Electro chemistry is the branch of chemistry, which deals with chemical applications of electricity. The passage of electricity through a substance is called electrical conductance. Electrical conductance involves movement of electrons or ions. A substance which allows electric current to pass through it, is called a conductor. Eg: all metals fused salts, acids, alkalis. The electrical conductors are of two types.

1. Metallic or Electronic conductors
2. Electrolytic conductors

**Metallic or Electronic conductors:**
Metallic conductors conduct electricity due to the movement of electrons from one end to another end. In a solid, the electrical conduction involves the free movement of electrons in the metallic lattice, without any movement of the lattice atom; this type pf conduction is called metallic conduction. In metallic conductors, the electricity is carried by the electrons, the atomic nuclei remaining stationary. These conductors are further sub classified in to three types.

A. Good conductor
B. Semi- conductor
C. Non- conductor or Insulator.

**Good conductor:** It is a substance, which conducts electricity fully and freely. Eg: Metals like Copper, Aluminum, and Iron.

**Semi- conductor:** It is a substance, which partially conducts electricity. Eg: Silicon, Germanium.

**Non- conductor or Insulators:** It is a substance, which does not conduct electric current i.e., which does not allow the passage of current through it. Eg: Wood, Graphite.

**Electrolytic conductor:** It is a substance, which in aqueous solution of in molten state liberates ions and allows electric current to pass through. Electrolytic conductors are further sub classified in to three types, depending upon the extent of dissociation at ordinary dilutions.

**Strong electrolytes:** Strong electrolytes are completely dissociated into ions at all concentrations. Eg. NaCl, HCl, NaOH.

**Weak Electrolytes:** Weak electrolytes dissociate only to a small extent even at very high dilutions. Eg: CH₃COOH, NH₄OH.

**Non-Electrolytes:** Non-Electrolytes do not dissociate into ions even at low dilutions. Eg: Glucose, Sugar.

<table>
<thead>
<tr>
<th>S.NO</th>
<th>Metallic conductors</th>
<th>Electrolytic conductors</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>It involves the flow of electrons in a conductor.</td>
<td>It involves the movement of ions in a solution.</td>
</tr>
<tr>
<td>2.</td>
<td>It does not involve any transfer of matter.</td>
<td>It involves transfer of electrolyte in the forms of ions.</td>
</tr>
<tr>
<td>3.</td>
<td>Generally metallic conduction shows an increase in resistance as the temperature is raised.</td>
<td>But the resistance of an electrolytic solution decreases as the temperature is raised.</td>
</tr>
<tr>
<td>4.</td>
<td>No net chemical change takes place</td>
<td>Chemical reactions takes place at the two electrodes.</td>
</tr>
</tbody>
</table>

**Conductivity of electrolytes:** Electrolytic conduction involves the transfer of electrons through the migration of positive and negative ions towards the electrodes. In an ionic solution, the cations and the anions are free to move and both can transport charge. When a current is passed through the solution, the ions carry a current. The ability of the ions in solution to carry current is conductivity. The conductivity of a solution depends on the number of anions and cations present in it and also on how readily these ions can move. Like electronic conductors, electrolytes also obey ohm’s law.
**Ohm’s law:** The resistance $\mathcal{R}$ of a conductor is directly proportional to its Length ($l$) and inversely proportional to its cross sectional area ($a$)

\[
\mathcal{R} \propto l \\
\mathcal{R} \propto a \\
\mathcal{R} \sim l/a \\
\mathcal{R} = \rho \, l/a \\
\rho = \text{specific resistance}
\]

Thus, if length of the conductor is 1 cm and its cross sectional area is 1 cm$^2$

\[
\mathcal{R} = \rho \, l/a = \rho \, 1/1 = \rho
\]

Units: Resistance = $\mathcal{R} =$ Ohm

**Specific Conductance:** reciprocal of specific resistance is known as Specific conductance, this type of conductivity is called specific conductivity.

\[
k = \frac{1}{\rho} \\
(R = \rho \, l/a \rightarrow \rho = Ra/l)
\]

Specific conductivity is defined as the conductance of a one centimeter cube of substance or solution. It is represented by the symbol ($k$) $k =$ kappa.

In CGS system the conductivity is expressed in S cm$^{-1}$ or mho cm$^{-1}$

\[
\text{Conductivity} \quad k = \frac{1}{\rho} = \frac{1}{Ra/l} = \text{mho cm}^{-1} = \text{S cm}^{-1}
\]

In SI system, meter being the fundamental unit of distance, the conductivity is expressed as S m$^{-1}$.

The conversion factor of both CGS & SI system is,

\[
1 \text{ S cm}^{-1} = 100 \text{ S m}^{-1} \quad \text{or} \quad 1 \text{ S m}^{-1} = 0.01 \text{ S cm}^{-1}
\]

**Equivalent Conductivity:**

Equivalence conductance is defined as the conductance of all ions present in one gram equivalent of the substance or electrolyte in the solution at the given concentration.

**Equivalent conductivity/ equivalent conductance** is represented by $\Lambda$ (Greek : Capital Lambda).

\[
\Lambda = 1000 \times k/C
\]
Units of Equivalent conductivity:

\[ \text{Ohm}^{-1} \text{ Cm}^2 \text{ eq}^{-1} \]

**Molar Conductivity:**

Molar conductivity is defined as the conductance of all the ions present in mole of the electrolyte in the solution.

\[ \mu = \frac{1000k}{M} \]

The units of molar conductivity:

- CGS system: \( \text{Ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1} \) or S cm^2 mol^1

** Ionic Conductivity and Ionic Mobilities:**

Equivalent conductivity of any electrolyte at any dilution is directly proportional to the charge carried by the ions and their velocities. The conductivity is thus given by the products of charge and velocity of individual ions. At infinite dilution the ionization is complete and the solution containing one equivalent of various electrolytes contains equivalent number of ions. Hence at infinite dilution total charge carried by all ions is same in every case. Because the total charge is constant at infinite dilution, the \( \Lambda_0 \) **must depend exclusively on ionic velocities.**

**Defining the ionic velocity or mobility** as the speed with which a charged a particle at infinite dilution moves under a potential gradient of one volt per cm, we have,

\[ \lambda_+ \alpha u_+ \quad \lambda_- \alpha u_- \]

Or \( \lambda_+ = ku_+ \) \( \lambda_- = ku_- \)

Where \( k \) is a proportionality constant and \( u_+ \) and \( u_- \) represent the ionic velocities at infinite dilution. Since 1 equivalent of an ion under unit potential gradient carries a charge of 1 Faraday per sec., the proportionality constant \( k = 96500 \) coulombs.

Therefore,

\[ u_+ = \frac{\lambda_+}{k} \quad \text{and} \quad u_- = \frac{\lambda_-}{k} \]

Ionic conductivity is expressed in S cm^2, while ionic mobility is expressed in cm s^{-1}. Calculated ionic mobilities of few common ions at 25°C are given in Table

2. What is Kohlrausch law? Give its applications (Or) what is Kohlrausch law of independent migrations? Give its application.

**Kohlrausch Law:**

In a state of infinite dilution all electrolytes ionize or dissociate cent percentage, and the ions can be carried by the ions independent of each other. During our discussion on the variation of equivalent conductivity with square root of concentration we noticed that equivalent conductivity increased with dilution to reach a limiting value characteristic of the electrolyte and named it as equivalent conductivity at infinite dilution. \( \Lambda_0 \). In 1875 Kohlrausch made a series of measurements, involving electrolytes with common cations, common anions and calculated their differences. He obtain a constant difference in \( \Lambda_0 \) values of an ion pair, irrespective of the nature of the common counter ion employed, as exemplified by following results obtained at 25°C.

Kohlrausch studied the equivalent conductance of some pairs of having the same anion and cation at infinite dilution and experimental results are given in the table.


From the experimental results, he noticed, replacement of Sodium by Potassium ion, irrespective of the nature of anion, gives the same difference in equivalent conductance.

Similarly, replacement of chloride by hydroxide ion, irrespective of the cation, gives the same difference in equivalent conductance at infinite dilutions.

Basing on similar observations, kohlrausch advised a hypothesis called **law of independent migration of ions**. This law states that at infinite dilution each ion makes a definite contribution towards the equivalent conductivity of an electrolyte, irrespective of nature of the co-ion with which it is associated in the solution.

Therefore equivalent conductivity at infinite dilution is made up of two independent terms, called ion conductivities, characteristic of each ionic constituent of an electrolyte in solution. We can express the same conclusion mathematically as

\[ \Lambda_0 = \lambda_0^+ + \lambda_0^- \]

Where \( \lambda_0^+ \) and \( \lambda_0^- \) are the contributions of cation and anion (or) ionic conductance of anion respectively.

### Applications of Kohlrausch law:
1. Determination of equivalent conductance for weak electrolytes at infinite dilutions:
2. Determination of equivalent conductance for sparingly soluble salt (AgCl):
3. Determination of the solubility of sparingly soluble salt:
4. Determination of degree of dissociation & calculate the ionic product of water.

### 1. Determination of equivalent conductance for weak electrolytes at infinite dilutions:

We can easily calculate the equivalent conductance of strong electrolyte at infinite dilution graphically by extrapolation to zero concentration, but impossible for weak electrolytes like acetic acid, ammonium hydroxide, because

(i) Even at high dilutions they are not fully dissociated, and
(ii) Can’t obtain straight line curve.

So Kohlrausch gave a simple method of calculating \( \Lambda_0 \) for weak electrolytes from measurements of strong electrolytes.

E.g Equivalent conductance of acetic acid is obtained from the knowledge of equivalent conductance of HCl, CH₃COONa & NaCl at infinite dilutions.

\[ \lambda^0 \text{CH}_3\text{COO}^- + \lambda^0 \text{H}^+ = \lambda^0 \text{Cl}^- + \lambda^0 \text{CH}_3\text{COO}^- + \lambda^0 \text{Na}^+ - (\lambda^0 \text{Na}^+ + \lambda^0 \text{Cl}^-) \]

i.e \( \Lambda_0 \text{CH}_3\text{COOH} = \Lambda_0 \text{HCl} + \Lambda_0 \text{CH}_3\text{COONa} - \Lambda_0 \text{NaCl} \)

Similarly \( \Lambda_0 \text{NH}_4\text{OH} = \Lambda_0 \text{NH}_4\text{Cl} + \Lambda_0 \text{NaOH} - \Lambda_0 \text{NaCl} \)

### 2. Determination of equivalent conductance for sparingly soluble salt (AgCl):

The equivalent conductance of sparingly soluble salt (AgCl) also can be obtained by the similar method.
\[ \Lambda_0 \text{AgCl} = \Lambda_0 \text{NH}_4 \text{Cl} + \Lambda_0 \text{AgNO}_3 - \Lambda_0 \text{NH}_4\text{NO}_3 \]

3. **Determination of the solubility of sparingly soluble salt:**

The solubility of the sparingly soluble salts like Gal, BaSO4 can calculate by using the following relation.

\[ \Lambda_0 = 1000 \frac{k}{S} \]

\[ S = \text{Solubility in gm eq lit}^{-1} \]

\( K \) is determined by using Wheatstone bridge, \( \Lambda_0 \) is calculated using Kohlrausch’s law,

\[ \Lambda_0 \text{ (salt)} = \Lambda_0^+ + \Lambda_0^- \]

4. **Determination of degree of dissociation:**

Degree of dissociation (\( \alpha \)) is the fraction of the total number of molecules ionized into ions.

\[ \alpha = \frac{\text{No. of molecules ionized into ions}}{\text{Total number of molecules taken}} \]

This equation may be written as

\[ \Lambda = \alpha \Lambda_0 = \frac{\text{No. of molecules ionized into ions at a particular dilution}}{\text{Total no. of Molecules taken}} \]

\( \Lambda \), can be obtained from conductivity measurements, \( \Lambda_0 \) can calculated using Kohlrausch’s law.

Thus degree of dissociation (\( \alpha \)), is the ratio of the equivalent conductivity at particular dilution to the equivalent conductivity at infinite dilution.

Similarly we may calculate the ionic product of water.

3. **What are galvanic cells? What is the cell reaction and how is it written? Illustrate your answer? Describe the Daniel cell? define emf & Calculate the emf of the cell.**

**Galvanic Cells or Electro-chemical Cells:**

Electro-chemical cells are entirely different from electrolytic cells. In electrolytic cell electrical energy is converted to chemical energy.

But in electro chemical cells or voltaic cells or galvanic cells chemical energy is converted to electrical energy. Daniel cell is an example for the galvanic cell.

It consists of Zinc electrode dipped in ZnSO₄ solution. Where oxidation takes place, known as oxidation half cell and copper electrode dipped in CuSO₄ solution. Where reduction takes place, known as reduction half cell. These two solutions are separated by a salt bridge (U-tube containing concentrated solution of KCl or NH₄NO₃ in an agar-agar gel). Or porous pot, it provides an electrical contact between two solutions.
The following chemical reactions take place

At Anode: Zn \(\rightarrow\) Zn\(^{2+}\) + 2e\(^-\) (Oxidation Half Reaction)

At Cathode: Cu\(^{+2}\) + 2e\(^-\) \(\rightarrow\) Cu (Reduction half reaction)

Net cell reaction Zn + Cu\(^{2+}\) \(\rightarrow\) Zn\(^{2+}\) + Cu

Representation of Galvanic cells or cell diagram:

It consists of two electrodes anode & cathode. It is represented by keeping in view the following points.

1. Anode must be written on the left hand side, cathode on the right hand side.
2. Left hand side electrode is written by writing the metal first and then electrolyte. These two are separated by vertical line or a semicolon. The electrolyte may be written by the formulae of the compounds or by ionic species.

\[\text{Zn/Zn}^{2+} \text{ (or) Zn/Zn}^{2+} \text{ (or) Zn/ZnSO}_4\]

3. Cathode is written on the right hand side. In this first case, electrolyte is represented then only electrode; these two are separated by a vertical line or a semicolon.

\[\text{Cu}^{2+}/\text{Cu} \text{ (or) Cu}^{2+}; \text{Cu} \text{ (or) CuSO}_4/\text{Cu}\]

4. A salt bridge is denoted by two vertical lines, which separates the two half cells. Eg: Daniel cells

\[\text{Zn/Zn}^{2+}||\text{Cu}^{2+};\text{Cu}\]

**EMF of Electrochemical cell:**

The difference of potential, which causes flow of electrons from the electrode of higher potential to the electrode of lower potential, is called electromotive force (EMF). The emf of galvanic cell is calculated from the reduction half-cell potentials using the following relation.

\[E_{(\text{cell})} = E_{(\text{right})} - E_{(\text{left})}\]

Where

\[E_{(\text{cell})} = \text{e.m.f of cell}\]
\[E_{(\text{right})} = \text{reduction potential of right hand side electrode}\]
\[E_{(\text{left})} = \text{reduction potential of left hand side electrode}\]

**Applications of EMF measurement:**

1. Potentiometer titrations can be carried out.
2. Transport number of the ions can be determined.
4. From the EMF data the free energy changes, equilibrium constant of a reaction can be found out.
5. Hydrolysis constant can be determined.
6. Solubility of a sparingly soluble salt can be found out.

**Calculation of emf of the cell.**

\[\text{Cu/ Cu}^{++} \text{ (0.1M) } || \text{ Cl}/1/2 \text{ Cl}^{-} \text{ (0.01M).pt}\]

\[E^0 \text{ Cu}^{++}/\text{Cu} = + 0.337V, E^0 \quad \frac{1}{2} \text{ Cl}_2/\text{Cl}^{-} = +1.36 V\]

\[E_{(\text{left})} \rightarrow E^0 \text{ Cu}^{++}/\text{Cu} = + 0.337V\]
\[
E_{(\text{right})} \rightarrow E^0 \frac{1}{2} \text{Cl}_2/\text{Cl}^- = +1.36 \text{ V}
\]
\[
E_{(\text{cell})} = E_{(\text{right})} - E_{(\text{left})}
\]
\[
E_{(\text{cell})} = 1.360 - 0.337 = 1.023
\]

\[
E_{(\text{cell})} = 1.023 \text{ V}
\]

4. To describe types of electrodes, What is Nernst equation?

**Types of Electrodes**
1. Metal/metal-ion electrode
2. Gas electrode
3. Redox electrode
4. Metal/metal insoluble salt electrode

1. **Metal/metal-ion electrode- Zn | Zn$$^{2+}$$ Electrode:** This electrode can be constructed by bringing a Zinc rod in contact with Zinc ions. Oxidation of Zinc atoms to give Zinc ions is expressed by the following equation:

\[
\text{Zn} \rightarrow \text{Zn}^{2+} + 2 \text{e}^-
\]

In the reaction two electrons are exchanged between both the zinc species in the overall redox reaction making \(n=2\). Therefore

\[
E_{\text{Zn | Zn}^{2+}} = E^0_{\text{Zn | Zn}^{2+}} - 0.05916 \log \frac{a_{\text{Zn}^{2+}}}{a_{\text{Zn}}}
\]

Since the activity of all the pure solids is unity (\(a=1\))

\[
E_{\text{Zn | Zn}^{2+}} = E^0_{\text{Zn | Zn}^{2+}} - 0.05916 \log \frac{a_{\text{Zn}^{2+}}}{2}
\]

This expression suggests that the oxidation electrode potential, \(E\), decrease with increase \(\ln [a_{\text{Zn}^{2+}}]\), and equals to standard electrode potential, \(E^0\), at unit concentration of the electrolyte.

2. **Gas electrode – Hydrogen electrode:**

The electrode reaction of this electrode is written as;

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

Applying Nernst equation

\[
E_{\text{H}_2 | \text{H}^+} = E^0_{\text{H}_2 | \text{H}^+} - 0.05916 \log \frac{a_{\text{H}^+}}{1}
\]

At 1 atm pressure

\[
E_{\text{H}_2 | \text{H}^+} = E^0_{\text{H}_2 | \text{H}^+} - 0.0592 \log a_{\text{H}^+}
\]

\[
E_{\text{H}_2 | \text{H}^+} = E^0_{\text{H}_2 | \text{H}^+} + 0.0592 \text{ pH}
\]

3. **Redox electrode-Quin-hydrone Electrode:**

Platinum rod dipped in a mixture of two different oxidation states of a metal or two redox states of any compound is called redox electrode. Platinum wire immersed in a mixture of ferrous and ferric ion mixture is a typical example of this class.

Electrode reaction:

\[
\text{Fe}^{2+} \rightarrow \text{Fe}^{3+} + \text{e}^-
\]

\[
a_{\text{Fe}^{2+}} \quad a_{\text{Fe}^{3+}}
\]

The electrode potential at any \([\text{Fe}^{2+}] / [\text{Fe}^{3+}]\) ratio is given by the expression,
Quin-hydrone electrode: This is a redox electrode reversible to protons and often replaces the hydrogen electrode. Quinhedron is a 1:1 molar mixture of quinine and hydroquinone. The electrode consists of a shiny platinum electrode dipped in an acid/base test solution, which is saturated with quinhydrone. The electrode reaction is given by

\[
E_\text{Pt|Q-H^+,QH}_2^- = E^0_\text{Pt|Q-H^+,QH}_2^- - 0.0592 \log \frac{a_{\text{QH}}^2}{a_{\text{Q}}} 2 a_{\text{H}^+}
\]

Since quinine and hydroquinone are taken in equimolar amounts, i.e., \(a_{\text{Q}} = a_{\text{QH}}\).

\[
E_{\text{Q,QH}_2^-} = E^0_{\text{Q,QH}_2^-} - 0.0592 \text{ pH}
\]

Quin-hydrone electrode can thus be used to measure pH of a solution. Due to instability of quinine in strong alkaline medium, this hydrogen ion indicator electrode is suitable only upto a pH of 8.

4. Metal/Metal insoluble Salt electrode- Calomel Electrode: This electrode has Hg in contact with its insoluble salt Hg_2Cl_2 and chloride ions. Construction, Electrode reaction and Nernst equation of calomel electrode is discussed below.

Electrode potential:
Potential difference is developed between the metal ions from metal to the solution (or) from solution to the metal. At equilibrium the potential difference remains constant, this is known as electrode potential of metal.
The electrode potential of a metal is defined as the direct measure of its tendency to get reduced is called reduction potential, its value is +x volts. Similarly the tendency of an electrode to lose electrons is a measure of its tendency to get oxidized is called oxidation potential, its value is –x volts.

Expression for electrode potential:
Consider the following redox reaction
\[
M^{n+} + ne^- \leftrightarrow M
\]
For such a redox reversible reaction, the free energy change (\(\Delta G\)) and its equilibrium constant (K) are related as;
\[
\Delta G = -RT \ln k + RT \ln \frac{[\text{product}]}{[\text{Reactant}]} \\
\Delta G^0 + RT \ln \frac{[\text{product}]}{[\text{Reactant}]}
\]

Where \(\Delta G^0 = \text{standard free energy change}
\]
The above equation is known as Van’t Hoff Isotherm.
The decrease in free energy in the reversible reaction will produce electrical energy i.e.
\[
\Delta G = nEF \text{ and} \\
\Delta G^0 = -nE^0F
\]
Where $E = $ Electrode potential  
$E^0 = $ Standard electrode potential  
$F = $ Faraday (96,500 coulombs)

Comparing equation 1 & 2

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

$$= -nE^0F + Rt \ln \frac{1}{[M^{n+}]}$$

Where, concentration of the metal is unity or

$$-nEF = -nE^0F - RT \ln [M^{n+}]$$

Dividing the equation by $-nF$

$$E = E^0 + \frac{RT}{nF} \ln [M^{n+}]$$

$$E = E^0 + 2.303RT \log [M^{n+}]$$

$$E = E^0 + 0.0591 \log [M^{n+}] \quad \cdots \cdots \text{Eq-(3)}$$

This equation-3 is known as “Nernst Equation” for electrode potential.

5. To write a short notes on a) Concentration cells b) Potentio-metric Titrations.

a) Concentration Cells

Concentration cell is an electrochemical cell that has two equivalent half-cells of the same material differing only in concentrations. One can calculate the potential developed by such a cell using the Nernst Equation similar to an electrochemical cell. In concentration cell the voltage comes from its attempts to reach equilibrium, which will stop when the concentration in both half-cells are equal.

Types of concentration cells: The concentration differences could be affected in the electrode material or in the electrolyte. Further they could be subdivide into cells with transference or without transference.

Concentration cells mainly divided in to two types, they are
1. Electrode concentration cells
2. Electrolyte concentration cells: again this cell are two type, they are
   a. Electrolyte concentration cells with transference
   b. Electrolyte concentration cells without transference

Electrode concentration cells: in these cells, the potential difference is developed between two electrodes at different concentrations dipped in the same solution of the electrolyte. For example, two hydrogen electrodes at different gas pressure in the same solution of hydrogen ions constitute a cell of this type.

$$\text{Pt} | \text{H}_2 \text{ (pressure P}_1\text{)} | \text{H}^+ \text{ (a) } | (\text{H}_2 \text{ (pressure P}_2\text{)} \text{ | Pt})$$

If oxidation occurs at L.H.S electrode and reduction occurs at R.H.S electrode. The Nernst equation can be used to derive an expression for the potential of this electrode concentration cell.
\[
\begin{align*}
H_2 (P_1) &= 2H^+ + 2e^- \\
2H^+ + 2e^- &= H_2 (P_2) \\
\hline
H_2 (P_1) &= H_2 (P_2)
\end{align*}
\]

\[E_{\text{cell}} = 0.0591/n \log \frac{p_2}{p_1} \text{ at } 25^\circ C\]

The standard cell potential is zero because a cell cannot derive a current through a circuit with identical electrodes. Similarly we can construct different gas concentration cells, when coupled with their counter ions.

Two amalgam of the same metal at two different concentrations in the same electrolyte solution also form this class of cells.

Na-Hg (activity \(a_1\)) | Na\(^+\) | Na-Hg (activity \(a_2\))
Zn-Hg (activity \(a_1\)) | Zn\(^{2+}\) | Zn-Hg (activity \(a_2\))

**Electrolyte concentration cells**: In these cells, electrodes are identical but these are immersed in solutions of the same electrolyte of different concentrations. The source of electrical energy in the cell is the tendency of the electrolyte of diffuse from a solution of higher concentration to that or lower concentration. With the expiry of time, the two concentrations tend to become equal. Thus, at the start the emf of the cell is maximum and it gradually falls to zero.

Such a cells are represented in the following manner.

\[
\begin{align*}
M &| Mn^{+} (c_1) \parallel Mn^{+} (c_2) | M & (c_2 \text{ is greater than } c_1) \\
Zn &| Zn^{2+} (c_1) \parallel Zn^{2+} (c_2) | Zn & (c_2 \text{ is greater than } c_1)
\end{align*}
\]

The emf of the cell is given by the following expression:

\[E_{\text{cell}} = 0.0591/n \log \frac{c_2}{c_1} \text{ at } 25^\circ C\]

The above examples are typical examples of electrolyte concentration cells with transference.

Transference indicates the presence of salt bridge or liquid-liquid contact of electrolytes.

Examples of electrolyte concentration cells without transference are difficult to comprehend at this stage and are not considered now.

**Applications of concentration cells**: The concentration cells are used to determine the solubility of sparingly soluble salts, valency of the cation of the electrolyte and transition point of the two allotropic forms of a metal used as electrodes, etc.

Concentration cell corrosion occurs when two or more areas of a metal surface are in contact with different concentrations of the same solution. There are three general types of concentration cell corrosion.

Water in contact with the metal surface will normally contain dissolved oxygen. At oxygen cell can develop at any point where the oxygen in the air is not allowed to diffuse uniformly into the solution, thereby creating a difference in oxygen concentration between two points. Corrosion will occur at the area of low-oxygen concentration which is anodic. This is the explanation for corrosion of iron piece when in contact of moisture.

**b. Potentio-metric titrations**

Potentio-metric titration is a very interesting application of electrode potentials. They involve a study of variation of emf with the volume of titrant added. Here we discuss the precipitation titration and acid base titration.

**Precipitation titrations**: Consider the titration of Ag\(^+\) ions with KCl. On addition of any chloride salt the silver ions fall out of the aqueous solution forming an insoluble precipitate of silver chloride. Hence we study the variation of silver electrode potential with the change in concentration of silver ions.

\[E_{Ag|Ag^+} = E^{0}_{Ag|Ag^+} - 0.0592 \log a_{Ag^+}\]
As the $E_{\text{Ag|Ag}^+}$ varies in a logarithmic scale of the concentration of silver ions, initially even for a hundred fold variation of silver concentration the emf variation is only 0.118V. With the approach of neutralization point, the $E_{\text{Ag}^+}$ gets smaller and smaller, while the emf, a log value of $\text{Ag}^+$, increases rapidly.

Thus we notice a sigmoid curve with the steep portion indicating the neutralization point.

The $\text{Ag|Ag}^+$ electrode which is reversible to silver ion concentration is termed as the indicator electrode.

**Acid-base titrations:** In case of acid – alkali titration a hydrogen electrode may be used as an indicator electrode. The suitable cell may be represented as

$$(\text{Pt}), \text{Hg, Hg}_2\text{Cl}_2(\text{s})|\text{KCl (satd)}||\text{H}^+|\text{H}_2(1 \text{ atm}), (\text{Pt})$$

The emf of indicator electrode is given as

$$E_{\text{H}_2|\text{H}^+} = E_{\text{H}_2|\text{H}^+}^0 + 0.0592 \log [\text{H}^+]$$

Since the standard emf of hydrogen electrode is zero, we have;

$$E_{\text{H}_2|\text{H}^+} = -0.0592 \log [\text{H}^+]$$

$$E_{\text{H}_2|\text{H}^+} = -0.0592 \text{pH}$$

From the above expression we draw the conclusion that the emf decreases with decrease in the concentration of hydrogen ions or increase in the pH of the solution. On plotting the electrode potential or cell potential against the volume of titrant added, a sigmoid curve is obtained. The volume corresponding to zero emf gives the titer value of the acid solution.

In the laboratory titration generally the quin-hydrone electrode is used in a place of SHE.

**Determination of pH:** The pH of a solution could be determined by employing any electrode reversible to $\text{H}^+$ ions. The hydrogen electrode and quin-hydrone electrode discussed above and glass electrode is popularly employed for estimation of pH of a solution. The hydrogen indicator electrode could be coupled either to a standard hydrogen electrode (SHE) or to a standard calomel electrode (SCE). The cell diagram, when SHE is used as reference electrode is given by

$$\text{H}_2(1 \text{ atm}) | \text{H}^+(a=1) || \text{H}^+ (a=x) | \text{H}_2 (1 \text{ atm})$$

The emf of the indicator electrode is given by
\[ E_{H_2|H^+} = \frac{RT \ln a_{H^+}}{F} p_{H_2} \]

When \( p_{H_2} = 1 \) atm and \( T = 298 \) K

Since by definition \( pH = -\log a_{H^+} \), the above expression in terms of \( pH \) is

\[ E_{H_2|H^+} = -0.0592 \text{ pH} \]

Because the electrode potential of the reference SHE is zero, for the present cell diagram.

The cell diagram when SCE is used as reference electrode is given by

\[ \text{H}_2 | \text{H}^+ (a=x) || \text{Calomel (saturated)} \]

For this arrangement of room temperature

\[ E_{H_2|H^+} = E_{\text{cell}} - E_{\text{SCE}} = 0.0592 \text{ pH} \]

6. Write a note on Reference Electrodes (SCE, Quinhydrone electrode, Glass electrode)

**Reference Electrodes:** The electrode of standard potential, with which we can compare the potentials of another electrode, is called a “Reference Electrode”. The best “Primary reference electrode” used is standard hydrogen electrode, whose electrode potential is taken as Zero. But it is not always convenient to use this gas electrode in day to day potentiometric measurements. The main difficulty with this primary reference electrode is;

(a) Inconvenience in handling gases  
(b) Maintenance of accurate pressures throughout the measurements  
(c) Availability of sufficiently pure hydrogen gas  
(d) Necessity to platinize the platinum electrode with a solution of chloro platonic acid quite often.

For these reasons some secondary reference electrodes like silver chloride electrode and calomel electrode whose standard potentials are very accurately determined against hydrogen electrode are widely used.

**a. Standard Calomel Electrode – SCE**

Calomel electrode is particularly very simple to construct, free from surface sensitivity and accurate to use even in a very normal laboratory.

The calomel electrode consists of an inner glass tube and an outer jacket. In the inner glass tube a platinum wire is dipped into mercury which rests on a paste of mercurous chloride, \( \text{Hg}_2\text{Cl}_2 \) (commercially known as calomel) and mercury. This paste is in contact with KCl present in the outer
jacket, through the glass frit plug fixed at the bottom of inner glass tube. The calomel electrode comes in contact with the experimental solution through a frit arranged to the outer jacket. The potential of this electrode depends on the concentration of KCl taken in the outer jacket. Some of the most popularly used concentrations of KCl and corresponding single electrode (reduction) potentials on the hydrogen scale at 25°C are given below;

<table>
<thead>
<tr>
<th>Concentration</th>
<th>Electrode</th>
<th>Potential (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1M KCl</td>
<td>Hg₂Cl₂(s)</td>
<td>0.3338 V</td>
</tr>
<tr>
<td>1.0M KCl</td>
<td>Hg₂Cl₂(s)</td>
<td>0.2800 V</td>
</tr>
<tr>
<td>Saturated KCl</td>
<td>Hg₂Cl₂(s)</td>
<td>0.2415 V</td>
</tr>
</tbody>
</table>

The corresponding electrode reaction is;

\[ \text{Hg}_2\text{Cl}_2 + 2e^- \rightarrow 2\text{Hg} + 2\text{Cl}^- \]

And corresponding Nernst’s expression is;

\[ E_{\text{Hg}_2\text{Cl}_2 | Cl^-} = E_{0_{\text{Hg}_2\text{Cl}_2 | Cl^-}} - \frac{2.303 \log a_{2\text{Cl}^-}}{F} \]

b. Quin-hydrone electrode: This is a redox electrode reversible to protons and often replaces the hydrogen electrode. Quinhydrone is a 1:1 molar mixture of quinone and hydroquinone. The electrode consists of a shiny platinum electrode dipped in a acid / base test solution, which is saturated with quinhydrone. The electrode reaction is given by

The electrode potential at 25°C is given by,

\[ E_{\text{Pt} | \text{Q}, \text{H}^+, \text{QH}_2^2} = E_{0_{\text{Pt} | \text{Q}, \text{H}^+, \text{QH}_2^2}} - 0.0592 \log a_{\text{QH}_2^2} + 2 a_Q a_{\text{H}^+} \]

Since quinine and hydroquinone are taken in equimolar amounts, i.e., \( a_Q = a_{\text{QH}_2^2} \).

We have

\[ E = E^0 - 0.05916 \log a_{\text{H}^+} \]

\[ E = E^0 + 2 \times 0.05916 \log a_{\text{H}^+} \]

\[ E_{\text{Q}, \text{QH}_2^2} = E^0_{\text{Q}, \text{QH}_2^2} - 0.0592 \text{ pH} \]

Quin-hydrone electrode can thus be used to measure pH of a solution. Due to instability of quinine in strong alkaline medium, this hydrogen ion indicator electrode is suitable only upto a pH of 8.

Advantages: The quin-hydrone electrode is simple to set up and needs no removal of air. The reversibility equilibrium is achieved faster than hydrogen gas electrode thereby allowing a quicker measurement. pH values of solutions containing reducible substances like Cu²⁺, Cd²⁺, unsaturated acids, NO₃⁻, etc., and catalytic poisons can be measured using quin-hydrone electrode, where hydrogen electrode can not be used.

Limitations: The electrode can not be used at pH values greater than 8. Even this electrode fails in the presence of strong oxidizing and reducing agents.

c. Ion Selective Electrodes – Glass electrode

Credit for the first glass sensing pH electrode is given to Cremer, who first described it in his paper published in 1906. Later several groups contributed for development of different ion selective
an ion-selective electrode (ISE) (also known as a specific ion electrode, or SIE) is a sensor which converts the activity of a specific ion dissolved in a solution into an electrical potential which can be measured by some potentiometric device like a voltmeter or pH meter. As we know, the emf is theoretically dependent on the logarithm of the ionic activity (concentration), in accordance with the Nernst equation. Basically a concentration cell is developed with respect to the ion under observation. The sensing part of the electrode is usually made as an ion-specific membrane which is coupled with a reference electrode. So we need to have different ISEs for different ions.

**Glass Electrode:** Most often used pH electrodes are called glass electrodes and belong to the family of ISEs. They are sensitive only to H$^+$ ions. Typical glass electrode is made of glass tube engaged with small glass bubble sensitive to protons. Inside of the electrode is usually filled with buffered solution of chlorides in which silver wire covered with silver chloride is immersed. pH of internal solution varies— for example it can be 1.0 (0.1M HCl) or 7.0.

![Diagram of a glass electrode](image)

Active part of the electrode is the glass bubble. While tube has strong and thick walls, bubble is made to be as thin as possible. Surface of the glass is protonated by both internal and external solution till equilibrium is achieved. Both sides of the glass are charged by the adsorbed protons, this charge is responsible for potential difference. This potential in turn is described by the Nernst equation and is directly proportional to the pH difference between solutions on both sides of the glass.

The majority of pH electrodes available now a day are combination electrodes that have both glass H$^+$ ion sensitive electrode and reference electrode compartments, conveniently placed in one housing.

**Range of a pH glass electrode**

The pH range at a constant concentration can be divided into 3 parts:

- **Useful Working Range:** Dependence of potential on pH has linear behavior and within which such electrode really works as ion-selective electrode for pH and obeys Nernst equation.

- **Alkali error range:** At very low concentration of hydrogen-ions (high values of pH) metal ions interfere. In this situation dependence of the potential on pH become non-linear.

- **Acidic error range:** At very high concentration of hydrogen-ions (low values of pH) the anions plays a big role as interfering ions, in addition to destruction of the glass matrix used for making glass bulb.

Almost all commonly used glass electrodes have a working pH range from pH = 1 till pH = 12. So specially designed electrodes should be used only for working in aggressive conditions.

7. Define batteries, classify batteries, describe the functioning of following cells a) Lead acid cell b) Ni-Cd cell c) Li cell and mention their applications?

**Battery**
When two or more electrochemical cells are electrically interconnected, each of which containing two electrodes and an electrolyte is called a Battery. In everyday usage, “battery” is also used to refer to a single cell. No one battery design is perfect for every application. There are many parameters like cost, voltage, duty cycle, dimension, stability with time and temperature, shelf life, etc., on which a battery is selected for a particular operation. It is important to prioritize our list of requirements before choosing one and requires compromise. Here duty cycle refers to conditions the battery experiences during use like, type of discharge and current drain, e.g. continuous, intermittent, continuous with pulses, etc.

Batteries are classified into two categories depending on their recharging capabilities.

a. Primary batteries
b. Secondary Batteries

**Primary batteries:** These are non-rechargeable and are meant for a single use and meant to be discarded after use.

Primary batteries are non-rechargeable and are less expensive and are often used in ordinary gadgets like torch lights, watches and toys. Commercially many kinds of primary batteries are available but our discussion only on Leclanche cell, Alkaline cell and Lithium cell.

**Secondary batteries:**
Secondary batteries are rechargeable and are meant for a multi cycle use. After every use the electrochemical reaction could be reversed by external application of voltage. The cycle is reversed till the capacity fades or lost due to leakage or internal short circuit.

These cells are rechargeable and reusable. A combination of all reversible electrochemical cells gives secondary batteries. Many kinds of secondary batteries are available in the market but we are restricting our discussion to Lead-acid cell, Ni/Cd cells, Ni-Metal hydride cell and Lithium ion cells.

**Lead-acid cells:**

- **Anode:** Sponge metallic Lead
- **Cathode:** Lead-dioxide (\(\text{PbO}_2\))
- **Electrolyte:** Dilute mixture of aqueous sulfuric acid.
- **Applications:** Automobiles and construction equipment, standby/backup systems

Used mainly for engine batteries, these cells represent over half of all battery sales. Some advantages are their low cost, long life cycle, and ability to withstand mistreatment. They also perform well in high and low temperatures and in high-drain applications.

The half-cell reactions are:

\[
Pb + \text{So}_4^{2-} \rightarrow \text{PbSo}_4 + 2e^- \quad 0.356 \\
PbO_2 + \text{SO}_4^{2-} + 4\text{H}^+ + 2e^- \rightarrow \text{PbSO}_4 + 2\text{H}_2\text{O} \quad 1.685
\]

There are a few problems with this design, if the cell voltages exceeds 2.39V, the water breaks down into hydrogen and oxygen and may lead to explosion. Another problem arising from this system is that fumes from the acid solution may have a corrosive effect on the area surrounding the battery. These problems are mostly solved by sealed cells, made commercially available in the 1970s. this sealing in reality is only valve regulated and allowing hydrogen and oxygen recombination using catalytic recombines. They convert these gases back into water achieving about 85% efficiency at best. In these batteries the water lost becomes so insignificant that no refill in needed fro the life of the battery. Also, this cell design prevents corrosive fumes from escaping.

These cells have a low cycle life, a quick self discharge, and low energy densities. However, with a nominal voltage of 2V and power densities of up 600 W/kg, the lead-acid cell is an adequate, if not perfect, design for car batteries.

