C (298K) containing all reactants and products at unit activity (conc. 1M and press. 1atm). It is denoted as E°.
The standard electrode potential for all metals can be obtained by preparing the cells in which one electrode is standard hydrogen electrode while the other metal is metal immersed in the solution of its ions. The standard electrode potentials are also known as standard oxidation potentials. It can be calculated using Nernst equation,
Consider a general redox reaction,

$M^{n+} + ne^- \rightarrow M$

Then,

$$E = E° + \frac{0.0592}{n} \log_{10}\frac{[M^{n+}]}{[M]}$$

**Electrode potential indicates tendency of a metal to behave as cathode or anode.**

**Nernst Equation:**

1. Consider a reaction, $M^{n+} + ne^- \rightarrow nM$

2. The equilibrium constant is given by,

$$K = \frac{[Product]}{[Reactant]} = \frac{[M^{n+}]}{[M\,]} \text{ --------(1)}$$

3. At equilibrium, Maximum work done

$W_{max} = nFE$

Where, n – number of electrons, F – Faraday(96500C), E – Cell potential

4. For a spontaneous reaction, change in free energy

$$\Delta G = -W_{max} = -nFE \text{----------}(2)$$

5. Under Standard Conditions,

$$\Delta G^\circ = -nFE^\circ \text{----------}(3)$$

6. According to Vant Hoff, the decrease in the above mentioned reaction can be given as

$$\Delta G = \Delta G^\circ + 2.303RT\log_{10} K$$

Substituting equations 1, 2,3

$$-nFE = -nFE^\circ + 2.303RT\log_{10}\frac{[M_{n+}]}{[M\,]}$$

Dividing by –nF,

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

OR

$$E_{cell} = E^\circ_{cell} - \frac{2.303RT}{nF}\log_{10}\frac{[M_{n+}]}{[M\,]}$$

or $$E_{cell} = E^\circ_{cell} - \frac{2.303RT}{nF}\log_{10}\frac{1_{n+}}{[M\,]}$$

Or $$E_{cell} = E^\circ_{cell} + \frac{2.303RT}{nF}\log_{10}[M^{n+}]$$

Or $$E_{cell} = E^\circ_{cell} + \frac{0.0592}{n}\log_{10}[M^{n+}]$$

Or $$E_{cell} = E^\circ_{cell} - \frac{0.0592}{n}\log_{10}\frac{[M_{n+}]}{[M\,]}$$

*A cell uses $Zn^{2+}/Zn$ and $Ag^{+}/Ag$ electrodes. Write the cell representation, Half-cell reactions, Net cell reactions and calculate the standard Emf of the cell.*

*Given:* $E^0_{Zn2+/Zn} = -0.76\ V$ *and* $E^0_{Ag+/Ag} = 0.8\ V$

ii) Cell representation

$Zn_{(s)}/Zn^{2+}{}_{(aq)}\ //Ag^{+}{}_{(aq)}\ /Ag_{(s)}$……………………………………………1M

Half Cell Reaction ,Net cell reaction……………………………………3M

$Zn_{(s)}$ ———$Zn^{2+}{}_{(aq)}$ +2e- At Anode

2 [$Ag^{+}{}_{(aq)}$ +2e- —— $Ag_{(s)}$] At Cathode

……………………………………………………

$Zn_{(s)}$ +2 $Ag^{+}{}_{(aq)}$ ——$Zn^{2+(}{}_{aq)}$ +2$Ag_{(s)}$ Net Cell Reaction

$E^0_{cell} = E^0_{Cathode} - E^0_{Anode}$

$= 0.8 - (-0.76)$

**$E^0_{cell}$= 1.56 V**……………………………………………………………………2M

*Write the Nernst Equation and calculate Emf of the following cell at 298K:*
*$Mg_{(s)}/Mg^{2+}(0.001M)\ ||\ Cu^{2+}(0.0001M)/Cu_{(s)}$.*
*Given:* $E^0_{Cu2+/Cu} = 0.34\ V$ *and* $E^0_{Mg2+/Mg} = -2.37\ V$

ii)Nernst equation……………………………………………………………………2M

Calculation :

$E_{cell} = E^0_{cell} - 0.0591/n \log [Mg^{2+}]/[Cu^{2+}]$

$E^0_{cell} = E_{cathode} - E_{anode}$

= 0.34-(-2.37

**$E^0$ cell = 2.71 V**………………………………………………………………1M

$E_{cell}$ = 0.34-(-2.37) -0.0591/2 log [10-3]/[10-4]

=2.71-0.02955(1log10)

=2.71-0.02955

**$E_{cell}$ =2.680 V**……………………………………………………………………2M

**Electrochemical series:**

In this the elements are arranged in the increasing order of their standard reduction potential.

| element | Std. electrode potential at 25°C | |
|---|---|---|
| Li | -3.052 | ↑ anodic ↓ |
| K | -2.93 | |
| Ca | -2.90 | |
| Na | -2.71 | |
| Mg | -2.37 | |
| Al | -1.66 | |
| Zn | -0.76 | |
| Cr | -0.74 | |
| Fe | -0.44 | |
| Ni | -0.23 | |
| Sn | -0.14 | |
| **H** | **0.00** | **Reference electrode** |
| Cu | 0.34 | ↑ cathodic |
| Hg | 0.79 | |
| Ag | 0.80 | |
| Pt | 0.86 | |
| Au | 1.69 | |

**Features of Electrochemical series:**

| **Elements at higher position** | **Elements at lower position** |
|---|---|
| Electropositive | Electronegative |
| Tendency to lose electrons (act as anode) | Tendency to gain electrons (act as cathode) |
| Easily oxidized | Easily reduced |
| Corrodes easily | Does not corrode easily |

**Limitations:**

- Iron corrodes faster than aluminium even though iron is placed below aluminium in electrochemical series because aluminium forms a nonporous, very thin, tightly adhering protective oxide film ($Al_2O_3$) on its surface and this film does not permit corrosion to occur. Such cases are not explained by electrochemical series.
- The standard electrode potentials are measured using SHE as the reference electrode whose electrode potential is taken as zero. But practically the electrode potential of SHE cannot be zero as it is impossible to get pure $H_2$ gas, 1M conc. Of HCl and 1atm pressure of $H_2$ gas.
- Also the standard electrode potentials are measured at 25°C, at 1atm pressure and at 1M conc.

of metal ions which may not be the practical conditions for corrosion of certain metal to occur.

## Galvanic Series

- In galvanic series the metals are arranged in the decreasing order of their activity.
- **For practical purpose, the electric potentials of many materials are obtained in a single environment mostly sea water using standard calomel electrode as reference. Such data in a tabular is called a 'galvanic series'**
- **Galvanic series in Sea water of metals & alloys.**

| **Anodic end (corroded)** | |
|---|---|
| Magnesium | Copper |
| Zinc | Bronze (Cu – Sn) |
| Aluminium | Copper – Nickel alloys |
| Cadmium | Monel Metal |
| Aluminium alloys | Nickel |
| Mild steel | Iconel |
| Alloy steel | Silver |
| Cast iron | Titanium |
| Stainless Steel | Graphite |
| Muntz Metal | Gold, Platinum |
| Brasses (Cu – Zn) | **Cathodic (protected) end** |

- In the galvanic series chemically more active metals are given higher position. These metals easily react with oxygen, sulphur etc. hence corrode readily.
- The noble metals at the lower end do not easily react.
- Greater the difference in their position in galvanic series the faster will be the corrosion.
- Metals close to each other in the galvanic series show fewer tendencies to corrode when in contact with each other.

**Distinguish between Electrochemical series and galvanic series.**

| **Electrochemical series** | **Galvanic series.** |
|---|---|
| 1. It is developed by arranging the electrode potentials of metals, which are measured by dipping pure metals in their salt solution of 1M concentration at 25°C & at 1 atm pressure. | 1. It is developed by studying corrosion of metals and alloys in unpolluted sea water using standard calomel electrode. |
| 2. Position of a given metal is fixed on the basis of its electrode potential. | 2. The position of a given metal may shift in galvanic series. |
| 3. It does not give any information regarding position of alloys. | 3. It gives information regarding position of alloys. |
| 4. This series comprises of both metals and nonmetals, but not alloys. | 4. This series comprises of both metals and alloys, but not non-metals. |
| 5. It is unable to predict correct corrosion behavior of metals. | 5. It predicts corrosion behavior more correctly. |

# MODULE 5 : FUELS (25 MARKS)

**Definition:**

It may be defined as a substance, which by oxidation is made a source of heat that can be used for any desired purpose.

**OR**

Fuel is a combustible substance, containing carbon as main constituent, which on proper burning gives large amount of heat which can be used economically for domestic and industrial purposes.

Fuel + $O_2$ → Products + Heat.

**OR**

According to modern concept, fuel is any fissionable material which produces energy that can be used for producing power.

Wood, charcoal, coal, kerosene, petrol, diesel, producer gas, oil gas etc. are some of the fuels.

**Classification:**

Fuels may be divided into two types,

i) Natural or primary fuels which are found in nature. Example wood, peat, coal, natural gas, petroleum etc.

ii) Artificial or secondary fuels which are derived from primary fuels. Examples coke, charcoal, kerosene, coal gas, producer gas, oil gas etc.

**Calorie:**

It is the amount of heat required to raise the temperature of one gram of water through one degree centigrade.

1000 cal = 1Kcal.

**Calorific value:**

**Q. 1 Define HCV or GCV and LCV or NCV.**

**Q.2 Why GCV is greater than NCV?**

It is the amount of heat liberated during complete combustion of unit weight or volume of the fuel. It is most important property because efficiency of fuel is judged by its calorific value.

Units of calorific value:

For solids and liquids – Kcal/Kg (MKS or SI units)

For gaseous fuel – Kcal/$m^3$

The calorific value of a fuel can be considered in two ways, **1. High calorific value (HCV) or gross calorific value (GCV):**

It is defined as a total amount of heat produced when a unit mass of fuel is burned completely and the products of combustion are cooled down to room temperature usually 60ºF or 15ºC. Explanation: Hydrogen is present in almost all fuel and when the fuel burns, hydrogen present in the fuel is converted into steam. Now, when the products of combustion are cooled down to 60ºF or 15ºC, the steam gets condensed into water and the latent heat is evolved on condensing the steam. This latent heat of condensation of the steam also gets included in the total heat and as a result more amount of heat is available.

**2. Low calorific value (LCV) or net calorific value (NCV):**

It is defined as a net amount of heat produced when a unit mass of fuel is burned completely and the products of combustion are allowed to escape into the atmosphere. In actual practice water (steam) is not condensed but escapes into the atmosphere along with other hot combustion gases and as a result lesser amount of heat is available.

If a fuel does not contain hydrogen, then, HCV = LCV.

**Characteristics of a good fuel:**

1. High calorific value: A fuel should possess high calorific value; since the amount of heat liberated and temperature attend thereby depend upon the calorific value of fuel.
2. Moderate ignition temperature: Ignition temperature is the lowest temperature to which the fuel must be preheated so that it starts burning smoothly. Low ignition temperature is dangerous for storage and transport of fuel, since it can catch fire easily. On the other hand high ignition temperature causes difficulty in igniting the fuel but the fuel is safe during storage, handling and transport. Hence an ideal fuel should have moderate ignition temperature.
3. Low moisture content: The moisture content of fuel reduces the calorific value. Hence fuel should have lower moisture content.
4. Low non-combustible matter: Non-combustible matter such as ash reduces the calorific value. Each percent of non-combustible matter in fuel means a heat loss of about 1.5%. Also it increases the cost of storage, transport and disposal of waste matter produced. Hence a good fuel should have low content of non-combustible matter.
5. Moderate velocity of combustion: Velocity of combustion is the rate or time taken by fuel to burn. If the fuel has high velocity of combustion, it burns so rapidly that it may not attain desired temperature. On the other hand if velocity of combustion is low then it burns so slowly that major part of heat is lost to the surrounding. Hence a good fuel must have moderate velocity of combustion.
6. Products of combustion should not be harmful: fuels on burning should not give out objectionable and harmful gases such as CO, $SO_2$, and H2S etc.
7. Low cost: A good fuel should be easily available in bulk at a cheap rate.
8. Easy to transport: Fuel must be easy to handle, store and transport at a low cost. Solid and liquid fuels can be easily transported while transportation of gaseous fuels is costly and can even cause fire hazards.
9. Combustion should be easily controllable that is combustion of fuel should be easy to start or stop when required.
10. Cleanliness in use : A good fuel should be ash less, smoke less, easily combustible.

**Dulong's formula:**

It is used for calculating gross value or HCV and net value or LCV from the chemical composition of fuel in MKS system.

1. HCV or GCV = 1/ 100 [ 8080 C + 34500 ( H – O/8) + 2240 S]

Where C, H, O and S are the percentage of carbon, hydrogen, oxygen and sulphur in the fuel respectively.

2. NCV or LCV = GCV – latent heat of condensation of water vapour formed.

= GCV – (weight of hydrogen x 9 x latent heat of steam)
Per unit weight of fuel
= GCV – [( H/ 100) x 9 x 587]
Where H = percentage of hydrogen in the fuel.

Problems based on Dulong's formula:

$$\text{HCV or GCV} = 1/100\ [\ 8080\ C + 34500\ (\ H - O/8) + 2240\ S]\ \text{Kcal/Kg}$$

$$\text{NCV or LCV} = \text{GCV} - [\ (H/\ 100) \times 9 \times 587]\ \text{Kcal/Kg}$$

Where, Where C, H, O and S are the percentage of carbon, hydrogen, oxygen and sulphur in the fuel respectively.

Solved example:

The ultimate analysis of coal gave the following results, C = 84%, S = 1.5%, N = 0.6%, H = 5.5% and O = 8.4%. Calculate the gross and net calorific value of the coal using Dulong's formula. Solution:

HCV or GCV = 1/100 [8080 C + 34500 (H – O/8 ) + 2240 S] Kcal/Kg

= 1/100 [8080 x 84 + 34500 (5.5 – (8.4/8)) + 2240 x 1.5] Kcal/Kg = 8356 Kcal/Kg.

NCV or LCV = GCV – ( H/100 x 9 x 587) Kcal/Kg

= 8356 – ( (5.5/100) x 9 x 587) Kcal/Kg

= 8356 – 290.56 = 8065.44 Kcal/Kg.

Ans. HCV or GCV = 8356 Kcal/Kg.

NCV or LCV = 8065.44 Kcal/Kg.

**Problems for practice:**

1. A sample of coal was found to have the following percentage composition. C = 75%, N = 3.2%, H = 5.2% O = 12.1% and ash = 4.5%. Calculate the gross and net calorific value of the coal using Dulong's formula. [Ans. GCV = 7332.18Kcal/Kg, NCV = 7057.47 Kcal/Kg]
2. A sample of coal contains. C = 76%, N = 1.5%, H = 5 % O = 16.2%, S = 0.3 %, and ash = 1.0%. Calculate the higher and lower calorific value of the coal. [Ans. GCV = 7173.895Kcal/Kg, NCV = 6909.745 Kcal/Kg]
3. Find the gross and net calorific value of a fuel, which an ultimate analysis gave the following results; C = 68.3%, N = 0.25%, H = 5% O = 25.6% and S = 0.3 %. Assume latent heat of steam is 600cal/gm. [Ans. GCV = 6146.36Kcal/Kg, NCV = 5876.36 Kcal/Kg]
4. Determine the gross and net calorific value of a fuel, which an ultimate analysis gave the following results; C = 92%, N = 1%, H = 4% O = 2% S = 0.3 %, and ash = 0.7%.Assume latent heat of condensation of steam is 580cal/gm. [Ans. GCV = 8734.07Kcal/Kg, NCV = 8525.27 Kcal/Kg]
5. Calculate the gross and net calorific value of a fuel having following composition: C = 86%, H = 6%, O = 0.5%, N = 3%, ash = 0.5%. [Ans. GCV = 8997.23Kcal/Kg, NCV = 8680.25 Kcal/Kg]
6. A sample of coal has the following percentage composition: C = 82%, H = 3.1%, O = 4%, N = 0.7%, ash = 9%, S = 1.2%. Calculate the gross calorific value. [Ans. GCV = 7549.48Kcal/Kg]

7. A sample of coal has the following percentage composition: C = 60%, H = 6%, O = 33%, N = 0.3%, ash = 0.2%, S = 0.5%. Calculate the gross calorific value. [Ans. GCV = 5506.07Kcal/Kg]
8. A coal having the following composition by weight: C = 90%, O = 0.3%, N = 0.5%, ash = 2.5%, S = 0.5%. The net calorific value was found to be 8925.28Kcal/kg. Calculate the %H and gross calorific value.

9. A coal sample contains C = 70%, H = 8%, O =20%, N = 0.2%, ash = 0.5%, S = 0.5%. Calculate GCV and NCV. [Ans. GCV = 7564.70Kcal/Kg, NCV = 7142.06 Kcal/Kg]

## Solid fuels

Solid fuels contain combustible organic material and incombustible or mineral part known as ballast. The organic part of fuel consists of carbon, hydrogen and sulphur. The organic portion may also include elements such as nitrogen and sulphur. The ratio of the various elements present in a fuel determines its properties. The incombustible or mineral part of the fuel consists of moisture and minerals. The mineral part of a fuel consists of carbonates, phosphates, sulphates, sulphides of Fe, Ca, Mg, Al, K, Na etc.

Solid fuels form a quite substantial part of total fuels. Solid natural fuels are wood, peat, lignite, anthracite coal, bituminous coal etc. and the most important artificial fuels are coke and charcoal, which are derived from natural coal.

### 1. Coal:

Coal is highly carbonaceous matter that has been formed as a result of alteration of vegetable matter (e. g. plants) under certain favorable conditions. It is mainly composed of C, H, N and O, besides non-combustible inorganic matter. There are several different types of coal, which have different properties depending upon their age and depth to which they have been buried under the other rocks. The degree of coal development is referred to as a coals “rank”, with peat being the lowest rank coal and anthracite being the highest. The ranks of coal from those with the least carbon to those with high carbon content are lignite, sub-bituminous, bituminous and anthracite.

### Analysis of coal:

There are two types of analysis, 1) Proximate analysis and 2) Ultimate analysis.

## 1) Proximate analysis:

It deals with the determination of moisture, volatile matter, ash and fixed carbon.

### a. Determination of moisture:

Presence of moisture in coal lowers its calorific value. Hence determination of moisture content is important. It is carried out as below, **Procedure:**

- About 1g of powdered sample coal is weighed in a clean and dry silica crucible with lid.
- The crucible, after **removing the lid** is placed inside the electric hot air oven maintained at **105-110ºC**.
- The crucible is allowed to remain in oven for about **an hour**.

- After one hour it is transferred to a desiccator by means of a pair of tongs and is allowed to remain there till it acquires room temperature.
- When the crucible with its contents attains the room temperature, it is taken out of the desiccator and weighed along with the lid.
- The process of heating followed by cooling to room temperature and weighing is continued till the constant weight is obtained.

During the process of heating, the crucible in the electric oven to a temperature in the range of 105-110ºC, the moisture associated with the coal gets vaporized. Thus

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

**b. Determination of volatile matter:**

Presence of volatile matter leads to lowering of calorific value. Determination of it involves the following procedure. **Procedure:**

- Crucible containing **<u>moisture free coal</u>** is **<u>covered with a lid</u>**.
- It is then transferred to a **<u>muffle furnace</u>**, which is maintained at a temperature of about **<u>925± 20 ºC for nearly seven minutes</u>**.
- The crucible after seven minutes is taken out and allowed to remain in air till it attains room temperature.
- It is then placed in a desiccator for some time to remove any moisture that may get associated with it during cooling.
- The crucible along with its content is then weighed to know the loss in weight corresponding to the amount of volatile matter evaporated.
- The process of heating followed by cooling and weighing is continued till constant weight is obtained.

$$\% \text{ of volatile matter} = \frac{\text{loss in weight at } 925 \pm 20\,^{\circ}\text{C} \times 100}{\text{Weight of coal taken}}$$

**c. Determination of ash:**

Presence of ash leads to the formation of clinkers (i. e. fused ash lumps), which are bad conductors of heat and create problems of its disposal. The fuel is then neither clean in use nor economic in labor. Determination of it involves the following procedure.

**Procedure:**

- After the determination of volatile matter, the **<u>crucible with contents, but without lid</u>**, is placed in the **<u>muffle furnace</u>** which is maintained at the temperature in the range of **<u>725750 ºC for nearly one hour</u>**. Hence the coal burns to form ash.
- The crucible along with its contents (ash) is then transferred to desiccator and allowed to attain room temperature.
- It is then taken out of the desiccator and weighed to know the weight of the ash formed.

- The process of heating followed by cooling and weighing is continued till the constant weight is obtained.

During the process of heating, the coal burns to form ash, which is the ultimate product of combustion. Its determination is important in the selection of proper quality of coal for a specific purpose, because the coal forming large amount of ash affects the calorific value and hence quantity of heat obtained is less.

$$\%\text{ of Ash} = \frac{\text{Weight of residue left in crucible} \times 100}{\text{Weight of coal taken}}$$

**d. Determination of fixed carbon:**

The percentage of fixed carbon in the given sample of coal is calculated by subtracting the sum of percentage moisture, percentage volatile matter and percentage ash from 100.

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

**Significance / Importance of proximate analysis:**

The proximate analysis plays a vital role in the selection of a specific variety of coal for a specific purpose and thereby in deciding the quality of coal. **A. Moisture:**

i) The high percentage of moisture reduces the calorific value of coal since a significant amount of liberated heat is wasted in evaporating the moisture. Therefore the net useful heat is less.

ii) Since the moisture is transported at the same cost as coal, fuel becomes expensive. iii) Due to excessive surface moisture, handling of coal becomes troublesome.

iv) However a small quantity of surface moisture up to 10% is desirable in coal as it improves yield and quantity of metallurgical coke.

v) It also produces a more uniform fuel bed and reduces the amount of fly ash. Hence a good quality of coal should have less amount of moisture. **B. Volatile matter:**

**i)** The volatile matter is produced as a result of thermal decomposition of coal.

**ii)** The volatile matter consists of combustible gases like CO, $H_2$, $CH_4$ and other hydrocarbons and incombustible gases like $CO_2$ and $N_2$.

**iii)** The incombustible gases do not have any heating value and are undesirable.

**iv)** Some coals having large amount of volatile matter burn with long, sooty (smoky) flame and have low heating value. Hence lesser the percentage of volatile matter better will be the rank of coal.

**v)** Coals with low volatile matter burn with a shorter flame. Thus information regarding the percentage of volatile matter is essential while designing a furnace, as combustion space required depends upon the nature of the flame.

**C. Ash:**

i) Ash is a non-combustible inorganic matter left after complete combustion of organic matter in the coal. Ash reduces the calorific value of coal.

ii) Ash also causes hindrance in the burning of coal. Hence lower the ash content, better the quality of coal.

iii) The presence of ash also increases the transporting, handling and storage costs. It also involves additional cost in ash disposal.

iv) The presence of ash also causes early wear of furnace walls, burning of apparatus and feeding mechanism. **D. Fixed carbon:**

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

**Numericals:**

1. A coal sample was analyzed as follows:

Exactly 2.5g was weighed into silica crucible. After heating for 1 hour at 110°C the residue weighed 2.415g, the crucible was then covered with a vented lid and strongly heated for exactly seven minutes at 950±20°c. The residue weighed 1.528g. The crucible was then heated without cover at 700°C until a constant weight was obtained. The last residue was found to weigh 0.245g. Calculate the percentage results of above analysis.