**Nickel/Cadmium Cells:**

- **Anode:** Cadmium
**Cathode:** Nickel oxy-hydroxide (NiOOH)

**Electrolyte:** Aqueous potassium hydroxide (KOH)

**Applications:** Calculators, digital cameras, pagers, laptops, tape recorders, flashlights, medical devices (defibrillators), electrical vehicles, space applications.

The cathode is Nickel-plated, woven mesh, and the anode is a Cadmium-plated net. The electrolyte, KOH, acts only as an ion conductor and does not contribute significantly to the cell’s reaction. That’s why not many electrolytes are needed, so this keeps the weight down.

The cell reactions are as follows:

\[
\begin{align*}
Cd + 2OH^- & \rightarrow Cd(OH)_2 + 2e^- \\
NiOOH + 2H_2O + 2e^- & \rightarrow Ni(OH)_2.H_2O + OH^- \\
Cd + NiOOH + 2H_2O +OH^- & \rightarrow Cd(OH)_2 + Ni(OH)_2.H_2O
\end{align*}
\]

0.81

0.45

1.26

Advantages include good performance in high-discharge and low-temperature applications. They also have long shelf and use life. Disadvantages are that they cost more than the lead–acid battery and have lower power densities. Possibly it’s most well-known limitation is a memory effect, where the cell retains the characteristics of the previous cycle. This term refers to a temporary loss of cell capacity, which occurs when a cell is recharged without being fully discharged. This can cause cadmium hydroxide to passive the electrode, or the battery to wear out. In the former case, a few cycles of discharging and charging the cell help correct the problem, but may shorten the lifetime of the battery.

**Lithium cell:** Lithium cell consists of lithium anode and either solid electrolyte or liquid electrolyte and solid or liquid cathode. A thin protective insulating film is formed on the lithium anode protecting the anode against corrosion as it is conductive to lithium ions but not electrons. Water and alcohol do not form such a protective film and hence cannot be used as solvents. Organic solvents such as dioxane, tetrahydrofuran, propylene carbonate ether, etc., and electrolyte salts of lithium such as perchlorate, tetrafluoroborate or hexafluorophosphohate are used.

Lithium-iodide solid cathode cell consists of iodine-PVP (polyvinyl pyrrolidone) cathode with voltage of 3V. It has low current densities but is highly stable and dependable and hence used in medical source for electronic flash guns of cameras. Lithium-sulphur dioxide cell consists of a liquid cathode of a mixture of acetonitrile or propylene carbonate with sulphur dioxide. Instead of the solvents acetonitrile or propylene carbonate, thionyl chloride has been found to be better as it generates a potential of 3.5 V and has high energy density.

**Lithium ion Cells:**

**Anode:** Carbon compound, Graphite

**Cathode:** Lithium oxide

**Applications:** Laptops, cellular phones, electrical vehicles.

Lithium metal batteries have some safety disadvantages, Lithium ion batteries overcomes that problem. Cathodes consists of a layered crystal (graphite) into which the lithium is intercalated. Experimental cells have also used lithiated metal oxides such as LiCoO$_2$, NiNi$_{0.3}$Co$_{0.7}$O$_2$, LiNiO$_2$, LiV$_2$O$_5$, LiV$_2$O$_{13}$, LiMn$_4$O$_9$, LiMn$_2$O$_4$, LiNiO$_{0.2}$Co$_2$.

Electrolytes are usually LiPF$_6$, although this has a problem with aluminum corrosion, and so alternatives are being sought. One such is LiBF$_4$. The electrolyte in current production batteries is a patented liquid, and uses an organic solvent. Membranes are necessary to separate the electrons from the ions. Currently the batteries in wide use have micro-porous polyethylene membranes.

Intercalation keeps the small ions such as Lithium, sodium and other alkali metals, into the interstitial spaces in a graphite crystal. This makes the graphite is conductive, dilutes the Lithium for
safety, is reasonably cheap, and does not allow dendrites or other unwanted crystal structures of Li to form.

8. Write a note on fuel cells? Describe Hydrogen-Oxygen cell, Mentions their advantages.

Fuel cells:
A cell in which one or both of the reactants are not permanently contained in the cell, but are continuously supplied from a source external to the cell and the reaction products continuously removed is called a fuel cell. Unlike the metal anodes typically used in batteries, the fuels in a fuel cell are usually gas or liquid, with oxygen as the oxidant.

Around 1900 Nernst and Haber attempted for a direct carbon oxidizing fuel cells but met with a limited success. Later in 1933 Bauer, a German scientist, proposed the first fuel cell that can use hydrogen as a fuel and can work at room temperature. This idea was forwarded by Bacon, a British engineer and developed a porous nickel electrode that can withstand high pressures and can give current in kilowatt range at moderate temperatures. This technology found a ready customer in Apollo program of NASA (USA). This fuel cell harnesses the chemical energy of hydrogen and oxygen to generate electricity without combustion or pollution. Hydrogen/Oxygen Fuel cell systems work well in space travel applications because of their high efficiency, high power-to-weight and volume ratios, and usable reaction product (water). In the near future, our vehicles may also be powered by fuel cells.

There are many kinds of H₂/O₂ fuel cells and are categorized on the basis of electrolytes used.
- a. Proton Exchange membrane fuel cells (PEMFC)
- b. Alkaline Fuel Cells (AFC)
- c. Molten Carbonate Fuel Cells
- d. Phosphoric acid Fuel Cells
- e. Solid oxide Fuels

Proton Exchange membrane fuel cells (PEMFC)
This typically used in automobiles is a proton exchange membrane (PEM) fuel cell, also called a polymer electrolyte membrane fuel cell. A fuel cell harnesses the chemical energy of hydrogen and oxygen to generate electricity without combustion or pollution.

At the anode: a platinum catalyst causes the hydrogen to split into positive hydrogen ions (protons) and negatively charged electrons.

Half reactions:
At anode \(2H_2 = 4H^+ + 4e^-\) 0
At cathode \(4H^+ + O_2 + 4e^- = 2H_2O\) 1.2

The proton exchange membrane (PEM) allows only the positively charged ions to pass through it to the cathode. The negatively charged electrons must travel along an external circuit to reach the cathode, creating an electrical current.

At the cathode: The negatively charged electrons and positively charged hydrogen ions combines with oxygen to form water, which flows out of the cell. Thus we get electricity from environmentally friendly reactants and products.

Alkaline fuel Cells (AFC)
Alkaline fuel cells, 30-45% aqueous solutions of potassium hydroxide are used as electrolyte, so acidic impurities such as CO₂ should be avoided. Generally this is done by passing the compressed air into lime solution before allowing it to enter the fuel cell. These fuel cells yield highest voltages at comparable current densities in comparison to other classes of fuel cells.
The following half reactions take place in these cells

**At cathode:** Oxygen passed is converted into hydroxide ions by consuming 4 electrons.

\[ \text{O}_2 + 2\text{H}_2\text{O} + 4e^- \rightarrow 4\text{OH}^- \]

In fact, this is a two step reaction with intermediate peroxy ions formation.

\[ \text{O}_2 + \text{H}_2\text{O} + 2e^- \rightarrow \text{HO}_2^- + \text{OH}^- \]

\[ \text{HO}_2^- \rightarrow \text{OH}^- + \frac{1}{2}\text{O}_2 \]

**At anode:** Anode involves oxidation of hydrogen in to water by reacting with hydroxide. Anions from the electrolyte.

\[ 2\text{H}_2 + 4\text{OH}^- \rightarrow 4\text{H}_2\text{O} + 4e^- \]

**Overall reaction:**

\[ 2\text{H}_2 + \text{O}_2 \rightarrow 2\text{H}_2\text{O} \]

**Advantages of Fuel Cells:**

- No emission of toxic gases and chemical wastes are in safe limits. The reactants and products are environment friendly and only we have to bother about disposal of cell material.
- High efficiency (75-85%) of energy conversion from chemical energy to electrical energy. So offer an excellent use of our renewable energy resources.
- No noise pollution like in generators and low thermal pollution.
- Low maintenance costs, fuel transportation costs, cell parts are modular and exchangeable.
- The fuels and electrolyte materials are available in plenty and inexhaustible unlike fossil fuels.
- Unlike solar cells, fuels cells are compact and transportable.
- Unlike acid cells used in automotives the fuel cells are far less corrosive.
- Unlike nuclear energy, fuel cell energy is economical and safe.
- Fuel cells are operatable to 2000°C and so find application in high temperature systems.
- Fuel cells promise as good storage devices for future nuclear and solar energy economies.
INTRODUCTION

Metals have a natural tendency to revert back to combined states. During this process mostly, oxides are formed though in some cases sulphides, carbonates, subparts etc. May result due to presence of impurities. Any process of deterioration and loss of solid metallic material by chemical or electrochemical attack by its environment is called corrosion. Corrosion is the reverse process of metallurgy.

Corrosion may be defined as “the destruction of a metallic material by chemical, electrochemical, or metallurgical interaction between the environment and the material”.

\[
\text{Corrosion (Oxidation)}
\]

Metal \[\rightarrow\] Metallic compound + energy

\[
\text{Metallurgy (Reduction)}
\]

e.g., rusting of iron when exposed to atmospheric conditions. Rust is hydrated oxide (Fe\(_2\)O\(_3\).xH\(_2\)O).

Q1. Describe the theory of Dry or Chemical corrosion.

Ans: Dry (or) Chemical Corrosion

This type of Corrosion occurs mainly through the direct chemical action of atmospheric gasses (O\(_2\), halogen, H\(_2\)S, SO\(_2\), N\(_2\) or anhydrous inorganic liquid) with metal surpasses in immediate proximity.

Three types of chemical Corrosion are as follows..

1. **Oxidation Corrosion**: This is carried out by the direct action of oxygen low or high temperatures on metals in absence of moisture at ordinary temperature metals or very slightly attacked. The Exceptions are Alkali metals and Alkaline earth metals. At high temperature all metals are oxidized. The exception is Ag, Au and Pt.

\[
\begin{align*}
2M & \rightarrow 2M^{n+}+2ne^- & \text{(De- electronation)}\\
\text{Metal ion} & \quad & \text{(Metal ion)}\\
nO_2+2ne^- & \rightarrow 2nO^2- & \text{(Electronation)}\\
\text{Oxide ion} & \quad & \text{(Oxide ion)}\\
2M+ nO_2 & \rightarrow 2M^{n+} + 2nO^2- & \text{(Metal oxide)}
\end{align*}
\]

**Mechanism:** At the surface of metal oxidation occurs and the resulting metal oxide scale forms a barrier which restricts further oxidation. For oxidation to continue either the metal must diffused outwards through the scale to the surface or the oxygen must defuse inwards through the scale to the underlying metal. Both the cases are possible. But the outward diffusion of metal is generally more rapid than inward diffusion of oxygen since metal ion is appreciably smaller than the oxygen ion and hence more mobile.

\[
\begin{align*}
\text{Metal + Oxygen} & \rightarrow \text{Metal oxide}
\end{align*}
\]

When oxidation starts, a thin layer of oxide is formed on the metal surface and the nature of this film decides further action.

If the film is,
a) Stable, it behaves as a protective coating in nature e.g., the oxide films on Al, Pb, Cu, Pt etc., are stable and therefore further oxidation corrosion of prohibited.

b) Unstable that is the oxide layer formed decomposes back into metal and oxygen. So, oxidation Corrosion is not possible.

\[
\text{Metal oxide} \xrightarrow{\text{Decomposes}} \text{Metal} + \text{Oxygen}
\]

e.g., Ag, Au and Pt do not undergo oxidation Corrosion.

c) Volatile that is oxide layer volatilizes after formation and as such leaves the underlying metal surface exposed further attack. This causes continuous which is excessive. e.g. Molybdenum oxide (MoO}_3\)

d) Porous that is the oxide layer formed having pores or cracks. In this case the atmospheric oxygen passes through the pores or cracks of the underlying metal surface. This causes continuous corrosion till complete conversion of metal into its oxide.

Q2. **What is corrosion, describe the mechanism of electro chemical corrosion by : a)hydrogen evolution b)oxygen absorption (Or) Explain the process of wet corrosion by evolution of hydrogen and absorption of oxygen (Or) Describe the electrochemical theory of corrosion.**

**Ans: Corrosion:** Metals have a natural tendency to revert back to combined states. During this process mostly, oxides are formed though in some cases sulphides, carbonates, subparts etc. May result due to presence of impurities. Any process of deterioration and loss of solid metallic material by chemical or electrochemical attack by its environment is called corrosion. Corrosion is the reverse process of metallurgy.

Corrosion may be defined as “the destruction of a metallic material by chemical, electrochemical, or metallurgical interaction between the environment and the material”.

**Wet or Electrochemical Corrosion.**

This type of Corrosion occurs

Where a conducting liquid is in contact with the metal or when two dissimilar metals or alloys are dipped partially in a solution.

This corrosion occurs due to the existence of separate anodic and cathodic parts, between which current flows through the conducting solution. At anodic area, oxidation reaction occurs thereby destroying the anodic metal either by dissolution or formation of compounds. Hence corrosion always occurs at anodic parts.

At Anode: \[M \xrightarrow{\text{Dissolution}} M^{n+} + ne^{-}\]

\[M^{n+} \xrightarrow{\text{Formation of compound}}\]

At cathodic part, reduction reaction (electro nation) occurs. It does not affect the cathode, since most metals cannot be further reduced. At cathodic part, the dissolved constituents in the conducting medium accepts the electrons forming ions (OH\(^{-}\), O\(^{2-}\)). The metallic ions formed at anodic part and the ions formed at cathodic part diffuse towards each other through conducting medium and form a corrosion product somewhere between anode and cathode.
Mechanism:  
Electrochemical corrosion involves flow of electrons between anode and cathode. The anodic reaction involves dissolution of metal liberating free electrons.

\[ M \rightarrow M^{n+} + ne^- \]

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

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

\[ \text{Fe} \rightarrow \text{Fe}^{2+} + 2e^- \quad (\text{Oxidation}) \]

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

\[ 2H^+ + 2e^- \rightarrow H_2 \uparrow \]

The overall reaction is

\[ \text{Fe} + \text{H}^+ \rightarrow \text{Fe}^{2+} + \text{H}_2 \uparrow \]

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

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

At anode:  
\[ \text{Fe} \rightarrow \text{Fe}^{2+} + 2e^- \quad (\text{Oxidation}) \]
At cathode:
The released electrons flow from anode to cathode through iron metal.

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

\[
\text{Fe}^{2+} + 2\text{OH}^- \rightarrow \text{Fe(OH)}_2
\]

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

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

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

### 3Q. To explain Different types of corrosion, and to describe in detail pitting and stress corrosion

**Ans: a) Pitting corrosion:**
Pitting corrosion is a localized accelerated attack, resulting in the formation of cavities around which the metal is relatively unattacked. Thus pitting corrosion results in the formation of pinholes, pits and cavities in the metal. Pitting is usually the result of the breakdown or cracking of the protective film on a metal at specific points. This gives rise to the formation of small anodic and large cathodic areas. In the corrosive environment this produces corrosion current.

\[
\text{Fe}^{2+} + 2\text{OH}^- \rightarrow \text{Fe(OH)}_2
\]

Corrosion product

More oxygenated cathode
\[
\text{H}_2\text{O} + \frac{1}{2} \text{O}_2 + 2e^- \rightarrow 2\text{OH}^-
\]

More oxygenated cathode

The presence of the extraneous impurities (like sand, dust, scale etc.), embedded on the surface of the metals, also lead to pitting once a small pit is formed, the rate of corrosion will be increased. If the presence of some extraneous impurities like sand, dust and scale is checked, pitting can be reduced. If the concentration of oxygen is uniform, then also pitting is reduced. Otherwise differential aeration corrosion takes place leading to pitting.

**Stress corrosion:** stress corrosion is the combined effect of static tensile stresses and the corrosive environment on the metal. It is characterized by a highly localized attack occurring, when overall corrosion is negligible. For stress corrosion to occur: 1. Presence of tensile stress, and 2. a specific corrosive environment are necessary. The corrosive agents are highly specific and selective such are a. Caustic alkalis and strong nitrate solution for mild steel. b. Traces of ammonia for brass, c. acid chloride solution for stainless steel.

This type of corrosion is seen in fabricated articles of certain alloys like high-zinc brasses and nickel brasses due to the presence of stresses caused by heavy working like rolling, drawing or insufficient annealing. However, pure metals are relatively immune to stress corrosion.
Stress corrosion involves in a localized electrochemical corrosion, occurring along narrow paths, forming anodic areas with respect to the more cathodic areas at the metal surface. Presence of stress produces strains, which result in localized zones of higher electrode potential. These become so chemically-active that they are attacked, even by a mild corrosive environment, resulting in the formation of attack, which grows and propagates in a plant, until failure occurs or it may stop, after progressing a finite distance.

**Concentration Cell Corrosion**

This type of corrosion is due to electrochemical attack on the metal surface exposed to an electrolyte of varying concentrations or of varying aeration. The most common type of concentration cell corrosion is the differential aeration corrosion which occurs when one part of metal is exposed to different air concentration from other part. This causes a difference in potential between the differently aerated areas. Experimentally it has been observed that poor oxygenated parts are anodic. Differential aeration of metal causes a flow of current called the differential current.

If a metal e.g., Zn is partially immersed in a dilute solution of a neutral salt e.g., NaCl and the solution is not agitated properly, then the parts above and adjacent to the waterline are strongly aerated and hence become cathodic. Whereas parts immersed show a smaller oxygen concentration and become anodic. so there is a difference of potential which causes flow of current between two differentially aerated areas of same metal. Zinc will dissolve at anodic areas and oxygen will take up electrons at the cathodic areas forming hydroxyl ions.

\[
\begin{align*}
\text{Zn} & \rightarrow \text{Zn}^{2+} + 2e^- \quad \text{(Oxidation)} \\
\frac{1}{2} \text{O}_2 + \text{H}_2\text{O} + 2e^- & \rightarrow 2\text{OH}^- \quad \text{(Reduction)}
\end{align*}
\]

Following are the facts about differential aeration corrosion:

(a) Less oxygenated part is the anode. Therefore cracks serve as foci for corrosion.

(b) Corrosion is accelerated under accumulation of dirt, scale or other contaminations. This restricts the access of oxygen resulting an anode to promise greater accumulation. The result is localized corrosion.

(c) Metals exposed to aqueous media corrode under blocks of wood or glass which restricts the access of oxygen.
Galvanic Corrosion

When two dissimilar metals are electrically connected and exposed to an electrolyte, the metal higher in electrochemical series undergoes corrosion. This type of corrosion is called Galvanic corrosion. e.g., Zinc (higher in electrochemical series) forms the anode and is attacked and gets dissolved; whereas copper (lower in electrochemical series) acts as cathode.

Mechanism: If the solution is acidic then corrosion occurs by hydrogen evolution process and if the solution is neutral or slightly alkaline in nature then corrosion occurs by oxygen absorption process. The electrons flow from the anodic metal to the cathodic metal.

\[
\text{Zn} \rightarrow \text{Zn}^{2+} + 2e^- \quad \text{(Oxidation)}
\]

Thus the corrosion is a localized accelerated attack resulting in the formation of pits, holes or cavities. Pitting corrosion therefore results in the formation of pinholes, pits and cavities in the metal. The pitting corrosion may be due to following reasons:

a) Metal surface are not homogeneous.
b) External environment is not homogeneous.
c) Films are not perfectly uniform.
d) Crystallography directions are not equal in the reactivity.
e) Environment is not uniform with respect to concentration.

Pitting is usually the result of the breakdown or cracking of the protective film on a metal at specific points. This gives rise to the formation of small anodic and large cathodic areas. In process of correct environment this produces corrosion current.

e.g., Stainless steel and aluminum show characteristic pitting on chloride solution. Pitting is caused by the presence of sand, dust scale and other extraneous impurities present on the metal surfaces. Because of differential amount of oxygen in contact with the metal, the small part (underneath the impurity) becomes the anodic areas and the surrounding large parts become the cathodic areas. Intense corrosion takes place in the anodic areas underneath the impurity. Once a small pit is generated, the rate of corrosion will be increased.

Waterline Corrosion

This is also known as differential oxygen concentration corrosion. In general, when water is stored in a steel tank, it is observed that the maximum amount of corrosion takes place along a line just beneath the level of the water meniscus. The area above the waterline (highly oxygenated) acts as cathodic and is not affected by corrosion. However, if the water is relatively free from acidity, little corrosion occurs. The problem of waterline corrosion is a matter of concern for marine engineers. This type of corrosion is prevented to a great extent by painting the sides of the ships by antifouling paints.
Erosion Corrosion

Erosion Corrosion results by the combined effect of the abrading action of vapours, gases and liquids and the mechanical rubbing action of solids over the surface of metals. This type of corrosion is caused by the breakdown of a protective film at the spot of impingement and its subsequent inability to repair itself under existing abrading action removes protective films from localized spots on the metal surface, thereby resulting in the formation of differential cell at such areas and localized corrosion at anodic points of the cells. Erosion corrosion is most common in agitators, piping, condensers, tubes and vessels in which steams of liquids or gases emerge from an opening and strike the side walls with high velocities.

Q4. Define corrosion? Explain any 4 factors that affect the rate of corrosion

Ans: FACTORS INFLUENCING CORROSION:

The rate and extent of corrosion depends on the nature of the metal and nature of corroding environment.

NATURE OF METAL:

a. Position in galvanic series: when 2 metals or alloys are in electrical contact in presence of an electrolyte the more active metal having higher position in the galvanic series undergoes corrosion. The greater is the difference in position, the faster is the corrosion.

Galvanic Series: it is used to provide sufficient information in predicting the corrosion behavior in a particular set of environmental conditions. Oxidation potential measurement of various metals and alloys has been made using standard calomel electrode as the reference electrode and immersing the metals and alloys in sea water. These are arranged in decreasing order of activity and this series is known as the galvanic series.

<table>
<thead>
<tr>
<th>Electrochemical series</th>
<th>Galvanic series</th>
</tr>
</thead>
<tbody>
<tr>
<td>a. This series consists of metals and non-metals</td>
<td>a. This series consists of metals and alloys.</td>
</tr>
<tr>
<td>b. The position of a metal in this series is permanently fixed.</td>
<td>b. Position of pure metal and when present in the form of alloy is different.</td>
</tr>
<tr>
<td>c. It predicts the relative displacement tendencies.</td>
<td>c. It predicts the relative corrosion tendencies.</td>
</tr>
<tr>
<td>d. Electrode potentials are measured by dipping pure metals in their salt solution of 1M concentration.</td>
<td>d. Corrosion of metals and alloys is studied in unpolluted sea water.</td>
</tr>
</tbody>
</table>

| Active (Anodic) | 1. Mg |
| Noble(Cathodic) | 2. Mg alloys |
|                | 3. Zn |
|                | 4. Al |
|                | 5. Al alloys |
|                | 6. Cu |
|                | 7. Bronze |
|                | 8. Copper Nickel alloys |
|                | 9. Au |
|                | 10. Pt |
b. **Over voltage:** reduction in overvoltage of the corroding metal accelerates the corrosion rate. E.g. Zn in 1N H₂SO₄ undergoes corrosion slowly because of high overvoltage of zinc metal (0.7 V) which reduces the effective potential to a small value. In presence of CuSO₄ the corrosion rate of zinc is accelerated.

c. **Nature of surface/oxide film:** In aerated atmosphere, all metals get covered with a thin surface film of metal oxides. The ratio of the volumes of metal oxides to the metal is known as specific volume ratio. Greater is this value lesser is the oxidation corrosion rate. Specific volume ratios of Ni, Cr and W are 1.6, 2.0 and 3.6 respectively suggesting Tungsten has least corrosion. Further the corrosion depends on nature of oxide film. Metals like Al have a firm oxide film in comparison to Fe and hence Al in less corrosive means it follows Pilling-Bedworth Rule. The iron oxide is porous in nature and this leads to extension of corrosion to inner surface.

d. **Nature of Corrosion Product:**

  **Solubility of corrosion products:** In electrochemical corrosion if the corrosion product is soluble in the corroding medium then corrosion is rapid. If the corrosion product is insoluble, then acts as barrier thereby suppressing further corrosion.

  **Volatility of corrosion products:** If the corrosion product is volatile, then the underlying surface is exposed for further attack. This causes rapid and continuous corrosion. E.g. MoO₃ is volatile.

e. **Nature of corroding environment:**

  a. **Temperature:** As the temperature of environment is increased the reaction rate is increased thereby accelerating corrosion. The effect of temperature on the corrosion rate is complicated because of the fact that it affects the various factors in different ways. The rate of chemical reaction increases, with rise in temperature but the solubility of gases, like oxygen which affect corrosion, decreases. The temperature may affect the protective coatings in different ways. In general, the rate of corrosion due to oxygen or oxidizing agents is decreased with rise in temperature but the rate of hydrogen type corrosion is increased.

  b. **Effect of pH:** In the corrosion reaction described H⁺ or OH⁻ are also involved. Therefore the effect of pH is obvious. It can be easily seen from the chemical equation for a reaction the direction in which it will shift by change in concentration of H⁺ or OH⁻. As a general rule, acids are more corrosive than neutral or alkaline solutions. Exceptions to the rule are amphoteric metals, aluminium, zinc and lead, which form anions as well as cations. In acid solutions these react quickly like other metals but in alkaline solutions they form complex ions and go into solution. Consequently these metals most resistant to corrosion in neutral solutions. In the case of other metals the corrosion rate is higher in acidic solutions than in alkaline solutions. The corrosion of iron or steel is quite slow in alkaline solutions and gradually increases as acidity increases and becomes rapid when the pH value is below, say, 4.5 to 3. This is the reason why the pH value of water for boiler feed or for cooling systems is kept in the alkaline range.

  c. **Effect of Oxidant:** Oxidizing agents may increase or decrease corrosion rates. Systems handling water. E.g. boilers, heat exchangers, etc., are faced with serious corrosion problems due to dissolved oxygen. In high pressure boilers less than 0.005 mg/l of dissolved oxygen is permissible. The oxidizing agents oxidize materials and are themselves reduced at cathodes and, thereby support cathode reaction and promote corrosion. It is noteworthy that on some metals, like stainless steels. Aluminum and magnesium, a thin film of oxide is deposited on the surface rendering the metal resistant to corrosion and makes it passive. Such metals and alloys are more resistant in oxidizing environments. Monel metals corrode rapidly in the presence of air whereas 18-8 stainless steel corrodes rapidly in the absence of air. It has been reported that in an experiment using 5% sulphuric acid at 30°C the corrosion rate of Monel metal was 240 mdd (mg per square decimeter per day). When the acid solution was saturated with air, but on exposure to the same solution free from air corrosion was 40 mdd. Under similar conditions the corrosion rates of stainless steel were 2 and 300 mdd. This illustrates the sharp difference in the behaviors of Monel and stainless steel both of which are known for their resistance to corrosion. Hence, care needs to be taken while using materials.
Humidity of air: critical humidity is defined as the relative humidity above which the atmosphere corrosion rate of metal increases sharply. The value of critical humidity depends on nature of metal and corrosion products.

Corrosion of a metal is furnished in humid atmosphere because gases (CO$_2$, O$_2$) and vapours present in atmosphere furnish water to the electrolyte essential to establish an electrochemical corrosion cell. The oxide film on the metal surface has the property to absorb moisture. In presence of this absorbed moisture, corrosion rate is enhanced. Rain water may also wash away the oxide film from the metal surface. This leads to enhanced atmospheric attack. The exceptions are Cr, Al.

A mild steel equipment handling water gets corroded at a faster rate as the temperature increases, because of a higher rate of chemical reaction, reaching the maximum rate 80$^0$. Above this temperature the effect of lower solubility of oxygen in water becomes dominant and the rate of corrosion falls sharply. Similar results have been reported for the corrosion of Monel metal in dilute sulphuric acid in the presence of air. The effect of temperature on the corrosion of zinc in distilled water is interesting. Up to 50$^0$ the protective coating formed by the corrosion protects zinc. Above 50$^0$ the protective coating gives way and rapid corrosion takes place up to about 65$^0$. Above 65$^0$ the effect of decreasing solubility of oxygen becomes pronounced and the corrosion rate falls.

Q5. Define corrosion? Explain any 3 corrosion control methods. (Or) Explain with examples how do you protect a metal or an alloy by a) cathodic protection b) sacrificial anode c) impressed current

**Ans:** CORROSION CONTROL METHODS:

The corrosion methods are as follows

Proper Designing

Cathodic Protection

Using Pure metal

Using Metal alloys

Modifying the Environment

Use of Inhibitors

Application of Protective coatings

1. **Proper Designing** The design of the material should be such that, even if the corrosion occurs, corrosion is uniform and doesn’t result in intense and localized corrosion. Important design principles are,

a. Avoid the contact of dissimilar metals in the presence of a corroding solution.

b. When 2 dissimilar metals are to be in contact, the anode metal should have as large area as possible, whereas the cathode metal should have as much smaller area as possible.

c. If 2 dissimilar metals in contact have to be used, they should be as close as possible to each other in the electrochemical series.

d. Whenever the direct joining of dissimilar metals, is unavoidable, an insulating fitting may be applied in-between them to avoid direct metal electrical contact.

e. The anode metal should not be painted or coated, when in contact with a dissimilar cathodic metal, because any break in coating would lead to rapid localized corrosion.

f. Prevent the occurrence of in homogenitics, both in the metal and in the corrosive environment.

g. It is desirable that the design allows for adequate clearing and flushing of the critical parts i.e., susceptible to dirt, deposition, etc. for the equipment.

h. Whenever possible, the equipment should be supported on legs to allow free circulation of air and prevent the formation of stagnant pools or damp areas.

i. Uniform flow of corrosion liquid is desirable, since both stagnant areas and highly turbulent flow and high velocities can cause accelerated corrosion. So, highly impingement conditions of flowing liquid should be avoided as much as practically possible.
A proper design should prevent condition subjecting some areas of structure to stress (cold-worked part).

2. CATHODIC PROTECTION:
The cathodic protection of metals is used to control corrosion metals where it is impracticable to alter the nature of the corrosion medium. The principle involved in this method is to protect metals and alloys from corrosion by making them completely cathodic. Since there will not be any anodic area on the metal, therefore corrosion does not occurs.
The following are 2 types of cathodic protections.
  a. Sacrificial anodic protection
  b. Impressed current cathodic protection

a. Sacrificial anodic protection: In this method, the metal structure can be protected from corrosion by connecting it with wire to a more anodic metal. As this more active metal is sacrificed in the process of saving metal from corrosion, it is known as sacrificial anode. The metals which are commonly used as sacrificial anodes are Mg, Zn, Al and their alloys. The important applications of this method are
  1. Protection of underground cables and pipelines from soil corrosion.
  2. Protection of ships and boat hulls from marine corrosion.
  3. Prevention of rusty water by inserting Mg sheets or rods into domestic water boilers or tanks.

b. Impressed current cathodic protection: As the name implies, an impressed current is applied to convert the corroding metal from anode to cathode. The applied current is in opposite direction since to nullify the corrosion current. This can be accomplished by applying sufficient amount of direct current source like battery or rectifier to an anode like graphite, high silica iron, stainless steel or platinum buried in the soil or immersed in the corrosion medium. And connected to the corroding metal structure which is to be protected as shown in the diagram below.
In impressed current cathodic protection, electrons are supplied from an external cell, so that the object itself becomes cathodic and not oxidized. This type of cathodic protection has been applied to buried structures such as tanks and pipelines, transmission line-towers, marine piers, laid-up ships etc. since, their operating and maintenance costs are less, they are well suited for large structures and long term operations.

3. USING PURE METAL:
Impurities in a metal cause heterogeneity, which decreases corrosion-resistance of the metal. Thus, the corrosion-resistance of a given metal may be improved by increasing its purity. Purification of metals like Al, Mg, etc., provides a coherent and impervious protective oxide film on their surface, when exposed to environment. However, corrosion-resistance of a purified metal depends on the nature of corrosive environment.

4. USING METAL ALLOYS:
Noble, but precious metals such as platinum and gold are corrosion-resistant. Corrosion-resistance of most metals is best increased by alloying them with suitable elements. But for maximum corrosion-resistance, alloy should completely homogeneous. Chromium is the best suitable alloying metal for iron or steel.

5. MODIFYING THE ENVIRONMENT:
The corrosive nature of the environment can be reduced either, a. by the removal of harmful constituents, or b. by the addition of substances, which neutralize the effect of corrosive constituents of the environment.

6. USE OF INHIBITORS:
A corrosion inhibitor is “a substance which when added in small quantities to the aqueous corrosive
environment effectively decreases the corrosion of a metal”.

Inhibitors are mainly 2 types
1. **Anodic Inhibitors:** Such as chromates, phosphates, tungstates or other ions of transition
   elements with high oxygen content are those that stifle the corrosion reaction occurring at
   the anode, by forming a sparingly soluble compound with a newly produced metal ion.
2. **Cathodic Inhibitors:** In acidic solutions, the main cathodic reaction is evolution of
   hydrogen.
   \[2H^+ (aq) + 2e^- \rightarrow H_2 (g)\]
   Consequently, corrosion may be reduced either by slowing down the diffusion of hydrated
   H+ ions to the cathode, and by increasing the over voltage of hydrogen evolution.

### 7. APPLICATION OF PROTECTIVE COATINGS:

Protecting the surface of an object by the application of coating is probably the oldest of the
common procedures for corrosion prevention. A coated-surface isolates the underlying metal from
the corroding environment.

**PROTECTIVE COATINGS AND THEIR APPLICATIONS**

**Metallic Coatings:** The metals used for coatings may be placed under two categories;
1. Metals which are anodic to the metal to be protected, i.e. metals standing above it in the galvanic
   series, or
2. Cathodic metals, which stand below it in the galvanic series. Metals like zinc, magnesium,
   cadmium and aluminum, when applied on iron and steel fall under the first category. These being
   anodic get themselves corroded, saving the iron which is to be protected. As explained under
   ‘formation of anodic areas’. In such cases even if the surface is scratched, the metal to be protected
   does not get corrode. These metals may be applied on the surface by hot dipping or spraying.
Metals like tin, nickel and chromium on iron and steel surfaces fall in the second category. These are
cathodic to iron or more resistant to corrosion and offer protection only so long as the surface is
completely covered. If the coating breaks or is applied in a manner so that pinholes are left, the points at
which the iron surface is exposed gets very severely corroded because they are anodic to the large
cathodic surface. Hence great care has to be exercised while applying these. Generally, the cathodic metal
coating is applied by electroplating because by this method a more uniform coating is protected which
completely covers the surface.

**SURFACE PREPARATIONS:**

Generally, there are two types of metallic coatings are protection from corrosion.
1. Anodic coatings
2. Cathodic coatings

Q6. Write a short note on hot dipping – galvanizing & tinning.

**Ans:** Hot-dipping: Hot dipping process is applicable to the metals having higher melting point than
the coating metal. It consists of immersing well cleaned base metal in a bath containing molten coating
metal, and a flux layer. The flux cleans the surface of the base metal and prevents the oxidation of the
molten coating metal.

Eg. Coating of Zn, Pb, Al on iron, steel surfaces. Most widely used hot dip process are
a. Galvanizing
   b. Tinning

**Galvanizing:** Galvanizing is a process in which the iron article is protected from corrosion by coating it
with a thin layer of zinc. In this process, at first iron or steel is cleaned by pickling with dilute sulphuric
acid solution \((H_2SO_4)\) at a temperature range of 60-90°C for 15 to 20 minutes. Therefore, it removes scale,
rust and other impurities present if any and then washed well and dried. Then after, dipped in the bath
molten zinc which is at 425-450°C. To prevent it from oxide formation, the surface of bath is covered with
a flux \((NH_4Cl)\). When the iron piece is taken out it is coated with a thin layer of zinc. And to remove
excess zinc, it is passed through a pair of hot rollers; lastly, it is annealed at a temperature of 450°C and
then cooled slowly.
Galvanizing is widely used for protecting iron exposed to the atmosphere, as is the case with roofs, wire fences, pipes and articles fabricated from galvanized sheets like buckets, tubes, etc. Galvanized ware is not used for keeping eatables because of the solubility of zinc. The popularity of galvanizing is due the low cost of zinc. Easy application and the anodic protection offered by the zinc.

TINNING: The process of coating tin over the iron or steel articles to protect it from corrosion is known as tinning. Tin is a nobler metal than iron, therefore, it is more resistance to chemical attack. In this process, at first Iron sheet is treated in dilute sulphuric acid (pickling) to remove any oxide film if present. A cleaned Iron sheet is passed through a bath molten flux. Like Zinc chloride, then through molten tin and finally through a suitable vegetable oil.

Tinning of mild steel plates is done mostly for the requirements of the foodstuff industry. Tin is a nobler metal than iron, therefore, it is more resistant to chemical attack. As already been explained, if the coating formed does not cover the surface completely during use and leaves iron exposed, more rapid corrosion of iron will take place.

A cleaned iron sheet is passed through a bath of molten flux, like zinc chloride, then through molten tin and finally through a suitable vegetable oil. Lastly it is passed between rolls to adjust the thickness of the tin layer, which may be about 0.002 mm thick.
Q7. Write a short note on a) Metal cladding b) Electroplating (Or) Write a short note on cathodic coatings.

Ans: CATHODIC COATINGS:

METAL CLADING: The surface to be protected is sandwiched between two thin layers of coat metal and pressed between rollers. The finished product may be welded at the edges or riveted at some points. The coat metal has to be anodic to the base metal and only plain surfaces can be cladded. This method is used for coating Al, Cr, Ni, Duralumin, etc.

Coating of a thin homogeneous layer of a coating metal on a base metal an fused so that it strongly binds permanently either on one side or on both sides and passed through rollers under heat and pressure. All corrosion-resistant metals like Ni, Cu, Ag, Au & Pt, and alloys like steel nickel alloys can be used as cladding materials. Base metals on which cladding is done are mild steel, aluminium, copper, nickel and other alloys Duralumin is very light metal alloys used in aircrafts industry. Terne plate is name given to the plate which has a coating of an alloy of tin and lead.

ELECTROPLATING: Electroplating is the process or method of coating metals and non-metals, to change their surface properties such as to improve the appearance, to properties such as to improve the appearance to corrosion and wear or chemical attack. Electroplating is the electro-deposition of metal, by means electrolysis over surface of metals, alloys or non-metals.

The wear resistance of a metal part can be improved by electroplating a harder metal on its surface. The metals most often plated on base metals or materials are chromium, Nickel and Rhodium. For example metals like Iron which are easily corroded by atmospheric air, moisture and CO₂ are coated electrolytically with base metals such as nickel or chromium which are more resistant to wear or chemical attack.

Some of the applications of electroplating are,
1. Plating for protection from corrosion and chemical attack.
2. Plating for decoration.
3. Plating for special for special surface and engineering effects.
4. Electroforming
5. Plating on non-metallic materials.

Therefore, this process is widely used in automobiles, aircrafts, refrigerators, jewellery, radios, cameras, type-writers, umbrellas, watches etc.
**Q8. Define paints. To write about paints constitution and their functions.**

**Ans: ORGANIC COATINGS**

**PAINTS:** Paint may be defined as the mechanical dispersion mixture of pigments and fillers which are in a liquid medium and later becomes film forming oil. The volatile liquids such as thinners are again added to these liquids.

**CONSTITUENTS OF PAINT:**

a. Pigment
b. Vehicle or drying oil
c. Thinners
d. Driers
e. Fillers or extenders
f. Plasticizers
g. Anti-skinning agents

a. **Pigment:**
   - It is a solid constituent present in paint which provides a decorative colour effect to protect it from ultraviolet rays. Pigment is one of the essential constituents of paint.
   - The essential functions of pigments are:
     - To provide desired color, opacity and strength to the paint.
     - To give aesthetic appeal to the paint film.
     - To provide protection to the paint film by reflecting harmful ultraviolet light.
     - To provide resistance to the paint film to moisture and
     - To increase the weather-resistance of the film.

b. **Vehicle or drying oil:**
   - It is a film-forming constituent of the paint. The liquid portion of the paint in which the pigment is dispersed is called as vehicle or drying oil.
   - The important functions of vehicle oil are:
     - They hold the pigment on the metal surface
     - They form the protective film.
     - They impart water-repellency, durability and toughness to the film, and
     - They give better adhesion to the metal surface.

c. **Thinners:**
   - Viscosity (or consistency) of the paints are reduced by the addition of thinners. So paints easily applied on the metal surface.
   - The important functions of thinners are:
     - Thinners reduce the viscosity of the paint to suitable consistency, so that it can be easily handled and applied to the metal surface.
     - They dissolve the film-forming material and also the other desirable additives in the vehicle.
     - They evaporate rapidly and help the drying of the paint film.
     - They increase the elasticity of the paint film.
     - They also increase the penetration power of the vehicle.

d. **Driers:**
   - The drying of the oil is accelerated or catalyzed by driers. They do this by oxidation, polymerization and condensation. In fact, driers are oxygen carrier catalysts.
   - The important functions of the driers are:
     - Linoleates, borates, naphthalene’s, resonates and tungstates of heavy metals like Pb, Zn, Co and Mn.
     - Surface driers: Cobalt substances,
     - Bottom- driers: Lead substances,
     - Through driers: Manganese substances.
e. **Fillers or extenders:** Fillers are inert materials which are used to improve the properties and reduce the cost of the paint.

The important functions of fillers are:
- They reducing the cost of the paint.(Expensive pigments which have excellent hiding power (like TiO2 and ZnSO4) are used in a admixture with cheap extenders for reducing the cost without reducing the efficiency),
- They serve to fill the voids in the film,
- They increase random arrangement of the primary pigment particles, and act as carriers for the pigment color,
- They improve the durability of the film by reducing the cracking of the paints after drying.

f. **Plasticizers:** Plasticizers are added to the paint film to give elasticity to the paint film and to prevent cracking of the film.
Ex: Tri cresyl phosphate, triphenyl phosphate, dibutyl tartarate, and tributyl phthalate.

g.. **Antiskinning agents:** antiskinning agents prevent the gelling and skinning of the paint film. E.g. Polyhydroxy phenols

**Requirements of a Paint:**
1. The adhesion capacity of the paint should be high to the material on which it is to be used.
2. The paint should spread easily over the surface to be protected.
3. On drying, the paint film should not be cracked.
4. The paint film should have high corrosion resistance property so as to protect the painted surface from the corrosion environment.
5. The paint film should be stable.
6. The paint film should be prepared such a way as to be applicable easily by spraying or brushing.
7. The paint film should yield a smooth and uniform surface.
8. The paint film obtained on the surface should be tough, uniform and adherent.
9. The colour of the film should be stable and should not get affected by the environment conditions.
10. The covering power of the paint should be high.
POLYMER SCIENCE AND TECHNOLOGY

Polymer is a macro molecule formed by the union of many small molecules. Depending upon the structure, a polymer may be linear or branched.

Ex. \(- \text{CH}_2 - \text{CH}_2 -\) Polyethylene Linear

Ex. \(- \text{CH}_2--\text{Si} - \text{O} - \text{Si} - \text{O} - \text{Si}\) Branched silicon resin.

Depending type of monomer, they may be homopolymer (made up of same monomer) or Co-polymer (made up of different monomers)

POLYMERISATION: It may be defined as the process of linking or joining together small molecules like monomers to make large molecules.

Basically there are 3 types of polymerizations.

1. Additional polymerization or Chain polymerization
2. Condensation polymerization or Step polymerization
3. Copolymerization

1. **Additional polymerization or Chain polymerization:** This polymerization yields an exact multiple of basic monomeric molecules. This monomeric molecule contains one or more double bonds. By intermolecular rearrangement of these double bonds makes the molecule bifunctional. In this polymerization process light, heat and pressure or catalyst is used to breakdown the double covalent bonds of monomers.

2. **Condensation polymerization or Step polymerization:** May be defined as “a reaction occurring between simple polar-group-containing monomers with the formation of polymer and elimination of small molecules like water, HCl, etc.” For example, hexamethylene diamine and adipic acid condense to form a polymer, Nylon6:6.

Additional polymerization is a chain reaction converting of a sequence of three steps. Initiation, propagation and termination.

a. Initiation step is considered to involve two reactions. The first is the production of free radicals, usually, by the hemolytic dissociation of an initiator (or catalyst) to yield a pair of radicals R’.

\[
\text{I} \rightarrow 2\text{R'} \quad \text{........(1)}
\]
The second part of initiation under the addition of this radical to the just moment molecule (M) to produce the chain initiating species M1.

\[
R + M \rightarrow M_1 \quad \ldots \ldots \ldots \ldots (2)
\]

Thus the polymerization of monomer \(CH_2=CHY\) taken in the form.

\[
H \quad R + CH_2=CHY \rightarrow R-CH_2-C \quad R
\]

b. Propagation step: Consists of the growth of M1 by successive additions of large numbers of monomer molecules according to equation.

\[
M_1 + M \rightarrow M_2
\]

\[
M_2 + M \rightarrow M_3
\]

\[
M_3 + M \rightarrow M_4 \quad \text{or in general terms} \quad Mn + M \rightarrow Mn + 1
\]

c. Termination step: At some time, the propagation polymer chain steps growing and terminates.

\[
-CH_2-C + C-CH_2 \rightarrow -CH_2-C-C-CH_2
\]

Disproportion in which a hydrogen atom of one radical center is transferred to another radical center. This results in the formations of two polymer molecules, are saturated and one unsaturated e.g.

\[
-CH_2-C + C-CH_2 \rightarrow CH_2-CH+C=C-CH
\]

The two different modes of terminations can be represented in general terms by:

\[
M^*n + M^*m \rightarrow M^{n+m} \quad \text{(Coupling)}
\]

\[
M^n + M_m^* \rightarrow Mn + M_m \quad \text{(Disproportionation)}
\]

Co-polymerization: Polymerization involving two different monomers.

Ex. Polymerization of butadiene and styrene to gave Buna –S.

\[
CH_2 = CH – CH = CH_2 + nx CH_2 = CH –Ph \rightarrow -C-CH = CH –CH - -CH2 –CH - \quad 1,3\text{-butadiene (75%)} \quad \text{Styrene(25%)} \quad H \quad \text{Ph}
\]

What is Plastic?

Plastics are the materials that show the property of plasticity and can be moulded into any desired shape and dimensions by the application of heat and pressure. Plastics having variety of properties are in use in present applications. The properties are low
thermal and electrical conductivities, easy to fabricate, low specific gravity etc. The plastics can be fabricated for large number of colours and can be used for decorative purpose. Plastics can be used to produce complicated shapes and accurate dimensions very cheaply by moulding process. Plastics are generally used for making automobile parts, goggle, telephones, electrical instruments, optical instruments, household appliances etc. plastics having high wear resistance properties can be used for making gears, bearings etc.

**Merits of Plastics**

1. Plastics have good shock absorption capacity compared with steel.
2. Plastics have high abrasion resistance.
3. Plastics are chemically inert.
4. Plastics have high corrosion resistance compared to metals.
5. Moulding, machining, drilling etc. can be easily done on plastic materials.
6. Plastics are light in weight having specific gravity from 1 to 2, 4.
7. Plastics can be made according to the order like hard, soft, rigid, tough, brittle, malleable etc.
8. Fabrication of plastics into desired shape and size is cheap.
9. Plastics are dimensionally stable.
10. Plastics are don’t absorb water.
11. Thermal coefficient of expansion of plastic is low.
12. Excellent outer finish can be obtained on plastic products.

**Demerits of Plastics**

1. Plastics are soft
2. Plastics have poor ductility.
3. Resistance to heat is less.
4. Cost of plastics is high.
5. Plastics can deform under load.

**THERMOSET PLASTICS:** They are formed by condensation polymerization. They have three dimensional network structures. The cross links and bonds retain their strength on heating and hence they do not soften on heating. On prolong heating however, charming of polymers is caused. They retain the shape and structure even on heating. Hence, they cannot be reshaped and reused. They are usually, hard, strong and more brittle. They cannot be reclaimed from wastes. Due to strong bonds and cross-links they are insoluble in almost all organic solvents.
Difference between thermo set and thermoplastics.

Plastics are materials that show the property of plasticity and can be moulded into any desired shape and dimension of articles by the application of heat and pressure.

<table>
<thead>
<tr>
<th>Thermoplastics</th>
<th>Thermoset plastics</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. These are processed by addition polymerization.</td>
<td>1. These are proceed by condensation Polymerization.</td>
</tr>
<tr>
<td>2. Softens on heating and retaining the same chain on cooling.</td>
<td>2. These are infusible and insoluble mass on heating i.e., heat resistance.</td>
</tr>
<tr>
<td>3. They are along chain linear polymers without any branched or cross linked chain.</td>
<td>3. They are branched or cross-linked Polymer.</td>
</tr>
<tr>
<td>4. On repeated heating and cooling, there is no change in chemical nature.</td>
<td>4. Some sort of chemical changes occur on heating.</td>
</tr>
<tr>
<td>5. These plastics undergo purely physical process.</td>
<td>5. These Plastics undergo physical as well As chemical process.</td>
</tr>
<tr>
<td>6. By heating the plastics, thy can be proceed.</td>
<td>6. These plastics cannot be proceed by heating.</td>
</tr>
<tr>
<td>7. Waste thermoplastics can be recovered.</td>
<td>7. Waste thermosetting cannot be recovered.</td>
</tr>
</tbody>
</table>

Compounding of plastics:

Compounding of the plastics may be defined as the mixing of different materials like plasticizers, fillers of extenders, lubricants, dies and pigments to the thermoplastic and thermosetting plastics to increase their useful properties like strength, toughness, etc. Resins have plasticity or binding property, but need other ingredients to be mixed with them for fabrication into useful shapes.

Compounding of plastics:

Many plastics are virtually useless along but are converted into highly serviceable products by combining them with a variety of additives, stabilizers etc., by the compounding process. The exact formulation will depend upon the specific application requirement. The different additives impart different physical properties which are used to improve the performance of the plastic materials. Additives are widely used for thermoplastics,
thermo sets and elastomers like phenolics or amino resins are useless alone but by the addition of fillers, resins etc., they give a reversible products. Some of the compounding materials are stabilizers, plasticizers, fillers, colorants or pigments, lubricants and accelerators.

**Ingredients used in compounding of plastics**

Some of the ingredients used in compounding of plastics are

i) Plasticizers.

ii) Fillers or extenders.

iii) Dyes and pigments.

iv) Lubricants.

i). **Plasticizers**

Plasticizers are substances added to enhance the plasticity of the material and to reduce the cracking on the surface. Plasticizers are added to the plastics to increase flexibility and toughness. Plasticizers also increase the flow property of the plastics.

**Example**

Dibutyltyle oxalate, Castor oil and Tricresyl phosphate

ii). **Fillers or Extenders**

Fillers are generally added to thermosetting plastics to increase elasticity and crack resistance. Fillers improve thermal stability, strength, non combustibility, water resistance, electrical insulation properties and external appearance.

**Example**

wood flour, Asbestos, Mica, Cotton, Carbon black, Graphite, Barium sulphate etc.

iii) **Dyes and pigments**

These are added to impart the desired colour to the plastics and give decorative effect.

iv) **Lubricants**

These are added to prevent the plastics from sticking to the moulds.

**Example**

Oils, Waxes, Soaps etc.

Thus the objective of compounding is to improve the properties of the basic resin, such that the fabrication is made easy.

**Fabrication of plastics:**

Many methods of fabricating plastics into desired shaped articles are employed. This production of plastics is known as fabrication of plastics. The methods, usually depends upon the types of resins used i.e., whether thermosetting or thermoplastic. Different fabrication techniques are described below.
Moulding of Plastics

Moulding of plastics comprises of forming an article to the desired shape by application of heat and pressure to the moulding compounds in a suitable mould and hardening the material in the mould. The method of moulding depends upon the type of resins used.

i) Compression moulding:
This method is applied to both thermoplastic and thermosetting resins. The predetermined quantity of plastic ingredients in proper properties are filled between the two half –pieces of mould which are capable of being moved relative to each other heat and pressure are than applied according to specifications. The containers filled with fluidized plastic. Two halves are closed very slowly. Finally curing is done either by heating or cooling. After curing the moulded article is taken out by opening the mould parts.

ii) Injection moulding:
In this method, the moulding plastic powder is fed into a heated cylinder from where it is injected at a controlled rate into the tightly locked mould by means of a screw arrangement or by a piston plunger. The mould is kept cold to allow the hot plastic to cure and become rigid.
When the materials have been cured sufficiently, half of the mould is opened to allow the injection of the finished article without any deformation, etc. Heating is done by oil or electricity.
iii) Transfer moulding:

Injection Molding

Injection Mold - Before Shot

Injection Mold - Filled

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In this method, the principle is like injection moulding. The moulding powder is heated in a chamber to become plastic. Later it is injected into a mould by plunger working at high pressure through orifice. Due to this heat is developed and the plastic melts, takes the shape of the mould.

d) Extrusion moulding:
This process is useful in the preparation of continuous wires with uniform cross section. The heated plastic is pushed into the die with the help of screw conveyor. In the die, the plastic gets cooled due to the exposure to atmosphere and by artificial air jets.
Extrusion moulding is used mainly for continuous moulding of thermoplastic materials into articles of uniform cross section like tubes, rods, strips, insulated electric cables. The thermoplastic ingredients are heated to plastic condition and then pushed by means of a screw conveyor into a die, having the required outer shape of the article to the manufactured. Here the plastic mass gets cooled, due to the atmospheric exposure (or artificially by air jets). A long conveyor carries away continuously the cooled product.
Moulding of insulated electric cable by vertical extrusion moulding

**Differences between compression and injection moulding techniques:**

<table>
<thead>
<tr>
<th>Compression Moulding</th>
<th>Injection moulding</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. The plastic ingredient in proper proportions are filled in between the two half portions of the mould. These portions are moved relative to each other and by the applying heat and pressure, the part can be manufactured.</td>
<td>1. In this, the heated plastic is injected into the mould cavity from where it is cooled and taken out.</td>
</tr>
<tr>
<td>2. It is applicable to both thermoplastic and thermosetting resins.</td>
<td>2. It is applicable to thermoplastic resins.</td>
</tr>
</tbody>
</table>
plastic resins

3. Moulding is often simpler.
4. It is less expensive.
5. Require more operation time.
7. There is no limitation to the design of articles to be moulded.
8. High moulding cost.

3. Moulding is somewhat complicated compared to compression moulding.
4. It is expensive.
5. Require less operation time.
6. High Production rate.
7. There is limitation to the design of articles to be moulded.
8. Less moulding cost.

**Polyethylene:**

This can be obtained by the polymerization of ethylene at 1500 atm and a temperature 150 – 250 °C in presence of traces of oxygen.

![Polyethylene structure](image)

**Properties:**
Depending upon the density, they may be LDPE and HDPE. If we use free radical initiator, LDPE is the product while use of ionic catalysts results in the formation of HDPE.
It is a rigid, waxy white solid. Translucent. It is permeable to many organic solvents. It crystallizes easily.
LDPE has a density 0.91 to 0.925 g/cm³
HDPE has a density 0.941 to 0.965 g/cm³
HDPE is linear and has better chemical resistance.
Uses: These are useful in the preparation of insulator parts, bottle caps, flexible bottles, pipes etc.
LDPE is used in making film and sheeting. Pipes made of LDPE are used for both agricultural, irrigation and domestic water line connections.
HDPE is used in manufacture of toys and other household articles.

**PVC:**
Poly Vinyl Chloride is obtained by heating a water emulsion of vinyl chloride in presence of a small amount of benzoyl peroxide or hydrogen peroxide in an auto clave under pressure.
Vinyl chloride, so needed is generally prepared by treating acetylene at 1 to 1.5 atmospheres with hydrogen chloride at 60°C to 80°C in the presence of metal chloride as catalyst.

\[
\text{CH} = \text{CH} + \text{HCl} \rightarrow \text{CH}_2 = \text{CH Cl}
\]

Properties: It occurs as a colourless rigid material. It is having high density and low softening point. It is resistant to light, atmospheric oxygen, inorganic acids and alkalis. It is most widely used synthetic plastic.

Uses: It is mainly used as cable insulation, leather cloth, packing and toys. It is used for manufacturing of film, sheet and floor covering. PVC pipes are used for carrying corrosive chemicals in petrochemical factories.

**Nylon-6,6:**

It is prepared by Hexamethylene diamine and Adipic acid are polymerized in 1:1 ratio.

Properties: This is linear polymer not resistant to alkali and mineral acids. Oxidising agents like hydrogen peroxide, potassium permanganate etc. are able to degrade the fibres.
**Applications:** Nylon-6,6 is mainly used for moulding purposes for gear bearings and making car tyres, used for fibres etc. This is mainly used in manufacture of tyre cord. Other uses include manufacture of carpets, rope, fibre cloth etc.

**POLYESTER**
Terylene is a polyester fibre made from ethylene glycol and terephthalic acid. Terephthalic acid required for the manufacture of Terylene is produced by the catalytic atmospheric oxidation of p-xylene.
Properties: This occurs as a colourless rigid substance. This is highly resistant to mineral and organic acids but is less resistant to alkalis. This is hydrophobic in nature. This has high melting point due to presence of aromatic ring.

Uses: It is mostly used for making synthetic fibres. It can be blended with wool, cotton for better use and wrinkle resistance. Other application of polyethylene terephthalate film is in electrical insulation.

TEFLON OR Poly tetra fluoro ethylene:
Teflon is obtained by polymerization of water-emulsion tetrafluoroethylene, under pressure in presence of benzoyl peroxide as catalyst.

Properties: Due to the presence of highly electronegative fluorine atoms and the regular configuration of the polytetrafluoro ethylene molecule results in very strong attractive forces between the different chains.
These strong attractive forces give the material extreme toughness, high softening point, exceptionally high chemical-resistance towards all chemicals, high density, waxy touch, and very low coefficient of friction, extremely good electrical and mechanical properties: It can be machined, punched and drilled. The material, however, has the disadvantage that it cannot be dissolved and cannot exist in a true molten state. Around 350°C, it sinters to form very viscous, opaque mass, which can be moulded into certain forms by applying high pressures.
**Uses:** as insulating material for motors, transformers, cables, wires, fittings, etc., and for making gaskets, packing, pump parts, tank linings, chemical-carrying pipes, tubing's and tanks, etc.; for coating and impregnating glass fibres, asbestos fibres and cloths; in non-lubricating bearings and non-sticking stop-cocks etc.

**POLY URETHANES:**
Poly urethanes are obtained, commercially, by treating diisocyanate and diol. For example, Perlon-U (a crystalline polymer) is obtained by the reaction of 1,4-butane diol with 1,6-hexane diisocyanate.

**Properties:**
1. Polyurethanes are less stable than polyamides at elevated temperature.
2. They are characterized by excellent resistance to abrasion and solvents.

**Uses:** Polyurethanes are used as coatings, films, foams, adhesives and elastomers. Resilient polyurethane fibres (spandex) are used for foundation garments and swim-suits. They also find use as a leather substitute (corfoam). They are used to cast to produce gaskets and seals.

**Bakelite:**
It is prepared by condensing phenol with formaldehyde in presence of acidic/alkaline catalyst.

The initial reaction results in the formation of O- and P- hydroxyl methyl/phenol which reacts to form linear polymer. During modeling hexamethylene tetramine is added, which converts to insoluble solid of cross-linked structure Bakelite.
**Applications:** It is used for making electric insulator parts like switches, plugs, switch boards etc. For making moulded articles like telephone parts cabinet of radio and television.

**Silicone resins:**
Silicone resins contain alternate silicone-oxygen structure, which has organic radicals attached to silicon atoms. Thus, their structure is:
Where R = alkyl or phenyl radical
Preparation: reacting silicon with alkyl halide or silicon halide with Grignard reagent.
The reaction product is fractionally distilled to get different organo-silicon chlorides, which are then polymerized by carefully controlled hydrolysis.

1. Dimethyl-silicon dichloride is ‘bifunctional’ and can yield very long chain polymers, E.g.
2. Trimethyl silicon chloride is ‘monofunctional’ and hence, a ‘chain-stopper’. This is, therefore, used in proportions to limit the chain-length.
3. Monomethyl silicon chlorides is ‘trifunctional’ and goes cross-linking to the final polymer. Its proportion used in polymerization, determines the amount of cross-linking that can be obtained.

**Characteristics of silicones:**
1. Depending on the proportion of various alkyl silicon halides used during their preparation, silicones may be liquids, viscous liquids, semi-solid, rubber-like and solids.
2. Because of silicon-oxygen links, they exhibit outstanding-stability at high temperatures, good water resistance, good oxidation-stability, but their chemical-resistance is generally lower than that of other plastics.
3. Their specific gravity ranges from 1.03 to 2.1.
4. Their physical properties are much less affected by variations in temperature.
5. They are non-toxic in nature.

Different types of silicones and their uses: Liquid silicones or silicone oils are relatively low molecular-weight silicones, generally of dimethyl silicones. They possess great wetting-power for metals, Low surface tension and show very small changes in viscosity with temperature.

**Uses:**
1. They are used as high temperature lubricants, antifoaming agents, water-repellent finishes for leather and textiles, heat transfer media, as damping and hydraulic fluids. They are also used in cosmetics and polishes.
2. Silicone greases are modified silicone oils, obtained by adding fillers like silica, carbon black, lithium soap, etc.
3. They are particularly used as lubricants in situations where very high and very low temperatures and encountered.

**Natural Rubber:** Rubbers also known as Elastomers, they are high polymers, which have elastic properties in excess of 300%.

Natural rubbers consist of basic material latex, which is a dispersion of isoprene. During the treatment, these isoprene molecules polymerize to form, long-coiled chains of cis-polyisoprene. Natural rubber is made from the saps of a wide range of plants like Hevea brasiliens and guayule.

Latex: is a milky white fluid that oozes out from the plant Hevea brasiliens when a cut is made on the steam of the plant. The latex is diluted with water. Then acetic or formic acid is added [1kg of acid per 200kgs of latex] to prepare coagulum. This is processed to give wither crepe rubber or smoked rubber.

**Vulcanization:**
Vulcanization discovered by Charles Goodyear in 1839.

It consists of heating the raw rubber at 100 – 140°C with sulphur. The combine chemically at the double bonds of different rubber spring and provides cross-linking between the chains. This cross-linking during vulcanization brings about a stiffening of the rubber by anchoring and consequently preventing intermolecular movement of rubber springs. The amount of sulphur added determines the extent of stiffness of vulcanized rubber. For example, ordinary rubber (say for battery case) may contain as much as 30% sulphur.

Advantages of vulcanization:
1. The tensile strength increase.
2. Vulcanized rubber has excellent resilience.
3. It has boardar useful temperature range (-40 to 100°C)
4. It has better resistance to moisture, oxidation and abrasion.
5. It is resistance to organic solvents like CCl4, Benzene petrol etc.
6. It has only slight thickness.
7. It has low elasticity.
Buna – S or STYRENE RUBBER:
Buna-S rubber is probably the most important type of synthetic rubber, which is produced by copolymerization of butadiene (about 75% by weight) and styrene (25% by weight).

\[
n\text{CH}_2 = \text{CH} - \text{CH} = \text{CH}_2 + \text{n CH}_2 = \text{CH} - \text{Ph} \rightarrow (-\text{H}_2\text{C}-\text{CH} - \text{CH} --\text{CH}_2 --\text{CH} - \text{PH})_n
\]

Properties: Styrene rubber resembles natural rubber in processing characteristics as well as quality of finished products.

It possesses high abrasion-resistance, high load-bearing capacity and resilience. However, it gets readily oxidized, especially in presence of traces of ozone present in the atmosphere. Moreover, it swells in oils and solvents. It can be vulcanized in the same way as natural rubber either by sulphur or sulphur monochloride (S\(_2\)Cl\(_2\)). However, it requires less sulphur, but more accelerators for vulcanization.

Uses: Mainly used for the manufacture of motor tyres. Other uses of these elastomers are floor tiles, shoe soles, gaskets, foot-wear components, wire and cable insulations, carpet backing, adhesives, tank-linings, etc.

Nitrile Rubber or GR-A or Buna – N or NBR:
Preparation: It is prepared by the copolymerization of butadiene and acrylonitrile in emulsion system.

\[
m\text{CH}_2=\text{CH}-\text{CH}=\text{CH}_2 + \text{nCH}_2=\text{CH}--\text{CN} \rightarrow (-\text{CH}_2-\text{CH}=\text{CH}-\text{CH}_2-\text{CN})_n
\]

---

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1,3-Butadiene  Acrylonitrile  Poly butadiene co-acrylonitrile
Compounding and vulcanization methods are similar to those of natural rubber.

**Properties:**

i. Due to the presence of cyano group, nitrile rubber is less resistance to alkalis than natural rubber;

ii. Excellent resistance to oils, chemicals, aging (sun light). As the acrylonitrile percentage is increased in nitrile rubber, its resistance to acids, salts, oils, solvents etc. increases. But the low temperature resilience suffers.

iii. Compared to natural rubber, nitrile rubber (vulcanized) has more heat resistance and it may be exposed to high temperatures.

iv. It has good abrasion resistance, even after immersion in gasoline or oils.

**USES:**

For making Conveyor belts, Lining of tanks, Gaskets

i. Printing rollers, Oil-resistance foams

ii. Automobile parts and high altitude air-craft components

iii. Hoses and adhesives.

**Thiokol:**

This also called as polysulphide rubber (or Gr-P). It can be prepared by the condensation polymerization of sodium polysulphide (Na2Sx) and ethylene dichloride.

\[
\text{S} \quad \text{S} \\
\text{Cl} - \text{CH}_2 - \text{CH}_2 - \text{Cl} + \text{Na} - \text{S} - \text{S} - \text{Na} + \text{Cl} - \text{CH}_2 - \text{CH}_2 - \text{Cl} \rightarrow \\
\text{Ethylene dichloride} \quad \text{Sodium polysulphide} \quad \text{Ethylene dichloride} \\
\text{S} \quad \text{S} \\
\text{\text{CH}_2 - \text{CH}_2 - \text{S} - \text{S} - \text{CH}_2 - \text{CH}_2-} \\
\text{Thiokol}
\]

It is used for the -

i. Manufacture of oils hoses, chemically resistant tubing and engine gaskets;

ii. Diaphragms and seals in contact with solvents and

iii. Printing rolls,

iv. Containers for transporting solvents and

v. Solid propellant fuels for rockets, etc.

**POLY URETHANES RUBBERS:**

Polyurethane or isocyanate rubber is produced by reacting polyalcohol with di-isocyanates.

\[
n[\text{OH}-(\text{CH}_2)_2-\text{OH}+\text{O}=\text{C}-(\text{CH}_2)_2-\text{N}=\text{C}=\text{O}] \rightarrow [-\text{O}-(\text{CH}_2)_2-\text{O}-(\text{CO})-\text{NH}-(\text{CH}_2)_2-\text{NH}-(\text{CO})-]_n
\]

**Properties:** Polyurethanes are highly resistant to oxidation, because of their saturated character. They also show good resistance to many organic solvents, but are attacked by acids and alkalis, especially concentrated and hot. The polyurethane foams are light, tough and resistant to heat, abrasion, chemicals and weathering.

______________________________________

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**Uses:** For surface coatings and manufacture of foams and spandex fibres.
WATER TECHNOLOGY-I

1. Introduction

Water is nature’s most wonderful, abundant and useful compound. Water is not only essential for the lives of animals and plants. But also occupies a unique position in industries.

Water is also used as a coolant in power and chemical plants. It is widely used in drinking, bathing, sanitary, washing, irrigation, fire-fights, air-conditioning and also production of industrial materials.

2. Effect of water on rocks and minerals:

   1. Dissolution: Some mineral constituents of rocks such as NaCl and CuSO₄·2H₂O readily dissolve in water.
   2. Hydration: Some minerals are easily hydrated with the consequent increase in volume leading to disintegration of the rocks in which these minerals are present. Eg.
      \[
      \text{CaSO}_4 \quad \text{Hydration} \rightarrow \text{CaSO}_4·2\text{H}_2\text{O} \quad \text{(Gypsum)}
      \]
      \[
      \text{Mg}_2\text{SiO}_4 \rightarrow \text{Mg}_2\text{SiO}_4·\text{XH}_2\text{O} \quad \text{(Serpentine)}
      \]
   3. Effect of dissolved oxygen: This leads to oxidation and Hydration
      \[
      \text{Fe}_3\text{O}_4 \rightarrow \text{Fe}_2\text{O}_3 \rightarrow 3 \text{Fe}_2\text{O}_3·2\text{H}_2\text{O} \quad \text{(Limonite)}
      \]
      \[
      2\text{FeS}_2 + 7\text{O}_2 + 2\text{H}_2\text{O} \rightarrow 2\text{FeSO}_4 + 2\text{H}_2\text{SO}_4
      \]
   4. Effect of dissolved CO₂: Water containing dissolved CO₂ converts the insoluble carbonate of calcium, Magnesium and iron into their relatively soluble bicarbonates.
      \[
      \text{CaCO}_3 + \text{H}_2\text{O} + \text{CO}_2 \rightarrow \text{Ca(HCO}_3)_2
      \]

3. Types of Impurities present in water:

   The natural water is usually contaminated by different types of impurities.

   They are mainly 3 types:
   1. Physical impurities
   2. Chemical impurities
   3. Biological impurities

   1. PHYSICAL IMPURITIES:
      a. Colour: Colour in water is caused by metallic substances like salts.
      b. Turbidity: is due to the colloidal, extremely fine suspensions such as insoluble substances like clay, silt, and micro-organisms.
      c. Taste: presence of dissolved minerals in water produces taste. Bitter taste can be due to the presence of Fe, Al, Mn, Sulphates, lime. Soap taste can be due to the presence of large amount of sodium bicarbonate.
      d. Odour: In water is undesirable for domestic as well as industrial purpose.

   2. CHEMICAL IMPURITIES:
      a. In-organic-organic chemicals:
         Inorganic chemicals:
         1. Cations: Ca²⁺, Mg²⁺, Na⁺, K⁺, Fe³⁺, Al³⁺, Zn²⁺, Cu²⁺
         2. Anions: Cl⁻, SO²⁻, NO₃⁻, HCO₃⁻, F⁻, NO₂⁻.

         Organic chemicals: dyes, paints, petroleum products, pesticides, detergents, drugs textile materials, other organic related materials.
Acidity: surface and ground water attains acidity from industrial wastes like acid, mine, drainage, pickling liquors, usually acidity caused by the presence of free CO\(_2\), mineral acids, and weakly dissociated acids.

b. Gases: All natural waters contains dissolved atmosphere CO\(_2\), O\(_2\), NH\(_3\) gases, pollutant and sewage water contains nitrogen in the form of nitrogenous organic compounds and urea, which are partially converted into NH\(_3\).
c. Mineral matters: have organs from rocks and industrial effluents. These include mineral acids, Ca\(_{+2}\), Mg\(_{+2}\), Na\(_{+}\), K\(_{+}\), Fe\(_{+2}\), Al\(_{+3}\), Zn\(_{+2}\), Cu\(_{+2}\), Mn\(_{+2}\), Cl\(_{-}\), SO\(_{4}\)\(_{-2}\), NO\(_3\)\(_{-}\), HCO\(_3\)\(_{-}\), F\(_{-}\), NO\(_3\)\(_{-}\), SiO\(_2\)\(_3\).

3. BIOLOGICAL IMPURITIES:

Biological impurities are Algae, pathogenic bacteria, fungi, viruses, pathogens, parasite-worms, etc. the source of these contamination is discharge of domestic and sewage wastes, excreta, etc.
A. Micro-organisms: algae, fungi, viruses, etc.
B. Water bodies in water include 1. Bacteria, organisms’ inhabiting the bottom sludge, and 2. Organisms and planktons developed at the water surfaces. These are inhibited by different groups of worms like flat worms, hair worms, tiny roundworms, oligochetes, etc.

**HARDNESS OF WATER**

Hardness of water defined as which prevent the lathering of soap. This is due to presence of in water of certain salts of Ca\(_{+2}\), Mg\(_{+2}\) and other Heavy metals dissolved in it. Soaps are Sodium or Potassium salts of higher fatty acids like Oleic acid or Palmitic acid or stearic acids. C\(_{17}\)H\(_{35}\)COONa

Temporary Hardness is mainly caused by Bicarbonates of Calcium, Magnesium and other heavy metals.

SOAP with HARDWATER REACTIONS

\[2C_{17}H_{35}COONa + CaCl_2 \rightarrow (C_{17}H_{35}COO)_2Ca + 2NaCl\]

\[2C_{17}H_{35}COONa + MgSO_4 \rightarrow (C_{17}H_{35}COO)_2Mg + Na_2SO_4\]

Hardness of water is mainly TWO types
1. Temporary Hardness
2. Permanent Hardness

1. **Temporary Hardness** mainly caused by the presence of dissolved Bicarbonates of Calcium, Magnesium and other Heavy metals and the carbonate of Iron.

Temporary hardness of water mainly responsible salts are…

1. Calcium bicarbonate \(\text{Ca(HCO}_3\text{)}_2\)
2. Magnesium bicarbonate \(\text{Mg(HCO}_3\text{)}_2\)

When bicarbonates are decomposed a, yielding insoluble carbonates or hydroxides, which are deposited as a crust at the bottom of vessel.

Temporary Hardness can be largely removed by mere Boiling of water.

Temporary Hardness is also known as….Carbonate Hardness or Alkaline Hardness

2. **Permanent harness**: It is due to the presence of dissolved Chlorides and sulphates of Calcium, Magnesium, Iron and other metals

Permanent hardness responsible salts are…. \(\text{CaCl}_2, \text{MgCl}_2, \text{CaSO}_4, \text{MgSO}_4, \text{FeSO}_4, \text{Al}_2(\text{SO}_4)_3\)

Permanent Hardness cannot remove by boiling but it can be removed by the use of chemical agents.

Permanenent Hardness also known as…. Non-Carbonate Hardness, Non-Alkaline

**Heat**

\[\text{Ca(HCO}_3\text{)}_2 \rightarrow \text{CaCO}_3 + \text{H}_2\text{O} + \text{CO}_2\]

Calcium bicarbonate

**Heat**
• \( Mg(HCO_3)_2 \rightarrow Mg(OH)_2 + 2CO_2 \)
Magnesium bicarbonate

5 UNITS OF HARDNESS

1. **Parts per million (ppm)** is the parts of calcium carbonate equivalent hardness per 10^6 parts of water, i.e., 1 ppm = 1 part of CaCO_3 eq hardness in 10^6 parts of water.

2. **Milligrams per litre (mg/L)** is the number of milligrams of CaCO_3 equivalent hardness present per litre of water. Thus:

   \[
   1 \text{ mg/L} = 1 \text{ mg of CaCO}_3 \text{ eq hardness of 1 L of water}
   \]

   But 1 L of water weighs

   \[
   = 1 \text{ kg} = 1,000 \text{ g} = 1,000 \times 1,000 \text{ mg} = 10^6 \text{ mg}.
   \]

   \[
   \therefore \; 1 \text{ mg/L} = 1 \text{ mg of CaCO}_3 \text{ eq per 10}^6 \text{ mg of water}.
   \]

   \[
   = 1 \text{ part of CaCO}_3 \text{ eq per 10}^6 \text{ parts of water} = 1 \text{ ppm}.
   \]

3. **Clarke’s degree (°Cl)** is number of grains (1/7000 lb) of CaCO_3 equivalent hardness per gallon (10 lb) of water. Or it is parts of CaCO_3 equivalent hardness per 70,000 parts of water. Thus:

   1° Cl = 1 grain of CaCO_3 eq hardness per gallon of water.

   or

   1° Cl = 1 part of CaCO_3 eq hardness per 70,000 parts of water.

4. **Degree French (°Fr)** is the parts of CaCO_3 equivalent hardness per 10^5 parts of water. Thus:

   1° Fr = 1 part of CaCO_3 hardness eq per 10^5 parts of water.

5. **Milliequivalent per litre (meq/L)** is the number of milli equivalents of hardness present per litre. Thus:

   \[
   1 \text{ meq/L} = 1 \text{ meq of CaCO}_3 \text{ per L of water}
   \]

   \[
   = 10^{-3} \times 50 \text{ g of CaCO}_3 \text{ eq per litre}
   \]

   \[
   = 50 \text{ mg of CaCO}_3 \text{ eq per litre}
   \]

   \[
   = 50 \text{ mg/L of CaCO}_3 \text{ eq} = 50 \text{ ppm}.
   \]

**Relationship between various units of hardness:**

<table>
<thead>
<tr>
<th>1 ppm</th>
<th>1 mg/L</th>
<th>1 mg/L</th>
<th>1 meq/L</th>
<th>1° Cl</th>
<th>1° Fr</th>
<th>0.07° Cl</th>
<th>0.07° Fr</th>
<th>0.02 meq/L</th>
<th>0.07° Cl</th>
<th>0.07° Fr</th>
<th>0.02 meq/L</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 ppm</td>
<td>1 mg/L</td>
<td>1 mg/L</td>
<td>1 meq/L</td>
<td>1° Cl</td>
<td>1° Fr</td>
<td>0.07° Cl</td>
<td>0.07° Fr</td>
<td>0.02 meq/L</td>
<td>0.07° Cl</td>
<td>0.07° Fr</td>
<td>0.02 meq/L</td>
</tr>
<tr>
<td>1° Cl</td>
<td>1.433° Fr</td>
<td>14.3 ppm</td>
<td>14.3 mg/L</td>
<td>0.286 meq/L</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1° Fr</td>
<td>10 ppm</td>
<td>10 mg/L</td>
<td>0.7° Cl</td>
<td>0.2 meq/L</td>
<td></td>
<td></td>
<td></td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1 meq/L</td>
<td>50 mg/L</td>
<td>50 ppm</td>
<td>5° Fr</td>
<td>0.35° Cl</td>
<td></td>
<td></td>
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</tbody>
</table>

**DISADVANTAGES OF HARDWATER:**

1. **In Domestic use:**
   a. **WASHING:** hardwater, when used for washing purposes, does not producing lather freely with soap. As a result cleansing quality of soap is decreased and a lot of it is wasted. Hardwater reacts with soap it produces sticky precipitates of calcium and magnesium soaps. These are insoluble formations.
   b. **Bathing:** hardwater does not lather freely with soap solution, but produces sticky scum on the bath-tub and body. Thus, the cleansing quality of soap is depressed and a lot of it is wasted.
   c. **Cooking:** the boiling point of water is increased because of presence of salts. Hence more fuel and time are required for cooking.
   d. **Drinking:** hardwater causes bad effects on our digestive system. Moreover, the possibility of forming calciumoxalate crystals in urinary tracks is increased.
2. **INDUSTRIAL USE:**
   a. **Textile Industry:** Hardwater causes wastage of soap. Precipitates of calcium and magnesium soaps adhere to the fabrics and cause problem.
   b. **Sugar Industry:** water containing sulphates, nitrates, alkali carbonates. Etc. if used in sugar refining, causes difficulties in the crystallization of sugar. Moreover, the sugar so produced may be de-liquefied.
   c. **Dyeing Industry:** The dissolved salts in hardwater may react with costly dyes forming precipitates.
   d. **Paper Industry:** Calcium, magnesium, Iron salts in water may affect the quality of paper.
   e. **Pharmaceutical Industry:** Hardwater may cause some undesirable products while preparation of pharmaceutical products.
   f. **Concrete Making:** Water containing chlorides and sulphates, if used for concrete making, affects the hydration of cement and the final strength of the hardened concrete.
   g. **Laundry:** Hardwater, if used in laundry, causes much of the soap used in washing to go as waste Iron salts may even cause coloration of the clothes.