**Solution**:-

**i) Determination of % moisture:**

Weight of coal taken = 2.5g

Mass of moisture in coal sample =2.5- 2.415

= 0.085g

Therefore % of moisture = loss in weight of coal sample x 100

Weight of coal taken

= 0.085 x 100

2.5

= 3.4%

**ii) Determination of % volatile matter:**

Mass of volatile matter = 2.145- 1.528

= 0.887g

% of volatile matter = loss in weight due to volatile matter x 100

Weight of coal taken

= 0.887 x 100

2.5

= 35.48%

**iii) Determination of % ash:**

Mass of residue = 0.245g

% of ash = weight of ash left x 100

Weight of coal taken

= 0.245 x 100

2.5

= 9.8%

**iv) Determination of % fixed carbon:**

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

= 100 – (3.4+35.48+9.8)

= 100 – 48.68

= 51.32%

2. 2.5g of air dried coal sample was taken in a silica crucible, after heating it in an electric oven at 105-110ºC for 1 hour; the residue was weighed 2.410g. The residue was heated in a silica crucible covered with vented lid at a temperature 950±20ºC for exactly 7 minutes. After cooling the weight of the residue was found to be 1.78g. The residue was then ignited at 700750ºC to a constant weight of 0.2469g. Calculate the percentage of fixed carbon in a coal sample.
3. One gram of dried sample of coal on heating at 110ºC for 1 hour produced a residue 0.850g and this residue on heating at 950 ºC for 7 minutes in absence of air left 0.72g mass which on combustion left 0.1g of non-combustible matter. Calculate the result of proximate analysis.
4. A sample of coal was analyzed for content of moisture, volatile matter and ash. From the following data, calculate the percentage of the above quantities.
   i) Weight of coal taken = 2.5g ii) Weight of coal
   after heating at 100ºC = 2.365g
   iii) Weight of coal after heating in an covered crucible at 950±20ºC = 1.165g iv)
   Constant weight obtained at the end of the experiment = 0.460g
5. 1.5g of coal was weighed into a silica crucible. After heating for 1 hour at 100ºC, the residue weighed 1.415g. The crucible was then covered with lid and strongly heated for exactly 7 minutes at 950±20ºC. The residue weighed 0.528g. The crucible was then heated without cover, until a constant weight was obtained. The residue was found to weigh 0.254g. Calculate the percentage results.
6. An air dried coal sample weighing 2.9g was taken for volatile matter determination. After losing volatile matter, the coal sample weighed 1.96 g. if it contains 4.5% moisture, find % volatile matter in it.

## Ultimate analysis:

This type of analysis deals with the determination of carbon, hydrogen, nitrogen, sulphur, oxygen as follows,

**a) Determination of percentage of carbon and hydrogen:**

Here the carbon is oxidized to carbon monoxide which is then oxidized to carbon dioxide, while the hydrogen is converted into water. From the weight of the products, percentage of respective components is determined.

**Principle:** A known weight of powdered sample of dry coal is heated in a combustion tube in a current of dry oxygen. Here carbon is oxidized to $CO_2$ while hydrogen is converted into water.

Chemical reactions taking place are,

$C + O_2 \rightarrow CO_2$

12 44

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

2 18

$CaCl_2 + 7\ H_2O \rightarrow CaCl_2 . 7\ H_2O$

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

These gaseous products are absorbed in U-tubes containing anhydrous calcium chloride and potassium hydroxide respectively. $CaCl_2$ tube absorbs water vapours formed, while the second tube containing potassium hydroxide absorbs $CO_2$. From the increase in weight of the respective tubes, % of carbon and hydrogen can be calculated as below, **Procedure**:

1. Weigh out accurately a small quantity of powdered sample of dry coal in a previously weighed crucible.
2. Place the crucible in a hard glass tube, open at both the ends. At one side CuO gauge and other side silver gauge is present. CuO gauge ensures complete oxidation of the sample and silver gauge retains the oxidation products other than $CO_2$ and $H_2O$. Close the ends by airtight rubber corks having a hole at the centre. Insert two small tubes through these holes. One glass tube is connected to oxygen supply, while the second tube is connected to two U-tubes connected in series.
3. In the first U-tube, introduce anhydrous $CaCl_2$ and in the second pour KOH solution. Weigh both these tubes before the experiment.
4. Strongly heat the hard glass tube containing the crucible. Pass a current of dry oxygen through one end of the tube. Allow the gases to escape and enter into the two U-tubes connected in series.
5. After definite span of time, stop the oxygen supply and cool the hard glass tube containing the crucible, to room temperature.
6. Disconnect the two U-tubes and weigh them separately. Find out the increase in their weights.

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

$$\%\ \text{of H} = \frac{\text{Increase in weight of } CaCl_2 \text{ tube} \times 2 \times 100}{\text{Weight of coal taken} \times 18}$$

**OR**

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

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

### b) Determination of nitrogen ( Kjeldhal's method):

**Principle:**

- A known quantity of powdered sample of coal is heated with concentrated $H_2SO_4$ in a Kjeldhal's flask, in presence of potassium sulphate and copper sulphate as a catalyst, till the solution becomes clear.
- Nitrogen present in the coal gets converted into ammonium sulphate [$(NH_4)_2SO_4$] hence the solution becomes colourless.
- The solution of ammonium sulphate is then boiled with KOH/NaOH solution to liberate ammonia, which is absorbed in a known volume of standard acid solution ($H_2SO_4$) with few drops of methyl red till colour changes to faint pink.
- The acid solution (unreacted acid) is then back titrated with standard NaOH solution (till the colour is completely discharged).
- Blank titration is carried out using same volume of $H_2SO_4$.
- From the volume of the acid consumed nitrogen present in the coal can be estimated.

$$(NH_4)_2SO_4 + 2\ NaOH \rightarrow Na_2SO_4 + 2\ NH_3 + 2\ H_2O$$

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

**c) Determination of sulphur:**

The method consists of the conversion of sulphur present in the coal into $BaSO_4$. From the weight of $BaSO_4$ obtained, sulphur can be estimated.

**Principle:**

A known mass of powdered sample of coal is heated in current of dry oxygen in the bomb calorimeter, where the sulphur present in the coal is oxidized to sulphates. These sulphates are then treated with $BaCl_2$ solution to obtain precipitate of $BaSO_4$. From the weight of dry $BaSO_4$, sulphur can be estimated.

**Procedure:**

1. Weigh carefully and accurately some quantity of powdered sample of dried coal.
2. Heat the sample in the bomb calorimeter in the current of dry oxygen. Ash formed is extracted with dil. HCl and extract is heated with solution of $BaCl_2$ to obtain the precipitate of $BaSO_4$.
3. The precipitate is washed thoroughly with water and separated on a filter paper and dried thoroughly.
4. The dry precipitate is weighed accurately. From the weight of dry $BaSO_4$, sulphur can be estimated.

$$\underset{32g}{S} + O_2 \rightarrow SO_4^{-2} + BaCl_2 \rightarrow \underset{233g}{BaSO_4}.$$

$$\%\ \text{of S} = \frac{\text{weight of } BaSO_4 \text{ formed x 32 x 100}}{\text{Weight of coal taken x 233}}$$

**d) Determination of oxygen:**

It is obtained by deducting the sum of the percentage of carbon, hydrogen, nitrogen and sulphur from 100.

% of $O_2$ = 100 – (% C + % H + % N+ % S + % ash) **Significance:**

1. Carbon: Calorific value of a fuel is related to its carbon content. Higher the percentage of carbon, greater is the calorific value and better is the quality of coal. It also helps in the ranking of coal and classification of coal.
2. Nitrogen: Nitrogen is an inert and incombustible gas; hence its presence is undesirable. Thus a good quality coal should have very little nitrogen content.
3. Sulphur: Although sulphur increases the calorific value, on oxidation it produces harmful and corrosion causing gases like $SO_2$ and $SO_3$. These oxides of sulphur pollute the atmosphere. Presence of sulphur is highly undesirable in coal which is used for making coke for iron industry since it is transferred to the iron metal and badly affects the quality and properties of steel.
4. Oxygen and hydrogen : Since hydrogen is mainly present in combination with oxygen as water which is not desirable as it lowers the calorific value of a fuel. Lesser the percentage of hydrogen better is the quality of coal. Further hydrogen is associated with volatile matter of the coal and affects the use of coal. Oxygen is present in combined form with hydrogen in coal. Coals having high oxygen content have high inherent moisture and low calorific value. Thus a good coal should have low percentage of oxygen.

**Problems based on ultimate analysis**:

**1. Determination of % of C and H**

- 0.250g of coal sample was burned in steam of oxygen at 1290ºC in a combustion tube. There was increase in weight of calcium chloride tube by 0.025g and that of KOH tube by 0.8g after combustion. Find out the % of C and H of sample. Solution:-

$$\text{\% of H} = \frac{\text{Increase in weight of } CaCl_2 \text{ tube x 2 x 100}}{\text{Weight of coal taken x 18}}$$

$$= \frac{0.025 \times 2 \times 100}{0.250 \times 18}$$

$$= 1.11\%$$

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

$$= \frac{0.8 \times 12 \times 100}{0.250 \times 44}$$

$$= 87.27\%$$

**Problems for practice:**

i) 0.2g of coal was burned in a combustion apparatus and the gaseous products of combustion were absorbed in a KOH bulb and $CaCl_2$ tube which were previously weighed. There was increase in weight of calcium chloride tube by 0.1g and that of KOH tube by 0.56g after combustion. Find out the % of C and H of sample.

ii) A 0.5g of coal sample on ultimate analysis produced 1.60g of $CO_2$ and 0.225g of $H_2O$. Find out the % of C and H of sample.

iii) 0.4g of coal sample was burned in a combustion tube. There was increase in weight of calcium chloride tube by 0.2g and that of KOH tube by 0.88g after combustion. Find out the % of C and H of sample. iv) A 0.5g of coal sample on ultimate analysis produced 1.35g of $CO_2$ and 0.225g of $H_2O$. Find out the % of C and H of sample.

v) 0.2g of coal was burned in a combustion apparatus and the gaseous products of combustion were absorbed in a potash bulb and $CaCl_2$ tube which were previously weighed. There was increase in weight of calcium chloride tube by 0.06g and that of potash bulb by 0.64g after combustion. Find out the % of C and H of sample.

2. **Determination of % of N and S**:

- 1.4g of coal sample in Kjeldhal's experiment liberated ammonia which was absorbed in 50ml N/10 $H_2SO_4$. The resultant solution required 10ml of N/10 NaOH solution for complete neutralization. Find out % of Nitrogen.

Solution:
Volume of acid taken = 50ml
Volume of acid unreacted (in terms of NaOH) = 10ml Therefore
volume of acid consumed = (50-10) = 40ml.

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

$$\% \text{ of N} = \frac{40 \times 0.1 \times 1.4}{1.4}$$

$$= 4\%$$

- 0.5g coal sample was burned completely in a bomb calorimeter. The ash formed was extracted with acid and the extract obtained was treated with barium chloride solution to get barium sulphate precipitate. The weight of dry precipitate was 0.04g. Calculate the % of S in the coal sample.

Solution:

$$\% \text{ of S} = \frac{\text{weight of } BaSO_4 \text{ formed x 32 x 100}}{\text{Weight of coal taken x 233}}$$

$$\% \text{ of S} = \frac{0.04 \times 32 \times 100}{0.5 \times 233}$$

$$= 1.09\%$$

**Problems for practice:**

**1.** 1g of coal sample in Kjeldhal's experiment liberated ammonia which was absorbed in 25ml N/5 $H_2SO_4$. The excess of acid required 40ml of N/10 NaOH solution for back titration. Find out % of Nitrogen.

**2.** 0.5g coal sample was burned completely in a bomb calorimeter. The ash formed was extracted with acid and the extract obtained was treated with barium chloride solution to get barium sulphate precipitate. The weight of dry precipitate was 0.025g. Calculate the % of S in the coal sample.

**3.** A coal sample on ultimate analysis gave following result:

**a)** 0.5g coal produces 1.35g $CO_2$ and 0.225g $H_2O$.

**b)** 0.4g coal in Kjeldhal's experiment liberated ammonia which was absorbed in 50ml 0.5N $H_2SO_4$. The resultant solution required 22ml of 1 N NaOH solution for complete neutralization.

**c)** 0.5g coal on combustion in a bomb calorimeter followed by the treatment with $BaCl_2$ produces 0.04g $BaSO_4$.Calculate the % of C, H, N,S and O assuming coal contents 3.6% ash and also find GCV.

**4.** A coal sample on ultimate analysis gave following result:

a) 0.5g coal produces 1.3g $CO_2$ and 0.2g $H_2O$.

b) 0.4g coal in Kjeldhal's experiment liberated ammonia which was absorbed in 50ml 0.5N $H_2SO_4$. The resultant solution required 23ml of 1 N NaOH solution for complete neutralization.

c) 0.5g coal on combustion in a bomb calorimeter followed by the treatment with $BaCl_2$ produces 0.06g $BaSO_4$.Calculate the % of C, H, N, S and O assuming coal contents 4.5% ash and also find GCV and NCV.

**5.** A coal sample on ultimate analysis gave following result:

a) 0.25g coal produces 0.782g $CO_2$ and 0.021g $H_2O$.

b) 1.4g coal in Kjeldhal's experiment liberated ammonia which was absorbed in 50ml N/10 $H_2SO_4$. The resultant solution required 15ml of N/10 NaOH solution for complete neutralization.

c) 3.2g coal on combustion in a bomb calorimeter followed by the treatment with $BaCl_2$ produces 0.233g $BaSO_4$. Find GCV and NCV.