3. **IN STEAM GENERATION IN BOILERS:**
   For steam generation, boilers are almost invariably employed. If the hardwater is fed directly to the boilers, there arise many troubles such as:
   a. **Scale and sludge formation:** the hardness of water fed to the boiler may cause scale and sludge formation.
   b. **Corrosion:** Hardwater may cause caustic embrittlement which is a type of boiler corrosion.
   c. **Priming and Foaming:** Hardwater used in boiler causes priming and foaming which results in the formation of wet stream.
   d. **Caustic embrittlement**

**ESTIMATION OF HARDNESS BY EDTA METHOD:**
The hardness of water is not a pollution parameter but indicate the water quality in terms of Calcium and magnesium expressed in terms of CaCO$_3$.

The analysis is done by complex metric titration using standard EDTA and EBT as an indicator. EDTA is Ethylene diamaine tetra acetic acid whose structural formulae is

EDTA can form 4 to 6 dative bonds with cations like Calcium Magnesium.

**PRINCIPLE:** In this complex metric Titration, the water sample is titrated with standard solution of Di sodium salt of EDTA using EBT indicator.

**PROCEDURE:** To 50 mL of sample add 10-15 mL buffer solutions adjust the pH about 10 and then warm the solution. Add 2 drops of Eriochrome Block-T and it is titrated with 0.01 M EDTA solution changes its colour from red-wine to blue.
**REACTIONS INVOLVED:** EBT indicator when added to hard water at pH = 10, forms weak complexes with calcium and magnesium present in hard water. It results in the formation of Ca-EBT or Mg-EBT complexes which is wine-red, these are unstable.

\[
(Ca^{2+} \text{ & or } Mg^{2+}) + \text{EBT} \rightarrow [Ca \text{ – EBT }] \text{ complex & or [Mg – EBT] complex}
\]

<table>
<thead>
<tr>
<th>Blue</th>
<th>Wine-red</th>
<th>Wine-red</th>
</tr>
</thead>
</table>

During titration with EDTA, calcium first reacts to form relatively stable followed by magnesium to give Mg-EDTA+2 complex releasing the free indicator(blue) the colour changes from wine-red to blue at the endpoint.

\[
\text{Metal-EBT + EDTA} \rightarrow \text{Metal – EDTA} + \text{EBT}
\]

Wine-red                                                          Blue

Various steps involved in this method are…

1. **Preparation of standard hard water:** dissolve 1g of pure, dry CaCO₃ in minimum quantity of dil.HCl and then evaporate the solution to dryness on a water bath. Dissolve the residue in distilled water to make 1 Litre solution. Each mL of this solution thus contains 1mg of CaCO₃ equalent hardness.

   1 mL hard water solution = 1mg of CaCO₃ equivalent hardness.

2. **Preparation of EDTA solution:** Dissolve 4 g of pure EDTA crystals + 0.1g MgCl₂ in 1 Litre of distilled water.

3. **Preparation of Indicator (EBT):** Dissolve 0.5 g of Eriochrome Black-T in 100mL alcohol.

4. **Preparation of Buffer solution:** add 67.5g of NH₄Cl to 570 mL of Con. Ammonia solution and then dilute with distilled water to 1 Litre.

5. **Standardization of EDTA solution:** Rinse and fill the burette with EDTA solution. Pipette out 50 mL of standard hard water in a conical flask. Add 10-15 mL of buffer solution and 4 to 5 drops indicator. Titrate with EDTA solution till wine-red colour changes to clear blue. Let volume used by V₁ mL.

6. **Titration of Unknown Hard water:** Titrate 50 mL of water sample just in Step-5. let volume used be V₂ mL.

7. **Titration of Permanent hardness:** take 250 mL of the water sample in a large beaker. Boil it. Till the volume is reduced to about 50 mL, filter it, wash the precipitate with distilled water, collecting filtrate and washing in a 250 mL measuring flask. Finally makeup the volume to 250 mL with distilled water. Then, titrate 50 mL of boiled water sample just as in Step (5). Let volume used by V₃ mL.

**CALCULATION:**

\[V_1 \text{ mL of EDTA is consumed by } 50 \text{ mL standard hardwater.}
\]

\[50 \text{ mL of standard hard water} = V_1 \text{ mL of EDTA}
\]

\[50 \times 1 \text{ mg of CaCO}_3 = V_1 \text{ mL of EDTA}
\]

\[1 \text{ mL of EDTA} = 50/V_1 \text{ mg of CaCO}_3 \text{ eq.}
\]

Now 50 mL of given/ unknown hard water = V₂ mL of EDTA

\[V_2 \times 50/V_1 \text{ mg of CaCO}_3 \text{ eq.}
\]

\[1 \text{ Lt or } 1000 \text{ mL of given hard water} = 1000 \times V_2/V_1 \text{ mg of CaCO}_3 \text{ eq.}
\]

Total hardness of water = 1000\times V₂/V₁ mg/L

1 mg/L = 1ppm so,

\[= 1000 \times V_2/V_1 \text{ ppm}
\]

Now 50 mL of boiled water = V₃ mL of EDTA

\[= V_3 \times 50/V_1 \text{ mg of CaCO}_3 \text{ eq.}
\]
1000 mL of boiled water = 1000*V3/V1 mg of CaCO3 eq. 
= 1000*V3/V1 ppm

So,
Permanent hardness = 1000*V3/V1 ppm
Temporary hardness = [Total hardness – Permanent hardness] = 1000*V2/V1 – 1000*V3/V1 = 1000[(V2-V3) V1] ppm
Total hardness of water = 1000*V2/V1 ppm
Permanent hardness = 1000*V3/V1 ppm
Temporary hardness = 1000[(V2-V3) V1] ppm

**Advantages of EDTA method:**
This method is definitely prep arable to the other methods, because of the
1. Greater accuracy
2. Convenience and 3. More rapid procedure

**Analysis of water**

1. **ALKALINITY:** Alkalinity of water is due to the presence of carbonates and bicarbonates of calcium and magnesium. So the carbonate and bicarbonates in water can be determined by titrating the solution with standard acid like N/50 H₂SO₄ using first Phenolphthalein and later methyl orange as an indicator conversion of carbonates into bicarbonates occur.

   In the II step to the solution using methyl orange as indicator (pH 4.2 to 5.4) bicarbonates present in the water and bicarbonates formed from carbonates gets neutralized.

   The alkalinity of water is attributed to the presence of the
   1. Caustic alkalinity (due to hydroxide & carbonate ions)
   2. Temporary hardness (due to Bicarbonate ions)

**PROCEDURE:** Pipette out 100 mL of the water sample in a clean titration flask. Add to it 2 to 3 drops of a phenolphthalein indicator. Run in N/50 H₂SO₄ from burette. Till the pink colour is just dis-charged. Then to the same pink colour reappears.

**CALCULATION:**
let volume of acid used to phenolphthalein endpoint = V₁ mL
And
Extra volume of acid used to Methyl orange endpoint = V₂ mL

Phenolphthalein alkalinity \( P = \frac{V_1 \times 50 \times 1000000}{50 \times 100 \times 1000} = 10 V_1 \) ppm

Methyl orange alkalinity \( M = \frac{(V_1+V_2) \times 50 \times 1000000}{50 \times 100 \times 1000} = 10(V_1+V_2) \) ppm

**CALCULATION OF ALKALINITY OF WATER:**

<table>
<thead>
<tr>
<th>ALKALINITY</th>
<th>OH- (ppm)</th>
<th>CARBONATE ion (ppm)</th>
<th>Bicarbonate ion (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P=0</td>
<td>0</td>
<td>0</td>
<td>M</td>
</tr>
<tr>
<td>P=1/2 M</td>
<td>0</td>
<td>2P</td>
<td>O</td>
</tr>
<tr>
<td>P&lt;1/2 M</td>
<td>0</td>
<td>2P</td>
<td>(M-2P)</td>
</tr>
</tbody>
</table>

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2. ESTIMATION OF CHLORIDES IN WATER

The chloride ions are present in water in the form of one or more of the compounds like CaCl₂, MgCl₂, NaCl etc. The estimation of chloride ions is generally made by titrating the water sample against a standard solution of silver nitrate using potassium chromate as indicator. The added silver nitrate precipitate chloride ions as white ppt of silver chloride,

\[ \text{NaCl} + \text{AgNO}_3 \rightarrow \text{AgCl} + \text{NaNO}_3 \]

\[ \text{Cl}^- + \text{Ag}^+ \rightarrow \text{AgCl} \]

When all the chlorine ions are removed as AgCl ppt, the excess drop of silver nitrate reacts with potassium chromate forming silver chromate, which is red in colour.

\[ \text{K}_2\text{CrO}_4 + 2\text{AgNO}_3 \rightarrow \text{Ag}_2\text{CrO}_4 + 2\text{KNO}_3 \]

\[ \text{CrO}_4^{2-} + 2\text{Ag}^+ \rightarrow \text{Ag}_2\text{CrO}_4 \]

The endpoint is therefore the change in colour from bright yellow due to brick red colour due to formation of Ag₂CrO₄ indicator. Then titrate it against N/50 AgNO₃ solution till the colour changes from yellow to permanent brick-red.

**Calculation:**

Let volume of N/50 AgNO₃ used = V mL

50 x Normality of free chlorine = V x [N/50]

Strength of free chlorine = \( \frac{V \times 35.5 \times 10^6}{25 \times 100 \times 1000} \) = 14.2 x V ppm.

3. DISSOLVED OXYGEN:

The oxidation of KI by dissolved Oxygen determines the amount of dissolved Oxygen in water. Iodine is titrated with standard sodium thiosulphate solution using starch as final indicator. The dissolved molecular Oxygen in water does not react with KI. So, an oxygen carrier is used to bring about the reaction between Oxygen and KI. Hence manganous hydroxide is produced as a result of the reaction of KOH and MnSO₄.

\[ 2\text{KOH} + \text{MnSO}_4 \rightarrow \text{Mn(OH)}_2 + \text{K}_2\text{SO}_4 \]

\[ 2\text{Mn(OH)}_2 + \text{O}_2 \rightarrow 2 \text{MnO(OH)}_2 \]

\[ \text{MnO(OH)}_2 + \text{H}_2\text{SO}_4 \rightarrow \text{MnSO}_4 + 2\text{H}_2\text{O} + \text{[O]} \]

\[ 2\text{KI} + \text{H}_2\text{SO}_4 + \text{[O]} \rightarrow \text{K}_2\text{SO}_4 + \text{H}_2\text{O} + \text{I}_2 \]

\[ 2\text{Na}_2\text{S}_2\text{O}_3 + \text{I}_2 \rightarrow 2\text{NaI} + \text{Na}_2\text{S}_4\text{O}_6 \]

The presence of sulphates, nitrates, etc. in rain water gives wrong results in determination of dissolved Oxygen in water because these ions also liberates iodine from KI. In order to prevent the liberation of Iodine solution from nitrate, if present in water, sodium-azide (NaN₃) is added to the alkaline Iodide solution. This reacts with nitrates and gives.

\[ 2\text{NaN}_3 + \text{H}_2\text{SO}_4 \rightarrow 2\text{HN}_3 + \text{Na}_2\text{SO}_4 \]

\[ \text{HNO}_2 + \text{HN}_3 \rightarrow \text{N}_2\text{O} + \text{N}_2 + \text{H}_2\text{O} \]

**PROCEDURE:** 250 mL of water is taken in bottle preventing it to contact with air. 2 mL of Manganous sulphate solution is added by means of pipette, and also 2 mL of alkaline iodine solution is also added. Shake the bottle thoroughly, and repeat the process thrice. The ppt is
allowed to settle half-way and mix again. Then add to it Conc. H₂SO₄ insert the stopper and shake the bottle again allow the yellow solution to stand for 5 min. Withdraw 100 mL of solution and titrate it against N/100 solution (Na₂S₂O₃ solution) using freshly prepared starch as indicator. The endpoint will be the disappearance of blue- colour. When the volume of Thiosulphate is V mL then dissolved oxygen content in water is 8 V ppm.

Methods of Treatment of Water for Domestic Purposes

SEDIMENTATION: Sedimentation is the process of removing large suspended particles at the bottom of the reservoir. Which are collected due to gravity.
Sedimentation is the process of allowing standing undisturbed in big tanks, about 5M deep, when most of the suspended particles settle down at the bottom, due to the force of gravity. The clear supernatant water is then drawn from tank with the help of pumps. The retention period in a sedimentation tank ranges from 2-6 hours.
In order to carry out the sedimentation process successfully, some of the chemicals are added to water before sedimentation. These chemicals are called Coagulants.
The coagulants when added to water, form an insoluble gelatinous, flocculent precipitates, which descends through the water and mixes-up into very fine suspended impurities forming bigger impurities forming bigger impurities or flocs, which easily settles down.
Some of the coagulants used for sedimentation process are alum, ferrous sulphate, sodium aluminate etc.

Chemical coagulants:
Alum: K₂SO₄. Al₂(SO₄)₃. 24H₂O
Alum is the most widely used in water treatment plants.

\[
\text{Al}_2\text{(SO}_4\text{)}_3 + \text{Ca(HCO}_3\text{)}_2 \rightarrow 2\text{Al(OH)}_3 + 3\text{CaSO}_4 + 6\text{CO}_2
\]

\[
\text{NaAlO}_2 + 2\text{H}_2\text{O} \rightarrow \text{Al(OH)}_3 + \text{NaOH}
\]

\[
\text{FeSO}_4 + \text{Mg(HCO}_3\text{)}_2 \rightarrow \text{Fe(OH)}_2 + \text{MgCO}_3 + \text{CO}_2
\]

2) FILTRATION: It is the process of removing colloidal matter and most of the bacteria, micro-organisms etc, by passing water through a bed of fine sand and other proper-sized granular materials. Filtration is carried out by using Sand-filter.
Sand filter is used for removing suspended particles, micro-organisms, bacteria etc., by passing through a finely graded sand bed. All the colloidal matter and sediments gets accumulated and water is purified.

OPERATION OF SAND FILTER: In sand filtration process, water is passed through different sized sand beds like fine, coarse and gravel beds. The suspended particles are unable to pass through the gaps in the sand bed, because of their size. Water is first passed through a fine sand-bed. The suspended particles are first collected and gets clogged in fine sand and then passed through sand-bed. Here colloidal matter gets collected and the water is free from sediments. After passing of water from coarse sand bed it enters through a bed of medium sized stones called gravel or gravel-bed. This is the last bed where water is filtered completely and the filtered water is collected at the filter outlet. During the filtration process the fine pores of sand bed gets seized and clogged. In order to continue the filtration process, 2-3 cm of fine sand at the top is scrapped, replaced and leveled with makeup sand.
3) REMOVAL OF MICROORGANISMS:
Water after passing through Sedimentation, Coagulation and Filtration operations still contains a small quantity of Pathogenic bacteria.

**Disinfection**: The process of destroying/killing the disease producing Bacteria, microorganisms, etc. from the water and making it safe for use, is called disinfection.

**Disinfectants**: the chemicals or substances which are added to water for killing the Bacteria.

The disinfection of water can be carried out by following methods:

A). **BOILING**: Water for 10-15 minutes, all the disease-producing bacteria are killed and water becomes safe for use.

B) **BLEACHING POWER**: It is used to purify the drinking water from microorganisms. The purification process is achieved by dissolving 1 kg of bleaching powder in 1000 kiloliters of water. This dissolved water solution is left undisturbed for many hours. When bleaching powder is mixed with water, the result of chemical reaction produces a powerful Germicide called Hypochlorous acid. The presence of chlorine in the bleaching powder produces disinfecting action, kills germs and purifies the drinking water effectively.

\[
\begin{align*}
\text{CaOCl}_2 + \text{H}_2\text{O} &\rightarrow \text{Ca(OH)}_2 + \text{Cl}_2 \\
\text{H}_2\text{O} + \text{Cl}_2 &\rightarrow \text{HCl} + \text{HOCl} \\
\text{HOCl} + \text{Germs} &\rightarrow \text{Germs are killed} \rightarrow \text{water purified.}
\end{align*}
\]

C) **CHLORINE**: Chlorination is the process of purifying the drinking water by producing a powerful Germicide like Hypochlorous acid. When this Chlorine is mixed with water it produces Hypochlorous acid which kills the germs present in water.

\[
\text{H}_2\text{O} + \text{Cl}_2 \rightarrow \text{HOCl} + \text{HCl}
\]

Chlorine is basic (means pH value is more than 7) disinfectant and is much effective over the germs. Hence Chlorine is widely used all over the world as a powerful disinfectant. Chlorinator is an apparatus, which is used to purify the water by chlorination process.

**BREAK-POINT CHLORINATION**:
Break-point chlorination is a controlled process. In this process suitable amount of Chlorine is added to water. In order to kill all the bacteria present in water, to oxidize the entire organic matter and to react with free ammonia the chlorine required should be appropriate. Break-point determines whether chlorine is further added or not. By Chlorination, organic matter and disease producing Bacteria are completely eliminated which are responsible for bad taste and bad odour in water.

When certain amount of Chlorine is added to the water, it leads to the formation of Chloro-organic compounds and chloramines. Addition of some more chlorine leads to destruction of
chloro-organic compounds and chloramines. The point at which free residual chlorine begins to appear is termed as “Break-point”.

**OZONISATION:** Ozone is a powerful disinfectant and is readily dissolved in water. Ozone being unstable decomposes by giving Nascent Oxygen which is capable of destroying the Bacteria. This Nascent Oxygen removes the colour and taste of water and oxidizes the organic matter present in water.

\[ \text{O}_3 \rightarrow \text{O}_2 + [\text{O}] \]
Q.No.5: Write a brief account of Zeolite process.

**Answer:** Zeolites are also known as Permutits;
Zeolites are mainly 2 types:
1. **Natural zeolites** are non-porous, eg. Natrolite- \( \text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 4\text{SiO}_2 \cdot 2\text{H}_2\text{O} \).
2. **Synthetic Zeolites** are porous and possess gel structure. Sodium zeolites are generally used for softening of water and are simply represented as \( \text{Na}_2\text{Ze} \), where ‘Ze’ stands for insoluble zeolite. In the process, when hard water is passed through a bed of zeolite placed in an closed cylinder, the hardness causing ions like Ca\(^+2\) and Mg\(^+2\) ions are taken up by the zeolite. Sodium salts are released during the reaction, as byproduct.

**Process:** For softening of water by zeolite process, hard water is percolated at a specified rate through a bed of zeolite, kept in a cylinder. The hardness causing ions like Ca\(^+2\), Mg\(^+2\) are retained by the zeolite as CaZe and MgZe; while the outgoing water contains sodium salts.
The various reactions taking place may be:

\[
\begin{align*}
\text{Na}_2\text{Ze} + \text{Ca(HCO}_3 \text{)}_2 & \rightarrow \text{CaZe} + 2\text{NaHCO}_3 \\
\text{Na}_2\text{Ze} + \text{Mg(HCO}_3 \text{)}_2 & \rightarrow \text{MgZe} + 2\text{NaHCO}_3 \\
\text{Na}_2\text{Ze} + \text{MgCl}_2 & \rightarrow \text{MgZe} + 2\text{NaCl} \\
\text{Na}_2\text{Ze} + \text{CaCl}_2 & \rightarrow \text{CaZe} + 2\text{NaCl} \\
\text{Na}_2\text{Ze} + \text{MgSO}_4 & \rightarrow \text{MgZe} + 2\text{Na}_2\text{SO}_4 \\
\text{Na}_2\text{Ze} + \text{CaSO}_4 & \rightarrow \text{CaZe} + 2\text{Na}_2\text{SO}_4 \\
\end{align*}
\]

Hence zeolite process removes the hardness of water effectively.

**Regeneration:** After some time, the Zeolite is completely converted into calcium and magnesium zeolites and it ceases to soften water, i.e., it gets exhausted. At this stage, the supply of hard water is stopped and the exhausted zeolite is reclaimed by treating the bed with a concentrated Brine solution (10% NaCl).

\[
\text{CaZe} + 2\text{NaCl} \rightarrow \text{Na}_2\text{Ze} + \text{CaCl}_2
\]
MgZe + 2 NaCl $\rightarrow$ Na$_2$Ze + MgCl$_2$

**Advantages:**

a. It removes the hardness completely and water of about 10 ppm hardness is produced.
b. The equipment used is compact, occupying a small space.
c. No impurities are precipitated, so there is no danger of sludge formation in the treated water at a later stage.
d. The process automatically adjusts itself for variation in hardness of incoming water.
e. It is quite clean
f. It requires less time for softening.
g. It requires less skill for maintenance as well as operation.

**Disadvantages:**

a. The treated water contains more sodium salts than in lime-soda process.
b. This method causes caustic embrittlement.
c. High turbidity water cannot be treated efficiently by this method.

**Limitations:**

1. If the supply of water is turbid, the suspended matter must be removed, before the water is admitted to the zeolite bed. Otherwise the turbidity will clog the pores of zeolite bed, thereby making it inactive.
2. If water contains large quantities of coloured ions such as Mn$^{+2}$ and Fe$^{+2}$ they must be removed first, because these ions produce magnesium and ferrous zeolites. This cannot be easily regenerated.
3. Mineral acids, if present in water, destroy the zeolite bed and therefore, they must be neutralized with soda, before admitting the water to the zeolite softening plant.

**Q.No.4: Write a brief account of Ion exchange process.**

**Answer:** Ion exchange process also known as demineralization or de-ionization process. Ion-Exchange resins are insoluble. Cross linked long chain organic polymers with a micro porous structure, and the “functional Groups” attached to the chains are responsible for the ion-exchanging properties.

In De-ionization process all the ions present in water are eliminated by using ion-exchange resins. Basically resins with acidic functional group are capable of exchanging H$^+$ ions with other cations. Resins with functional groups are capable of exchanging OH$^-$ ions with other anions.

Resins are classified as

1. Cation Exchange Resins
2. Anion Exchange Resins

1. **Cation Exchange Resins:** These are mainly styrene divinyl benzene co-polymers, which on sulphonation or carboxylation. These are capable of exchanging their hydrogen ions with cations in water.
2. **Anion Exchange Resins:** Anion exchange resins are styrene-divinyl benzene or amine-formaldehyde copolymers, which contain amino, quaternary ammonium or quaternary phosphonium or tertiary sulphonium groups as an internal part of the resin matrix. These after treatment with dilute NaOH solution become capable of exchanging their OH\(^-\) ions with anions in water.

**In ion-exchange process,** hard water is allowed to pass through cation exchange resins, which remove Ca\(^{+2}\) and Mg\(^{+2}\) ions and exchange equivalent amount of H\(^+\) ions. Anions exchange resins remove bicarbonates, chlorides and sulphates from water exchange equivalent amount of OH ions. Thus by passing hard water through cation hardness is observed by the following reactions.

**Cation Exchange Resins**

\[
2\text{RH}^+ + \text{Ca}^{+2} \rightarrow \text{R}2\text{Ca}^{+2} + 2\text{H}^+
\]

\[
2\text{RH}^+ + \text{Mg}^{+2} \rightarrow \text{R}2\text{Mg}^{+2} + 2\text{H}^+ \quad (\text{RH}^+ = \text{cation exchange resin})
\]

**Anion Exchange Resins**

\[
\text{R'}\text{OH} + \text{Cl}^{-2} \rightarrow \text{R'}\text{Cl}^{-} + \text{OH}^{-}
\]

\[
2\text{R'}\text{OH}^{-} + \text{SO}_4^{-2} \rightarrow \text{R}2\text{SO}_4^{-2} + 2\text{OH}^{-}
\]

\[
2\text{R'}\text{OH}^{-} + \text{CO}_3^{-2} \rightarrow \text{R}2\text{CO}_3^{-2} + 2\text{OH}^{-} \quad (\text{R'}\text{OH}^{-} = \text{anion exchange resin})
\]

H\(^+\) and OH\(^-\) ions, thus released in water from respective cation and anion exchange columns, get combined to produce water molecules.

\[
\text{H}^+ + \text{OH}^- \rightarrow \text{H}_2\text{O}
\]

The water coming out from the exchanger is ion free i.e., free from anions and cations. Thus water of zero hardness is obtained.
**REGENERATION:** When cation exchanger loses capacity of producing $\text{H}^+$ ions and exchanger loses capacity of producing $\text{OH}^-$ ions, they are said to be exhausted. The exhausted cation exchanger is regenerated by passing it through dilute sulphuric acid.

$$R_2\text{Ca}^{+2} + 2\text{H}^+ \rightarrow 2\text{RH}^+ + \text{Ca}^{+2}$$

The exhausted anion exchanger is regenerated by passing a dilute solution of NaOH.

$$R_2\text{SO}_4^{+2} + 2\text{OH}^- \rightarrow 2\text{R'}\text{OH}^- + \text{SO}$$

**Merits of Ion-exchange process:**

a. The process can be used to soften highly acidic or alkaline water.

b. It produces water of very low hardness (2 ppm)

c. So it is very good for treating water for use in high-pressure boilers.

**Demerits of Ion-exchange process:**

a. The equipment is costly and more expensive chemicals are needed.

b. If water contains turbidity, the output of the process is reduced. The turbidity must be below 10 ppm; else it has to be removed by coagulation and filtration.
Q. No. 6: What are Boiler troubles? Write short notes on scale & sludge formation and caustic embrittlement?

Answer: BOILER TROUBLES: In treatment of water complete elimination of all the impurities is not possible. The impurity that gives rise to certain troubles will be removed to certain extent. In modern pressure boilers and laboratories, water purer than the distilled water is required. Some of the boiler troubles caused by the use of unsuitable water are:
1. Carryover – Priming and Foaming
2. Scale formation
3. Boiler corrosion and
4. Caustic embrittlement

Carryover – Priming and Foaming
a. Priming: It may defined as the violent or rapid boiling of water occurring in the boiler which results in carrying out of water with steam in the form of a spray. When a boiler is producing steam rapidly, some particles of liquid water are carried along with the steam. This process of wet steam formation is called priming.

Priming mainly caused due to very high water level. The presence of large amount of dissolved solids, high steam velocities, sudden increase in steam production rate. Sudden steam demand which leads to sudden boiling, presence of excessive foam filling the foam spare, and due to faulty boiler design.

Priming can be controlled by proper boiler design, fitting mechanical steam purifier, avoiding rapid change in steam-rate, proper evaporation and adequate heating surfaces, uniform distribution of fuel and providing anti priming pipes, keeping the water level low and avoid sudden steam demands. Efficient softening and filtration of the boiler feed water.

b. Foaming: Foaming is the formation of small but stable bubbles above the surface. The main reason for foaming is being presence of fatty acids and other impurities.

Foaming can be controlled by using anti-foaming chemicals, removal of concentrated boiler water and replacing it by fresh feed water. Removing oil from boiler water by adding compounds like sodium aluminate.

SLUDGE FORMATION IN BOILERS:
In boilers, because of continuous evaporation of water, the concentration of salts increase progressively and after the saturation point is reached, precipitate form on the inner walls of boiler.

SLUDGE: Sludge is a soft, loose and slimy precipitate formed within the boiler. It is formed at comparatively colder portions of the boiler and collects in the area where flow rate is slow. These are formed by substances which have greater solubilities in hot water than in cold-water.

Eg. MgCO₃, MgCl₂, CaCl₂, MgSO₄.
**DIS-ADVANTAGES:**

a. As the sludge’s are poor conductor of heat they cause loss of heat.

b. The working of the boiler is disturbed because of choking of pipes by the sludge.

**PREVENTION:**

a. By using well softened water.

b. By drawing off a portion of concentrated water frequently.

---

**SCALES:** Scales are hard, adhering precipitates formed on the inner walls of the boilers. They stick very firmly on to the inner wall surface and are difficult to remove with chisel and hammer.

**causes of scale formation:** Following are the causes

**a.** Decomposition of calcium bicarbonate:

\[
\text{Ca(HCO}_3\text{)}_2 \rightarrow \text{CaCO}_3 + \text{H}_2\text{O} + \text{CO}_2
\]

In low pressure boilers, \(\text{CaCO}_3\) causes scale formation.

In high pressure boilers, \(\text{CaCO}_3\) becomes soluble.

\[
\text{CaCO}_3 + \text{H}_2\text{O} \rightarrow \text{Ca(OH)}_2 + \text{CO}_2
\]

**b.** Decomposition of calcium sulphate:

The solubility of \(\text{CaSO}_4\) in water decreases with rise of Temperature. In super heated water \(\text{CaSO}_4\) is insoluble.

This is the main cause in high-pressure boilers.

**c.** Hydrolysis of Magnesium salts:

Dissolved Magnesium salts undergo hydrolysis forming \(\text{Mg(OH)}_2\) precipitate.

\[
\text{MgCl}_2 + 2\text{H}_2\text{O} \rightarrow \text{Mg(OH)}_2 + 2\text{HCl}
\]

\(\text{Mg(OH)}_2\) so found by hydrolysis of Magnesium salts is a soft type of scale.

**d.** Presence of Silica: Silica present in small quantities deposits as silicates like \(\text{CaSiO}_3\) and \(\text{MgSiO}_3\). These are very difficult to remove.

---

**Disadvantages:**

a. **wastage of fuel:** The scale formation causes decreases of heat transfer. As a result over heating is required this causes consumption of fuel.

b. **danger of Explosion:** The hot scale cracks because of expansion and water suddenly comes in contact with overheated Iron plates. This causes in formation of large amount of steam suddenly. This results high pressure causing boiler to burst.

**PREVENTION:**

a. **External treatment:** Efficient softening of water is to be carried out.

b. **Internal treatment:** Suitable chemicals are added to the boiler water either to precipitate or to convert the scale into compounds.

---

**Boiler Corrosion:** The chemical or electro chemical eating away of metal by its environment in a boiler is known as boiler corrosion. The main reason for this problem is the presence of excess of oxygen in water. It can be prevented by mechanical deaerator, pre-heating and chemical treatment.

**a. Dissolved oxygen:** Water usually contains about 8 ml of dissolved oxygen per liter at room temperature. Dissolved oxygen in water, in presence of prevailing high temperature, attacks boiler material:

\[
2\text{Fe} + 2\text{H}_2\text{O} + \text{O}_2 \rightarrow 2\text{Fe(OH)}_2
\]

\[
4\text{Fe(OH)}_2 + \text{O}_2 \rightarrow 2[\text{Fe}_2\text{O}_3.2\text{H}_2\text{O}]
\]
Removal of dissolved oxygen: 1. By adding calculated quantity of sodium sulphite or hydrazine or sodium sulphide.

\[
2\text{Na}_2\text{SO}_3 + \text{O}_2 \rightarrow 2\text{Na}_2\text{SO}_4 \\
\text{N}_2\text{H}_4 \rightarrow \text{N}_2 + 2\text{H}_2\text{O} \\
\text{Na}_2\text{S} + \text{O}_2 \rightarrow \text{Na}_2\text{SO}_4
\]

Hydrazine is an ideal internal treatment chemical for the removal of dissolved oxygen. It reacts with oxygen, forming nitrogen and water. Nitrogen is harmless. Recently Azamina 8001-RD a poly organic compound, has been employed for degassing of water.

**b. Dissolved carbon dioxide:** Carbon dioxide is carbonic acid,

\[
\text{CO}_2 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{CO}_3
\]

This has a slow corrosive effect on the boiler material. Carbon dioxide is also released inside the boiler, if water used for steam generation contains bicarbonate,

Heat

\[
\text{Mg(HCO}_3\text{)}_2 \rightarrow \text{MgCO}_3 + \text{H}_2\text{O} + \text{CO}_2
\]

**Removal of carbon dioxide:**
1. By adding calculated quantity of ammonia,
   \[
   2\text{NH}_4\text{OH} + \text{CO}_2 \rightarrow (\text{NH}_4)_2\text{CO}_3 + \text{H}_2\text{O}
   \]
2. By mechanical – aeration process along with oxygen.

**c. Acids from dissolved salts:** Water containing dissolved magnesium salts liberates acids on hydrolysis.

\[
\text{MgCl}_2 + 2\text{H}_2\text{O} \rightarrow \text{Mg(OH)}_2 + 2\text{HCl}
\]

The liberated acid reacts with iron in chain – like reactions producing HCl again and again.

\[
\text{Fe} + 2\text{HCl} \rightarrow \text{FeCl}_2 + \text{H}_2
\]

\[
\text{FeCl}_2 + 2\text{H}_2\text{O} \rightarrow \text{Fe(OH)}_2 + 2\text{HCl}
\]

Consequently, presence of even a small amount of MgCl₂ will cause corrosion of iron to a large extent.

**Caustic Embrittlement:** The formation of brittle and incrystalline cracks in the boiler shell is called caustic embrittlement.

It is a type of boiler corrosion and the main reason for this, is the presence of alkali-metal carbonates and bicarbonates in feed water and also the presence of sodium sulphate.

In lime-soda process, it is likely that, some residual Na₂CO₃ is still present in the softened water. This Na₂CO₃ decomposes to give NaOH and CO₂, due to which the boiler water becomes “Caustic”.

\[
\text{Na}_2\text{CO}_3 + \text{H}_2\text{O} \rightarrow \text{NaOH} + \text{CO}_2
\]

This caustic water flows inside the boiler and causes some minutes hair-cracks, by capillary action. On evaporation of water, the dissolved caustic soda increases its concentration which attacks the surrounding area, thereby dissolving Iron of boiler as Sodium ferroate.

This causes embrittlement of boiler parts such as bends, joints, reverts etc, due to which the boiler gets fail. Caustic cracking can be explained by considering the following concentration cell:

\[
\begin{align*}
\text{Iron at bends, joints, reverts etc,} & + \text{Concentrated NaOH solution} & \text{Dilute NaOH solution} & - \text{Iron at plane surfaces} \\
\end{align*}
\]

Therefore, caustic embrittlement can be prevented.

- By maintaining the pH value of water and neutralization of alkali.
- By using Sodium Phosphate as softening reagents, in the external treatment of boilers.
Caustic embrittlement can also be prevented by adding Tannin or Lignin or Sodium sulphate which prevents the infiltration of caustic-soda solution blocking the hair-cracks.

Q. No. 7: Write a brief account of internal treatment of water.

Answer: INTERNAL TREATMENT:

Internal treatment of boiler water is carried out by adding proper chemicals to precipitate the scale forming impurities in the form of sludge and to convert the scale forming chemicals into compounds which will stay in dissolved form in water. This process is mainly used as a corrective treatment to remove the slight residual hardness and also sometimes to remove the corrosive tendencies in water. Some of the internal treatment methods used for the removed of scale formation in boilers are.

**COLLODIAL CONDITIONING:** The addition of organic substances such as Kerosene, tannin, Gel etc., to the surface in low pressure boilers may prevent the scale formation. These substances gets coated over the scale forming precipitates and gives a loose and non-sticky precipitates which can be removed by using blow-down operation.

**PHOSPHATE CONDITIONING:** The addition of sodium phosphate in hard water reacts with the hardness causing agents and gives calcium and magnesium phosphates which are soft and non-adhere and can be removed easily by blow-down operation. In this way, scale formation is removed in high-pressure boilers.

\[ 3\text{CaCl}_2 + 2 \text{Na}_3\text{PO}_4 \rightarrow \text{Ca}_3(\text{PO}_4)_2 + 6\text{NaCl} \]

**CARBONATE CONDITIONING:** In low-pressure boilers, scale-formation can be avoided by adding sodium carbonate to boiler water, when CaSO4 is converted into calcium carbonate in equilibrium.

\[ \text{CaSO}_4 + \text{Na}_2\text{CO}_3 \rightarrow \text{CaCO}_3 + \text{Na}_2\text{SO}_4 \]

Consequently, deposition of CaSO4 as scale doesn’t take place and calcium is precipitated as loose sludge of CaCO3 which can be removed by blow-down operation.

**CALGON CONDITIONING:** Involves in adding calgon to boiler water. it prevents the scale and sludge formation by forming soluble complex compound with CaSO4.

Calgon = Sodium hexa Meta phosphate = \((\text{NaPO}_3)_6\)

\[ \text{Na}_3 [\text{Na}_4 (\text{PO}_3)_6] \equiv 2\text{Na}^+ + [\text{Na}_4\text{P}_6\text{O}_{18}]^- \]

\[ 2\text{CaSO}_4 [\text{Na}_4\text{P}_6\text{O}_{18}]^2 \rightarrow [\text{Ca}_2\text{P}_6\text{O}_{18}]^2^- + 2\text{Na}_2\text{SO}_4 \]

**SODIUM ALUMINATE:** Sodium aluminate gets hydrolyzed yielding NaOH and a gelatinous precipitate of aluminum hydroxide.

Thus \[ \text{NaAlO}_2 + 2\text{H}_2\text{O} \rightarrow \text{NaOH} + \text{Al(OH)}_3 \]

The sodium hydroxide, so-formed, precipitates some of the magnesium as Mg (OH)2, i.e.,

\[ \text{MgCl}_2 + 2\text{NaOH} \rightarrow \text{Mg(OH)}_2 + 2\text{NaCl} \]

The flocculent precipitate of Mg (OH)2 plus aluminum hydroxide, produced inside the boiler, entraps finely suspended and colloidal impurities, including oil drops and silica. The loose precipitate can be removed by pre-determined blow-down operation.

Q. No.8: Write a short note on Reverse osmosis & electrodialysis.

Desalination of Brackish water: The process of removing common salt from the water is known as desalination. The water containing dissolved salts with a peculiar salty taste is called brackish water. Sea water, containing on an average about 3.5% salts, comes under this category. Brackish water is totally unfit for drinking purpose. Commonly used methods for the desalination of brackish water is: 1. Reverse Osmosis & 2. Electrodialysis.

1. **Reverse Osmosis:** Osmosis is the phenomenon by virtue of which flow of solvent takes place from a region of low concentration to high concentration when two solutions of different concentrations are
separated by a semi-permeable membrane. The flow continues till the concentration is equal on both the sides. The driving force for osmosis is osmotic pressure. However, if a hydrostatic pressure in excess of osmotic pressure is applied on the concentrated side, the flow of solvent reverses as it is forced to move from concentrated side to dilute side across the membrane. This is the basis of reverse osmosis.

![Diagram of reverse osmosis](image)

For practical purposes, semi-permeable membrane based on thin films of cellulose acetate, polymethyl acrylate and polyamide polymers are used. A pressure of the order of 15-40 kg/cm$^2$ is applied for separating the water from its contaminants. The process is also known as super or hyper filtration.

**Advantages:**
- Colloidal SiO$_2$ can be removed by reverse osmosis which even cannot be removed by demineralization.
- It is simple and reliable process.
- Capital and operating expenses are low.
- The life of the semi-permeable membrane is about 2 years and it can be easily replaced within a few minutes, thereby nearly uninterrupted water supply can be provided.

**2. Electrodialysis:** Electrodialysis is based on the fact that the ions present in saline water migrate towards their respective electrodes, through ion-selective membrane under the influence of applied emf.
The unit consists of electrodes and thin and rigid ion-selective membranes which are permeable to either cation or anion. The anode is placed the anion-selective membrane while the cathode is placed near the cation-selective membrane. Under the influence of fixed functional groups, which carry positive charge, inside the membrane. Similarly, a cation selective membrane is based on polystyrene resin embedded with negatively charged functional groups such as RSO3- or RCOO- and is permeable only to cations.

Under the influence of an applied emf across the electrodes the cations move towards the cathodes through cation selective membrane and anions move towards the anode through anion selective membrane the net result is the depletion of ions in the central compartment while it increases in the two side compartments. Desalinated water is periodically drawn out from the central compartment while the concentrated brackish water.

**Advantages of desalination by electrodialysis:**

- This process is economical as per the capital cost and operational expenses are concerned.
- The unit is compact and the method is best suited.

1. Calculate the quantities of lime and soda required in kgs for softening 10,000 lit of water using 82 ppm of NaAlO2 as coagulant. Analysis of water was as follows:

   CaCl2 = 111 ppm; Mg(HCO3)2 = 146ppm; NaCl = 58.5ppm; KCl = 74.5ppm; Dissolved CO2 = 44ppm. (At. Wt of Na = 23, Mg = 24, K = 39, Ca = 40 and Al = 27)

**Ans.**

<table>
<thead>
<tr>
<th>S.No.</th>
<th>Constituent</th>
<th>Amount(ppm)</th>
<th>MF *</th>
<th>CaCO3 equivalent</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>CaCl2</td>
<td>111</td>
<td>100/111</td>
<td>100</td>
</tr>
<tr>
<td>2.</td>
<td>Mg(HCO3)2</td>
<td>146</td>
<td>100/146</td>
<td>100</td>
</tr>
<tr>
<td>3.</td>
<td>NaCl</td>
<td>58.5</td>
<td></td>
<td>Do not contribute</td>
</tr>
<tr>
<td>4.</td>
<td>KCl</td>
<td>74.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5.</td>
<td>CO2</td>
<td>44</td>
<td>100/44</td>
<td>100</td>
</tr>
<tr>
<td>6.</td>
<td>NaAlO2</td>
<td>82</td>
<td>100/164</td>
<td>50</td>
</tr>
</tbody>
</table>

We have to consider atomic weight of metal ion.

\[
\text{Lime required} = \frac{74}{[\text{Mg}^{2+} + \text{CO}_2 + \text{NaAlO}_2]} \cdot \frac{100}{100}
\]
2. Calculate the lime and soda needed for softening 50,000 litres of water containing the following salts: CaSO$_4$ = 136 mg/lit; MgCl$_2$ = 95 mg/lit; Mg(HCO$_3$)$_2$ = 73 mg/lit; Ca(HCO$_3$)$_2$ = 162 mg/lit. Given that the molar mass of Ca(HCO$_3$)$_2$ is 162 and that of MgCl$_2$ is 95.

Ans:

<table>
<thead>
<tr>
<th>S.No.</th>
<th>Constituent</th>
<th>Amount (mg/lit)</th>
<th>MF</th>
<th>CaCO$_3$ equivalent</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>CaSO$_4$</td>
<td>136</td>
<td>100/136</td>
<td>100</td>
</tr>
<tr>
<td>2.</td>
<td>MgCl$_2$</td>
<td>95</td>
<td>100/95</td>
<td>100</td>
</tr>
<tr>
<td>3.</td>
<td>Mg(HCO$_3$)$_2$</td>
<td>73</td>
<td>100/146</td>
<td>50</td>
</tr>
<tr>
<td>4.</td>
<td>Ca(HCO$_3$)$_2$</td>
<td>162</td>
<td>100/162</td>
<td>100</td>
</tr>
</tbody>
</table>

Lime required = \( \frac{74}{100} \times [\text{Ca(HCO}_3\text{)}_2 + 2 \text{Mg(HCO}_3\text{)}_2 + \text{MgCl}_2] \)

\( \frac{74}{100} \times [100 + 2 \times 50 + 100 + 100] \)

\( \frac{74}{100} \times \frac{400}{1} = 296 \text{ mg/l} \)

For 50000 lit of water: 50000 x 296 = 14.8 Kg of lime required.

Soda required = \( \frac{106}{100} \times [\text{CaSO}_4 + \text{MgCl}_2] \)

\( \frac{106}{100} \times \frac{200}{1} = 212 \text{ mg/l} \)

For 50000 lit of water: 50000 x 212 = 10.6 kg of soda required.
### DIFFERENCES between lime-soda and zeolite process

<table>
<thead>
<tr>
<th>S.NO</th>
<th>LIME-SODA PROCESS</th>
<th>PERMUTIT/ZEOLITE</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Water treatment plant occupies more area or place.</td>
<td>Water treatment plant occupies less area.</td>
</tr>
<tr>
<td>2</td>
<td>Water after treatment has lesser dissolved solids.</td>
<td>Water after treatment has much more dissolved solids.</td>
</tr>
<tr>
<td>3</td>
<td>This method of water treatment plants is not much expensive and material used is cheap.</td>
<td>This method of water treatment plants is more expensive and material used for softening is expensive.</td>
</tr>
<tr>
<td>4</td>
<td>Operation expenses are higher</td>
<td>Operation expenses are low</td>
</tr>
<tr>
<td>5</td>
<td>The cost incurred on softening of water is high.</td>
<td>The cost incurred on softening of water is low.</td>
</tr>
<tr>
<td>6</td>
<td>It cannot operate in under pressure.</td>
<td>It can even operate in under pressure.</td>
</tr>
<tr>
<td>7</td>
<td>It can be used for treating acidic water also.</td>
<td>This method of softening the water is not used for treating acidic water.</td>
</tr>
<tr>
<td>8</td>
<td>There is a problem of settling, coagulation and removal of sludge.</td>
<td>There is no problem of settling, coagulation and removal of sludge.</td>
</tr>
<tr>
<td>9</td>
<td>It is not possible.</td>
<td>This method can be made automatic.</td>
</tr>
<tr>
<td>10</td>
<td>In order to meet the changing hardness of incoming water, frequent control and adjustment of reagents is needed.</td>
<td>Control test comprises only in checking the hardness of treated-water.</td>
</tr>
<tr>
<td>11</td>
<td>Residual hardness is low about 15 to 50 ppm</td>
<td>Residual hardness is low about 10 to 15 ppm</td>
</tr>
</tbody>
</table>
### DIFFERENCES between lime-soda and ion-exchange process

<table>
<thead>
<tr>
<th>S.NO</th>
<th>LIME-SODA PROCESS</th>
<th>ION-EXCHANGE/RESIN</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Water treatment plant occupies more area or place.</td>
<td>Water treatment plant occupies less area.</td>
</tr>
<tr>
<td>2</td>
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<td>3</td>
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</tr>
<tr>
<td>6</td>
<td>It cannot operate in under pressure.</td>
<td>It can even operate in under pressure.</td>
</tr>
<tr>
<td>7</td>
<td>It can be used for treating acidic water also.</td>
<td>It can be used for treating acidic and alkaline water also.</td>
</tr>
<tr>
<td>8</td>
<td>There is a problem of settling, coagulation and removal of sludge.</td>
<td>There is problem of turbidity.</td>
</tr>
<tr>
<td>9</td>
<td>It is not possible.</td>
<td>This method can be made automatic.</td>
</tr>
<tr>
<td>10</td>
<td>In order to meet the changing hardness of incoming water, frequent control and adjustment of reagents is needed.</td>
<td>Control test comprises only in checking the hardness of treated-water.</td>
</tr>
<tr>
<td>11</td>
<td>Residual hardness is low about 15 to 50 ppm</td>
<td>Residual hardness is low about 0 to 2 ppm</td>
</tr>
<tr>
<td></td>
<td>It is not good for boilers</td>
<td>It is very good for treating water for use in high pressure boilers.</td>
</tr>
<tr>
<td>---</td>
<td>-----------------------------</td>
<td>------------------------------------------------------------------</td>
</tr>
<tr>
<td>12</td>
<td>Skilled persons required</td>
<td>It required less skill for maintenance as well as operation</td>
</tr>
</tbody>
</table>

**Adsorption:** It is a phenomenon of concentration or assimilation of a gas or a liquid at the surface of a solid or liquid.

<table>
<thead>
<tr>
<th>Adsorption</th>
<th>Absorption</th>
</tr>
</thead>
<tbody>
<tr>
<td>a. It is a phenomenon of concentration or assimilation of a gas or a liquid at the surface of a solid or liquid.</td>
<td>It is the phenomenon in which the substance assimilated is uniformly distributed throughout the body of the solid or liquid.</td>
</tr>
<tr>
<td>c. A fast process.</td>
<td>A slow process.</td>
</tr>
<tr>
<td>d. Equilibrium is attained easily.</td>
<td>Attainment of equilibrium takes some time.</td>
</tr>
<tr>
<td>e. It depends upon the surface area of the adsorbent. Consequently, adsorption is more rapid on finely divided or more surface of adsorbent.</td>
<td>No such effect is there.</td>
</tr>
</tbody>
</table>

**Types of Adsorption:**
Adsorption is mainly two types, 1. Physical adsorption, 2. Chemical adsorption.

<table>
<thead>
<tr>
<th>Physical adsorption</th>
<th>Chemical adsorption</th>
</tr>
</thead>
<tbody>
<tr>
<td>a. Heat of adsorption is about 20-40 kcal/mol</td>
<td>Heat of adsorption is about 40-400 kcal/mol.</td>
</tr>
<tr>
<td>b. Adsorption is completely reversible, since the molecules are not tightly retained by the adsorbent.</td>
<td>Adsorption is reversible, since molecules are tightly retained by adsorbent.</td>
</tr>
<tr>
<td>c. Adsorption is appreciable only at temperature below the boiling point of the adsorbate; and it decreases with rise temperature.</td>
<td>Adsorption can occur at high temperatures.</td>
</tr>
<tr>
<td>d. Multilayer adsorption occurs, i.e., adsorbed layer may be several molecules thick, since the Vander Waal’s forces can extend from one layer to another.</td>
<td>Adsorption leads to almost, a mono-layer.</td>
</tr>
<tr>
<td>e. Forces responsible for such adsorption are very weak.</td>
<td>Forces responsible for such adsorption are quite strong.</td>
</tr>
<tr>
<td>f. The rate of adsorption increases for pressure or concentration of the adsorbate. Near saturation pressure, multilayers are formed.</td>
<td>The rate of adsorption decreases with the increase of pressure or concentration of the adsorbate. Near saturation pressure, adsorption rate decreases, since the adsorption is continued only to upper surface layer of adsorbent.</td>
</tr>
<tr>
<td>g. The amount of adsorption on a surfaced is</td>
<td></td>
</tr>
</tbody>
</table>
more a function of the adsorbate than the adsorbent. Degree of adsorption is high for more easily liquefiable and soluble gases.

h. Such adsorption involves very small or little activation energy.

i. No surface compound formation takes place.

j. It is not very specific in nature.

Such adsorption, generally, involves appreciable activation energy. Establishment of equilibrium requires time. Actual surface compound formation between the adsorbent and adsorbate takes place. It is highly specific in nature.

2. Q. Write a short note on Langmuir adsorption isotherm. Or Write a short note on mono layer adsorption.

**The Langmuir’s theory of adsorption – Mono-layer adsorption:**

According to Langmuir (1916), the phenomenon of adsorption can be explained theoretically on the basis of the following assumptions:

(i) Valences at the surface of adsorbent atoms are not fully satisfied and, therefore, they can share electrons with atoms present in the adsorbate to form bonds resembling a covalent linkage. If this bond is weak, a physical adsorption takes place. On the other hand, if bond is stronger, chemisorptions occur.

(ii) The residual valency force on the surface of adsorbent is effective only up to a small distance (about 2\(\times\)10\(-8\) cm) and hence, the adsorbed gas layer is only one molecule thick.

(iii) The phenomenon of adsorption consists of two opposing processes, namely, condensation of the molecules of the adsorbate on the surface of the adsorbent and evaporation or (desorption) of the adsorbed molecules from the surface of the adsorbent.

(iv) When the adsorption starts, the whole adsorbent surface is bare and consequently, the initial rate of absorption or condensation is highest; while the rate of desorption is smallest. As the surface becomes progressively covered, the rate of condensation gradually decreases; while the rate of evaporation of the condensed molecules gradually increases. Ultimately a dynamic equilibrium is set up, when the rate of condensation becomes equal to the rate of evaporation.

Based on the above postulates, the rate of adsorption depends on the pressure (P) and the number of vacant sites on the surface (1 - \(\theta\)), where \(\theta\) is the fraction of surface occupied by gas molecules.

Now, since the rate of adsorption is proportional to the pressure (P) of the gas as well as uncovered surface (1 - \(\theta\)) of the adsorbent available for adsorption.

\[
\text{Rate of adsorption} = \alpha P(1 - \theta)
\]

Rate of adsorption = \(k_1 P(1 - \theta) \rightarrow \text{(Eq.1)}\)

\[
\text{Rate of desorption} = \frac{x \alpha \theta}{M} \rightarrow \text{(Eq.2)}
\]

Where \(k_1\) is a proportionality constant.
Rate desorption $\propto \theta$
Rate desorption $= k_2 \theta$
Where $k_2$ is a proportionality constant.
At equilibrium:
Rate of adsorption $=$ Rate of desorption

$k_1 P (1 - \theta) = k_2 \theta$

$k_1 P - k_1 P \theta = k_2 \theta$

$k_1 P = k_2 \theta + k_1 P \theta$

$k_1 P = \theta (k_2 + k_1 P)$

$\theta = \frac{k_1 P}{(k_2 + k_1 P)}$

$\theta = \frac{k_1/ k_2 P}{(1 + k_1/ k_2 P)}$

$k_1/ k_2 = a$, which is another constant.

$\theta = \frac{a P}{(1 + a P)}$ \quad \rightarrow \quad (Eq.3)$

Since the adsorbed molecules form unimolecular layer, the amount of gas adsorbed per unit area or per unit mass of adsorbent must be proportional to the fraction of the surface covered, i.e.

$x/m = \theta$

$x/m = k_3 \theta$ \quad \rightarrow \quad (Eq.4)$

Where $x$ is the mass of gas adsorbed on ‘m’ grams of adsorbent and $k_3$ is the proportionality constant.

Equilibrium exists between free molecules and adsorbed molecules on the fraction of adsorbed surface.

Substituting the value of $\theta$ from Equation – 4 in the above equation.

We get

$x/m = k_3 \frac{a P}{(1 + a P)}$

$x/m = \frac{b P}{(1 + a P)}$ \quad \rightarrow \quad (Eq.5)$

Where $b = k_3 a$

In the equation-5 in the Langmuir adsorption isotherm the values of $a$ and $b$ depends upon the nature of the adsorbate gas and nature of solid adsorbent and the temperature. Their value can be determined from experimental data.

$\frac{x}{m}/P = \frac{b P}{(1 + a P)}$

Taking reciprocal $P/\frac{x}{m} = \frac{1}{b} + \frac{a}{b} P$

Since ‘$a$’ and ‘$b$’ are constant, a plot of $P/x/m$ against $P$ should give a straight line with slope equal to $a/b$ and intercept on y-axis is equal to $1/b$.

Or plot $P/x/m$ against $P$ is a straight line.

The extent of adsorption $x/m$ increases with increase in pressure ($P$) and becomes maximum at saturation.
At \( P_0 \), the rate of adsorption becomes equal to the rate of desorption. Further increase of pressure has no effect on adsorption.

**Advantages of the theory:**

a. Langmuir explained chemisorption.
b. This theory is more satisfactory than Freundlich’s isotherm while explaining physical adsorption of gases on different adsorbents when saturation is approached.

**Limitations:**

a. According to Langmuir’s adsorption is independent of temperature, but in reality decreases with temperature.
b. Instead of mono-layers, much thicker films have been reported.

---

**3. Q. To explain BET isotherm & write the BET equation.**

**B.E.T. theory of multi layer adsorption:**

The Langmuir theory of adsorption is restricted to the formation of mono-molecular layer of gas molecules on the solid surface. The adsorption theory proposed by B.E.T (Brunauer, Emmett and Teller) assumes that physical adsorption always results in multi layer adsorption. In the B.E.T. theory, it is assumed that the solid surface possesses uniform, localized sites and adsorption at one site does not affect adsorption at neighbouring sites as assumed in Langmuir theory. This theory further assumed that molecules can be adsorbed in second, third and nth layers. The surface area available for nth layer is equal to the area covered by (n-1)th layer. The energy of adsorption in the first layer \( E_1 \) is assumed to be constant and the energy of adsorption in the succeeding layers is assumed to be same as \( E_2 \). Based on the above assumption, B.E.T. derived an equation known after them as B.E.T. equation.

\[
\frac{P}{V_{\text{total}} X (P_0 - P)} = \frac{1}{V_{\text{mono}} X C} + \frac{C - 1}{V_{\text{mono}} X C} \left( \frac{P}{P_0} \right)
\]

Where \( V_{\text{total}} \) in the volume of gas adsorbed at the pressure \( P \), \( V_{\text{mono}} \) is the volume of gas adsorbed when the surface of solid is covered completely with a monolayer of adsorbed molecules of gas and ‘\( C \)’ is the constant depending upon the nature of gas. The numerical value of ‘\( C \)’ is expressed as \( C = \exp (E_1 - E_2)/Rt \) where \( E_1 \) is the heat of adsorption in the first layer and \( E_2 \) is the heat of liquefaction of gas.

Since ‘\( C \)’ is a constant for a given gas and \( V_{\text{mono}} \) is a constant for a given gas solid system, the plot of \( P/V_{\text{total}} (P_0 - P) \) against \( P/P_0 \) is a straight line.

The adsorption of nitrogen on silica gel occurs at \(-183^0\text{C.}\)

As long as the pressure \( P \) exceeds \( 1/3 \)rd of \( P_0 \), saturation pressure is the required to condense gas into liquid state at the prevailing temperature. Deviation occurs at high pressure.

The slope of the linear plot gives the value of \( C - 1 / (V_{\text{mono}} X C) \), the intercept gives the value of \( 1/(V_{\text{mono}} X C) \). Thus, from the slope and intercept, both \( V_{\text{mono}} \) and \( C \) can be evaluated.
4. Q. How to calculate the surface area of adsorbent with using BET method.

**Determination of surface area of a solid:**

Knowing $V_{\text{mono}}$, the surface area of adsorbent can be calculated as given under; the assumption is that the molecules of the gas adsorbed in the first layer are closely packed on the surface.

**Example:** At $0^\circ C$ and 1 atmosphere pressure, the volume of Nitrogen required to cover the sample on adsorbent, i.e. silica gel is 130 cm$^3$ g$^{-1}$ of gel, assuming Langmuir unimolecular adsorption. Calculate the surface area per gram of silica gel. Given that the area occupied by nitrogen molecule is 0.162 nm$^2$.

**Solution:**

\[ V_{\text{mono}} = 130 \text{ cm}^3 \text{ g}^{-1} = 0.130 \text{ dm}^3 \text{ g}^{-1}. \]
\[ V_{m} = 22.414 \text{ dm}^3 \text{ mol}^{-1}. \]

Number of molecules contained in $V_{\text{mono}} = \frac{6.023 \times 10^{23} \times 0.130}{22.414} = 3.49 \times 10^{22} \text{ g}^{-1}.

Area of cross section of one molecule = 0.162 nm$^2$ = 0.162 X 10$^{-8}$ m$^2$.

Area covered by 3.49 X 10$^{22}$ molecules.

i.e. surface area = 0.162 X 10$^{-18}$ m$^2$ X 3.49 X 10$^{22}$ g$^{-1}$

= 565.8 m$^2$ g$^{-1}$.

The area of cross section ‘a’ of the molecule can be determined from the density of liquefied or solidified adsorbate. Thus, if $\rho$ is the density, then the volumes ‘V’ occupied by a single molecule, assuming the adsorbate to be closely packed with no void volume, can be obtained as:

\[ \rho = \frac{Mm}{V} = \frac{Mm}{(N_{A}X\rho)}. \]

Assuming the molecule to be spherical with radius ‘r’, we have

\[ V = \frac{4\pi r^3}{3} = \frac{Mm}{(N_{A}X\rho)}. \]

Hence,

\[ r = \left( \frac{3Mm}{4\pi N_{A} \rho} \right)^{\frac{1}{3}}. \]

\[ a = \left( \frac{3Mm}{4\pi N_{A} \rho} \right)^{\frac{2}{3}}. \]

5. Q. Write postulates of Langmuir adsorption isotherm & write the applications adsorption

**The Langmuir’s theory of adsorption – Mono-layer adsorption:**

According to Langmuir (1916), the phenomenon of adsorption can be explained theoretically on the basis of the following assumptions:

(v) Valences at the surface of adsorbent atoms are not fully satisfied and, therefore, they can share electrons with atoms present in the adsorbate to form bonds resembling a covalent linkage. If this bond is weak, a physical adsorption takes place. On the other hand, if bond is stronger, chemisorptions occur.

(vi) The residual valency force on the surface of adsorbent is effective only upto a small distance (about 2X10$^{-8}$ cm) and hence, the adsorbed gas layer is only one molecule thick.

(vii) The phenomenon of adsorption consists of two opposing processes, namely, condensation of the molecules of the adsorbate on the surface of the adsorbent and evaporation or (desorption) of the adsorbed molecules from the surface of the adsorbent.

(viii) When the adsorption starts, the whole adsorbent surface is bare and consequently, the initial rate of absorption or condensation is highest; while the rate of desorption is smallest. As the surface becomes progressively covered, the rate of condensation gradually decreases; while the rate of
evaporation of the condensed molecules gradually increases. Ultimately a dynamic equilibrium is
set up, when the rate of condensation becomes equal to the rate of evaporation.

Based on the above postulates, the rate of adsorption depends on the pressure (P) and the number of
vacant sites on the surface (1 - θ), where θ is the fraction of surface occupied by gas molecules.

\[
\frac{x}{m} = k_3 \frac{aP}{(1 + aP)} \\
\frac{x}{m} = \frac{bP}{(1 + aP)}
\]

Where \(b = k_3a\)

Since ‘a’ and ‘b’ are constant, a plot of \(P/x/m\) against \(P\) should give a straight line with slope equal to \(a/b\)
and intercept on y-axis is equal to \(1/b\).

Or plot \(P/x/m\) against \(P\) is a straight line.

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pressure \(P_0\). At \(P_0\), the rate of adsorption becomes equal to the rate of desorption. Further increase of pressure has
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**Advantages of the theory:**

- Langmuir explained chemisorption.
- This theory is ore satisfactory than Freundlich’s isotherm while explaining physical adsorption of gases on
  different adsorbents when saturation is approached.

**Limitations:**

- According to Langmuir’s adsorption is independent of temperature, but in reality decreases with
temperature.
- Instead of mono-layers, much thicker films have been reported.
APPLICATIONS OF ADSORPTION

(1) Activated charcoal is used in gas masks in which all undesirable (toxic gases are adsorbed selectively by charcoal; while purified air passes through its pores.

(2) Activated charcoal is used removing colouring matter of sugar solution and the discoloration of vinegar.

(3) Silica and alumina gels are used as absorbent for removing moisture and for controlling humidities of room. Silica gel has been employed for drying air, used in blasts furnaces.

(4) Charcoal adsorption filters are used for removing organic matter from drinking water.

(5) Selective adsorption by alumina, magnesia, etc., has been used for separating different pigments by adsorption chromatography.

(6) During arsenic poisoning, colloidal ferric hydroxide is administered. The latter adsorbs the arsenic poison and retains it and can thus be removed from the body by vomiting.

(7) Fuller’s earth is used in large quantities for refining petroleum and vegetable oils, due to its good adsorption capacity for unwanted materials.

(8) The phenomenon of adsorption is useful in heterogeneous catalysis, e.g., contact process, Haber’s process, hydrogenation of oils, etc. based on an adsorption process.

(9) Adsorption process is used production by vacuum by using activated charcoal in Dewar’s flask.

(10) Lake test for Al\(^{3+}\) is based upon adsorption of litmus colour by Al(OH)\(_3\) precipitate:

(11) Mordant (like alum) used in dying cloth, adsorb the dye particles, which otherwise do not stick to the cloth.

COLLOIDAL CHEMISTRY:

Thomas Graham (1861), from investigations on diffusion of various substances in a liquid medium, classified substances as:

1. **Crystalloids**, which diffuse readily in solution and whose solution can readily pass through animal or vegetable membranes, e.g., urea, sugar, salts, acids, bases and other crystalline substances.

2. **Colloids** (from the Greek words kola and eidos, which means glue and like respectively), which diffuse very slowly in solution and whose solution cannot pass through animal or vegetable membranes, e.g., starch, glue, albumin, gelatin, silicic acid, proteins and other amorphous substances.

In recent years, Graham’s view about the classification of substances has undergone a great change, because it has been shown that every substance, irrespective of its nature, can be colloid under suitable conditions. Thus, we now talk of colloidal state, which may be defined as follows: A substance is said to be in the colloidal state, when it is dispersed in another medium in the form of very small particles having diameter of \(2 \times 10^{-4}\) to \(1 \times 10^{-7}\) cm.

**Types of solutions:** On the basis of size of particle dispersed size, the solutions may be following three types:

1. **True solution** is a “homogenous” solution containing dispersed particles of molecular size (i.e., less than 10 A or 1 nm), e.g., sodium chloride or glucose solution in water. The particles of solute (molecules/ions) are invisible even under ultramicroscope and can pass through an ordinary filter paper as well as animal/vegetable membrane.

2. **Suspension** is a “heterogeneous” mixture containing suspended insoluble particles of size greater than 1000 A or 100 nm. The particles of a suspension cannot pass through an ordinary filter paper as well as animal/vegetable membrane. The particles may be visible even to the naked eye, but are visible
3. **Colloidal solution** is a “heterogeneous” two phase system, in which a substance is distributed in colloidal state (i.e., of diameter 2X10^{-4} to 1X10^{-7} cm) in an insoluble medium. The particles of the dispersed substance in internal or discontinuous phase, are called dispersed phase; while insoluble medium or external phase, in which they are dispersed, it is called dispersion medium. Besides these, a colloidal solution may also contain a stabilizing agent – a substance which tends to keep the colloidal particles apart thereby avoiding their coalescence and consequent settling.

<table>
<thead>
<tr>
<th>S.no</th>
<th>Dispersed phase</th>
<th>Dispersion medium</th>
<th>Colloidal system</th>
<th>Examples</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Gas</td>
<td>Liquid</td>
<td>Foam</td>
<td>Foam, froth, soap sol, detergent sud</td>
</tr>
<tr>
<td>2</td>
<td>Gas</td>
<td>Solid</td>
<td>Solid foam</td>
<td>Rubber, biscuit, cake, bread, lava</td>
</tr>
<tr>
<td>3</td>
<td>Liquid</td>
<td>Gas</td>
<td>Liquid aerosol</td>
<td>Fog, cloud</td>
</tr>
<tr>
<td>4</td>
<td>Liquid</td>
<td>Liquid</td>
<td>Emulsion</td>
<td>Milk, cream</td>
</tr>
<tr>
<td>5</td>
<td>Liquid</td>
<td>Solid</td>
<td>Gel</td>
<td>Gel, curd, cheese, butter, pearl</td>
</tr>
<tr>
<td>6</td>
<td>Solid</td>
<td>Gas</td>
<td>Solid aerosol</td>
<td>Smoke, fume</td>
</tr>
<tr>
<td>7</td>
<td>Solid</td>
<td>Liquid</td>
<td>Sol</td>
<td>Indian ink, glue, gold sol</td>
</tr>
<tr>
<td>8</td>
<td>solid</td>
<td>solid</td>
<td>Solid sol</td>
<td>Black diamond, alloys, minerals</td>
</tr>
</tbody>
</table>

6. **Q. Define & classify colloids.**

**Colloids** (from the Greek words kola and eidos, which means gule and like respectively), which diffuse very slowly in solution and whose solution cannot pass through animal or vegetable membranes, e.g., starch, glue, albumin, gelatin, silicic acid, proteins and other amorphous substances.

In recent years, Graham’s view about the classification of substances has undergone a great change, because it has been shown that every substance, irrespective of its nature, can be colloid under suitable conditions. Thus, we now talk of colloidal state, which may be defined as follows: A substance is said to be in the colloidal state, when it is dispersed in another medium in the form of very small particles having diameter of 2X10^{-4} to 1X10^{-7} cm.

**Types of colloidal solutions:**
Sols or colloidal solutions are frequently classified, on the basis of their solvent affinity, into two classes:
1. Lyophilic or solvent – loving sols
2. Lyophobic or solvent – heating sols.

**Lyophilic or solvent – loving sols:** are those in which the dispersion medium possesses great affinity (or love) for the dispersed phase.
Examples: Starch, gelatin, glue, and agar sols in water.

**Characteristics:**
- They have tendency to pass directly into colloidal sol from, when dispersed phase is brought in contact with the dispersion medium.
- They are quite stable sols.
- They are reversible sols, i.e., solid residue of a lyophilic sol (obtained by evaporation) can be brought back to the sol from by merely shaking it with the dispersion medium.
- They are self-stabilized, due to the existence of strong attractive forces between the two phases.
- They are not easily precipitated by addition of electrolytes.

**Lyophobic (or solvent-heating) sols** are those in which there is no apparent affinity / interaction between the dispersion medium and the dispersed phase.
Examples: Gold sol, silver sol, and arsenic sulphide sol in water.

**Characteristics:**
- They cannot be prepared by bringing the dispersed phase in direct contact with dispersion medium.
- They are irreversible sols.
- They are comparatively much less stable, and are coagulated (or precipitated) more easily by addition of
even a little electrolyte.
- Their surface tension is almost identical to that of dispersion medium.
- For their stability, addition of stabilizer is essential.

<table>
<thead>
<tr>
<th>Property</th>
<th>Lyophilic sols</th>
<th>Lyophobic sols</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ease of preparation</td>
<td>Formed easily by mere shaking or warming the disperse phase in the dispersion medium (i.e., solvent). No stabilizer is needed to preserve them.</td>
<td>They are difficult to prepare. They are formed only by special methods. Addition of stabilizer is essential for their stability.</td>
</tr>
<tr>
<td>Nature of particle</td>
<td>Particles are solvent-loving and in the form of single molecules.</td>
<td>Particles are solvent-hating and consist of aggregates of large number of associated molecules.</td>
</tr>
<tr>
<td>Surface tension</td>
<td>Surface tension is, generally, lower than that of the medium itself.</td>
<td>Surface tension is almost the same as that of dispersion medium.</td>
</tr>
<tr>
<td>Viscosity</td>
<td>Viscosity is higher than that of solvent.</td>
<td>Viscosity is about the same as that of medium.</td>
</tr>
<tr>
<td>Visibility</td>
<td>The particles cannot be detected readily, even under ultra microscope, i.e., they show faint Tyndall effect.</td>
<td>The particles can be readily detected under ultra microscope, because they show distinct Tyndall effect.</td>
</tr>
<tr>
<td>Charge</td>
<td>The charge on the particles depends upon the pH of the medium and it may be +ve, or –ve or even neutral.</td>
<td>The particles have a characteristic either +ve charge, e.g., As₂S₃ sol particles possess –ve charge.</td>
</tr>
<tr>
<td>Migration in the electric field</td>
<td>The particles may migrate in either direction or even not at all, under the influence of an electric field.</td>
<td>The particles move in definite direction, i.e., either towards anode or cathode, depending on the type of their charge.</td>
</tr>
<tr>
<td>Action of electrolyte</td>
<td>Coagulation can be brought about only by the addition of large quantities of electrolytes.</td>
<td>The addition of even small quantity of electrolyte can cause coagulation.</td>
</tr>
<tr>
<td>Nature of its coagulate</td>
<td>The coagulation is reversible.</td>
<td>Coagulation is irreversible, i.e., coagulated mass cannot be dispersed into colloidal form.</td>
</tr>
<tr>
<td>Gel formation</td>
<td>Such sols can set to jelly.</td>
<td>These do not set to jelly.</td>
</tr>
<tr>
<td>Colloagative properties</td>
<td>They have relatively high osmotic pressure, depression of freezing point, elevation of boiling point, and lowering of vapour pressure.</td>
<td>They have high osmotic pressure, small depression of freezing point, less elevation of boiling point, and less lowering of vapour pressure.</td>
</tr>
<tr>
<td>Reversibility</td>
<td>Reversible.</td>
<td>Irreversible.</td>
</tr>
<tr>
<td>Example</td>
<td>Gelatin sol in water</td>
<td>As₂S₃ or Au sol in water</td>
</tr>
</tbody>
</table>

7. Q. Give a detailed account on the properties of Colloids.

**Optical properties or Tyndall effect:** If a powerful beam of light is passed through a colloidal solution (contained in a glass cell), placed in a dark room, the path of the beam becomes visible, when viewed through a microscope placed at a right angles to the path of light. The colloidal particles appear as pin-points of light moving against the dark background. This phenomenon is known as Tyndall effect and the microscope with a dark background, used for viewing the colloidal particles, is called ultra microscope.

Cause of Tyndall effect is believed to be due to scattering of light by the colloidal particles. The colloidal particles absorb the incident light energy, become self-luminous and scatter this absorbed light from their surfaces. As the intensity of scattering is maximum in the plane at right angles to the direction of incident beam, so the path becomes visible, when viewed from the sides. The molecules constituting a true solution do not scatter light, as their size is comparatively very small.
**Electrical properties:**

**Electrophoresis:** colloid particles (both lyophilic and lyophobic) are electrically charged either positive or negative. Table gives the kind of charge on some colloidal particles:

When a high potential gradient is applied between a U-tube, filled partly with a colloidal solution and rest with distilled water, the colloidal particles move towards oppositely charged electrode with a speed of the order of about 1 micron (10^-4 cm) per second per unit potential gradient. On reaching the electrode, they lose their charge and get coagulated or precipitated. The movement of the colloidal particles under the influence of an electric field is known as electrophoresis. If the movement of colloidal particles is towards cathode, the phenomenon is called cataphoresis as in case of negatively charged sols like As$_2$S$_3$.

**Electro-osmosis:** when an electric current is passed through colloidal solution in such a way that the dispersed particles are prevented from movement, it is observed that the dispersion medium moves. This phenomenon of movement of the dispersion medium of a colloidal solution, under the influence of an electric field, when the dispersed particles are prevented from moving, it called electro-osmosis.

**Isoelectric point:** Lyophilic colloids (solvent-loving) like albumin, gelatin, starch, etc., are positively charged in strongly acidic solution and negatively charged in alkaline solution. However, at a certain H$^+$ ion concentration (or pH), called the isoelectric point, the colloidal particles of a lyophilic move neither to the cathode nor to the
anode, under the influence of electric field. Hence, isoelectric point of a lyophilic sol is the pH (or H+ ion concentration) of the dispersion medium at which the dispersed particles are neutral and hence, they do not migrate, when subjected to an electric field. In fact, at the isoelectric point, coagulation of colloidal particles starts.

**Brownian motion:**

The molecules of dispersion medium are in a constant motion. These molecules keep on bombarding the colloidal particles. Occasional difference of impact forces causes a translator motion to the colloidal particles. These colloidal particles keep on moving in straight line until they encounter other collisions. Because of the frequent collisions, there is no preference of direction, direction changes with every collision. Thus, colloidal particles execute continuous, zigzag and random motion. This phenomenon was first noticed by Robert Brown (an English Botanist in 1827) when he examined colloidal solution under an ultra microscope and hence this motion is called the “Brownian motion”.

Brownian motion is rapid in particles of smaller sizes and in less viscous dispersion medium. Brownian motion disappears in coarse suspensions. This is because the bombardment of the molecules of the dispersion medium produces little effect on the particles of suspension. If a large number of molecules of dispersion medium, move in the vicinity of the suspended coarse particle and that too in the same direction, then a displacement comparable with the Brownian motion results, but this probability is very rare.

8. Q. Give a detailed account on the applications of colloidal chemistry.

**APPLICATION OF COLOIDS**

**In everyday life:** Colloids play an important role in our daily life. Protoplasm (out of which the plant cells and animal tissues are made) and blood (which flows through our veins) are all colloidal in character. The food (milk, butter, cheese, fruits, etc.) that we eat, the clothes and shoes that we wear are based on colloids. In fact, there is hardly any product that we use in everyday life, which does not depend on colloids.

**In analytical chemistry:**

(i) colloidal S, obtained by passing H2S in qualitative analysis, cannot be ordinarily filtered off, but it is coagulated by heating with the electrolyte like NH4NO3 or NH4Cl.

(ii) Micro analysis for detection of traces of noble metals in solution depends on the formation of their colloidal solution and observation of their colours.

(iii) Silica and alumina gels are used as adsorbent for gases and as drying agents in laboratory.

**In medicine:** Because of their easy assimilation and adsorption, the colloidal medicines are found to be much more effective, e.g.,

(i) argyrols and protargrol are colloidal sols of Ag and used as eye-lotions;

(ii) colloidal gold, calcium and iron are used as oral medicines as well as injectibles for raising the vitality of human system;

(iii) colloidal antimony is an effective medicine for kalazar;

(iv) Blood from minor wounds, cuts is stopped, by coagulation with alum or ferric chloride. The trivalent Al3+ or Fe3+ ions neutralize the negative charge on the albumioid particles, which constitute the blood, and thus coagulate it.

**In industry:** (a) Electrophoresis has been utilized in the following:
(i) **Smoke precipitation:** In big industrial cities, smoke is a nuisance, as it pollutes the atmosphere as well as injurious to health. Smoke is a negatively charged colloidal solution, consisting of carbon particles dispersed in air. For the precipitation of carbon particles of the smoke, it is passed through a chamber, provided with a highly positively charged metallic knob. The negatively charged smoke (or carbon) particles, on coming in contact with the knob, lose their charge and settle down on the floor of the chamber; while hot gases (free from the smoke) pass out to the chimney. The precipitated carbon is used as a by-product for making Indian ink, paints, etc.

(ii) **Removal of dirt from sewage:** The sewage of the towns consists of charged dirt particles dispersed in water. For effecting separation of dirt particles, sewage is passed through a system of two tanks, fitted with oppositely charged metallic electrodes. The suspended dirt particles get coagulated and deposited on the oppositely charged electrodes. The deposited dirt is the used as good manure.

(iii) **Purification of water:** When alum is added to impure water containing suspended negatively charged clay particles, bacterial, etc., the Al\(^{3+}\) ions (furnished by alum) brings about precipitation of negatively charged colloidal impurities; while the clear water is decanted off.