# COMBUSTION:

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

$$C_{(s)} + O_{2\,(g)} \rightarrow CO_{2\,(g)} + 97Kcal$$

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

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

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

For e.g. when carbon combines with oxygen to form carbon dioxide.

| | $C_{(s)}$ + | $O_{2\,(g)}$ → | $CO_{2\,(g)}$ |
|---|---|---|---|
| Mass proportion | 12 | 32 | 44 |
| Volume proportion | 1vol | 1 vol | 1vol |

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

**OR**

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

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

$2H_2 + O_2 \rightarrow 2H_2O$

$2CO + O_2 \rightarrow 2CO_2$

$2C_2H_6 + 7O_2 \rightarrow 4CO_2 + 6H_2O$

$2C_2H_2 + 5O_2 \rightarrow 4CO_2 + 2H_2O$

$2C_4H_{10} + 13O_2 \rightarrow 8CO_2 + 10H_2O$

$C_3H_8 + 5O_2 \rightarrow 3CO_2 + 4H_2O$

$S + O_2 \rightarrow SO_2$

$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$

$C_2H_4 + 3O_2 \rightarrow 2CO_2 + 2H_2O$

$C_4H_8 + 6O_2 \rightarrow 4CO_2 + 4H_2O$

$2C_3H_6 + 9O_2 \rightarrow 6CO_2 + 6H_2O$

Nitrogen, ash and carbon dioxide, if any, present in the fuel or air are incombustible matters and hence they do not take oxygen during combustion reaction. The total amount of oxygen required by the fuel can be given by sum of the amounts of oxygen required by individual constituent present in the fuel and these calculations are shown below:

**(ONLY FOR UNDERSTANDING, NOT REQUIRED FOR EXAM)**

**a) Combustion of carbon:**

Combustion of carbon is expressed by the equation

$$2C + O_2 \rightarrow CO_2$$

**12 Kg** of carbon requires for complete combustion **32 Kg** of oxygen.

Therefore, **C Kg** of carbon requires for complete combustion = $\mathbf{\frac{C \times 32}{12}}$

$= 2.67\ C$ Kg of $O_2$

Therefore, quantity of oxygen required for C Kg of carbon = 2.67 C Kg.

**b) Combustion of hydrogen**

Combustion of hydrogen is expressed by the equation

$$2H_2 + O_2 \rightarrow 2H_2O$$

**4 Kg** of hydrogen requires for complete combustion **32 Kg** of oxygen Therefore, **H Kg** of hydrogen requires for complete combustion **8H Kg** of Oxygen.

**c) Combustion of sulphur:**

Combustion of sulphur is expressed by the equation

$$S + O_2 \rightarrow SO_2$$

**32 Kg** of sulphur requires for complete combustion **32 Kg** of oxygen

Therefore, **S Kg** of sulphur requires for complete combustion **S Kg** of oxygen.

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

**(2.67C+8H+S)Kg**

**2.** But some quantity of oxygen is already present in the fuel. Therefore the minimum corrected quantity of oxygen required for complete combustion of 1 Kg of fuel will be ; (2.67C+8H+S-O)

**3.** Air contains 23% oxygen by weight and 21% oxygen by volume

From the above total quantity of air required for combustion of 1 Kg of fuel can be calculated. Since 23kg oxygen is present in100 Kg of air. Therefore (2.67C+8H+S-O) Kg is present in (2.67C+8H+S-O) x 100/23 Kg.

**4.** Further it should be noted that weight can be converted into volume in the following ways: At N.T.P. (i.e. at 0ºC and 760 mm pressure), 22.4 litre of any gas will weigh one gram molecule i.e. its molecular weight in grams.

For example, 22.4 liters of $CO_2$ at N.T.P. will weigh 44g of $CO_2$ (44 being the molecular weight of $CO_2$)

OR

$$22.4\text{m}^3 \text{ of } CO_2 = 44\text{Kg of } CO_2$$

**5.** The average molecular weight of air is taken as 28.94

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

$$\text{Weight of air needed} = 32C/12 + 16H/2 + 32S/32 - O \quad \times \frac{100}{23}$$

(O is oxygen present in the fuel)

$$\text{Volume of air required} = (\text{number of moles of air}) \times 22.4\ \text{m}^3 \text{ at N.T.P.}$$

$$= \frac{\text{weight of air needed in kg}}{28.94} \times 22.4\ \text{m}^3 \text{ at N.T.P.}$$

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

$$PV = nRT$$

Where P = pressure of gas in
atmosphere V = volume of gas in
liters n = number of moles of gas
T = Temperature on Kelvin scale.

**8.** To calculate the volume of gas at given temperature and pressure, following relation is used.

$$\frac{P_0V_0}{T_0} = \frac{P_1V_1}{T_1} \text{ (From Boyle's and Charles law)}$$

Where $P_0$, $V_0$ and $T_0$ are standard pressure, volume and temperature, $P_1$ and $T_1$ are the given pressure and temperature. Thus, $V_1$ volume at given pressure and temperature can be easily calculated.

**NOTE:** ***students should read the numerical carefully. If only elemental composition of each constituent of fuel is given, then it can be directly substituted in the formula, if not, then you can find amount of oxygen and air, by writing down the combustion reactions and calculating the total amount of oxygen and air. For this, students must write the correct combustion reactions.***

**NUMERICALS:**

**Formula Based:**

**1.** A liquid fuel has C =80%, H= 12%, $O_2$= 8%. Find the minimum quantity of air needed for complete combustion of 1 Kg of the above liquid fuel. (Ans: 13.11kg)

**2.** A coal sample was found to contain the following constituents: C =81%, H= 6%, O= 7%, S= 1%, N=1%, ash= 4%. Calculate the minimum amount of air required for complete combustion of 1 kg of coal.(Ans: 11.2kg)

**3.** Calculate the weight and volume of air needed for complete combustion of 1 Kg of coal containing has C =65%, H= 4%, $O_2$= 7%, N= 3.0%, moisture= 15% and remaining is ash. Molecular weight of air = 28.949g.

**4.** Calculate the volume of air by weight and volume for combustion of 2 Kg of carbon.

**5.** The percentage composition by mass of a sample of coal is as follows: C =75%, H= 10%, $O_2$= 10%, S= 1%, N=2% and remaining is ash. Calculate a) Amount of air required for complete combustion of 1kg of fuel. b) GCV and NCV.

**6.** A sample of coal contains: C =65%, H= 15%, $O_2$= 10%, S= 4%, N=2% and ash=4%. Calculate the minimum amount of air required for complete combustion of 2kg of fuel.

**7.** A sample of coal contains: C =80%, H= 6%, $O_2$= 8%, S= 2.5% and ash=3.5%. Calculate the gross and net calorific value of coal. Also calculate the minimum amount of air required for complete combustion of 1kg of above coal.

**8.** Calculate the weight and volume of air required for complete combustion of 5kg of coal with following composition: C =85%, H= 10%, $O_2$= 5%.

**9.** Calculate the weight and volume of air required for complete combustion of 1kg of coal with following composition: C =54%, H= 6.5%, $O_2$=3%, N=1.8%, moisture=17.3%, ash=17.4%. (given molecular weight of air =28.949)

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

**11.** Calculate the weight of air required for complete combustion of 5kg of coal with following composition: C =80%, H= 15%, O= remaining.

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

**13.** Calculate volume of air containing 20% oxygen by volume at 27ºC and 760mm pressure which will be required for complete combustion of 4 kg of fuel containing C=80%, H=15% and incombustible matter= 5%.

**14.** The percentage composition of coal sample was C =88%, H= 3.5%, $O_2$= 5%, S= 0.5%, N=1%. Calculate the theoretical quantity of oxygen and air (in volume) required at 27ºC and 1 atm pressure for the combustion of 2kg of coal.

**Equation Based:**

**15.** Calculate the volume of air required for complete combustion of $6m^3$ of gaseous fuel with following composition. CO= 46%, $C_2H_4$=1%, $CH_4$=8%, $N_2$=3%, $H_2$=6%, $CO_2$= remaining.
**16.** Calculate the volume of air required for complete combustion of $1m^3$ of gaseous fuel, which possess by volume $CH_4$=35%, $C_2H_4$=4%, CO=10%, $H_2$=45%, $N_2$=2%, Water vapour=4%.
**17.** The composition of gas was found to be $H_2$=10%, $CH_4$=15%, $C_2H_6$=25%, $N_2$=5%, CO=20%, and $O_2$= 5%. Calculate the volume of oxygen and air required for complete combustion of $8m^3$ of this gas.
**18.** A gas has following composition by volume $H_2$=20%, $CH_4$=5%, CO=25%, $CO_2$=10%, $O_2$= 6%, $N_2$=34%. If 20% excess air is used, find the weight of air supplied per $m^3$ of gas.
**19.** A gaseous fuel has following composition by volume $H_2$=30%, $CH_4$=40%, $C_2H_6$=10%, CO=10%, $N_2$=5%. Calculate volume of air required if 20% excess air is used for complete combustion assuming air contains20% oxygen by volume.

## Liquid fuels:

In the modern era, liquid fuels have become more popular for their use as domestic as well as industrial fuels since they are better, more convenient for use, more economical than solid fuels. Petroleum is one of the most important sources of liquid fuels.

**Petroleum or crude oil:**

The word petroleum is derived from petra meaning rock and oleum meaning oil. It is a dark, greenish-brown, viscous oil found deep in earth's crust, may be off shore or on shore. It is composed of many hydrocarbons (like straight chain paraffin, cyclo-paraffin or naphthalene, olefins and aromatics), together with small amount of organic compounds containing oxygen, nitrogen and sulphur. The oil is usually found floating upon a layer of brine and has a layer of gas at the top of it.

**The average composition of crude petroleum is**
C = 79.5-87.1% H
= 11.5-14.8%
S = 0.1-3.5% N +
O = 0.1-0.5% **Importance**
**of petroleum:**

1. It is the main fuel, which can be used in I. C. engines and runs the automobiles, airships, ships and practically all types of machines.

2. It is also a source of lubricating oils which reduces friction between the moving parts of machines and thereby increases the life and efficiency of machines. Such machines may either be of automobiles or those used in industries.
3. Commonly used products such as paints, cold creams, lotions, ointment, shampoos etc. are obtained from petroleum products.
4. It is also used as a source of asphalt or pitch, which is commonly used for road making, in the manufacture of paraffin wax, waterproofing compounds, waterproofing papers, in making cheap candles etc.

**Classification of petroleum:**

According to its chemical nature, petroleum has been classified as:

- **Paraffin base petroleum:** It consists of a number of either straight chain or branched chain saturated hydrocarbons thatA coal sample has C =70%, H= 10%, O= 0.05%, S= 3%, N=2% and ash= 6.5%. Calculate the minimum amount of air required for complete combustion of 1kg of coal. is paraffin from $CH_4$ to $C_{35}H_{72}$. The series of hydrocarbons from $C_{18}H_{38}$ to $C_{35}H_{72}$ are semisolids hence they are known as waxes. When ignited they burn with a long sooty flame. Hence, this type of petroleum is known as paraffin base petroleum.
- **Naphthalene base petroleum:** It consists of naphthalene or substituted naphthalene product with little quantity of paraffin and aromatic hydrocarbons. It burns with a short, non-sooty flame.
- **Mixed base petroleum:** It is a mixture of both, paraffin base and naphthalene base petroleum. It generally contains large amount of semisolid waxes.

**Mining of petroleum:**

Mining of petroleum is done by drilling holes in the earth's crusts and sinking pipes up to the oil-bearing porous rocks. Oil, usually, comes out itself due to hydrostatic pressure of natural gas. Alternatively it may be mechanically pumped up by using either lift pump or air-lift pump. The latter consists of two co-axial pipes, lowered into the base of the oil bed. Compressed air is forced through the outer pipe whereby oil comes out through the inner pipe. The oil is conveyed to refinery by a system of pipelines.

**Refining of petroleum:**

The crude oil, itself, cannot be used directly as a fuel, since it contains lot of impurities, which must be removed. The process in which petroleum is separated into different fractions having different boiling points is called "refining of petroleum". The plant set up for refining is called refinery.