(iv) **Electroplating of rubber:** Latex (obtained from saps of certain trees, from which rubber is made) is a colloidal suspension of negatively charged rubber particles in water. Metals and wooden articles can be rubber-plated by making them anode in the electrophoresis of latex, when the negatively charged rubber particles get deposited on the articles.

(b) **Leather tanning** of leather is based on the mutual coagulation of oppositely charged colloids. The raw animal skin is positively charged colloidal system, consisting of proteins in the colloidal form. The extract of barks, wood, leaves, etc., is a negatively charged colloidal solution of tannin. When the two are mixed, in adequate proportions, mutual coagulation of two oppositely charged sols takes place and the surface of leather becomes hard, which does not putrefy easily.

(c) **In laundry:** Soap, etc., used for washing, yields a colloidal solution in water, which removes the dirt of the cotton, etc., by adsorption of greasy materials by emulsion formation.

(d) **Artificial rains** have been obtained by throwing electrically charged sand into clouds.

(e) **In warfare:** Animals charcoal is used in gas masks for adsorption of poisonous gases. Smoke screens, used in warfare, consist of colloidal titanium oxide particles dispersed in air.

In nature:

- The blue of sky, tails of comets, etc., are due to scattering of light by the colloidal particles of dust or smoke in air.
- The fertility of soils can also be explained on the basis of its colloidal properties.
- The formation of deltas in rivers is due to coagulation of negatively charged fine sand particles present in river water by the Na\(^+\), K\(^+\), Mg\(^{2+}\) and Ca\(^{2+}\) ions of sea water at the junction of two. The precipitated sand, etc., forms delta. This also causes self-purification of river.

9. Q. Define nano materials & discuss properties, preparation of nano materials.

**NANO MATERIALS**

Nano means \(10^{-9}\). A nanometre (nm) is one thousand millionth of a metre (i.e. \(10^{-9}\)). Atoms are extremely small and the diameter of a single atom can vary from 0.1 to 0.5 nm depending on the type of the element. For example, one carbon atom is approximately 0.15 nm in diameter. The radius of the atom can be considered as half the distance between neighbouring atoms when they are present in the solid phase.

To understand how small one nm is let us see few comparisons. A red blood cell is approximately 7,000 nm wide and a water molecule is almost 0.3 nm across. Quite often people make a comparison with a human hair, which is about 80,000 nm wide.

**What are Nanomaterials?**
All materials are composed of grains, which in turn comprise of many atoms. Depending on the size, these grains may be visible or invisible to the naked eye. Conventional materials have grains of size varying from hundreds of microns to centimeters. Any bulk material we take, its size can be expressed in three dimensions. Any planar material we take, its area can be expressed in two dimensions. Any linear material we take, its length can be expressed in one dimension. Nanomaterials could be defined as those materials which have structured components with size less than 100 nm at least in one dimension.

- Materials that are nanoscale in one dimension (and are extended in the other two dimensions) are layers, such as thin films or surface coatings.
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Nanoscience can be defined as the study of phenomena and manipulation of materials at atomic, molecular and macromolecular scales, where properties differ significantly from those at a larger scale.

Nanotechnology can be defined as the design, characterization, production and application of structures, devices and systems by controlling shape and size at the nanometre scale.

Physical Properties: How does the geometrical arrangement of atoms and their stability change with size?
Starting from the bulk, the first effect of reducing particle size is to create more surface sites i.e. surface to volume ratio increases. This changes the surface pressure and results in a change in the inter particle spacing.

Chemical Properties: The large surface-to-volume ratio, the variations in geometry and the electronic structure have a strong effect on catalytic properties. As an example, the reactivity of small clusters has been found to vary by orders of magnitude when the cluster size is changed by only a few atoms. Fig.4 shows this for the case of Fen clusters reacting with hydrogen.

Production of Nanomaterials
Materials can be produced that are nanoscale in one dimension (for example, very thin surface coatings), in two dimensions (for example, nanowires and nanotubes) or in all three dimensions (for example, nanoparticles). Nanomaterials can be synthesized by 'top down' techniques, producing very small structures from larger pieces of material. One way of doing this is mechanical crushing of solid into fine nanopowder (ball milling)' Nanomaterials may also be synthesized by 'bottom up' techniques, atom by atom or molecule by molecule. One way of doing this is to allow the atoms or molecules arrange themselves into a structure due to their natural properties e.g. Crystals grown.

Preparation: Now there are many known methods to produce nanomaterials. Let us study briefly few these methods.

i) Plasma arcing Plasma is an ionized gas. To produce plasma potential difference is applied across two electrodes. The gas yields up its electrons and gets ionized. Ionised gas (plasma) conducts electricity. A typical plasma arcing device consists of two electrodes. An arc passes from one electrode to the other. From the first electrode (anode) due to the potential difference electrons are emitted. Positively charged ions pass to the other electrode (cathode) pick up the electrons and are deposited to form nano particles. As a surface deposit, the depth of the coating must be only a few atoms. Each particle must be nanosized and independent. The interaction
among them must be by hydrogen bonding or Vander Waal’s forces. Plasma arcing is used to produce carbon nanotubes.

ii) Chemical Vapour Deposition (CVD): In this method nanoparticles are deposited from the gas phase. Material is heated to form a gas and then allowed to deposit on a solid surface, usually under vacuum condition. The deposition may be either physical or chemical. In deposition by chemical reaction new product is formed. Nanopowders of oxides and carbides of metals can be formed if vapors of carbon or oxygen are present with the metal.

Production of pure metal powders is also possible using this method. Now the metal is melted exciting with microwave frequency and vapourised to produce plasma at 1500°C. This plasma then enters the reaction column cooled by water where nanosized particles are formed.

Chemical vapour deposition can also be used to grow surfaces. If the object to be coated is introduced inside the chemical vapour, the atoms/molecules coated may react with the substrate atoms/molecules. The way the atoms/molecules grow on the surface of the substrate depends on the alignment of the atoms/molecules of the substrate. Surfaces with unique characteristics can be growth with this technique. (a) Hydrolysis (b) condensation and polymerization of monomers to form particles (c) agglomeration of particles. This is followed by the formation of networks which extends throughout the liquid medium and forms a gel. The rates of hydrolysis and condensation reactions are governed by various factors such as pH, temperature, H2O/Si molar ratio, nature and concentration of catalyst and process of drying. Under proper conditions spherical nanoparticles are produced. Nanoparticles prepared by sol-gel method are Si(OR)₃ where R is alkyl groups of various types.

iv) Electro-deposition: Electro deposition technique is used to electroplate a material. In many liquids called electrolytes (aqueous solutions of salts, acids etc.), when current is passed through two electrodes immersed inside the electrolyte, certain mass of the substance liberated at one electrode gets deposited on the surface of the other. By controlling the current and other parameters, it is possible to deposit even a single layer of atoms. Nano-structured films of copper, platinum nickel, gold etc. can be produced by electro-deposition. The films thus obtained are mechanically robust, highly flat and uniform. Since these films have larger surface areas, they exhibit quite different and favorable electrical properties. They have very wide range of applications. These include batteries, fuel cells, solar cells, magnetic read heads, etc.

v) Ball Milling: In ball milling, also called mechanical crushing, small balls are allowed to rotate around the inside of a drum and then fall on a solid with gravity force and crush the solid into nano-crystallites. Ball milling can be used to prepare a wide range of elemental and oxide powders. For example, iron with grain sizes of 10-30 nm can be formed. Other crystallites, such as iron nitriles, can be made using ammonia gas. A variety of inter-metallic compounds based on nickel and aluminium can be formed. Ball milling is the preferred method for preparing metal oxides.


Carbon Nanotubes (CNTs):
Carbon nanotubes were first observed by Sumio Iijima in 1991. So far we know only three forms of carbon, namely diamond, graphite, and amorphous carbon. Now we come to know that there is a whole family of other forms of carbon known as Carbon nanotubes, which are related to graphite. The molecular structure of graphite is one atom-thick a planar network of interconnected hexagonal rings of carbon atoms. In conventional graphite, the sheets of carbon are stacked on top of one another. They can easily slide over each other. That is why graphite is not hard, and can be used as a lubricant. When graphite sheets are rolled into a cylinder and their edges joined, they form carbon nanotubes. i.e. Carbon nanotubes are extended tubes of rolled graphite sheets.

Types of CNTs: A nanotube may consist of one tube of graphite, a one-atom thick single-wall nanotubes, or a number of concentric tubes called multiwalled nano-tubes. Both of these are typically a few nano-metres in diameter. There length may vary from several micro-metres to centi-metres. There are different types of CNTs, because the graphitic sheets can be rolled in different ways. The three types of CNTs are zigzag, Armchair, and chiral. It is possible to recognize type by analyzing their cross-sectional structure. Multi walled nanotubes can
come in an even more complex array of forms. Each concentric single-walled nanotube can have different structures, and hence there are a variety of sequential arrangements. The simplest sequence is when concentric layers are identical but differs in diameter. However, mixed variants are possible, consisting of two or more types of concentric CNTs arranged in different orders. These can have either regular layering or random layering. The structure of the nanotube influences its properties - including electrical and thermal conductivity, density, and lattice structure. Both type and diameter are important. The wider the diameter of the nano-tube, the more it behaves like graphite. The narrower the diameter of the nano-tube, the more its intrinsic properties depends upon its specific type.

**Carbon nanotubes have assumed an important role because of their novel chemical and physical properties.** They are mechanically very strong, flexible (about their axis), and can conduct electricity extremely-well. The helicity of the graphite sheet determines whether the CNT is a semiconductor or metallic. All of these remarkable properties give CNTs a range of potential applications: for example, in reinforced composites, sensors, nano-electronics and display devices. CNTs come in a variety of diameters, lengths, and functional group content. They are available for industrial applications in bulk (metric ton). Several CNT manufacturers have > 100 ton per year production capacity for multi walled nanotubes.

**Production of CNTs:** There are a number of methods of making CNT's. CNT's have probably been around us for a quite longer time but we didn't realize their existence. They may have been made during various carbon combustion and vapor deposition processes. But electron microscopy at that time was not advanced enough to distinguish them from other types of tubes. Now let us few methods presently adopted for the production of CNTs.

**a) Arc Method:** This method creates CNTs through arc-vaporization of two carbon rods placed end to end, separated by approximately 1mm, in an enclosure that is usually filled with inert gas at low pressure. Recent investigations have shown that it is also possible to create CNTs with the arc method in liquid nitrogen. A direct current of 50 to 100 A, driven by a potential difference of approximately 20 V, creates a high temperature discharge between the two electrodes. The discharge vaporizes the surface of one of the carbon electrodes, and forms a small rod-shaped deposit on the other electrode. Producing CNTs in high yield depends on the uniformity of the plasma arc, and the temperature of the deposit forming on the carbon electrode.

**b) Laser Method:** In 1996 CNTs were first synthesized using a dual-pulsed laser and achieved yields of >70wt% purity. Samples were prepared by laser vaporization of graphite rods with a 50:50 catalyst mixture of Cobalt and Nickel at 12000C in flowing argon. The initial laser vaporization pulse was followed by a second pulse, to vaporize the target more uniformly. The use of two successive laser pulses minimizes the amount of carbon deposited as soot. The second laser pulse breaks up the larger particles ablated by the first one, and feeds them into the growing nanotube structure. The CNTs produced by this method are 10-20 nm in diameter and up to 100m or more in length. By varying the growth temperature, the catalyst composition, and other process parameters, the average nanotube diameter and size distribution can be varied.

**c) Chemical Vapor Deposition(CVD):** Large amounts of CNTs can be formed by catalytic CVD of acetylene over cobalt and iron catalysts supported on silica or zeolite. The carbon deposition activity seems to relate to the cobalt content of the catalyst, whereas the CNTs' selectivity seems to be a function of the pH in catalyst preparation. Bundles of single walled nanotubes were also found among the multi walled nanotubes produced on the carbon/zeolite catalyst.. CNTs can be formed from ethylene. Supported catalysts such as iron, cobalt, and nickel, containing either a single metal or a mixture of metals, seem to induce the growth of isolated single walled nanotubes or single walled nanotubes bundles in the ethylene atmosphere. The production of single walled nanotubes, as well as double-walled CNTs, on molybdenum and molybdenum-iron alloy catalysts has also been demonstrated.
11. Q. To explain Nano chemistry & write some applications of nano materials.

NANO MATERIALS

Nano means $10^{-9}$. A nanometre (nm) is one thousand millionth of a metre (i.e. $10^{-9}$). Atoms are extremely small and the diameter of a single atom can vary from 0.1 to 0.5 nm depending on the type of the element. For example, one carbon atom is approximately 0.15 nm in diameter. The radius of the atom can be considered as half the distance between neighbouring atoms when they are present in the solid phase.

To understand how small one nm is let us see few comparisons. A red blood cell is approximately 7,000 nm wide and a water molecule is almost 0.3 nm across. Quite often people make a comparison with a human hair, which is about 80,000 nm wide.

What are Nanomaterials?

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Applications of Nanomaterials:

Nanoparticles are “the small particles with a big future”. Because of their extremely small particle size, they have extremely large specific surface area. Hence they are chemically very active. They are stronger and more ductile. They have electronic states quite different from those of bulk. In dispersed state nanoparticles are used as fillers, paints, magnetic recording media, Ferro fluids, drugs, phosphors, rocket propellants, fuel additives, etc.

In consolidate state nanoparticles are used as catalysts, and fuel cells, sensors, adsorbents, synthetic bone, self cleaning glass etc.

In ordered assembly form nanoparticles are used as quantum electronic devices, photonic crystals, DNA chips, biosensors etc.

In very dense phase nanoparticles are used in synthesis of flexible/dense ceramics and insulators, harder metals etc.

Materials Technology

Magnets made of nano-crystalline yttrium-samarium-cobalt possess unusual magnetic properties due to their extremely large grain interface area. High coercivity can be obtained because magnetization flips cannot easily propagate boundaries. This could lead to applications in motors, analytical instruments like magnetic resonance imaging (MRI).

Ceramics are hard, brittle and difficult to machine. However, with a reduction in grain size to the nanoscale, ceramic ductility can be increased. Zirconia, normally a hard, brittle ceramic, has even been rendered super plastic (for example, able to be deformed up to 300% of its original length)

* Nano-crystalline ceramics, such as silicon nitride and silicon carbide, have been used in such automotive
applications as high strength springs, ball bearings and valve lifters, because they can be easily formed and
machined, as well as exhibiting excellent chemical and high temperature properties.
They are also used as components in high-temperature furnaces.
* Nano-engineered membranes could potentially lead to more energy-efficient water purification processes,
notably in desalination by reverse osmosis.
* Nanosized titanium dioxide and zinc oxide are currently used in sun screens. They absorb and reflect ultra-
violet (UV) rays and yet are transparent to visible at light. Nanosized iron oxide is present in some lipsticks as a
pigment.
* An important use of nanoparticles and nano-tubes in composites. Composite materials combine one or more
separate components and are designed to exhibit overall the best properties of each component. Currently, carbon
fibers and bundles of multi-walled CNTs are used in composites having potential long-term applications
i A carbon nanoparticles act as fillers in a matrix; for example, they are used as a filler to reinforce car tyres. Clay
particle based composites containing plastics and nano-sized flakes of clay are also finding applications such as
use in car bumpers.
* Recently developed applications include the self-cleaning windows. Nano-coating of highly activated titanium
dioxide is highly hydrophobic (water repellent) and antibacterial. Coatings based on nano-particulate oxides
catalytically destroy chemical agents
* Wear and scratch-resistant hard coatings are significantly improved by nanoscale intermediate layers (or multi-
layers) between are hard outer layer and the substrate material. The intermediate layers give good bonding and
graded matching of elastic and thermal properties, thus improving adhesion.
* Improved control of porosity at the nanoscale has important applications. A range of enhanced textiles, such as
breathable, waterproof and stain resistant fabrics, have been enabled by this technique in variety of polymers and
in-organics.
* Cutting tools made of nano-crystalline materials, such as tungsten carbide, tantalum carbide and titanium
carbide, are more wear and erosion resistant, and last longer than their conventional (large grained) counter parts.
They are finding applications in the drills used to bore holes in circuit boards.
* Other novel, and more long-term, applications for nanoparticles lie in paints that change colour in response to
change in temperature or chemical environment, or paints that have reduced infrared absorptivity and so reduce
heat loss.
+ It is now possible to synthesis harder metals having hardness 5 times higher then normal metals using
nanoparticles-
* Flexible/dense ceramics and insulators have started replacing metals.
* Stronger, light ware resistant, tougher and flame retardant polymers are synthesized with nanoparticles as
fillers. They are used in replacement of body parts and metals.
* It is possible to produce unusual color paints using nanoparticles since nanoparticles exhibit entirely different
optical properties.
Smart magnetic fluids are used as vacuum seals, viscous dampers, cooling fluids, magnetic separators etc.

Nano-metallic colloids are used as film precursors.

Useful as magneto resistance spin valves.

**Information Technology**

Nano-scale fabricated magnetic materials also have applications in data storage. If the area required to record one piece of information can be shrunk in the nanoscale (and can be written and read reliably), the storage capacity of the disk can be improved dramatically. The devices on computer chips which operate using flows of electrons could use the magnetic properties of these electrons, called spin, with numerous advantages.

Coatings with thickness controlled at the nano or atomic-scale have been used in optoelectronic devices or in catalytically active and chemically functionalized surfaces.

Nanocrystalline zincselenide, zincsulphide, cadmiurnsulphide and lead telluride synthesized by sol-gel techniques are candidates for the next generation of light emitting phosphors, they will have huge market for displays.

CNTs are being investigated for low voltage field emission displays; their strength, sharpness, conductivity and inertness make them potentially very efficient and long-lasting emitters.

Nanoparticles are used for information storage.

Quantum electronic devices have started placing bulky conventional devices.

Nanodimensional photonic crystals are used in chemical/optical computers.

**Biomedicals**

Nanocrystalline zirconiumoxide (zirconia) is hard, wear resistant, and bio-compatible. If therefore presents an attractive alternative material for implants. It and other nano-ceramics can also be made as strong, light aero-gels by sol-gel techniques. Nano-crystalline silicon carbide is a candidate material for artificial heart valves primarily because of its low weight, high strength and inertness.

Bio-sensitive nanoparticles are used for tagging of DNA and DNA chips.

Controlled drug delivery is possible using nanotechnology. Diffusion of medicine through nano-porous polymer reservoir as per the requirement is very useful in controlling the disease.

Nano-structured ceramics readily interact with bone cells and hence find application as an implant.

**Energy storage material.**

Addition of nano-particulate ceria (ceriumoxide) to diesel fuel improves fuel the degradation of fuel economy by reducing consumption.

In Fuel cells, the external surface properties over time and the pore structure affect performance. The hydrogen used as the immediate fuel in cells is generated from hydrocarbons by catalytic reforming.

Metal nanoparticles are very useful in fabrication of ionic batteries. Infact, the ability to control properties by changing size, composition, or dimension shows that nanoscale materials will form the basis of a new class of atomically engineered materials with tailored properties.
ENERGY RESOURCES (UNIT-VI)

Q.No.1. define fuels? Classify it, discuss characteristic properties of fuels?

A fuel can be defined as any combustible substance which during combustion gives large amount of industrially or domestically useful heat.

The fuels have been classified according to their:
1. Occurrence (and preparation), and
2. The state of aggregation.

According to the first classification, we have:
A. natural or primary fuels, which are found in nature as such e.g., wood, peat, coal, petroleum, natural gas etc.
B. artificial or secondary fuels are those which are prepared from the primary fuels. For example, charcoal, coke, kerosene, diesel, petrol, coal gas, oil gas, producer gas, blast furnace gas, etc.

The second classification is based upon their state of aggregation like:
a) Solid fuels;
b) Liquid fuels, and
c) Gaseous fuels.

<table>
<thead>
<tr>
<th>Type of fuel</th>
<th>Natural or primary</th>
<th>Artificial or secondary</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solid</td>
<td>Wood, peat, lignite, dung, bituminous coal and anthracite coal</td>
<td>Charcoal, coke etc.</td>
</tr>
<tr>
<td>Liquid</td>
<td>Crude oil</td>
<td>Petrol, diesel and various other fractions of petroleum</td>
</tr>
<tr>
<td>Gaseous</td>
<td>Natural gas</td>
<td>Coal gas, oil gas, bio gas, water gas etc.</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>S.NO</th>
<th>Characteristic property of a fuel</th>
<th>Solid fuels</th>
<th>Liquid fuels</th>
<th>Gaseous fuels</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>example</td>
<td>Coal</td>
<td>Crude oil</td>
<td>Coal gas</td>
</tr>
<tr>
<td>2</td>
<td>Cost</td>
<td>Cheap</td>
<td>Costlier than solid fuels</td>
<td>Costly</td>
</tr>
<tr>
<td>3</td>
<td>Storage</td>
<td>Easy to store</td>
<td>Closed containers should be used for storing</td>
<td>Storage space required is huge and should be leak proof.</td>
</tr>
<tr>
<td>4</td>
<td>Risk towards fire hazards</td>
<td>Less</td>
<td>More</td>
<td>Very high, since these fuels are highly inflammable</td>
</tr>
<tr>
<td>5</td>
<td>Combustion rate</td>
<td>It is a slow process</td>
<td>Fast process</td>
<td>Very rapid and efficient</td>
</tr>
<tr>
<td>6</td>
<td>Combustion control</td>
<td>Cannot be controlled</td>
<td>Cannot be controlled or stopped when necessary</td>
<td>Controlled by Regulating the supply of air</td>
</tr>
<tr>
<td>7</td>
<td>Handling cost</td>
<td>High since labour is required in their storage &amp; transport.</td>
<td>Low, since the fuel can be transported through pipes</td>
<td>Low, similar to liquid fuels, these can be transported through pipes</td>
</tr>
<tr>
<td>8</td>
<td>Ash</td>
<td>Ash is produced and its disposal also possess problems</td>
<td>No problem of ash</td>
<td>No problem of ash</td>
</tr>
<tr>
<td>9</td>
<td>Smoke</td>
<td>Produce smoke invariably</td>
<td>Clean, but liquids associated with high carbon and aromatic fuels produce smoke</td>
<td>Smoke is not produced</td>
</tr>
<tr>
<td>10</td>
<td>Thermal efficiency</td>
<td>Least</td>
<td>High</td>
<td>Highest</td>
</tr>
<tr>
<td>11</td>
<td>Calorific value</td>
<td>Least</td>
<td>High</td>
<td>highest</td>
</tr>
<tr>
<td>12</td>
<td>Use in internal combustion engine</td>
<td>Cannot be used</td>
<td>Can be used</td>
<td>Can be used</td>
</tr>
</tbody>
</table>
Characteristics of good fuel: A good fuel should satisfy the following requirements:

- It should have a high calorific value per unit weight i.e. it should evolve a large amount of heat when a unit weight of it is burnt under the conditions in which it is to be used as a fuel.
- Its moisture content should be low, so that its heating value should be high.
- It should not produce harmful products like CO$_2$, SO$_2$, H$_2$S and other poisonous gases on burning since they pollute the atmosphere.
- A fuel should have low content of non-combustible matter in the form of ash or clinker. The presence of non-combustible matter will enhance the cost of storage, handling and disposal of the waste.
- In case of solid fuel, the size should be controllable so that it can be started or stopped.
- It should be economical and easily available.
- It should not give any offensive odour.
- An ideal fuel should have moderate ignition temperature. Normally low ignition temperature during storage and transport of fuel leads to fire hazards on the other hand, fuel with high ignition temperature is safe for storage, handling and transport.

Coal is highly carbonaceous matter and is regarded as a fossil fuel produced from large accumulations of vegetable debris and alternation of vegetable matter like plants etc. under certain favorable conditions by the action of heat and pressure over millions of years. Coal is mainly composed of carbon, oxygen, hydrogen and nitrogen.

Its formation can be explained by the following theories.

i) In-situ theory: this theory states that the coal formation took place at the same area where vegetation grew and accumulated originally. The great purity of coal appear more reasonable on the basis of this theory.

ii) Drift theory: according to this theory, trees when uprooted due climating conditions, in the deeper parts of the soil under transformation to coal due to high temperature, pressure absence of oxygen and presence of bacteria.

Qualities of good coal:

1. High calorific value.
2. Less moisture content
3. Low ash content
4. High calorific intensity
5. Uniform size of coal
6. Good coking quality
7. Less sulphur and phosphorous contents

Coal has been classified in several ways. The most common method of classification is on the basis of rank. From the origin of coal it is clear the wood, after a long interval of time and under certain conditions was converted into coal. The successive stages in the transformation of vegetable matter into coal are wood, peat, lignite, bituminous coal and anthracite coal.

Coal is classified based on the carbon content. The following is sequence of conversion.

Peat $\rightarrow$ Lignite $\rightarrow$ Bituminous $\rightarrow$ Anthracite

Peat: peat is regarded as the first stage in the transformation of wood into coal. Brown, fibrous, jelly like mass. Un-economical fuel. Contains 80-90% of H$_2$O. Composition C = 57%, H= 6%, O = 35%, ash 2.5 to 6%. Calorific value = 5400 kcal/kg.

Lignite: (Brown coal) soft, brown, colored lowest rank coal moisture content is 20 to 60%.
Composition: C = 60%, O = 20%, Calorific value = 6,500 to 7,100 k.cal/kg
**Bituminous coal:** Bituminous coal (common coal) Black to dark colored. This coal is largely used in industries for making metallurgical coke, coal gas and for domestic heating. It has laminated structure it is sub classified based on carbon content. Composition is % of C = 78 to 90%, VM = 20 to 45%, CV = 8000 to 8500 kcal/kg.

**Anthracite:** Highest rank of coal. These coals have very low volatile matter, ash & moisture. This coal is very hard, dense and lustrous in appearance. % of C = 98% has lowest volatile matter hardest, dense, lustrous. CV = 8650 to 8700 k.cal/kg.

**Grading:** Coal is graded as caking coal and coking coal.
- The coal which on heating becomes soft, plastic and fuse together are known as caking coal.
- The coal which on heating gives porous, hard and strong residues are called coking coals.

**Analysis of coal:**
The composition of coal varies widely and hence it is necessary to analyze the coal samples so that types of coal can be selected for a particular industrial use. The following methods of analysis can be utilized for the selection of coal.
1. **Proximate analysis:** This analysis records moisture, volatile matter, ash and fixed carbon as percentages of the original weight of the coal sample. Proximate analysis is of significance in commercial classification and industrial utilization of coal.
2. **Ultimate analysis:** This consists of determination of C, H, S, N and O. The ultimate analysis is essential for calculating heat balances in any process for which coal is employed as a fuel.

2. Q. Explain the determination & significance of the following constituents present in coal. i. Moisture ii. Volatile matter iii. Ash and iv. Fixed carbon. Or Explain in detail an account of proximate analysis of coal.

1. **Proximate analysis:** It is a quantitative analysis of the following parameters.
1. Moisture
2. Volatile matter
3. Ash
4. Fixed carbon
   1. **Moisture:** About 1 gram of finely powdered air-dried coal sample is weighed in a crucible. The crucible is placed inside an electric hot air-oven, maintained at 105 to 110°C. The crucible is allowed to remain in oven for 1 hour and then taken out, cooled in desiccators and weighed. Loss in weight is reported as moisture.  
   
   \[
   \text{Percentage of Moisture} = \frac{\text{Loss in weight}}{\text{Weight of coal taken}} \times 100
   \]

   2. **Volatile Matter:** The dried sample taken in a crucible in and then covered with a lid and placed in an electric furnace or muffle furnace, maintained at 925 ± 20°C. The crucible is taken out of the oven after 7 minutes of heating. The crucible is cooled first in air, then inside desiccators and weighed again. Loss in weight is reported as volatile matter on percentage-basis.  
   
   \[
   \text{Percentage of volatile matter} = \frac{\text{Loss in weight due to removal of volatile matter}}{\text{Weight of coal sample taken}} \times 100
   \]

   3. **Ash:** The residual coal sample taken in a crucible and then heated without lid in a muffle furnace at 700 ± 50°C for ½ hour. The crucible is then taken out, cooled first in air, then in desiccators and weighed. Hearing, cooling and weighing is repeated, till a constant weight is obtained. The residue is reported as ash on percentage-basis. Thus,  
   
   \[
   \text{Percentage of ash} = \frac{\text{Weight of ash left}}{\text{Weight of coal taken}} \times 100
   \]

   4. **Fixed carbon:**  
   \[
   \text{Percentage of fixed carbon} = 100 - \% \text{ of (Moisture + Volatile matter + ash)}
   \]
Importance of proximate analysis: Proximate analysis provides following valuable information’s in assessing the quality of coal.

1. **Moisture**: Moisture is coal evaporates during the burning of coal and it takes some of the liberated heat in the form of latent heat of evaporation. Therefore, moisture lowers the effective calorific value of coal. Moreover, it quenches the fire in the furnace, hence, lesser, the moisture content, better the quality of coal as a fuel. However, presence of moisture, up to 10%, produces a more uniform fuel-bed and less of “fly-ash”.

2. **Volatile matter**: A high volatile matter content means that a high proportion of fuel will distil over as gas or vapour, a large proportion of which escapes un-burnt, so, higher volatile content in coal’s undesirable. A high volatile matter containing coal burns with a long flame, high smoke and has low calorific value. Hence, lesser the volatile matter, better the rank of the coal.

3. **Ash**: Ash is a useless, non-combustible matter, which reduces the calorific value of coal. Moreover, ash causes the hindrance to the flow of air and heat, thereby lowering the temperature. Also, it often causes trouble during firing by forming clinkers, which block the interspaces of the grate, on which coal is being burnt. This in-turn causes obstruction to air supply; thereby the burning of coal becomes irregular. Hence, lower the ash content, better the quality of coal. The presence of ash also increases transporting, handling and storage costs. It also involves additional cost in ash disposal. The presence of ash also causes early wear of furnace walls, burning of apparatus and feeding mechanism.

4. **Fixed carbon**: Higher the percentage of fixed carbon, greater is it’s calorific and better the quality coal. Greater the percentage of fixed carbon, smaller is the percentage of volatile matter. This also represents the quantity of carbon that can be burnt by a primary current of air drawn through the hot bed of a fuel. Hence, high percentage of fixed carbon is desirable. The percentage of fixed carbon helps in designing the furnace and the shape of the fire-box, because it is the fixed carbon that burns in the solid state.

3. **Q. Explain the determination & significance of the following constituents present in coal. i. Total carbon ii. Hydrogen iii. Nitrogen iv. Sulphur and v. Oxygen.**

   **Or explain in detail an account of ultimate analysis of coal.**

**Ultimate analysis**: This is the elemental analysis and often called as qualitative analysis of coal. This analysis involves the determination of carbon and hydrogen, nitrogen, sulphur and oxygen.

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

   $$\text{C} + \text{O}_2 \rightarrow \text{CO}_2$$

   $$\text{2KOH} + \text{CO}_2 \rightarrow \text{K}_2\text{CO}_3 + \text{H}_2\text{O}$$

   $$\text{H}_2 + \frac{1}{2} \text{O}_2 \rightarrow \text{H}_2\text{O}$$

   $$\text{CaCl}_2 + 7 \text{H}_2\text{O} \rightarrow \text{CaCl}_2\cdot7\text{H}_2\text{O}$$

   **Percentage of C** = Increase in weight of KOH tube X 12 X 100  
   Weight of Coal sample taken X 44

   **And**  Percentage of H = Increase in weight of CaCl$_2$ tube X 2 X 100  
   Weight of Coal sample taken X 18

2. **Nitrogen**: About 1 gram of accurately weighed powdered coal is heated with concentrated H$_2$SO$_4$ along with K$_2$SO$_4$ (catalyst) in a long-necked Kjeldahl’s flask. After the solution becomes clear, it is treated with excess of KOH and the liberated ammonia is distilled over and absorbed in a known volume of standard acid solution. The unused acid is then determined by back titration with standard NaOH
solution. From the volume of acid used by ammonia liberated, the percentage of N in coal is calculated as follows:

\[
\text{Percentage of N} = \frac{\text{Volume acid} \times \text{Normality of acid} \times 1.4}{\text{Weight of coal taken}}
\]

3. **Sulphur**: Sulphur is determined from the washings obtained from the known mass of coal, used in bomb calorimeter for determination of a calorific value. During this determination, S is converted into Sulphate. The washings are treated with Barium chloride solution, when Barium-sulphate is precipitated. This precipitate is filtered, washed and heated to constant weight.

\[
\text{Percentage of Sulphur} = \frac{\text{Weight of BaSO}_4 \text{ obtained} \times 32 \times 100}{\text{Weight of coal sample taken in bomb} \times 233}
\]

4. **Ash**: The residual coal taken in the crucible and then heated without lid in a muffle furnace at 700 ± 50 C for ½ hour. The crucible is then taken out, cooled first in air, then in desiccators and weighed. Hearing, cooling and weighing is repeated, till a constant weight is obtained. The residue is reported as ash on percentage-basis.

Thus,

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

5. **Oxygen**: It is determined indirectly by deducting the combined percentage of carbon, hydrogen, nitrogen, sulphur and ash from 100.

\[
\text{Percentage of Oxygen} = 100 - \text{percentage of (C + H + S + N + Ash)}
\]

**Importance of ultimate analysis**:

- **Carbon and Hydrogen**: Greater the percentage of carbon and hydrogen, better is the coal in quality and calorific value. However, hydrogen is mostly associated with the volatile matter and hence, it affects the use to which the coal is put.

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

- **Sulphur**: Sulphur, although contributes to the heating value of coal, yet on combustion produces acids like SO\(_2\), SO\(_3\), which have harmful effects of corroding the equipments and also cause atmospheric pollution. Sulphur is, usually, present to the extent of 0.5 to 0.3% and derived from ores like iron, pyrites, gypsum, etc., mines along with the coal. Presence of sulphur is highly undesirable in coal to be used for making coke for iron industry. Since it is transferred to the iron metal and badly affects the quality and properties of steel. Moveover, oxides of sulphur pollute the atmosphere and leads to corrosion.

- **Ash**: Ash is a useless, non-combustible matter, which reduces the calorific value of coal. Moreover, ash causes the hindrance to the flow of air and heat, thereby lowering the temperature. Hence, lower the ash content, better the quality of coal. The presence of ash also increases transporting, handling and storage costs. It also involves additional cost in ash disposal. The presence of ash also causes early wear of furnace walls, burning of apparatus and feeding mechanism.

- **Oxygen**: Oxygen content decreases the calorific value of coal. High oxygen-content coals are characterized by high inherent moisture, low calorific value, and low coking power. Moreover, oxygen is a combined form with hydrogen in coal and thus, hydrogen available for combustion is lesser than
actual one. An increase in 1% oxygen content decreases the calorific value by about 1.7% and hence, oxygen is undesirable. Thus, a good quality coal should have low percentage of oxygen.

4. Q. a) What knocking? What are its adverse affects? How it is prevented?
   b) What is octane number & cetane number c) What is leaded petrol? Discuss its advantages and disadvantages.
   Ans: a) Premature and instantaneous ignition of petrol – air (fuel-air) mixture in a petrol engine, leading to production of an explosive violence is known as knocking.
   The resistance offered by gasoline to knocking cannot be defined in absolute terms. It is generally expressed on an arbitrary scale known as Octane rating.
   In an internal combustion engine, a mixture of gasoline vapor and air is used as a fuel. After the initiation of the combustion reaction, by spark in the cylinder, the flame should spread rapidly and smoothly through the gaseous mixture; thereby the expanding gas drives the piston down the cylinder. The ratio of the gaseous volume in the cylinder at the end of the suction-stroke to the volume at the end of compression ratio. The efficiency of an internal combustion engine increases with the compression ratio, which is dependent on the nature of the constituents present in the gasoline used. In certain circumstances (due to the presence of some constituents in the gasoline used), the rate of oxidation becomes so great that the last portion of the fuel air mixture gets ignited instantaneously, producing an explosive violence, known as knocking. The knocking results in loss of efficiency.

   Some of the effects of knocking or detonation are:
   1. Carbon deposits on liners and combustion chamber
   2. Mechanical damage
   3. increase in heat transfer
   4. Noise and roughness
   5. decrease in power output and efficiency
   6. preignition

   The knocking can be controlled or even stopped by the following methods:
   1. increasing engine r.p.m
   2. reducing pressure in the inlet manifold by throttling
   3. Retarding spark
   4. Making the ratio too lean or rich, preferably latter.
   5. Water injection increases the delay period as well as reduces the flame temperature.
   6. Use of high octane fuel can eliminates detonation. High octane fuels are obtained by adding additives known as dopes like tetraethyl lead, benzol, xylene to petrol

   Chemical structure and knocking: The tendency of fuel constituents to knock in the following order.
   Straight – chain paraffins > Branched- chain paraffins (i.e.,iso paraffins)> Olefines> Cycloparaffins (i.e.,naphthalenes)> aromatics.
   Thus, olefins of the same carbon chain length possess better anti knock properties than the corresponding paraffins and so on.

   Octane rating: It has been found that n-heptane,

   \[
   \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \\
   \text{H} - \text{C} - \text{C} - \text{C} - \text{C} - \text{C} - \text{C} - \text{C} - \text{H} \\
   \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{H}
   \]

   Knocks very badly and hence, its anti-knock value has arbitrarily been given zero. On the other hand, isoocetane (2: 2: 4 – trimethyl pentane). Gives very little knocking, so its anti-knock value has been given as ‘100’. Thus, octane number (or rating) of a gasoline (or any other internal combustion engine fuel) is the percentage of isoocetane in a mixture of isoocetane and n-heptane, which matches the fuel under test in knocking
characteristics. In this way, an “80-octane” fuel is one which has the same combustion characteristics as an 80:20 mixture of iso-octane and n-heptane.

**Octane number:** The knocking characteristic of a fuel can be easily expressed by octane number. The anti-knocking value of n-heptane is taken as 0 (zero) because n-heptane knocks very badly. Where as the anti-knock value of iso-octane is approximately taken as 100 because iso-octane knocks very little. Actually the octane number is the percentage of iso-octane in a mixture of n-heptane in order to matches the knocking characteristics of the fuel.

In this way, an “80-octane” fuel is one which has the same combustion characteristics as a 80:20 mixture in iso-octane and n-heptane. Gasoline with octane rating as high as 135 are used for aviation purposes. The octane number of poor fuels can be raised by the addition of extremely poisonous materials as tetra ethylene lead (C₂H₅)₄Pb and diethyl-telluride (C₂H₅)₂Te

\[
\begin{align*}
&\text{CH₃} \\
&\text{CH₃ – C – CH₂ – CH₂ – CH₃} \\
&\text{CH₃} \\
&\text{CH₃} \\
&\text{2,2,4- trimethyl pentane} \\
&\text{isooctane octane number 100 (good fuel)}
\end{align*}
\]

\[
\begin{align*}
&\text{CH₃ – (CH₂)₅ – CH₃} \\
&\text{n-heptane} \\
&\text{octane number zero (bad fuel)}
\end{align*}
\]

**Cetane Number:** The knocking characteristics of diesel oil are expressed in terms of cetane number. Cetane, C₁₆H₃₄, is a saturated hydrocarbon which has a very short ignition lag as compared to any commercial diesel fuel. Hence, its cetane number is taken as 100. On the contrary, Alpha-methyl naphthalene. C₁₁H₁₀ has a very long ignition lag as compared to any commercial diesel oil. Hence its cetane number is taken zero. Then the cetane number of diesel oil is defined as the percentage by volume of cetane in a mixture of cetane and Alpha-methyl naphthalene which exactly matches in its knocking characteristics with the oil under test.