The crude oil is an emulsion having greenish red to black colour mixed with sandy oil and water. It contains dissolved gases, liquids of low, medium and high boiling points, of widely different viscosities and solids as well as semi-solids waxes. The steps involved in the process of refining consist of:

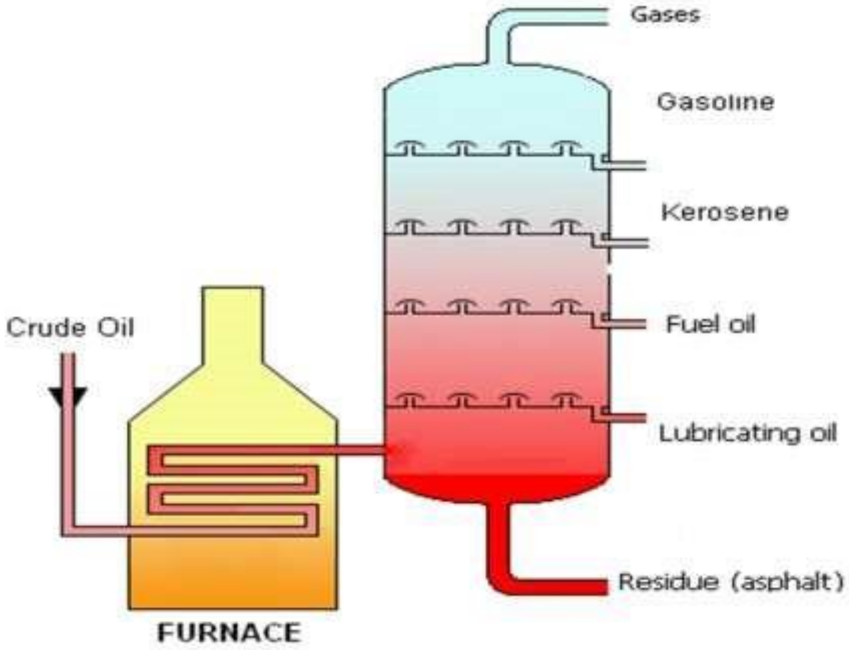
**Step- I) Separation of water or De-emulsification or Cottrell's process:**

The crude oil is as obtained from oil wells is an extremely stable emulsion of oil and salty water. Such an oil and water mixture is allowed to flow through cylindrical tanks fitted with charged electrodes. This causes the breaking of emulsion forming two different layers. The layers are withdrawn separately. Dissolved salts that may be present in oil are removed by thorough washing with water.

**Step- II) Removal of sulphur compounds :( desulphurization)**

Sulphur present in crude causes corrosion, hence needs to be removed during refining of crude petroleum. For this purpose the oil is treated with copper oxide, which forms insoluble precipitate of copper sulphide that can be removed by simple filtration. Complete removal of sulphur may be effected by the treatment of oil with alcoholic caustic soda and sodium butyrate.

**Step –III) Fractional distillation:**



- The crude oil, after removal of sulphur and water, is heated in an iron retort to a temperature of about 400ºC. In such heating volatile components of the crude oil gets evaporated.
- The vapours are then cooled by passing them up a tall cylindrical tower (bubble tower) consisting of a number of horizontal stainless steel trays, called fractionating columns.
- Each tray is provided with a small chimney, which is covered with a loose cap.
- As the vapours move up the tower, condensation of different fractions takes place, as per their boiling points i.e. high boiling fraction condenses first, followed by the one having somewhat lower boiling point and so on, i.e. higher boiling fractions condenses at lower plates and lower boiling fraction condenses at higher one.
- Each fraction is collected separately finally the residue left in the retort is black tarry mass called asphalt or pitch.

Thus, the various fractions between the temperature range of 20ºC-350ºC and above are separated.

## Gasoline or Petrol:

The fraction which is obtained between 40ºC to 120ºC is known as petrol or gasoline.

It is associated with impurities of thiocompounds, colour and few unsaturated hydrocarbons which are essential to be removed for further purification. In addition to this it also contains $H_2S$ and thioalcohols, which are responsible for the bad odour of the oil.Thus gasoline is first made free from bad odour by washing with NaOH and adding salts such as sodium butyrate which mask the undesirable odours. Sulphur can be removed by treatment with alcoholic caustic soda and sodium butyrate.The colouring matter is removed by treating the fractions at about 450ºC, with bauxite or liquid sulphur dioxide.

**Give the characteristics of ideal gasoline.**

i. It must be cheap and readily available.
ii. It must burn clean and produce less harmful combustion products. iii. It
should easily mix with air and should easily vaporize. iv. It must have high
calorific value.
v. It must be knock resistant.
vi. It should be stable and safe in storage.

| | **Diesel oil** | | **Gasoline** |
|---|---|---|---|
| 1 | It is the fraction collected at 250320°C | 1 | It is the fraction collected at 40-120°C |
| 2 | Its calorific value is 11,000Kcal/Kg. | 2 | Its calorific value is 11,250Kcal/Kg. |
| 3 | It is cheaper than gasoline. | 3 | It is costlier |
| 4 | Its consumption per unit of power produced is less. | 4 | Its consumption is more. |
| 5 | Its thermal efficiency is higher by about 30-35% than gasoline. | 5 | It has lower thermal efficiency. |

# Knocking:

It is a term related to internal combustion engine working on petrol.

1. In an internal combustion engine, a mixture of air and petrol vapour is compressed and ignited by an electric spark and the essential chemical reaction is the oxidation of hydrocarbon molecules.
2. Due to combustion or oxidation , gases are produced which move the piston down the cylinder.
3. It is essential that the combustion of the fuel in the cylinder of an I.C. engine should proceed in a smooth and regular way.
4. But sometimes, the rate of oxidation is so great that the mixture detonates (i.e. the mixture on ignition produces a sudden increase in gaseous volume) which causes uneven moving of the piston producing a sound called as engine 'Knock'.
5. Thus knocking is defined as, '**the rattling noise or sharp metallic noise produced in an internal combustion engine (I.C. engine) and which results into the loss of energy. Thus it is the abnormal type of combustion.'**

**6.** Knocking causes A) loss of large amount of energy.
B) Damage to piston and cylinder.

**7.** It is observed that straight chain saturated hydrocarbons have more knocking tendency than straight chain unsaturated hydrocarbon.

With normal paraffin, the anti-knock properties decrease with increase in the length of hydrocarbon chain (number of carbon atoms). E.g. n-propane, n-butane, n-pentane, n-hexane and n-heptane have octane numbers 100, 92, 62, 26 and 0 respectively. Also cyclic compounds have fewer tendencies to knock than straight chain compounds. Further Aromatic hydrocarbons like benzene, toluene, naphthalene and alcohols show good anti-knock properties.

Straight chain paraffin > branched chain paraffin > olefins > cyclo-paraffin > aromatics.

| | |
|---|---|
| High knocking | low knocking |
| Low octane number | High octane number |
| Low anti-knocking property | High anti-knocking property |

Thus knocking can be minimized by using fuel of high octane number and by adding a small amount of anti-knocking agents like tetra ethyl lead to gasoline.

## Anti-knocking agents:

**1.** Knocking can be decreased by addition of certain compounds to the fuels and these compounds are known as anti-knocking agents and the process of adding these compounds is called 'doping'.

**2.** Examples of anti-knocking agents are tetra ethyl lead (TEL), tetra methyl lead, diethyl zinc (DEZ) etc.

**3.** Methyl tertiary butyl ether (MTBE): **{same is the answer of unleaded petrol}**

- Octane rating of petrol is increased by adding TEL. However, combustion of leaded petrol causes formation of lead oxide which gets deposited on inner walls of cylinder and jams the piston.
- Also leaded petrol cannot be used in automobiles equipped with catalytic converters (a device which is used in motor vehicle exhaust systems which converters toxic combustion by-products into less toxic substances), because lead present in exhaust gas poisons the catalyst, thereby destroying its active sites.
- Alternative method of increasing octane number of petrol is to add high octane compounds like iso-pentane, iso-octane, ethyl benzene, MTBE etc.
- Out of these MTBE is preferred because it contains oxygen in the form of ether group which supplies oxygen for the combustion of petrol in I.C engines, thereby reducing the extent of per-oxy compound formation.
- Thus petrol added with such compounds is called as 'unleaded petrol' where higher octane rating is obtained without addition of lead compounds.
- An advantage of unleaded petrol is that it permits the use of catalytic converter attached to the exhaust in automobiles.

## Octane value or octane number:

1. It is a measure of anti-knocking property of gasoline or petrol. It is a number given to petrol that signifies its anti-knocking property. Fuel having high octane number will have good antiknocking property
2. Octane number of a fuel was introduced by Edger in 1927.
3. He found that, straight hydrocarbons such as n-heptane ($C_7H_{16}$), knocks very badly (poor antiknocking property). On the other hand iso-octane ($C_8H_{18}$) burns smoothly without producing any knock (highest anti-knocking property).
4. Therefore he rated; n- heptanes as zero.
   And Iso-octane as 100.
5. Thus if two hydrocarbons such as iso-octane and n-heptane are mixed in all proportions then a series of fuels having anti-knocking property from 0-100 octane are obtained. Such mixtures of iso-octane and n-heptane are taken as standard and the knocking property of gasoline and other fuels are compared with them.
6. Definition: - **octane value is defined as percentage of iso-octane in the mixture of isooctane and n-heptane that knocks with the same intensity as petrol being tested.**
7. The octane number scale has been extended by treating a mixture of iso-octane and n-heptane with the addition of tetra ethyl lead (TEL) which mixes thoroughly with gasoline and increases the octane rating of the gasoline.
8. Nowadays fuels with octane number above 100 are available E.g. Aviation gasoline. Octane number of few of the hydrocarbons is given below:

## Cetane value or Cetane number:

1. Knocking characteristics of diesel are expressed in terms of Cetane number.
2. Diesel engine is a compression ignition engine in which fuel is ignited by the application of heat and pressure.
3. In diesel engine first only the air is forced into the cylinder and compressed at high pressure due to which air temperature is raised to 500°C to 600°C. At this stage the fuel is injected in the form of spray into the very hot air. The droplets vaporize and get heated to the temperature at which spontaneous ignition takes place.
4. The time gap between the beginning of fuel injection and the beginning of combustion is called as ‘ignition delay’ or ‘ignition lag’.
5. If the fuel does not ignite fast i.e. it has long ignition delay, a large portion of injected oil gets accumulated into the cylinder before ignition as a result a violent combustion and sudden increase in pressure takes place on ignition resulting in rough and bumpy running of engine called as diesel knock.
6. Thus, it is desirable for a diesel fuel to ignite very quickly (without any delay) when injected into the cylinder of a compression ignition engine.
7. Thus ignition quality of diesel oil is measured in terms of Cetane number. Higher the Cetane number shorter is the ignition delay.

8. Ignition delay depends upon engine design, type of the injector, size of oil droplets, the way in which air and diesel are mixed and chemical nature of the fuel
9. In order to grade diesel fuels, Cetane number scale was introduced
10. Cetane ($C_{16}H_{34}$) is a saturated hydrocarbon which ignites very quickly (without delay).
11. While α- methyl naphthalene ($C_{11}H_{10}$), an aromatic hydrocarbon, does not ignite quickly (with long delay).
12. Thus, Cetane is rated as 100 and α-methyl naphthalene is rated as zero.
13. Thus Cetane and α-methyl naphthalene are mixed in all proportions then a series of fuels having Cetane number from 0-100 Cetane are obtained. Such mixtures are taken as standard and the ignition quality of diesel are compared with them.
14. Definition: **Thus Cetane number is defined as percentage by volume of Cetane in the mixture Cetane and α-methyl naphthalene which has same ignition delay as fuel being tested.**
15. The Cetane number of diesel oil can be improved by using the additive like acetylene, ethyl nitrite; ethyl nitrate, acetone, diethyl ether etc. (reduce the ignition delay by reducing flash point).

**Distinguish between Octane value and Cetane value:**

| | Octane value | | Cetane value |
|---|---|---|---|
| 1 | It is defined as, percentage of iso-octane in the mixture of iso-octane and n-heptane that knocks with the same intensity as petrol being tested. | 1 | It is defined as, percentage by volume of Cetane in the mixture Cetane and α-methyl naphthalene which has same ignition delay as fuel being tested. |
| 2 | It is a measure of **Anti-knocking** property of petrol. | 2 | It is a measure of **ignition quality** of diesel. |
| 3 | Octane number of petrol can be increased by addition of **TEL.** | 3 | Cetane number of diesel oil can be improved by using the additive like **acetylene, ethyl nitrite, ethyl nitrate, acetone, diethyl ether** |
| 4 | Petrol containing aromatics have highest octane number. | 4 | Diesel containing n- paraffins have highest Cetane number. |
| 5 | Oils having high Octane number have a low Cetane number. | 5 | Oils having high Cetane number have a low Octane number. |

## • Catalytic converters

A catalytic converter is a device used to reduce the toxicity of emissions from an I.C engine. Catalytic converters are most commonly used in motor vehicle exhaust systems. They are also used on generator sets, mining equipments, trucks, buses, trains and other engine-equipped machines. A catalytic converter provides an environment for a chemical reaction wherein toxic combustion by-products are converted to less toxic substances.