Cetane number, it can indicate the purity of diesel oil.

The percentage of cetane in a mixture of cetane and n-hexadecane which has same ignition characteristics as the diesel fuel under test is certain number.

\[
\begin{align*}
&\text{2-methyl naphthalene} \\
&\text{Cetane number = 0 (bad fuel)}
\end{align*}
\]

\[
\begin{align*}
&\text{n-hexadecane} \\
&\text{Cetane number = 100 (good fuel)}
\end{align*}
\]

**Lead petrol:** The variety of petrol in which tetra ethyl lead is added, it is leaded petrol.

\[
\begin{align*}
&C₂H₅ \\
&C₂H₅ – Pb – C₂H₅ \\
&C₂H₅
\end{align*}
\]

**Tetra ethyl lead (TEL)**

**Advantages:** Usually petrol with low octane number is not good quality petrol. It often knocks (i.e., produces huge noise due to improper combustion). As a result of knocking, petrol is wasted; the energy produced cannot be used in a proper way.

When tetra ethyl lead is added, it prevents knocking, there by saves money and energy. Usually 1 to 1.5 ml of TEL is added per 1lit of petrol.

The mechanism of action is as follows:

First TEL will be transformed into finely divided particles of PbO which looks like a cloud. This takes place in the cylinder. Then the PbO particles react with hydrocarbon peroxide molecules formed, thus slowing down the oxidation process and prevent early detonation. Thus either knocking may be stopped or greatly reduced.

**Disadvantages:** Deposits of PbO are harmful to engine. So PbO must be eliminated from the engine. For this purpose, little amount of ethylene dibromide is added to petrol. It converts the harmful PbO to volatile PbBr₂ and eliminated through exhaust. Presence of any sulphur compounds reduces the efficiency of TEL.
5. Q. Write a short note on refining of petroleum products & write a note on synthetic petrol.

Refining of petroleum:

Crude oil obtained from the mine is not fit to be marked. It contains a lot of soluble and insoluble impurities which must be removed. Previously the purification of crude oil is done by simple fractional distillation. Further treatment of the products is done by refining. Refining can be defined as the process by which petroleum is made free of impurities, division of petroleum into different fractions having different boiling points and their further treatment to impart specific properties.

Refining of petroleum is done in different stages:

a. Removal of solid impurities: The crude oil is a mixture of solid, liquid and gaseous substances. This is allowed to stand undisturbed for some time, when the heavy solid particles settle down and gases evaporate. The supernant liquid is then centrifuged where in the solids get removed.

b. Removal of water (Cottrell's process): The crude oil obtained from the earth's crust is in the form of stable emulsion of oil and brine. This mixture when passed between two highly charged electrodes will destroy the emulsion films and the colloidal water droplets coalesce into bigger drops and get separated out from the oil.

c. Removal of harmful impurities: In order to remove sulphur compounds in the crude oil. It is treated with copper oxide. The sulphur compounds get converted to insoluble copper sulphide, which can be removed by filtration. Substances like NaCl and MgCl₂ it present will corrode the refining equipment and result in scale formation. These can be removed by techniques like electrical desalting and dehydration.

d. Fractional distillation: Heating of crude oil around 400°C in an iron retort, produces hot vapor which is allowed to pass through fractionating column. It is a tall cylindrical tower containing a number of horizontal stainless trays at short distances and is provided with small chimney covered with loose cap. As the vapors go up they get cooled gradually and fractional condensation takes place. Higher boiling fraction condenses first later the lower boiling fractions.

Synthetic petrol: because of the increasing of petrol, the synthetic methods of preparation of petrol gain more importance. The important processes commonly used for synthesis of petrol are

1. **Fischer-tropsch method**: This method was developed by Franz Fischer & Hans tropsch (German scientists). The raw material is the hard coke which is converted into water gas (CO + H₂) by passing steam over red hot coke.

The water gas so obtained is mixed with hydrogen. This mixture after the removal of impurities is heated in a furnace maintained at a temperature of 200 – 300 °C and a pressure of 30 atm. The mixture is then led to converter containing the catalyst consisting of Fe, Ni or CO. The product formed depends upon the catalyst used. A cobalt catalyst gives more olefins. Iron oxide with K₂CO₃ as promoter gives heavier hydrocarbons than those obtained from iron oxide and Na₂CO₃. Mixed catalysts such as cobalt magnesia are used to produce high-grade diesel fuel from the enriched water gas.

In general, the mechanism of the reactions can be represented as:

\[
\text{Ni or Co} \\
n\text{CO} + 2n\text{H}_2 \rightarrow C_n\text{H}_{2n} + n\text{H}_2\text{O} \\
n\text{CO} + (2n + 1)\text{H}_2 \rightarrow C_n\text{H}_{2n-2} + n\text{H}_2\text{O}
\]

The reactions taking place in the converter are exothermic, and the heat thus evolved raises the temperature of the coming out mixture, which is then led through cooling water and hence gets cooled. In the modern synthetic process the catalytic chamber is provided with tubes through which cold water is circulated. The products are then passed to a fractionating column and separated into different fractions such as heavy oil, kerosene oil and gasoline. The heavy oil can be reused for cracking to get more gasoline.

2. **Bergius process**: this process also known as hydrogenation of coal. This method is introduced by Bergius (German). In this process the low ash is finely powdered and turned into a paste using heavy oil and a catalyst (5% iron oxide or nickel oleate) is mixed with it. The paste is then heated in a converter maintained at a temperature of 350 – 500°C and mixed with H₂ under a pressure of 200 – 250 atmospheres for 1 ½ hours. Initially hydrogen combines with the different impurities like S, N, O present along with C in the coal i.e. H₂ +

\[
\text{S} \rightarrow \text{H}_2\text{S} \\
\text{H}_2 + \text{O} \rightarrow \text{H}_2\text{O} \\
3\text{H}_2 + \text{N}_2 \rightarrow 2\text{NH}_3
\]
The combination of the hydrogen with the carbon of the coal yields various hydrocarbons from wax to gases, which on cracking yield lower hydrocarbons. The vapours so obtained are condensed to give crude oil which is fractionated in a fractionating still resulting in the formation of gasoline or petrol, middle oil and heavy oil. The top fraction is condensed, and synthetic gasoline is recovered. The middle oil is then hydrogenated in presence of a solid catalyst to give more gasoline and the heavy oil fraction is recycled to make a paste with fresh batch of coal powder. The yield of gasoline is about 60\% of the coal dust used.

6. Q. What is cracking? Discuss fixed bed catalytic cracking & Moving bed method? Or discuss catalytic cracking.

Decomposition of larger hydrocarbon molecules to smaller molecules is cracking.

\[
\text{Cracking}\quad \text{Ex.}\quad \begin{array}{c}
\text{C}_{10}\text{H}_{12} \\
\text{Decane}
\end{array} \quad \rightarrow \quad \begin{array}{c}
\text{C}_5\text{H}_{12}\quad \text{C}_5\text{H}_{10}
\end{array}\quad \text{Pentane}\quad \text{Pentene}
\]

Cracking is mainly two types:

a. \textbf{Thermal cracking of pyrolysis:} If the cracking takes place at high temperature then it is thermal cracking. It may take place at liquid phase or at vapour phase.

The liquid phase cracking takes place at 475\(^\circ\)C to 530\(^\circ\)C at a pressure 100kg/cm\(^2\). While the vapor phase cracking occurs at 600 to 650\(^\circ\)C at a low pressure of 10 to 20 kg/cm\(^2\).

b. \textbf{Catalytic cracking:} If the cracking takes place due to the presence of catalyst than it is named as catalytic cracking. Catalytic cracking may be fixed bed type or moving bed type.

\textbf{Fixed bed catalytic cracking:} The oil vapours are heated in a pre-heater to cracking temperatures (420 – 450 \(^\circ\)C) and then forced through a catalytic chamber maintained at 425 – 450 \(^\circ\)C and 1.5 kg/cm\(^2\) pressure. During their passage through the tower, about 40\% of the charge is converted into gasoline and about 2 – 4\% carbon is formed. The latter adsorbed on the catalyst bed. The vapour produced is then passed through a fractionating column, where heavy oil fractions condense. The vapours are then led through a cooler, where some of the gases are condensed along – with gasoline and uncondensed gases move on. The gasoline containing some dissolved gases is then sent to a ‘stabilizer’, where the dissolved gases are removed and pure gasoline is obtained.

The catalyst, after 8 to 10 hours, stops functioning, due to the deposition of black layer of carbon, formed during cracking. This is re-activated by burning off the deposited carbon. During the re-activated interval, the vapours are diverted through another catalyst chamber.
Moving-bed catalytic cracking: The solid catalyst is very finely powdered, so that it behaves almost as a fluid, which can be circulated in gas stream. The vapours of cracking stock mixed with fluidized catalyst is forced up into a large reactor ‘bed’ in which cracking of the heavier into lighter molecules occurs. Near the top of the reactor, there is a centrifugal separator, which allows only the cracked oil vapours to pass on to the fractionating column, but retains all the catalyst powder in the reactor itself. The catalyst powder gradually becomes heavier, due to coating with carbon, and settles to the bottom, form where it is forced by an air blast to regenerator it maintained at 600 °C.

In regenerator, carbon is burnt and the regenerated catalyst then flows through a stand-pipe for fixing with fresh batch of incoming cracking oil. At the top of the regenerator, there is a separator, which permits only gases like CO₂ to pass out, but holds back catalyst particles.

Natural gas: The natural gas is obtained from the wells dug in the earth during mining of petroleum. It is mainly composed of methane and small quantities of ethane along with other hydrocarbons. If the lower hydrocarbons are present the gas is called dry gas or lean gas, but if the hydrocarbons having the higher molecular weights are present the gas is known as rich gas or wet gas. It is also known by the name of marsh gas as a major portion of it is contributed by methane. The average composition of natural gas is as follows:

- Methane (CH₄) – 88.5%
- Ethane (C₂H₆) – 5.5%
- Propane (C₃H₈) – 3.7%
- Butane (C₄H₁₀) – 1.8%
- pentane, H₂, CO, CO₂ and higher hydrocarbons – 0.5%

The calorific value of natural gas varies from 8000 – 14000 k.cal/m³. Natural gas is subjected to various treatments before it reaches the consumer. For example sour natural gas contains appreciable quantities of H₂S which can be removed by scrubbing with monoethanolamine.

\[ \text{H}_2\text{S} + 2 \text{HO-CH}_2\text{-CH}_2\text{-NH}_2 \rightarrow [\text{HO-CH}_2\text{-CH}_2\text{-NH}_2]^2\cdot\text{H}_2\text{S} \]

On heating, H₂S is liberated. Natural gas is an excellent domestic fuel which can carry to long distances in pipelines as town gas in U.S., U.K. and Mumbai highway and also as an industrial fuel. It is also used for manufacturing a number of chemicals like carbon black, methanol, and formaldehyde etc. methane on
microbiological fermentation give synthetic proteins which are used as animal feed. It is also used for generation of electricity in fuel cells. Natural gas is also used as a source of H\textsubscript{2}. Hence ammonia can be made by reacting N\textsubscript{2} with H\textsubscript{2} obtained from natural gas.

**Analysis of fuel gas:**
Gases after combustion contain CO, CO\textsubscript{2}, N\textsubscript{2} etc. in order to know the exact details about any fuel it is essential to analyze the fuel gases. The mixture of gases mostly CO\textsubscript{2} issuing out of the combustion chamber is called fuel gas. The efficiency of combustion can be well understood by the analysis of fuel gas. For instance, if the presence of CO is indicated then carbon is suffering incomplete combustion due to insufficient supply of oxygen. But if the analysis shows the excess of CO\textsubscript{2}, more so of O\textsubscript{2}, it implies that oxidation is complete and the supply of oxygen may be excessive. The analysis of fuel gases is carried out with the help of Orsat’s apparatus.

**7. Q. With a neat diagram describe the Orsat's gas analysis method.**
**Ans: Orsat’s apparatus:** It consists of water – jacketed measuring burette, connected in series to a set of three absorption bulbs, through stop cocks. The other end is provided with a three way stop cock, the free end of which is further connected to a U – tube packed with glass wool (for avoiding the incoming of any smoke particles, etc.) The graduated burette is surrounded by a water jacket to keep the temperature constant of gas during the experiment. The lower end of the burette is connected to a water reservoir by means of a long rubber tubing. The absorption bulbs are usually filled with glass tubes, so that the surface area of contact between the gas and the solution is increased.

![Diagram of Orsat's apparatus](image)

The absorption bulbs have solutions for the absorption of CO\textsubscript{2}, O\textsubscript{2} and CO respectively. First bulb has potassium hydroxide solution (250 g KOH in 500ml of boiled distilled water), and it absorbs only CO\textsubscript{2}. The second bulb has solution of alkaline pyrogallic acid (25 g pyrogallic acid + 200g KOH in 500 ml of distilled water) and it can absorb CO\textsubscript{2} and O\textsubscript{2}. The third bulb contains ammonium cuprous chloride (100g cuprous chloride + 125ml liquor ammonia + 375 ml of water) and it can absorb CO\textsubscript{2}, O\textsubscript{2} and CO.

Hence, it is necessary that the flue gas it passed first through potassium hydroxide bulb, where CO\textsubscript{2} is absorbed, then through alkaline pyrogallic acid bulb, when only O\textsubscript{2} will be absorbed (because CO\textsubscript{2} has already been removed) and finally through ammonical cuprous chloride bulb, where only CO will be absorbed.

**Working:**
**Step 1:** To start with, the whole apparatus is thoroughly cleaned, stoppers greased and then tested for air tightness. The absorption bulbs are filled with their respective solutions to level just below their rubber connections. Their stop cocks are then closed. The jacket and leveling reservoir are filled with water. There three way stop cock is opened to the atmosphere and reservoir is raised, till the burette is completely filled with water and air is excluded from the burette. The three way stop cocks is now connected to the flue gas supply and the reservoir is lowered to draw in the gas, to be analyzed, in the burette. However, the sample gas mixed with some air present in the apparatus. So the three way stop cock is opened to the atmosphere, and the gas expelled out by raising the reservoir. This process of sucking and exhausting of gas is repeated 3-4 times, so as to expel the air from the capillary connecting tubes etc. Finally, gas is sucked in the burette and the volume of the flue gas is adjusted to 100ml at atmospheric pressure. For adjusting final volume, the three way stop cock is opened to atmosphere and the reservoir is carefully raised, till the level of water in it is the same as in the burette, which stands at 100ml mark. The three ways stop cock is then closed.

**Step 2:** The stopper of the absorption bulb, containing caustic potash solution, is opened and all the gas is forced into the bulb by raising the water reservoir. The gas is again sent to the burette. This process is repeated several times to ensure complete absorption of CO$_2$ [KOH solution]. The unabsorbed gas is finally taken back to the burette, till the level of solution in the CO$_2$ absorption bulb stands at the fixed mark and then, its stop cock is closed. The levels of water in the burette and reservoir are equalized and the volume of residual gas is noted. The decrease in volume gives the volume of CO$_2$ in 100ml of the gas sample.

**Step 3:** The volumes of O$_2$ and CO are similarly determined by passing the remaining gas through alkaline pyrogalllic acid bulb and ammonical cuprous chloride bulb respectively. The gas remaining in burette after absorption of CO$_2$, O$_2$ and CO is taken as nitrogen.

**Calorific value:** The prime property of a fuel is its capacity to supply heat. Fuels essentially consists of carbon, hydrogen, oxygen and some hydrocarbons and the heat that a particular fuel can give is due to the oxidation of carbon and hydrogen. Normally when a combustible substance burns the total heat depends upon the quantity of fuel burnt, its nature, air supplied for combustion and certain other conditions governing the combustion. Further the heat produced is different for different fuels and is termed as its calorific value.

Calorific value of a fuel may be defined as “the total quantity of heat liberated, when a unit mass (or volume) of a fuel is burnt completely”. Or

“Calorific value is the amount of heat liberated by the complete combustion of a unit weight of the fuel and in usually expressed as cal gm$^{-1}$ or kcal gm$^{-1}$ or B.Th.U. Or

The calorific value of a fuel can be defined as “the total quantity of heat liberated when a unit mass of the fuel is completely burnt in air or oxygen”.

There are different units for measuring the quantity of heat. They are:

1. Calorie
2. Kilocalorie
3. British thermal unit (B.Th.U)
4. Centigrade heat unit (C.H.U)

**1. Calorie:** It is the amount of heat required to increase the temperature of 1 gram of water through one degree centigrade.

**2. Kilocalorie:** This is the unit of heat in metric system, and is defined as the quantity of heat required to raise the temperature of one kilogram of water through one degree centigrade.

\[1 \text{ k.cal} = 1000 \text{ cal}\]
\[1 \text{ k.cal} = 3.968 \text{ B.Th.U}\]

**3. British thermal unit (B.Th.U):** This is the unit of heat in English system, it is defined as “the quantity of heat required to increase the temperature of one pound of water through of one degree of Fahrenheit.”

\[1 \text{ B.Th.U} = 252 \text{ cal} = 0.252 \text{ k.cal}\]
4. Centigrade heat unit (C.H.U): It is the quantity of heat required to raise the temperature of one pound of water through one degree centigrade.

\[1 \text{ k.cal} = 3.968 \text{ B.Th.U} = 2.2 \text{ C.H.U}\]

**Inter conversion of various units of heat:**

On the basis that 1 kg = 2.2 lb and 1 °C = 1.8 °F we have

\[1 \text{ k.cal} = 1000 \text{ cals} = 3.968 \text{ B.Th.U} = 2.2 \text{ C.H.U}\]

\[1 \text{ B.Th.U} = 252 \text{ cals}\]

**Units of calorific value:**

For solid or liquid fuels: cal/g or k.cal/kg, B.Th.U/lb

For gaseous fuels: k.cal/cubic meter or k.cal/m³

B.Th.U/ft³ or B.Th.U/cubic feet

**Relation between various units:**

\[1 \text{ k.cal/kg} = 1.8 \text{ B.Th.U/lb} = 1 \text{ cal/g}\]

\[1 \text{ k.cal/m}^3 = 0.1077 \text{ B.Th.U/ft}^3\]

\[1 \text{ B.Th.U/ft}^3 = 9.3 \text{ k.cal/m}^3\]

**Gross calorific value** is the heat liberated when a unit quantity of fuel is completely burnt and the products of combustion are cooled to room temperature. This heat includes the latest heat of condensation of water. Because when a fuel containing hydrogen is burnt, the hydrogen present is converted to steam. As the products of combustion are cooled to room temperature, the steam gets condensed into water and the latent heat is evolved. Thus the latent heat of condensation of steam, so liberated, is included in the gross calorific value.

**Higher calorific value or gross calorific value** is defined as the total amount of heat liberated, when unit mass or unit volume of the fuel has been burnt completely and the products of combustion are cooled down to 60 °F or 15 °C.

**Net calorific value or lower calorific value:** lower calorific value is defined as “the net heat produced, when unit mass or unit volume of the fuel is burnt completely and the combustion products are allowed to escape. Net calorific value is the gross calorific value excluding the latent heat of condensation of water (the weight of water formed is nine times the weight of hydrogen in the fuel).

Therefore,

\[\text{LCV or NCV} = \text{HCV} – \text{Latent heat of water vapour formed}\]

Net calorific value = Gross calorific value – (Mass of hydrogen per weight of fuel burnt x 9 x latent heat of vaporization of water).

Latent heat of steam is 587 kcal/g.

\[
\frac{H}{100} \\
= \text{Gross calorific value} – 52.83 \times \%H
\]

Where \(\% H\) = percentage of hydrogen.

The gross and net calorific values of coal can be calculated by bomb calorimeter.

**Bomb calorimeter:** It consists of a strong cylindrical stainless steel bomb in which the combustion of fuel is made to take place. The bomb has a lid, which can be screwed to the body of bomb so as to make a perfect gas-tight seal. The lid is provided with two stainless steel electrodes and an oxygen inlet value. To one of the electrode, a small ring is attaches. In this ring, a nickel or stainless steel crucible can be supported. The bomb is placed in a copper calorimeter, which is surrounded by an air-jacket and water-jackets to prevent heat losses due to radiation. The calorimeter is provided with an electrically operated stirrer and Beckmann’s thermometer, which can read accurately temperature difference upto 1/100th of a degree.
Working: A known mass (0.5 or 1 gram) of the given fuel is taken in clean crucible. The crucible is then supported over the ring. A fine magnesium wire, touching the fuel sample, is then stretched across the electrodes. The bomb lid is tightly screwed and bomb filled with oxygen to 25 atmospheric pressure. The bomb is then lowered into copper calorimeter, containing a known mass of water. The stirrer is worked and initial temperature of the water is noted. The electrodes are then connected to 6-volt battery and circuit completed. The sample burns and heat is liberated. Uniform stirring of water is continued and the maximum temperature attained is recorded.

Calculations:
Let mass of fuel sample taken in crucible = \( x \) g
Mass of water in the calorimeter = \( W \) g
Water equivalent in g of calorimeter + Stirrer + thermometer + bomb, etc. = \( w \) g
Initial temperature of water in calorie meter = \( T_1 \)°C
Final temperature of water in calorie meter = \( T_2 \)°C
Higher calorific value of fuel = \( L \) cal/g
Heat liberated by burning of fuel = \( xL \)
And heat absorbed by water + apparatus = \((W + w) (T_2 – T_1)\)
But heat liberated by the fuel = Heat absorbed by water and apparatus.
\[ xL = (W + w) (T_2 – T_1) \]

or HCV of fuel (Gross calorific value) = \( \text{GCV} = \frac{(W + w) (T_2 – T_1)}{x} \) cal/g  .............(1)

If ‘H’ is the percentage of hydrogen in fuel
\[ \frac{9H}{100} \] g = mass of \( H_2O \) from 1 gm of fuel = 0.09 H gram.

Heat taken by water in forming steam = \( 0.09 H \times 587 \) cal.  \[ \text{[Latent heat of steam = 587 cal/g]} \]

LVC (or Net calorific value) = HVC – latent heat of water formed
\[ = (L – 0.09 H \times 587 \text{ (cal/g)}) \]  ..........(2)

After corrections, we get more accurate results,
\[ L = \frac{(W+w) (T_2 – T_1 + \text{cooling correction}) – (\text{Acid + fuse correction})}{x} \] cal/g

Mass of fuel (\( x \))

8. Q. a) How calorific value of a gaseous fuel is determined by Junker’s gas calorimeter. Describe the experiment with a neat diagram.
Ans: a) Calorific value of a fuel may be defined as “the total quantity of heat liberated, when a unit mass (or volume) of a fuel is burnt completely”.

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Calorific value of gaseous fuel can be determined by using Junker's calorimeter; it consists of a vertical cylindrical combustion chamber where combustion of gaseous fuel can be carried out with the help of Bunsen burner. The supply of gaseous fuel is regulated with the help of pressure governor. The volume of gas, flowing in a particular time, is measured with the help of gasometer. The combustion chamber is surrounded by an annular water space. Inside the outer flues, heat exchanger coil are also fitted. Radioactive and convective heat loss from the calorimeter is prevented with the help of outer jacket which is chromium plated. Moreover, the outer jacket contains air which is very good heat insulator. Around the combustion chamber, there is an annular space where water is made to circulate. At the appropriate places there are the openings where thermometers are placed for measuring the temperatures of the inlet and outlet water.

A known volume of gas is burned in excess of air at a constant rate in combustion chamber in such a manner that all the heat produced is absorbed in water. Water is flowing at a constant rate in annular space around the combustion chamber. The increase in the temperature of the water is measured and the heat evolved from the burning of the gas can be readily calculated. The weight of water flowing is also recorded for the calculation of calorific value of gaseous fuel.

Let

\[ V = \text{Volume of gas burnt in certain time } t \text{ at S.T.P.} \]
\[ T_1 = \text{Temperature of incoming water,} \]
\[ T_2 = \text{Temperature of outgoing water,} \]
\[ W = \text{Weight of water collected in that time } t. \]

Then, Higher calorific value (HCV) = \( \frac{W(T_2 - T_1)}{V} \) kcal/m\(^3\)

Now suppose, \( m \) = mass of steam condensed in certain time \( t \) in graduated cylinder from \( V \) m\(^3\) of gas. And as latent heat of steam = 587 kcal/kg.

Thus, lower calorific value (LCV) = \( \frac{[HCV - m \times 587]}{V} \) kcal/m\(^3\)

6.b) Mass of cooling water = 25, \( T_2 = 30 \), \( T_1 = 25 \), \( V = 0.09 \) m\(^3\); \( m = 0.02 \);

\[ \frac{W(T_2 - T_1)}{V} = \frac{25(30-25)}{0.09} = 1388.88 \]
\[ M = 0.02 \text{ kg (water condensed)} \]
\[ V = 0.09 \text{ m}^3 \]
Combustion: Combustion may be defined as the exothermic chemical reaction, which is accompanied by heat and light. It is the union of an element or a compound with oxygen.

Example: C(s) + O\(_2\)(g) \(\rightarrow\) CO\(_2\) (g) + 97 kcal

In common fuels it involves the burning of carbon and hydrogen in air and also to a much smaller extent of sulphur.

The presence of moisture in coal is undesirable, because it causes waste of heat; moisture may be present in coal naturally or by adding i.e. moisturing the coal before use. The presence of some sort of moisture in coal helps to keep the temperature of the fire bars low and prevents the formation of clinkers. The excess presence of moisture leads to heavy smoking and leads to slow starting of combustion process. Optimum free moisture content is 7 to 9% when coal has minimum density. The presence of moisture in combustion makes the combustion process successful.

9. the percentage composition of a sample of coal found to contains C = 76%, H\(_2\) = 5.2%, O\(_2\) = 12.8%, N\(_2\) = 2.7%, S = 1.2% and ash = 2.2%. Calculate the minimum a. weight, b. volume of air at STP, required for complete combustion of 1 kg of coal and % composition by weight of dry products

Answer:

1. Weights of elements per kg of fuel:
   - C = 76% = 0.76 kg
   - H\(_2\) = 5.2% = 0.052 kg
   - O\(_2\) = 12.8% = 0.128 kg
   - N\(_2\) = 2.7% = 0.027 kg
   - S = 1.2% = 0.012 kg
   - Ash = 2.2% = 0.022 kg

2. Weight of oxygen need for
   - C = 0.76 x 32 = 2.026 kg
     \(\frac{12}{2}\)
   - H\(_2\) = 0.052 x 16 = 0.416 kg
     \(\frac{2}{32}\)
   - S = 0.012 x 32 = 0.012 kg
   - Total weight of O\(_2\) needed = 2.026 + 0.416 + 0.012 = 2.474 kg

3. Weight of dry products of combustion for
   - C = 0.76 x 44 = 2.786 kg (CO\(_2\))
     \(\frac{12}{2}\)
   - N\(_2\) = 0.027 kg (N\(_2\))
   - S = 0.012 x 64 = 0.024 kg (SO\(_2\))
     \(\frac{32}{32}\)
   - Weight of oxygen to be supplied = weight of oxygen needed – weight of oxygen present
     = 2.474 – 0.128
     = 2.326 kg
   - Weight of air needed = 2.326 x 100 = 10.113 kg
Weight of nitrogen supplied with air = Weight of air – weight of oxygen
= 10.113 – 2.326 = 7.787 kg

Products of combustion mean gaseous products of combustion but not ash.
Products in the combustion gases, excluding water are:
CO$_2$ = 2.786 kg
SO$_2$ = 0.024 kg
N$_2$ = 0.027 kg (from coal) + 7.787 kg (from air) = 7.814 kg

Total products = 2.786 + 0.042 + 7.814 = 10.624 kg

Percentage composition by weight
CO$_2$ = $\frac{2.786 \times 100}{10.624} = 26.22\%$
SO$_2$ = $\frac{0.024 \times 100}{10.624} = 0.23\%$
N$_2$ = $\frac{7.814 \times 100}{10.624} = 73.55\%$

10. A producer gas has the following composition by volume. H$_2$ = 10.4%, CH$_4$ = 35%, CO = 25%, CO$_2$ = 10.8%, N$_2$ = 50.3%. Calculate the quantity of air required per m$^3$ of gas. If 20% excess air is supplied, find the percentage composition of the products of combustion.

Solution: Combustion reaction

\[
\begin{align*}
\text{H}_2 + \frac{1}{2} \text{O}_2 & \rightarrow \text{H}_2\text{O} & 0.104 \times \frac{1}{2} = 0.052 \text{m}^3 \\
\text{CH}_4 + 2\text{O}_2 & \rightarrow \text{CO}_2 + 2\text{H}_2\text{O} & 0.35 \times 2 = 0.7 \text{m}^3 \\
\text{CO} + \frac{1}{2} \text{O}_2 & \rightarrow \text{CO}_2 & 0.25 \times \frac{1}{2} = 0.125 \text{m}^3
\end{align*}
\]
Total = 0.877m$^3$

Volume of air required = $\frac{0.877 \times 100}{23} = 3.81 \text{ m}^3$

Volume of air supplied = $3.81 \times 120 = 4.5$

In moles = $\frac{4500}{22.4} = 200.9 \text{ moles}$

In gms = $200.9 \times 28.94 = 5813.89 = 5.8 \text{ kg}$.

Percentage of products of combustion.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Products</th>
<th>Percentage</th>
</tr>
</thead>
</table>
| \( \text{H}_2 + \frac{1}{2} \text{O}_2 \rightarrow \text{H}_2\text{O} \) | 18  \\
|                           | 0.4 x --- = 3.78 kg 2 | \% age of \( \text{H}_2 \) = 7.78 \times 100 \frac{\text{---}}{6.4} = 59\% |
| \( \text{CH}_4 + 2\text{O}_2 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O} \) | 80  \\
|                           | 0.35 x --- = 1.75 16 | \( \text{CH}_4 \) = 27\% |
| \( \text{CO} + \frac{1}{2} \text{O}_2 \rightarrow \text{CO}_2 \) | 44  \\
<p>|                           | 0.25 x --- = 0.39 | ( \text{CO} ) = 6% |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
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</tr>
</thead>
<tbody>
<tr>
<td><strong>CO₂</strong></td>
<td>0.108 kg</td>
<td><strong>CO₂ = 1.68%</strong></td>
</tr>
<tr>
<td><strong>N₂</strong></td>
<td>77</td>
<td><strong>N₂ = 6%</strong></td>
</tr>
<tr>
<td></td>
<td>0.5kg x ---- = 0.385</td>
<td></td>
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<tr>
<td></td>
<td>100</td>
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</tr>
</tbody>
</table>

Total = 6.4kg
The Phase rule is given by Willard Gibbs. It is defined as, In heterogeneous systems, if equilibrium between phases are not influenced by gravity, magnetic & electrical forces, but are influenced only by pressure, temperature and concentration, then the number of degree of freedom (F) of the system is related to number of components (C) and number of phases(P) by the following phase rule equation \( F = C - P + 2 \)

Q.NO.1 Define phase, component, degree of freedom, phase rule equation & Merits – demerits of phase rule.

1. Phase: It is defined as, “any homogenous, physically distinct and mechanically separable portion of the system, which is separated from other such parts of the system by definite boundary surfaces”.
   Examples:
   - Water consists of three phases
     Ice (S) ↔ Water (L) ↔ Water vapour (g)
   - A gaseous mixture, miscible in all proportions, will constitute only one phase.
   - The two immiscible liquids (benzene and water) will form two liquid phases.
   - The two miscible liquids (i.e. alcohol and water) will form one separate phase.
   - A solution of a substance in a solvent consists of one phase only e.g.: Sugar solution in water.
   - A heterogeneous mixture like
     \( \text{CaCO}_3 \text{ (S)} \rightarrow \text{CaO}(S) + \text{CO}_2 \text{(g)} \)
     Consists of three phases (i.e. two solids and one gaseous)

2. Component: It is defined as, “the smallest number of independent variable constituents, by the means of which the composition of each phase can be expressed in the form of chemical equation”.
   Examples:
   In the water system, the chemical composition of all the three phases is \( \text{H}_2\text{O} \). Hence, it is one component system.
   Ice (S) ↔ Water (l) ↔ vapour (g)
   - The sulphur system consists of four phases, rhombic, monoclinic, liquid and vapour, the chemical composition of all the phases is ‘S’. Hence, it is also one component system.
   - A saturated solution of \( \text{NaCl} \) consists of solid \( \text{NaCl} \), \( \text{NaCl} \) solution, and water vapour. The chemical composition of all the three phases is \( \text{NaCl} \) & \( \text{H}_2\text{O} \). Hence, it is a two component system.

3. Degree of freedom: It is defined as, “the minimum number of independently variable factors, such as pressure temperature and composition, which must be specified to represent the condition of a system”.
   Examples:
   a. In the water system
     Ice (S) ↔ Water (l) ↔ Vapour (g)
     Three phases will be in equilibrium only at particular temperature and pressure. The system is, zero variant, or non-variant or invariant and has no degree of freedom.

   b. For a system consisting of water in contact with its vapour.
     Water (l) ↔ Vapour (g)
     We must state either temperature or pressure to define the system completely. Hence; the degree of freedom is one (or) the system is invariant.

   c. For a system consisting of
     \( \text{NaCl} \text{ (S)} \leftrightarrow \text{NaCl} \text{– Water (aq)} \leftrightarrow \text{Water vapour (g)} \)
     We must state either temperature or pressure. Hence the system is univariant (degree of freedom is one).
     For a gaseous mixture of \( \text{N}_2 \) and \( \text{H}_2 \), we must state both the temperature and pressure. Hence, the system is bivariant (degree of freedom is two).
Phase rule: is defined as, In heterogeneous systems, if equilibrium between phases are not influenced by gravity, magnetic & electrical forces, but are influenced only by pressure, temperature and concentration, then the number of degree of freedom (F) of the system is related to number of components (C) and number of phases (P) by the following phase rule equation \[ F = C - P + 2 \]

Merits of phase rule
1. It is applicable to both physical and chemical equilibria.
2. It is a convenient method of classifying the equilibrium states in terms of phases, components and degree of freedom.
3. It indicates different system with same degree of freedom behave similarly.
4. It helps us to predict the behaviours of a system, under different sets of variables.
5. It helps in deciding whether the number of substances remains in equilibrium or not.

Limitations of phase rule
1. It can be applied only for the system in equilibrium.
2. Only three variables like P, T, & C are considered, but not electrical, magnetic and gravitational forces.
3. It is applied only to a single equilibrium system.
4. It requires utmost care in deciding the number of phases existing in equilibrium.
5. Solid and liquid phases must not be in finely divided state; otherwise deviations occur.

Q. NO.2 Define phase diagram & classify systems. To explain one component system phase diagram with using one suitable example.

Phase diagram: Phase diagram is a graph obtained by plotting one degree of freedom against another. If temperature is plotted against pressure, the diagram is called P-T diagram. Similarly, a plot of temperature against composition is known as T-C diagram. By the phase diagram, we may understand the behaviour of the system, stability and equilibrium between phases.

Classification of system:
Systems are classified, on the basis of number of components, into three types.
1. One component systems.
2. Two component systems.
3. Three component systems.

One-component systems:
In any system, the minimum number of phases is one. It is evident from the phase rule equation 
\[ F = C - P + 2 \]
\[ = 1 - 1 + 2 = 2 \]
For one component system the maximum number of degree of freedom is two.
The maximum number of phases in any system is three, from the phase rule equation 
\[ F = C - P + 2 \]
\[ = 1 - 3 + 2 = 0 \]
The minimum number of degree of freedom is zero for one component system.
From the above calculations, it is clear that for any one-component system the maximum number of degree of freedom is two. Therefore, such a system can be presented completely by a two dimensional diagram. Hence, we may draw the phase diagram by taking pressure and temperature as the two axes. These are known as pressure-temperature (P-T) diagrams, concentration (or) composition remains constant.

The Water system:
Water can exist in three possible phases, namely, solid, liquid and vapour. Hence, there can be three equilibriums:
1. Liquid ↔ vapour
2. Solid ↔ Vapour
3. Solid ↔ Liquid
Each equilibrium involves two phases.
The curve OA
It is called the vapourization curve of water; it represents the equilibrium between liquid water and vapour. At any point on the curve the following equilibrium will exist.
Liquid water ↔ vapour

The degree of freedom of the system is one, i.e., univariant. This is predicted by the phase rule.
\[ F = C - P + 2; \quad F = 1 \]

This equilibrium will extend up to the critical temperature \((374^0C)\). Beyond the critical temperature, the equilibrium will disappear only water vapour will exist.

The curve OB
It is called the sublimation curve of ice; it represents the equilibrium between ice and vapour. At any point on the curve the following equilibrium will exist.
Ice ↔ Vapour.

The degree of freedom of the system is one i.e., univariant. This is predicted by the phase rule.
\[ F = C - P + 2; \quad F = 1 - 2 + 2; \quad F = 1 \]

This equilibrium will extend up to the absolute zero.

Triple point
The vaporization curve (OA) and the sublimation curve (OB) meet at point O, where three phases, namely solid, liquid and vapour will coexist. Such a point is known as the “triple point”. Temperature and pressure at the triple point of water are 0.0098 and 4.58mm respectively, according to phase rule, the degree of freedom is zero i.e., invariant.
\[ F = C - P + 2; \quad F = 1 - 3 + 2; \quad F = 0 \]

The curve OC
It is called the fusion curve of ice; it represents the equilibrium between ice and water. At any point on the curve the following equilibrium will exist.
Ice ↔ water

The curve OC shows how is the melting point of ice increased by increasing pressure. The degree of freedom of the system is one, i.e., univariant.
The curve OA’

It is called vapour pressure curve of the super-cool water (or) metastable equilibrium. Some times water can be cooled below 0°C without the formation of ice; this water is known as super-cool water. The super-cool water can be preserved if the system is not subjected to stirring (or) “Seeding” by solid. At any point on the curve the following equilibrium will exist.

Super-cool water ↔ vapour

The degree of freedom of the system is one i.e., univariant.

Area

AOB, AOC and BOC contain vapour, liquid and ice phases respectively, with in these single-phase areas, the system is bivariant. This is predicted by the phase rule.

F=C-P+2; F=1-1+2; F=2

To locate any point in an area, temperature and pressure needs to be known.

Q. NO.3. Define phase. To explain two component system phase diagram with using one suitable example. (OR) State phase rule & explain the terms involved. Apply the phase rule to silver-lead system.

Answer: Phase: It is defined as, “any homogenous, physically distinct and mechanically separable portion of the system, which is separated from other such parts of the system by definite boundary surfaces”.

TWO COMPONENT SYSTEMS: In a two – component system, minimum number of phases is one, i.e., P = 1, according to the phase rule equation, the maximum degree of freedom is three

F = C – P + 2; F = 2 – 1; F = 3

So, the phase diagram of a binary system should be represented by a three dimensional diagram of temperatures, pressure and composition, which can not be drawn on paper.

Generally solid-liquid equilibrium of an alloy has “no gas phase” and the effect of pressure is small. Therefore, experiments are conducted under atmospheric pressure. Thus, the system in which the pressure is constant (vapour phase is not considered) is known as condensed system. The phase rule becomes.