Catalytic converters are mainly of two types:

a) **Three –way catalytic converter:** It is used in spark ignition engines (petrol engine or I.C engine). It performs three simultaneous tasks i.e. it converts three main pollutants- CO, HC (hydrocarbon) and $NO_x$ (nitrogen oxides) to less toxic substances.

$$2NO_X \rightarrow {}_X O_2 + N_2$$

$$2CO + O_2 \rightarrow 2CO_2$$

$$\text{Hydrocarbon} + O_2 \rightarrow CO_2 + H_2O$$

b) **Two –way catalytic converter:** It is used in compression ignition engines (diesel engine). It performs two simultaneous tasks i.e. it converts two main pollutants- CO and HC (hydrocarbon) to less toxic substances. This catalyst uses excess oxygen in the exhaust gas stream to carry out following reactions.

$$2CO + O_2 \rightarrow 2CO_2$$

$$\text{Hydrocarbon} + O_2 \rightarrow CO_2 + H_2O$$

- Here for NOx, Selective Catalytic or NOx traps are used.

It consists of three parts,

a. Core or substrate ( catalyst support) eg. Honeycomb core.
b. Washcoat ( mixture of silica and alumina) this coating forms many rough surfaces over the substrate increasing the number of active sites. Hence efficiency increases. c. Catalyst Pt, Pd, Rh.

# MODULE VI: GREEN CHEMISTRY (16 MARKS)

**Q. What is green chemistry? List the principles of green chemistry. (3marks) May'08.**

**Definition:**

**Green chemistry is "The use of chemistry for pollution prevention by means of proper design of chemical products and processes that reduce or eliminate the use and generation of hazardous substances".**

## Principles of green chemistry:

Anastas and Warner have developed the twelve principles of green chemistry. They are as follows;

1. **Prevention of waste**
2. **Maximize Atom economy**
3. **Less hazardous chemical synthesis**
4. **Designing safer chemicals**
5. **Safer solvents and auxiliaries**
6. **Design for energy efficiency**
7. **Use of renewable feedstock**
8. **Reduce derivatives**
9. **Use of catalyst**
10. **Design for degradation**
11. **Real time analysis for pollution prevention**
12. **Safer chemistry for accident prevention**

## Explanation of twelve principles of green chemistry:

### 1. Prevention of waste:

Hundreds of tons of hazardous waste are released into the air, water and land by industry every hour, every day. **It is better to prevent waste than to treat or clean up waste after it has been created**. The ability of chemist to redesign chemical transformation to minimize the generation of the hazardous waste is an important first step in pollution prevention. By preventing waste generation, we minimize hazards associated with storage, transportation and treatment. Hence the chemical processes should be designed in such a way that less or no byproducts are formed.

### 2.Maximize Atom economy:

- It is a measure of how many atoms of the reactant end up in by product or waste.
- The most common way to judge the efficiency of the reaction is to calculate the yield.

$$\text{Percentage yield} = \frac{\text{Actual yield}}{\text{Theoretical yield}} \times 100$$

In general, organic chemists considers yields of 90% or better as excellent while 20% or less as poor.

Atom economy is a ratio of total mass of atoms in the desired product to the total mass of atoms in the reactants.

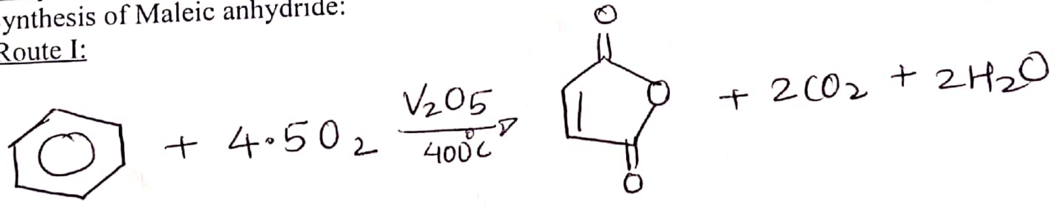
$$\%\text{ of Atom economy} = \frac{\text{Relative molecular mass of desired product}}{\text{Relative molecular mass of all reactant.}} \times 100$$

Synthetic methods should be designed to maximize the incorporation of all materials used in the process into the final product, resulting in few (if any) wasted atoms.

**Examples of atom economy reaction:**

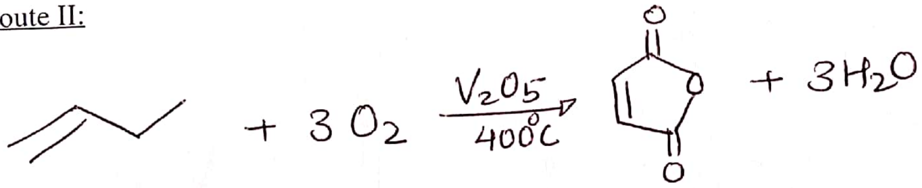
Synthesis of Maleic anhydride:

Route I:



$$\% \text{ atom economy} = \frac{100 \times 98}{(78+144)} = 44.1\%$$

Route II:



$$\% \text{ atom economy} = \frac{100 \times 98}{(56+96)} = 64.5\%$$

Comparison between the two routes shows that oxidation of butene is more atom efficient than oxidation of benzene (both are carried out at 400°Cand in presence of $V_2O_5$) because butane oxidation avoids wasting two carbon atoms as $CO_2$.

Q. **Find the atom economy of the following reactions :( 3-4 marks)**

① $H_3C-CH=CH_2 + Br_2 \xrightarrow{CCl_4} H_3C-\overset{Br}{CH}-CH_2-Br$ $= \frac{201.8}{(42+159.8)} \times 100 = 100\%.$

~~159~~ 42   159.8   201.8

② $H_3C-CH=CH_2 + Cl_2 \longrightarrow Cl-CH_2-CH=CH_2 + HCl$

e=42   71   76.5   Ans 67-69%

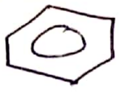
③ $H_3C-CH=CH_2 + H_2 \xrightarrow{Ni} CH_3-CH_2-CH_3$

42   2   44   Ans 100%

④ $C_6H_5NH_2 + (CH_3CO)_2O \longrightarrow C_6H_5NHCOCH_3 + CH_3COOH$

93   102   135   ~~60~~

Ans 69.23

⑤  + $CH_3COCl \longrightarrow C_6H_5COCH_3 + HCl$ Ans 76·67%

78

⑥ $C_6H_5CHO + CH_3CHO \longrightarrow C_6H_5CH{=}CH{-}CHO + H_2O$ Ans 88%

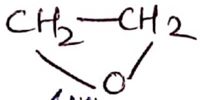
106 44 132

⑦ $CH_3NH_2 + COCl_2 \longrightarrow H_3C{-}N{=}C{=}O + 2HCl$ Ans 43·84%

43

⑧ $C_6H_6 + CH_3Cl \xrightarrow{AlCl_3} C_6H_5CH_3 + HCl$ Ans 71·5%

78 50·5 92

⑨ $C_2H_4 + \frac{1}{2}O_2 \longrightarrow$  Ans 100%

28 16 44

⑩ $C_6H_6 + Cl_2 \longrightarrow C_6H_5Cl + HCl$ Ans 75·5%

78 71 112·5

⑪ $C_6H_5NH_2 + C_6H_5COCl \longrightarrow C_6H_5NHCOC_6H_5 + HCl$ Ans 84·36

93 140·5 197

⑫ $CH_3CH_2Br + KOH \xrightarrow{H_2O} CH_3CH_2OH + KBr$ Ans 27·89

108·9 56 46

⑬ $CH_3CH_2CH_2Br + KOH \xrightarrow{alcohol} CH_3{-}CH{=}CH_2 + KBr + H_2O$ Ans 23·47

122·9 56 42

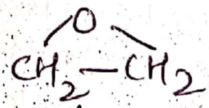
⑭ $CH_3CH_2CH_2OH + NaBr + H_2SO_4 \longrightarrow CH_3CH_2CH_2Br + NaHSO_4 + H_2O$ Ans 75·5%

60 103 Solvent 123

⑮ $C_2H_4 + Cl_2 + H_2O \longrightarrow CH_2Cl{-}CH_2OH + HCl$

28 71 18

~~$CH_2Cl$~~

$CH_2Cl{-}CH_2OH + Ca(OH)_2 \longrightarrow$  $+ CaCl_2 + 2H_2O$

74 44

$$\%\ \text{atom economy} = \frac{44}{(28+71+18+74)} \times 100$$

Ans = 23·03

**3. Less -hazardous chemical synthesis:**

According to this principle, the synthetic method should be designed in such a way that substances having little or no toxicity to humans' health or environment should be used wherever possible.

Starting materials such as aniline, pyridine should not be used as they are carcinogenic and toxic.

The reaction, in which intermediates or reagents or products are toxic, should not be followed. In this case alternative method or pathway should be used for synthesis. E.g. In 1984, due to leakage of MIC (Methyl isocynate) caused major damage. MIC is an intermediate in the manufacture of agricultural pesticides and it is highly poisonous.

Hence green chemistry recommends the design of synthesis to use and generate substances with little or no toxicity.

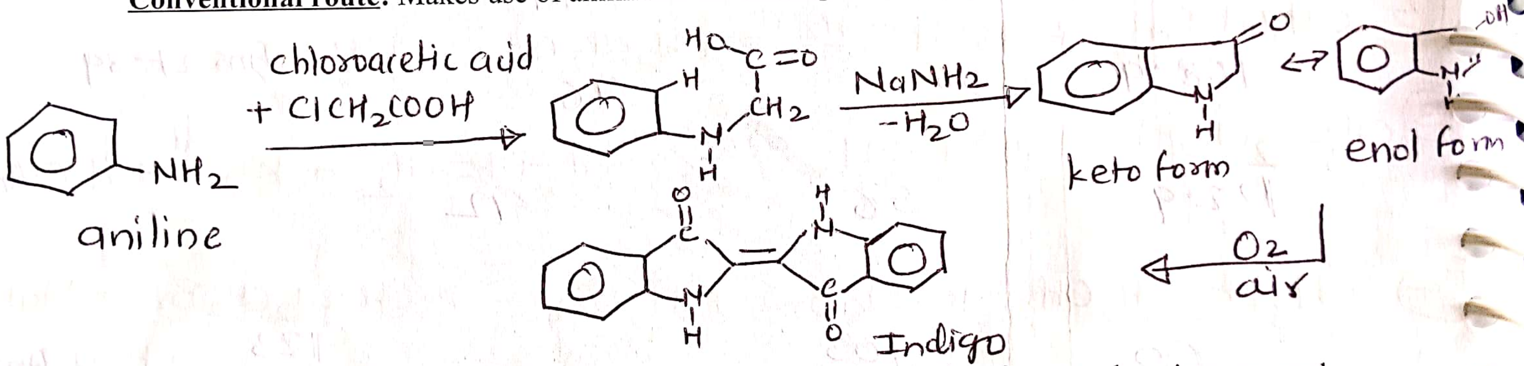
Other example is

**Synthesis of Indigo:**

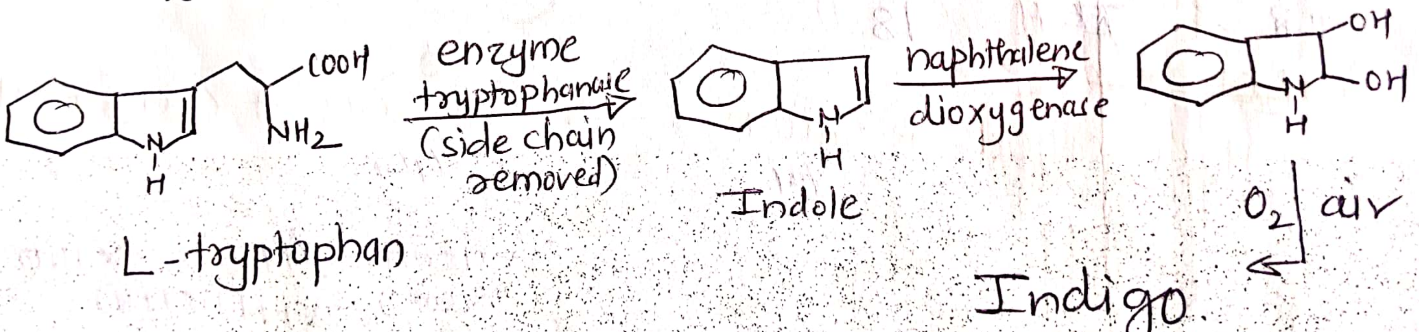
**Explain basic ideas in the field of green chemistry research with the help of synthesis of indigo dye. (May'08)**

Indigo is the dye which is used to colour blue jeans.

**Conventional route:** Makes use of aniline as the starting material.



**Greener route:** makes use of the reaction in which the side chain of tryptophan is removed enzymatically to give indole. It can be dehydroxylated enzymatically and then oxidized with oxygen to indigo.



Synthesis of CARBARYL

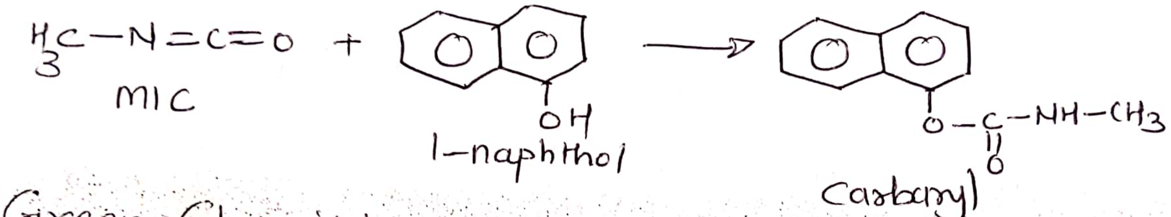
The Bhopal gas tragedy occurred on Dec 3,1984 was attributed to the catastrophic release of methyl isocyanate. The union carbide was manufacturing a pesticide called carbaryl (1-naphthyl-methyl carbamate) by the traditional method using 1-naphthol and phosgene are used as reactant to produce 1-naphtholenyl chloroformate, which when treated with methyl amine yields carbaryl. Although the reactants used are same, this alternative process eliminates the formation of methyl isocyanate, which is highly hazardous. Further insights and innovations in synthetic organic chemistry are needed to avoid the use of phosgene which is also toxic.

A] Traditional Synthesis :-

i] $CH_3NH_2 + COCl_2 \longrightarrow H_3C-N=C=O + 2HCl$

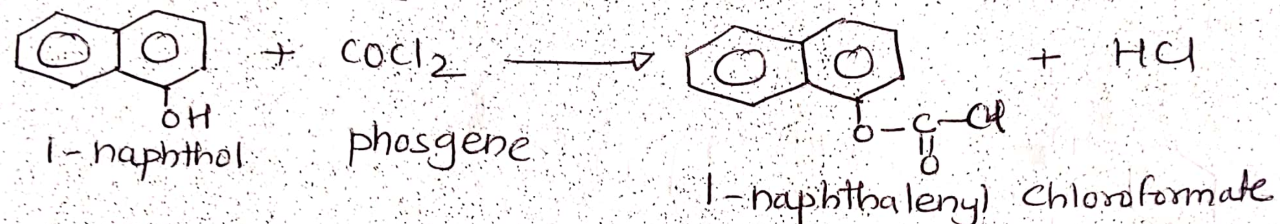
methylamine phosgene MIC (methyl isocyanate)

ii]

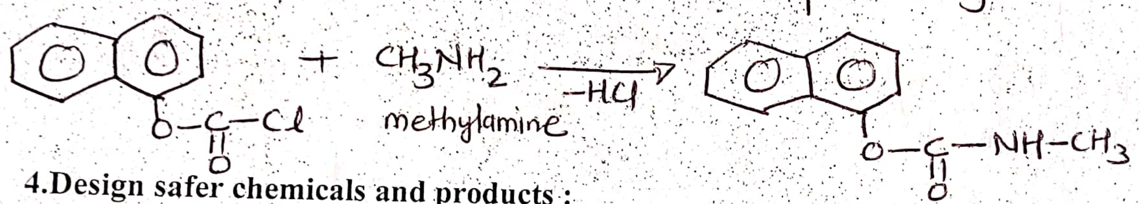


B] Green Chemistry Synthesis :-

i]



ii]



**4.Design safer chemicals and products :**

The chemical products should be designed in such a way that they have high efficiency and low toxicity.

When any medicinal drugs are to be introduced in the market, they are first put on trials to check their toxic effects on humans.

If they are found to be toxic then alternatives are prepared in such a way that only toxicity is reduced and not the efficiency.

**5. Use of safer solvents and auxiliaries:**

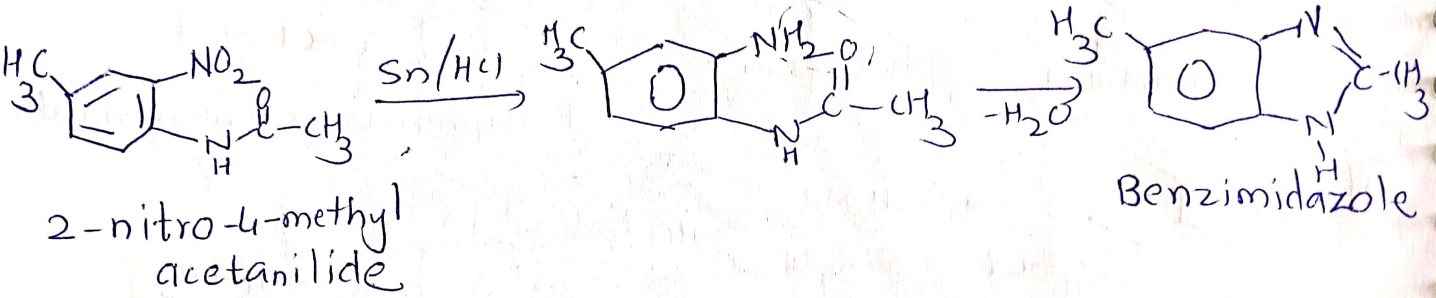
- According to this principle use of auxiliary substance like solvents, separating agents etc. should be avoided wherever possible.
- Solvents such as acetone, benzene, ether are highly inflammable and should be avoided.
- Other chemicals such as $CCl_4$, CHcl3, aniline, benzene are harmful for health. Some of them are carcinogenic in nature hence should be avoided.
- If a solvent is necessary, water is a good medium. Certain eco-friendly solvents which do not contribute in smog formation or destroy the ozone layer can be used.

- For e.g. for dry-cleaning the fabrics, toxic solvents like perchloroethylene was used, which is replaced during recent years by liquid $CO_2$.

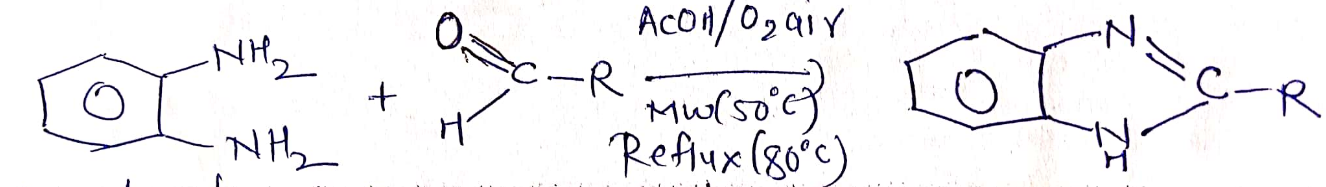
**6. Energy efficiency:**

- The aim of green chemistry is to increase energy efficiency.
- For this the energy requirements of chemical processes should be minimized
- This can be achieved by carrying out the reaction at ambient temperature and pressure wherever possible, by using catalyst and by stopping the excessive use of fossil fuels.
- The recently found substitutes are microwave radiations and ultrasound, which are used in the processes requiring very less energy.
- The fermentation process for producing many chemicals is also a good alternative since it requires less energy.
- Better energy efficiency can be achieved by proper heat transfer and minimum wastage of energy during the process.

**Eg. Synthesis of Benzimidazole**

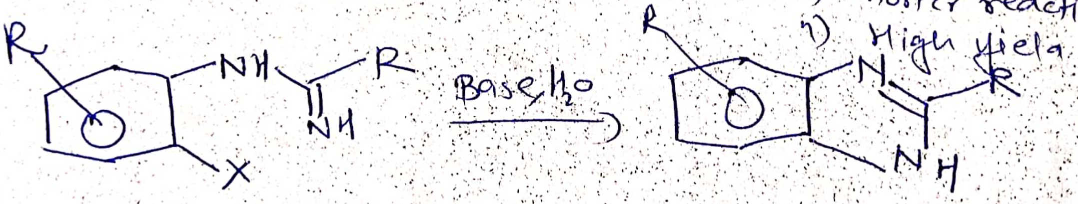


Green Route



phenylenediamine

↳ 1) Eco friendly
2) Avoiding hazardous solvent
3) shorter reaction time
4) High yield

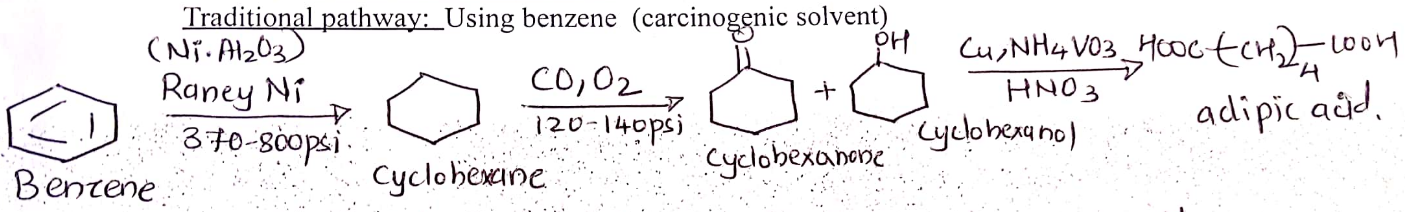


**7. Use of renewable feed-stock:**

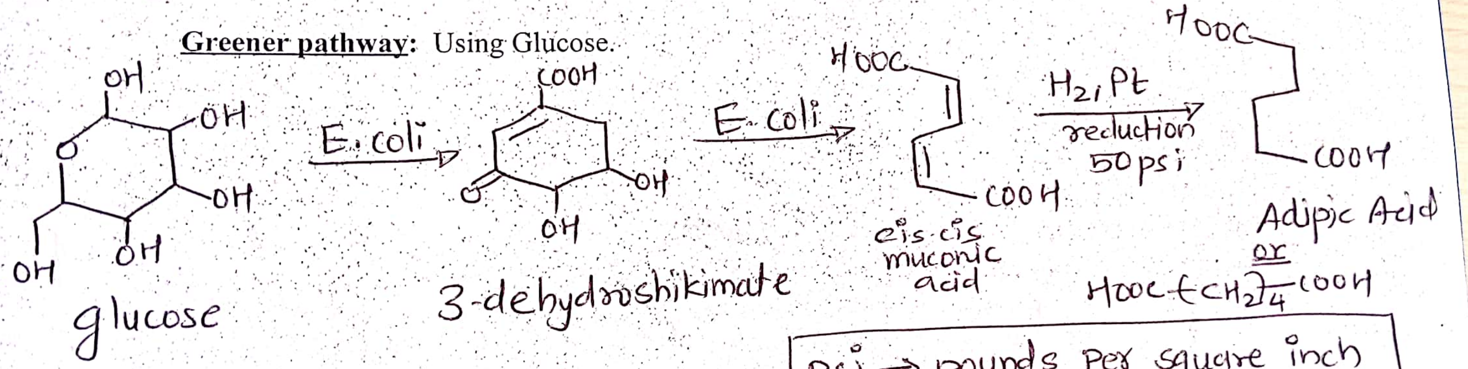
- The feed-stock or raw material should be renewable rather than depleting.
- Renewable feed-stock is often made from agricultural products or they are the waste from other processes.

- For e.g. **Synthesis of Adipic acid :**

Traditional pathway: Using benzene (carcinogenic solvent)



**Greener pathway:** Using Glucose.



psi ⇒ pounds per square inch

The first method is traditional method using benzene as a starting material which is carcinogenic in nature whereas in second method glucose is used which is easily available.

**8.Avoid chemical derivatives:**

During synthesis unnecessary derivatization such as blocking or protecting group should be avoided if possible.

The use of derivatives increase the steps of the process, hence additional reagents are required, it also generates more waste products. Hence to avoid these effects, alternative reagents should be used which are more selective.

For e.g. **Synthesis of Ibuprofen**

20
21
24
22
25
23
26
27

**9.Use of catalysts:**

- The catalytic reagents which are selective are preferred over stoichiometric reagents Minimize waste by using catalytic reactions.
  Catalysts are used in small amounts and can carry out single reaction many times.
  They are preferable to stoichiometric reagents which are used in excess and work only once.
  Catalytic reactions are faster and hence require less energy.

In recent years many processes have been developed which use non-toxic recoverable catalyst and also biocatalysis.

**10. Design chemicals and products to degrade after use:**

Chemical products should be designed in such a way that they break down to non-hazardous substances after use, so that they do not accumulate in the environment.

For e.g.

A) Pesticides: DDT when used as pesticide, its residue remains in the soil for many years causing pollution. The alternative to this is biological insecticides.

B) Plastic: The packing material such as plastic or polystyrene is non biodegradable and cause solid waste. The alternative to this is the biodegradable plastic containing cellulose and the packing pellets made up of starch.

**11.Real time analysis for pollution prevention:**

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

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

**12. Safer chemistry for accidents prevention:**

The substances and its forms used in the chemical process should be chosen to minimize the potential for the chemical release, accidents, explosion and fire.

The use of safer chemicals, minimizing temperature, pressure and using catalyst helps in minimizing the potential of accidents which is desirable.

**Synthesis of IBUPROFEN**

Principle highlighted:

1) reducing number of derivatives,

The traditional method involves many steps for which excessive chemicals are required. But in greener route less chemicals are needed.

2) Maximize atom economy.

Traditional method involving larger number of steps with atom economy of 40%. Alternative method which is simpler and employs recoverable strong acid as catalysts. The atom economy is 77%.

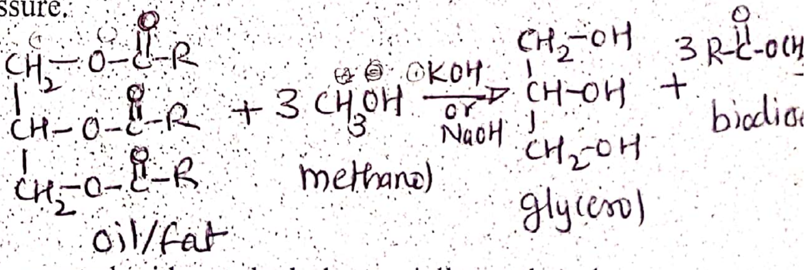
## GREEN FUELS eg.Biodiesel:

**Definition:** They are the monoalkyl esters of fatty acids derived from vegetable oils or animal fats via a catalytic reaction called as transesterification. In simple terms, biodiesel is the product you get when a vegetable oil or animal fat is chemically reacted with an alcohol to produce a new compound that is known as a fatty acid alkyl ester.

**Feedstock:** It is a clean burning alternative fuel produced from domestic renewable feedstock such as soya bean oil, corn oil, cottonseed oil, mustard oil, palm oil, restaurant waste oil. Animal fats, waste grease from water treatment plants etc.

**Properties:**

- Biodiesel is a liquid having colour between golden to dark brown depending upon the feedstock.
- It is practically immiscible with water.
- Has high boiling point and low vapour pressure.
- Its flash point is approximately 150°C.
- Its density is approximately 0.88g/cm$^3$.



**Synthesis of biodiesel (transesterification):**

- In this process, a vegetable oil or animal fat is reacted with an alcohol especially methanol in presence of catalyst such as potassium or sodium hydroxide to give methyl esters (biodiesel) and glycerol is produced as the byproduct.

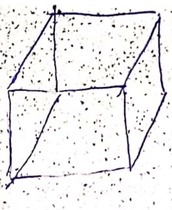
- **Steps involved in transesterification:**
  1. Catalyst i.e KOH or NaOH is dissolved in the alcohol (methanol) in a mixer, where alcohol is deprotonated by the base to a stronger nucleophile i.e potassium or sodium methoxide. → $CH_3OH + NaOH \rightarrow CH_3ONa + H_2O$
  2. This mixture is then taken into a close reaction vessel and the vegetable or animal oil/fat (Trans fatty acid) is added to it. The system is kept totally closed to prevent the loss of alcohol.
  3. potassium methoxide($K^+ CH_3O^-$) having strong polar bonds breaks the trans fatty acid into glycerol and ester chains(biodiesel) $\text{Oil/fat} + CH_3ONa \rightarrow \text{Biodiesel} + \text{glycerol}$.
  4. Generally the reaction mixture is kept just above the boiling point of alcohol (around 70°C) to increase the rate of the reaction.
  5. The reaction time is from 1 to 8 hrs and under normal conditions the reaction rate doubles with every 10°C increase in reaction temperature.
  6. Excess of alcohol is normally used to ensure total conversion fat/oil to its esters.
  7. The glycerol obtained as the byproduct settles at the bottom of the vessel because it is denser than biodiesel phase.Glycerol is removed from the bottom.
  8. The biodiesel fraction is then washed and dried.It is then checked for its purity.

**Advantages of biodiesel:**

1. It is prepared from renewable resources.
2. It is biodegradable and non-toxic.
3. It gives lesser combustion products such as CO, unburnt hydrocarbon, particulate matter etc. as compared to the conventional diesel fuel.
4. Like any other fuel, biodiesel can also be used as a heating fuel in domestic and commercial boilers.

**Disadvantages of bio-diesel:**

1. It is expensive than petroleum diesel.
2. It can harm rubber hose in some engines.
3. It has high $NO_x$ emissions.
4. It gels in cold weather.



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# MODULE 1: PRINCIPLES OF SPECTROSCOPY (8 MARKS)

## Introduction

### What is Spectroscopy?

Spectroscopy deals with interaction of electromagnetic radiation scattered, absorbed or emitted by the molecule giving rise to molecular spectra.

### What is the principle of spectroscopy?

The basic principle shared by all spectroscopic techniques is to shine a beam of **electromagnetic radiation** onto a sample, and observe how it responds to such a stimulus.

### What is Spectrum?

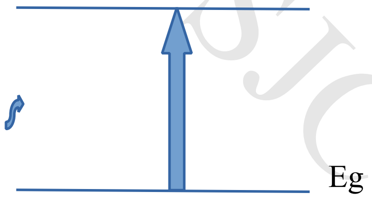
The response is usually recorded as a function of radiation wavelength. A plot of the response as a function of wavelength is referred to as a **spectrum**.

### Origin of spectrum:

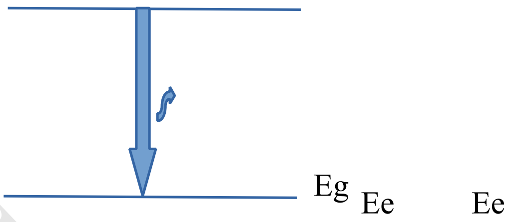
Consider two energy level of atoms or molecules. The one with low energy is called ground state energy level (Eg) and one with higher energy level is called excited state energy level (Ee).

**1)** **Absorption spectrum** results when an atom or molecule undergo transition from lower energy level to higher one with absorption of photon of energy h□□ h□ is equal to energy difference (□E = Ee – Eg)

**2)** **Emission spectrum** results when an atom or molecule undergo transition from higher energy level to lower one with emission of photon of energy h□□



Absorption Spectrum



Emission Spectrum

### What are the different types of spectra?

Spectra can be broadly classified into two categories viz. Atomic spectra and Molecular spectra

1) Atomic spectra arises from the transition of electron between the atomic energy levels.

2) Molecular spectra arises from the transition of electron between the molecular energy levels.

**What is the difference between atomic and molecular spectroscopy?**

In atomic spectroscopy, only electronic transitions are involved while in molecular spectroscopy electronic as well as rotational and vibrational transitions are involved. Thus molecular spectra is more complicated than atomic spectra, also it contains more information.

**What are the applications of molecular spectroscopy?**

1. It is used in structural investigation. We can determine electronic energy levels, bond lengths, bond angles and bond strengths.
2. It is used to monitor the changing concentrations of reactants or products.
3. It is also the basis of our understanding of colours in the world around us.

## Selection Rules

When light falls on certain molecule or atom, whether it will be absorbed or not depends on certain rules. These rules are called as selection rules.

A photon of light is absorbed by an electron, the electron jump to higher energy level. Conversely, if the electron releases a photon of light it will jump to lower energy state.

If electron move from lower to higher energy level or higher to lower energy level after absorbing or emitting certain amount of energy, the transition that occurs are called allowed transition. While transition which are less likely to takes place are called forbidden transition.

Probability of allowed transition can be determined by selection rule.

### 1. Laporte selection rule –

This rule say that the change in the orbital quantum number during transition is either +1 or -1,

$\Delta l = +1$ or -1 only

S(0) → p(1) → d(2) → f(3)

Transition from s to P, P to d and d to f are allowed transition.

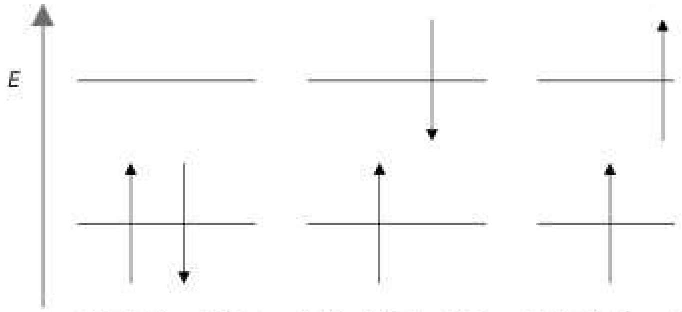
But transition from s to d and p to f are forbidden transition.

### 2. Spin selection rule

There must be no change in the spin multiplicity during transition, $\Delta S = 0$ only. i. e the spin of the electron must not change during transition.

Singlet → Singlet and Triplet → Triplet are allowed transitions.

But Singlet→ Triple and Triple →Singlet are forbidden transitions.(Refer diagram given below)



(a) Singlet Ground State
S = 0
Mutiplicity (2S+1) = 1

(b) Singlet Excited State
S = 0
Mutiplicity (2S+1) = 1

(c) Singlet Ground State
S = 1
Mutiplicity (2S+1) = 3

**Give classification of Spectroscopy**

**1. Atomic spectroscopy- in this case the energy changes take place at atomic levels.**

**a. Atomic Absorption Spectroscopy (AAS)** – In AAS, the atom absorbs uv light to get excited to higher energy level. AAS determine the amount of light absorption of ground state atoms in the gaseous state. AAS is used in detection of metals.

**b. Atomic Emission Spectroscopy (AES)-** In AES, the atoms are excited by the heat of flame to higher energy level and emit the light energy when come back to lower energy level. AES determine the amount of light emitted by the sample. ASE is used to determine the quantity of an element in a sample.

**c. Atomic Fluorescence Spectroscopy (AFS)-** In AFS depends on the measurement of fluorescence emitted from gas phase atom that have been excited to higher energy levels by absorption of electromagnetic radiation. The florescence from a sample is then analyzed using a fluorometer. AFS is commonly used to analyze the organic compounds.

**2. Molecular Spectroscopy- In this case the energy changes take place at molecular levels**

**a. Microwave spectroscopy** – Microwave spectroscopy uses microwave radiation, which result in rotational transitions of molecules in the gas phase. A type of spectroscopy which gives information related to structure and chemical bonding of molecules.

**b. Infrared spectroscopy -** Infrared spectroscopy uses infrared radiation, which result in Vibrational transitions of molecules. A type of spectroscopy used to determine the functional group present in the molecule.

**c. UV- vis spectroscopy-** UV- vis spectroscopy uses UV radiation, which result in electronic transitions of molecules. A type of spectroscopy used to determine presence of double or triple bond in the molecule.

**d. Nuclear Magnetic Spectroscopy-** NMR spectroscopy uses magnetic property of specific atoms to determine the structure, concentration and behavior of molecules in solid or liquid sample.

1. What is spectroscopy.
2. What is Principle of spectroscopy.
3. What is spectrum.
4. Explain electromagnetic radiation and give the characteristics of electromagnetic radiation.
5. What is electromagnetic spectrum? Explain with the diagram?
6. What are the different types of spectra.
7. What is the difference between atomic and molecular spectroscopy.
8. What are the application of molecular spectroscopy.
9. Explain Selection Rule