F’=C-P+1

This is known as reduced phase rule (or) condensed phase rule. The phase diagram can be drawn by taking temperature and composition as the two axis. This is known as (T-C) diagram.

The reduced phase rule is used only when atmospheric pressure is larger than actual vapour pressure of the component.

Depending upon the solubility of the two components and their reactive ability, two component systems are classified into three types

1. Simple Eutectic formation
2. Solid solution formation.
3. Compound formation.

Simple Eutectic: If two substances are completely miscible in the liquid state, but completely immiscible in the solid state, form a simple eutectic. Of the various mixture, one mixture has the lowest melting point such a mixture is known as a eutectic mixture (eutectic means easy melting).

Solid Solution: When two substances, especially metals, are completely miscible in both the solid and liquid states, they form solid solutions, where mixing takes place in the atomic levels. A condition for the formation of solid solution is, the two metals should not differ in atomic radius by more than 15%.

Compound formation: Under some conditions, two metals chemically react to give one or more compounds with definite proportions. Of the compounds, a compound is said to possess congruent (constant) melting point, if it melts exactly at a constant temperature into liquid, having the same composition as that of solid.

A compound is said to possess incongruent melting point, if it decomposes completely at a temperature below its melting point yielding a new solid phase with a composition different from that of the original.
Thermal Analysis or Cooling Curves: The shape of the cooling curves can be determined by thermal analysis. Thermal analysis is a method involving a study of cooling curves of various compositions of a system during solidification. The cooling curve is obtained by plotting fall of temperature with time. The principle of the method can be understood from the following examples.

1. When a pure substance in the liquid state is allowed to cool slowly and the temperature is noted at definite times. The cooling curve (fig) shows the rate of cooling is continuous up to the point ‘b’ the solid begins to separate, and the temperature will remain constant, until the liquid is completely solidified (indicated by the line ‘b’). Thereafter, the fall in temperature will again become continuous (indicated by the line ‘cd’).

2. If a mixture of two solids in the liquid state is cooled slowly and the cooling curve is obtained in a similar manner (fig). The cooling curve shows the rate of cooling is continuous up to the point ‘b’. At the point ‘b’ one of the solids begins to separate, this separation will extent up to the point ‘c’. At the point ‘c’ the eutectic compound begins to separate. The temperature remains constant along cd until the solidification completes. Thereafter the fall of temperature becomes uniform, but the rate of fall is quite different from the previous one.

Uses
1. Melting point and eutectic temperature can be noted from the cooling curve.
2. Percentage purity of the compounds can be known.
3. The behaviour of the compounds can be clearly understood from the cooling curves.
4. The procedure of thermal analysis can also be used to derive the phase diagram of any two component system.

Simple Eutectic (Pb-Ag system)
It is a two-component system. The phase diagram of the Pb-Ag system is shown in the fig.

Curve AO
Point A is the melting point of pure Silver. Curve AO shows melting point depression of silver by the addition of lead. At any point in this curve there is equilibrium between solid Ag and liquids part. According to reduced phase rule equation. The system is univariant.

\[ F' = C - P + 1; \]
\[ F' = 2 - 2 + 1; \]
\[ F' = 1 \]

Curve BO
Point B is the melting point of pure lead, (327°C), curve BO shows the melting point depression of lead on gradual addition of silver to it. Along this curve solid lead and solution co – exist and hence the system is univariant.
**Point O:** The two curves AO & BO meet at point O, where three phases solid Pb, solid Ag and their solution co-exist, according to condensed phase rule the system is invariant.

\[ F' = C - P + 1; \quad F' = 2 - 1 + 1; \quad F' = 2 \]

The point ‘O’ is known as eutectic point, its composition (Ag=2.6%; Pb=97.4%) and temperature (303°C) is known as eutectic composition and eutectic temperature respectively. Further cooling below the eutectic temperature respectively. Further cooling below the eutectic temperature will cause simultaneous crystallization of a mixture of lead and silver.

**Area AOB:** Consists of only one phases namely pb-Ag solution. According to reduced phase rule equation.

\[ F' = C - P + 1; \quad F' = 2 - 1 + 1; \quad F' = 2 \]

The system is bivariant i.e., both T & composition has to be specified to define the system.

Let us consider a point p, which represents a sample of lead containing less than 2.6% silver. On cooling the temperature falls gradually till point p’. On further cooling lead begins to separate and the concentration of Ag increase in the solution till the point O is reached, after that whole mass solidifies (2.6% Ag; 97.4% Pb). This process is utilized in the pattinson’s process of desilverization of lead.

Below the eutectic point (O), area COEF consists of solid and eutectic compound, where crystalline silver and eutectic compounds are stable. Similarly the area ODFG consists of solid Pb and eutectic compound, where crystalline lead eutectic compounds are stable.

**Applications to pattinson’s process:** If a sample of argentiferrous lead, containing less than 2.6% Ag is allowed to cool gradually, lead will separate out and the solution will become progressively richer in Ag, till the percentage 2.6 of Ag is reached; and on further cooling, the whole mass will solidify as such. On the other hand, if lead-silver allow containing Ag greater than 2.6% is allowed to cool, and then pure silver separates along the curve AO, till the eutectic composition at O is reached.

**Merits of phase rule**

1. It is applicable to both physical and chemical equilibria.
2. It is a convenient method of classifying the equilibrium states in terms of phases, components and degree of freedom.
3. It indicates different systems with the same degree of freedom behave similarly.
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5. It helps in deciding whether the number of substances remains in equilibrium or not.
Limitations of phase rule
1. It can be applied only for the system in equilibrium.
2. Only three variables like P, T, & C are considered, but not electrical, magnetic and gravitational forces.
3. It is applied only to a single equilibrium system.
4. It requires utmost care in deciding the number of phases existing in equilibrium.
5. Solid and liquid phases must not be in finely – divided state; otherwise deviations occur.

Q. NO. 4. Define phase. To explain two component system phase diagram with using one suitable example (OR) To discuss Pb -Ag two component system.

**Answer:** Phase: It is defined as, “any homogenous, physically distinct and mechanically separable portion of the system, which is separated from other such parts of the system by definite boundary surfaces”.

**TWO COMPONENT SYSTEMS:** In a two – component system, minimum number of phases is one, i.e., P = 1, according to the phase rule equation, the maximum degree of freedom is three

\[
F = C - P + 2; \quad F = 2 - 1; \quad F = 3
\]

So, the phase diagram of a binary system should be represented by a three dimensional diagram of temperatures, pressure and composition, which can not be drawn on paper.

Generally solid-liquid equilibrium of an alloy has “no gas phase” and the effect of pressure is small. Therefore, experiments are conducted under atmospheric pressure. Thus, the system in which the pressure is constant (vapour phase is not considered) is known as condensed system. The phase rule becomes.

\[
F' = C - P + 1
\]

This is known as reduced phase rule (or) condensed phase rule. The phase diagram can be drawn by taking temperature and composition as the two axis. This is known as (T-C) diagram.

The reduced phase rule is used only when atmospheric pressure is larger than actual vapour pressure of the component.

**Pb-Ag system:** It is a two-component system. The phase diagram of the Pb-Ag system is shown in the fig.

![Phase Diagram](www.hitam.webs.com)
Curve AO: Point A is the melting point of pure Silver. Curve AO shows melting point depression of silver by the addition of lead. At any point in this curve there is equilibrium between solid Ag and liquids part. According to reduced phase rule equation. The system is univariant.

\[ F' = C - P + 1; \quad F' = 2 - 2 + 1; \quad F' = 1 \]

Curve BO: Point B is the melting point of pure lead, (327°C), curve BO shows the melting point depression of lead on gradual addition of silver to it. Along this curve solid lead and solution co-exist and hence the system is univariant.

Point O: The two curves AO & BO meet at point O, where three phases solid pb, solid Ag and their solution co-exist, according to condensed phase rule the system is invariant.

\[ F' = C - P + 1; \quad F' = 2 - 1 + 1; \quad F' = 2 \]

The point ‘O’ is known as eutectic point, its composition (Ag=2.6%; Pb=97.4%) and temperature (303°C) is known as eutectic composition and eutectic temperature respectively. Further cooling below the eutectic temperature will cause simultaneous crystallization of a mixture of lead and silver.

Area AOB: Consists of only one phases namely pb-Ag solution. According to reduced phase rule equation.

\[ F' = C - P + 1; \quad F' = 2 - 1 + 1; \quad F' = 2 \]

The system is bivariant i.e., both T & composition has to be specified to define the system.

Let us consider a point p, which represents a sample of lead containing less than 2.6% silver. On cooling the temperature falls gradually till point p’. On further cooling lead begins to separate and the concentration of Ag increase in the solution till the point O is reached, after that whole mass solidifies (2.6% Ag; 97.4% pb). This process is utilized in the pattinson’s process of desilverization of lead.

Below the eutectic point (O), area COEF consists of solid and eutectic compound, where crystalline silver and eutectic compounds are stable. Similarly the area ODFG consists of solid Pb and eutectic compound, where crystalline lead eutectic compounds are stable.

Applications to pattinson’s process: If a sample of argent ferrous lead, containing less than 2.6% Ag is allowed to cool gradually, lead will separate out and the solution will become progressively richer in Ag, till the percentage 2.6 of Ag is reached; and on further cooling, the whole mass will solidify as such. On the other hand, if lead-silver alloy containing Ag greater than 2.6% is allowed to cool, and then pure silver separates along the curve AO, till the eutectic composition at O is reached.

Merits of phase rule
1. It is applicable to both physical and chemical equilibria.
2. It is a convenient method of classifying the equilibrium states in terms of phases, components and degree of freedom.
3. It indicates different systems with same degree of freedom behave similarly.
4. It helps us to predict the behaviours of a system, under different sets of variables.
5. It helps in deciding whether the number of substances remains in equilibrium or not.

Limitations of phase rule
1. It can be applied only for the system in equilibrium.
2. Only three variables like P, T, & C are considered, but not electrical, magnetic and gravitational forces.
3. It is applied only to a single equilibrium system.
4. It requires utmost care in deciding the number of phases existing in equilibrium.
5. Solid and liquid phases must not be in finely divided state; otherwise deviations occur.
Q.No. 5. Write in detail an account of heat treatment based on iron-carbon phase diagram.

**Iron–Carbon Phase Diagram:**
Iron-carbon system represents interstitial solid solutions, which are formed when the alloying elements differ widely in their atomic sizes.

Pure iron is not suitable for fabrication of structural components because of its weak mechanical properties. Carbon, though a non-metallic element forms alloys with iron to give various types of steel and improves the mechanical properties of the base metal to a large extent. The size of carbon atom is small compared to that of iron atoms and hence occupies interstitial positions in the lattice formed by the iron atoms. The miscibility or solubility of carbon in iron depends on the crystal structure of iron, which in turn depends on the temperature, as pure iron exists in three allotropic forms.

The cooling curve of pure molten iron

None of the allotropic forms of pure iron are as useful as their alloys with carbon. Iron melts at 1535°C and the liquid iron boils at about 3000°C. Iron–carbon alloys containing up to 1.7% of carbon are classified as steels while those containing over 1.7% carbon are called cast irons. The solid solutions of carbon are the various forms of iron are interstitial solutions.

The various important micro constituents are as follows:

- **Austenite:** It is a solid solution of carbon in γ–iron. The γ–iron can dissolve carbon to an increased extent of 1.7% w/w. austenite does not exist in equilibrium below 723°C, as it decomposes on cooling.
- **Cementite:** Cementite is iron carbide with a specific composition of Fe3C and a complex orthorhombic structure. It exists at all temperatures studied from 0 to 1800°C. It undergoes a magnetic change at 200°C. It is hard, brittle and wears resistance.
- **Ferrite:** This is the solution of carbon in α–iron with a maximum carbon content of 0.035% at 723°C and 0.007% at room temperature. Ferrite is often considered to be pure α–iron, but even by this minute amount of dissolved carbon, some of its properties are strongly affected.
- **Pearlite:** This is the eutectoid of ferrite and cementite formed by the decomposition of austite. It contains 0.8% carbon. Further it is a fine grained mixture of ferrite and cementite and has a lamellar structure. More of ferrite makes pearlite soft and more of cementite makes it hard.
- **Martensite:** This is a transformed form of austenite. It is named so after the German metallurgist Martens. Martensite is a supersaturated interstitial solid solution of carbon in α–ferrite with a distorted BCC or tetragonal structure. Microscopic examination of martensite reveals a series of fine needles like structures. Martensite is extremely hard and strong, the hardness being attributed to the efficient filling up of the void space in the BCC structure with carbon atoms which prevents slippage between planes of iron atoms.
- **Troostite:** This is formed when the martensite is tempered in the range of 230 to 400°C. It consists of finely dispersed aggregate or superfine particles of cementite and ferrite. It is softer but tougher than martensite.
Bainite: It is the transformed form of austenite in the temperature range of 260 to 540°C. It has a ferrite matrix in which cementite is embedded. It is magnetic, moderately ductile and harder than pearlite and tougher than martensite.

Sorbite: It is formed when martensite is tempered at 400 to 600°C. It is an important constituent in some special steels such as rails. It consists of ferrite and globules of iron carbide.

A simple iron-carbide phase diagram is depicted in the below figure, which tells about the formation of different phases in the iron carbide system.

![Iron-carbide phase diagram]

Any point in the diagram represents a definite alloy at a definite temperature. The carbon content is shown on the vertical axis perpendicular to the point while the temperature is shown on the vertical axis perpendicular to the point. Further whenever an alloy is heated or cooled in such a way that a line on the diagram is crossed, a phase change occurs. All alloys corresponding to any point in the region above ACD in the diagram exist in the liquid phase only.

When any liquid alloy containing below 4.3% of carbon is cooled to temperatures on the curve AE, solid crystals begin to form. Hence AC is called the ‘liquidus’ for these alloys, above which there is only one liquid phase.

If the liquid alloys containing 0 to 0.55% carbon is cooled, the first crystals formed will be of the solid solution of carbon in δ-iron. If the liquid alloys containing 0.55 to 4.3% carbon are cooled, the first crystals formed are of “austenite” which is the solid solution of carbon in γ-iron. AEC is the region where the liquid melt and austenite exist in equilibrium.

When an alloy containing up to 4.3% carbon is cooled to conditions represented by AE or EC, it is completely converted into solid. These lines represent the “solidus” for alloys of this composition range, below which various Fe-C compositions are completely solid.

When liquid alloys containing greater than 4.3% carbon are cooled to temperatures represented on the curve CD, solid crystals of cementite (Fe₃C) start separating out. When an alloy containing greater than 4.3% of carbon is cooled the temperatures on the curve represented by CF, it is completely solidified.

The alloy containing 4.3% carbon is the eutectic alloy and it will completely solidify at ‘C’ which corresponds to the temperature 1130°C. This point represents the simultaneous formation of the solid eutectic mixture containing austenite and cementite.

Therefore with the help of iron-carbon phase diagram, the cause of events taking place and the various phase transformations occurring, while cooling liquid alloys having different carbon contents can be understood clearly.

**Heat treatment of steel:**
Heat treatment involves the combination of heating and cooling of a metal or alloy in one or more temperature cycles to confer desirable physical properties to the metal or alloy. Heat treatment of steel may be carried out under near equilibrium conditions to improve the ductility or under non equilibrium conditions to enhance the hardness. During heat treatment the size and shape of the grains or the composition of the phase undergoes changes with respect to the micro constituents and also in addition, the internal stresses will be relieved.

**Hardening:** Hardening involves the transformation of austenite to martensite or the bainite phase, making the steel hard. If steel is quenched by plunging into water or oil to $204^\circ C$ or lower temperature the carbon atoms do not have sufficient time to form cementite but remain trapped in the lattice. The excess carbon precipitates out in hot metal and prevents the slipping of the planes. Thus quenched steel is quite hard and strong but has lower ductility. This heat treatment is called transformation hardening. Further the quenched steel is not useful for construction purposes, because of its brittleness. Therefore quenching is always followed by another heat treatment process called tempering. The quenched steel is tempered by reheating to below $\alpha$–iron or $\gamma$–iron transition temperature. Normally on tempering, the steel becomes tougher and ductile. Tempering is carried out at about $200^\circ C$ to make hard steel resistant to abrasion or at higher temperature (~ $540^\circ C$) to make tough steel capable of withstanding shock loads.

**Case hardening:** is a surface treatment by which the inside soft core of steel is hardened on the surface. Low carbon steels are case hardened because they cannot be hardened by quenching.

**Cyaniding:** also produces case hardened, medium carbon steel articles. Here the article is immersed in a molten bath of sodium or potassium cyanide at about $850^\circ C$ for some times to facilitate the adsorption of both carbon and nitrogen and then quenched in oil or water.

**Nitriding:** produces a hard surface on alloy steels. The process involves heating the alloy in the presence of ammonia to about $550^\circ C$. Ammonia decomposes and nitrogen formed combines with alloying elements to form hard nitrides on the surface of the alloy.

**Annealing:** Annealing involves heating and holding the steel at a suitable temperature for some times to facilitate the dissolution of carbon in $\gamma$–iron followed by a slow cooling in a controlled manner in a furnace. Steel is softened and becomes ductile and machineable. However annealing decreases the hardness and strength of steel. Annealed hypereutectoid steels contain cementite. They are not soft but can be machined easily. In contrast annealed hypo eutectoid steels contain ferrite and are relatively soft and malleable.
MATERIAL SCIENCE (UNIT-VIII)

Q.No.1: With the help of flow diagram explain the manufacture of Portland cement by Dry & wet process

Answer: The manufacture of cement consists of the following steps.

Mixing of raw materials or slurry: An intimate mixture of finely ground limestone and clay (3:1) is made into thin slurry with water by any of the following methods.

a. Dry process
b. Wet process

Dry process: If the lime stone and clay are hard, then the dry process is used. In this process the lime stone is first broken into small pieces. It is then mixed with clay in the proper proportion (3:1) and finally pulverized to such a fineness that 90-95% passes through a 100 mesh sieve. Then the raw mix is fed to a rotary kiln.

Wet process: If lime stone and clay are soft, the wet process is preferred. In this process, the clay is washed with water in wash mill to remove the foreign materials, organic matters etc. The powdered limestone is then mixed with the clay paste in the proper proportion (3:1) and the two ingredients are finely ground and homogenized. In this process, the slurry contains about 40% of water. Now the slurry can be fed to rotary Kiln.

Burning: The dry pulverized raw mixture or slurry is introduced into a rotary kiln which consists of an inclined steel rotating cylinder. 150-200 feet long and 10 feet in diameter lined with fire bricks. The water evaporates at the upper ends of kiln by means of hot gases. The Kiln rotates on its axis at the rate of ½ to 1 revolution per minute. As the Kiln rotates the charge slowly moves downwards due to the rotary motion of the Kiln. Now the charge is heated by blast of air charged with coal dust is admitted. This produces a temperature range of 1500 to 1700°C in step wise process as:

a. At 750°C the moisture is completely eliminated.

b. At 1000°C the limestone is completely decomposed to CaO.

c. At 1500 to 1700°C the mixture is partly fused and sintered and chemical combinations between lime, alumina, ferric oxide and silica.

The charge takes 2 to 3 hrs. to cover the journey in the Kiln.

Chemical reactions: In the rotary Kiln the chemical reactions can be divided into the following parts.

Drying zone: In this zone temperature raises to maximum 750°C so that entire moisture in the slurry gets evaporated. The clay is broken into Al₂O₃, SiO₂ and Fe₂O₃.

\[ \text{Al}_2\text{O}_3 + 2\text{SiO}_2 + 2\text{Fe}_2\text{O}_3 + 2\text{H}_2\text{O} \rightarrow 4\text{O}_2 + 2\text{SiO}_2 + 2\text{Fe}_2\text{O}_3 + 2\text{H}_2\text{O} \]

Calcinations zone: When the temperature rises at 1000°C, the limestone is completely decomposed into CaO.

\[ \text{CaCO}_3 \rightarrow \text{CaO} + \text{CO}_2 \]

Reaction zone (Clinkering zone): When the temperature reaches about 1600°C, the mixture is partly fused and chemical combinations between lime, alumina, ferric oxide and silica, resulting in the formation of calcium aluminates and silicates occur.

\[ 2\text{CaO} + \text{SiO}_2 \rightarrow 2\text{CaO} . \text{SiO}_2 \text{ (di calcium silicate)} \]
The resulting product is known as cement clinkers and as it comes out into the cooler. The clinkers are very hot (1000°C). The clinkers have the appearance of small greenish black or grey colored.

**Mixing of cement clinkers with gypsum:** The cooled clinker is ground and almost 3% of gypsum is mixed with it in order to reduce the rate of setting. After the initial setting, Al₂O₃ which is a fast setting constituent of clinker reacts with gypsum to form the crystals of calcium sulfo aluminate.

\[
3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 3(\text{CaSO}_4 \cdot 2\text{H}_2\text{O}) + 2\text{H}_2\text{O} \rightarrow 3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{CaSO}_4 \cdot 2\text{H}_2\text{O} + 6\text{H}_2\text{O}
\]

At the initial setting, gypsum removes the fast setting elements and hence the process of setting cement gets retarded and the results in better strength of the mass which sets.

**Packing:** The ground cement is stored in silos, from which it is fed to automatic packing machines. Each bag, usually, contains 50 kg of cement.

**Flow-chart of Manufacturing of cement:**

- **Calcareous materials (Lime stone)**
- **Argillaceous materials (clay or Shale)**
- **Crushing and powdering**
- **Proportioning**
- **Grinding**
- **Slurr**
- **Rotary Kiln**
- **Cement clinkers**
- **Cooler**
- **Gypsum**
- **Clinkers grinding elevators**
- **Cement soils**

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Q.No. 2: Write the chemical composition and setting and hardening of cement.

**Answer:**

### a. Chemical composition of cement:

The essential constituents are lime, silica and alumina. For a good quality of cement the following ratio should be maintained.

\[
\frac{\text{%SiO}_2}{\text{%Al}_2\text{O}_3} = 2.5 \text{ to } 4.0
\]

\[
\frac{\text{%CaO} - \text{%SO}_3}{\text{%SiO}_2 + \text{%Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3} = 1.9 \text{ to } 2.
\]

- a. The ratio of silica to alumina lies between 2.5 and 4.
- b. The ratio of calcium oxide to silica + alumina + ferric oxide should be close to 2.5 and 4.
- c. Total percentage of magnesia should be \(< 6\%\)
- d. Total sulphur content should not be more than 2.75\%
- e. The ratio of Alumina to Iron oxide should be close to 0.65
- f. Total loss on ignition shall not exceed 4\%.

### b. Setting and Hardening of Cement:

Cement has the property of setting to hard mass after being mixed with water which is called cement paste. After mixing with water, hydration reaction starts and the mass becomes hard and very resistant to pressure. This is called as the setting of cement. The first setting takes place within 24 hours. The subsequent hardening requires about a fortnight. Setting is defined as stiffening of the original plastic mass and hardening is development of strength due to crystallization. Both these processes are due to hydration and hydrolysis reactions.

**Initial setting:** primarily the reactions involved are the hydration of calcium aluminates and calcium silicates which change into their colloidal gel. At the same time some calcium hydroxide and aluminium hydroxide are formed as precipitates due to hydrolysis.

\[
3\text{CaO Al}_2\text{O}_3 + 6\text{H}_2\text{O} \rightarrow 3\text{CaO.Al}_2\text{O}_3.6\text{H}_2\text{O} + 880 \text{ Kj/kg}
\]

\[
4\text{CaO Al}_2\text{O}_3\text{Fe}_2\text{O}_3 + 7\text{H}_2\text{O} \rightarrow 3\text{CaO.Al}_2\text{O}_3.6\text{H}_2\text{O} + 3\text{CaO Fe}_2\text{O}_3 \text{H}_2\text{O} + 420 \text{ Kj/kg}
\]

\[
3\text{CaO Al}_2\text{O}_3 + 3(\text{CaSO}_4 + 2\text{H}_2\text{O}) \rightarrow 3\text{CaO.Al}_2\text{O}_3.3\text{CaSO}_4.2\text{H}_2\text{O}
\]

Addition of gypsum removes the fast setting elements.

Reaction takes place between 1 and 7 days:

**Hydrolysis reaction:** \(3\text{CaOSiO}_2 + \text{H}_2\text{O} \rightarrow \text{Ca(OH)}_2 + 2\text{CaOSiO}_2\)

**Final setting (between 7 to 28 days):** begins to hydrate and forms the hydrated colloidal gel of the composition.

\[
2\text{CaOSiO}_2 + \text{XH}_2\text{O} \rightarrow 2\text{CaOSiO}_2\text{XH}_2\text{O} + 500\text{Kj/kg}
\]

**Sequence of chemical reactions during setting and hardening of cement:** when water is added to cement, its various constituents undergo hydration and crystallization at different rates.

1. At first, hydration of tricalcium aluminate and tetra calcium aluminoferrite takes place.
2. Next, the hydration of tricalcium silicate begins within 24 hours and gets completed in 7 days.
3. The gel of aluminate begins to crystallize and at the same time, dicalcium silicate begins to hydrate in 7 to 28 days. Thus, the initial set of cement is due to the hydration of aluminate. The development of early-strength, between 1 to 7 days, is due to the hydration of tricalcium silicate and the further hydration of aluminate. The increase of strength, between 7 to 28 days, is due to hydration of dicalcium silicate and continued hydration of tricalcium silicates.
Q.No.3 What are Refractories? Explain thermal-spalling, porosity, & strength of refractories (Pyrometric cone).

**Answer:** Refractories are ceramic materials that can withstand high temperatures as well as abrasive and corrosive action of molten metals; slag’s and gases, without suffering a deformation in shape. The main objective of a refractory is to confine heat.

**Criteria of good refractory material or essential properties of good refractory materials:**

The important properties are:

1. **Porosity:** Porosity of a refractory material is the ratio of its pore’s volume to the bulk volume. Porosity can also increase the thermal shock resistance. The least porous bricks have the highest thermal conductivity, strength, resistance to abrasion and corrosion. All refractories contain pores, either due to manufacturing methods or deliberately by incorporating saw-dust or cork during manufacture. The pores may be open or closed; the latter are encountered in an oven-fired refractory. Porosity in the ratio of its pore’s volume to the bulk volume. Thus, porosity,

   \[ P = \frac{[(W - D) - (W - A)]}{W} \]  

   W= Weight of saturated specimen  
   D= Weight of dry specimen  
   A = weight of saturated specimen submerged in water.

2. **Thermal spalling:** Rapid changes in temperature, cause uneven expansion and contraction of refractory material, thereby leading to development of internal stresses and strains. This is in turn are responsible for cracking, breaking or fracturing of a refractory brick or block under high temperature, collectively known as thermal spalling. Thermal spalling can also caused by the variation in the coefficient of expansion due to slag penetration in the refractory brick. A good refractory must show a good resistance to thermal spalling. Spalling can be decreased by

1. Avoiding sudden temperature changes. 
2. Over firing the refractories. 
3. Modifying the furnace design. 
4. Using high porosity, low coefficient of expansion, and good thermal conductivity refractory bricks.

3. **Strength of refractories:**

   **Refractoriness** is the ability of a refractory material to withstand the heat without appreciable softening or deformation under given service conditions. It is generally measured as the softening temperature. It is necessary that a refractory material should have a softening temperature higher than the operating temperature of the furnace in which it is to be used. Sometimes, it can be employed to withstand a temperature higher than
its softening temperature since the outer part of refractory is at a lower temperature and still in solid state, providing strength. Thus, refractory material does not melt away although inner refractory lining in a furnace is at a much higher temperatures than the outer ones. Most of the commercial refractories do not exhibit sharp melting points and they soften gradually over a range of temperatures.

**Measurement of refractoriness:** The softening temperatures of refractories are generally determined by seger cones also called pyrometric cones test. In this test, behaviour of heat on cone of refractory and series of seger cones of standard dimensions are compared. These cones are small pyramid shaped with triangular base, 38 mm high with 19 mm long sides.

The test refractory in the form of a cone is kept alongside similar sized standard cones and all are heated uniformly at 20\(^\circ\)C/hour or 100\(^\circ\)C/hour or 150\(^\circ\)C/hour or occasionally at 600\(^\circ\)C/hour. As seger cones are made of a particular refractory of a definite softening temperature so they are assigned ascending seger cone numbers with increasing softening temperature. When the test cone softens and loses its shape, one of the standard seger cones also softens and loses its shape provided its refractoriness is close to that of the test cone. The serial number of this standard seger cone is noted and this number is the pyrometric cone equivalent (PCE) of the refractory under that test. When the test cone softens earlier than one standard cone, but later than the previous one, the PCE value of the test sample is approximated as average of the two.

The temperature at which the softening or fusion of the test-cone occurs is indicated by its apex touching the base.

<table>
<thead>
<tr>
<th>Seger-cone number</th>
<th>Temperature ((^\circ)C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1110</td>
</tr>
<tr>
<td>5</td>
<td>1180</td>
</tr>
<tr>
<td>10</td>
<td>1300</td>
</tr>
<tr>
<td>15</td>
<td>1435</td>
</tr>
<tr>
<td>20</td>
<td>1530</td>
</tr>
<tr>
<td>30</td>
<td>1670</td>
</tr>
<tr>
<td>35</td>
<td>1770</td>
</tr>
</tbody>
</table>

**Refractoriness-under-load:** Temperature resistance and load bearing capacity are the two essential qualities of a refractory. This is due to the fact that commercial refractories which are used for lining high temperature furnace are expected to withstand varying loads of the charge. Hence they should possess high strength and excellent temperature resistance.

**Measurement:** Seger cone test is not applicable for the measurement of strength. Because, some refractories soften gradually over a range of temperature, but under appreciable load, they collapse, far below their true fusion temperature. High alumina bricks and fire-clay are examples of such refractory materials. There are some other refractory materials like silica bricks which exert good load bearing characteristics up to their fusion temperatures as they soften over a relatively narrow range of temperature. Thus, for good results, refractoriness-under-load test is performed by applying a load of (3.5 or 1.75 kg/cm\(^2\)) to the refractory specimen (of size 5cm\(^2\) and 75cm high). The sample is then kept in carbon-resistance furnace and heating is stated at the rate of 100\(^\circ\)C/minute. The height of the specimen is plotted vs. temperature and RUL is expressed as the temperature at which 10% deformation takes place.
Q.No. 4: Define Insulators? What are thermal insulators? Discuss their engineering applications and characteristics

**Answer: Insulators:** The substances which are capable of retarding or prohibiting the flow of heat or electricity or sound through them are known as insulators or Insulating materials.

Insulators can be broadly classified into three categories.

- Thermal Insulators
- Sound Insulators
- Electrical Insulators

**Thermal Insulators:** Thermal insulators are those materials with very low thermal conductivities. These essentially prevent heat loss. Insulation capacity is inversely proportional to conductivity. The properties of a thermal insulator depends on
  
  i. **Pores:** Most of the insulators are fibrous or granular bodies. They have pores. If the pore size is big, then heat transfer by convection is possible. So low pore size is preferred.
  
  ii. **Presence of moisture:** Moisture enhance thermal conductivity because, water has more thermal conductivity than air. If the pores are closed type then water can water cannot enter. Thermal insulator should not react with water.

An ideal thermal insulator should have the following characteristics:

  a. Thermal conductivity should be low
  b. It should be fire proof
  c. Should resist moisture absorption
  d. Chemically inert
  e. Low dense material
  f. Should be able to bear strong load
  g. Should be stable
  h. Should be odorless
  i. Should be inexpensive

Thermal insulators are two types:

- **Organic:** An organic thermal insulator poses large number of small pores. These are naturally occurring compounds.
- **Inorganic:** Inorganic thermal insulators are asbestos, glass, calcium silicate etc.

<table>
<thead>
<tr>
<th>Thermal Insulators</th>
<th>Characteristic properties</th>
<th>Engg. Applications.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glass wool</td>
<td>Soft and flexible, fire and heat proof, insect proof</td>
<td>Used as thermal insulating material in industrial and domestic appliances like ovens, motors and vacuum cleaners.</td>
</tr>
<tr>
<td>Cork</td>
<td>Possesses good porosity, compressibility and water resistance a part from good thermal resistance.</td>
<td>Used in the lining of cold storage, bottle stoppers, refrigerators.</td>
</tr>
<tr>
<td>Asbestos</td>
<td>Fire and weather proof, durable, light in weight.</td>
<td>Used as heat insulator in boilers, for roof covering in the form of sheets.</td>
</tr>
<tr>
<td>Cellular rubber</td>
<td>Possess large number of cellular cavities.</td>
<td>Used for heat insulation in cold storage and refrigerators.</td>
</tr>
<tr>
<td>Vermiculites</td>
<td>Mica like minerals</td>
<td>Used as heat insulators for furnace and also as sound insulators.</td>
</tr>
</tbody>
</table>
Q.No. 5: Define insulators? What are electrical insulators? Discuss their characteristics & engineering applications.

Answer: Insulators: The substances which are capable of retarding or prohibiting the flow of heat or electricity or sound through them are known as insulators or Insulating materials. Insulators can be broadly classified into three categories.

Thermal Insulators
Sound Insulators
Electrical Insulators

Electrical Insulators: The materials which are used to prevent the loss of electricity through certain parts in an electrical system are known as electrical insulating materials or Dielectrics. These materials apart from acting as electrical insulators can also store electric charge. Thus, these materials have two functions, Insulation and Storage of charge.

Characteristics:

1. A good insulator possesses low electrical conductivity or high resistivity. Typical values being 10^9 to 10^20 ohm-cm at room temperature.
2. Dielectrics used in capacitor should have high dielectric constant so that greater amount of energy can be stored in relatively thin insulation.
3. In an insulating material dielectric loss are caused by a. the absorption of electrical energy and leakage of current through the material. This due to the fact that the absorption of electrical energy, under an alternating field gives rise to dissipation of the electrical energy in the insulating material. The leakage of current through the insulating material takes place as a result of conduction, especially at higher temperature.
4. Good dielectric materials should have low porosity. This is due to the fact that higher porosity increases the moisture holding capacity and moisture adversely affects the electrical properties.
5. An ideal insulator should have least thermal expansion and contraction.
6. Good insulating materials should be chemically inert to acids, alkalies, oils, solvents, moisture, gas fumes etc.

Important electrical insulating materials and their engineering applications:

<table>
<thead>
<tr>
<th>Insulator</th>
<th>Engg. Applications</th>
</tr>
</thead>
<tbody>
<tr>
<td>Air</td>
<td>It provides insulation between the overhead transmission lines.</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>It is used in transformers to replace the harmful oxidising atmosphere.</td>
</tr>
<tr>
<td></td>
<td>under high pressure, it is also used as dielectric in certain electrical capacitors.</td>
</tr>
<tr>
<td>Electronegative gases like SF6 &amp; CCl4</td>
<td>SF6 is used in electrical devices like capacitors, cables.</td>
</tr>
<tr>
<td>Mineral oils</td>
<td>In transformers, light fraction oil like transit oil is used to allow converting cooling. Under pressure, light oils are also used in oil filled high voltage cables. More viscous or talky oils are used to impregnate the paper in solid type of cable.</td>
</tr>
<tr>
<td>Silicone fluids</td>
<td>Used as coolants in radio, pulse and aircraft transformers.</td>
</tr>
<tr>
<td>Fluorinated liquids</td>
<td>Used in transformers and small electric and radio devices.</td>
</tr>
<tr>
<td>Drying oils</td>
<td>Used in transformers and motor coils.</td>
</tr>
<tr>
<td>Non drying oils</td>
<td>Used in insulating resin compositions</td>
</tr>
<tr>
<td>Paper &amp; press boards</td>
<td>Used for winding, cable coil insulation, primary dielectrics in capacitors, windings and mica insulations, slot insulations of electrical machines etc.</td>
</tr>
<tr>
<td>Inorganic fibrous insulators (asbestos)</td>
<td>Below red heat it is used in woven cloth tape, paper and wire covering.</td>
</tr>
</tbody>
</table>
**Q.No.6**: Define Refractories; classify it, to explain Conditional for failure of a refractory material.

**Answer**: Refractories are ceramic materials that can withstand high temperatures as well as abrasive and corrosive action of molten metals; slag’s and gases, without suffering a deformation in shape. The main objective of a refractory is to confine heat.

On the basis of the chemical properties of their constituent substances, refractories are classified into three categories:

i. Neutral refractories
ii. Acid refractories
iii. Basic refractories

**Neutral refractories** like graphite, zirconia and SiC refractories. These refractories are made from weakly basic/acidic materials like carbon, zirconia (ZiO₂) and chromite (FeO.CrO₂)

**Acid refractories** like alumina, silica and fire clay refractories. These refractories consist of acidic materials like alumina (Al₂O₃) and silica (SiO₂). These refractory materials are resistant to acidic slag (like silica) and are often used as contaminant vessel for them. On the other hand, they are readily attacked by basic slag’s (like CaO, MgO etc.) and contact with these oxide materials should be avoided.

**Basic refractories** like Magnetite and Dolomite refractories. These refractories consist of basic materials like CaO, MgO etc. and are especially resistant to basic slags. That’s why they find extensive use in some steel making open hearth furnaces. The presence of acidic materials like silica is deleterious to their high-temperature performance.

**Conditional for failure of a refractory material:**

i. Using a refractory material which does not have required heat, corrosion and abrasion resistance;

ii. Using refractory material of higher thermal expansion;

iii. Using a refractory of refractoriness less than that of the operating temperature;

iv. Using basic refractory in a furnace in which acidic reactants and/or products are being processed and vice-versa;

v. Using lower-duty refractory bricks in a furnace than the actual load of raw materials in products;

vi. Using refractories which undergo considerable volume changes during their use at high temperature.
Q.No. 7. Explain the mechanism of lubricants: a) Boundary lubricants  b) Extreme pressure lubricants  
   c) Hydrodynamic or fluid film or Thick-film lubrication

**Answer: a. Boundary or Thin-Film lubrication:**

When the lubricant is not viscous enough to generate a film of sufficient thickness to separate the surfaces under heavy loads, friction may yet be reduced with the proper lubricant. Such an application is known as boundary lubrication.

A thin layer of lubricant is adsorbed on the metallic surfaces which avoids direct metal to metal contact. The load is carried by the layer of the adsorbed lubricant on both the metal surfaces. In boundary lubrication, the distance between moving/sliding surface is very small of the order of the height of the space asperities. The contact between the metal surfaces is possible by the squeezing out of lubricating oil film. When this occurs the load would be taken on the high spots of the journal and the bearing, and the two surfaces tend to because welded together by appreciable heat generated. This prevents motion as the two surfaces adhere together. For boundary lubrication the lubricant molecules should have long hydrocarbon chains, high viscosity index, resistance to heat and oxidation, good oiliness, low pour and oxidation. Graphite and MoS2, Vegetable and animal oils and their soaps are used for boundary lubrication.

**b. Extreme pressure lubrication:**

Is done by incorporating extreme pressure additives in mineral oils for applications in which high temperature is generated due to high speed of moving/sliding surfaces under high pressure. Chlorinated esters, sulphurised oils and tricrysyl phosphate are examples of such additives. These additives react with metallic surfaces, at prevailing high temperatures, to form metallic chlorides, sulphides or phosphates in the form of durable film. These films can withstand very high loads and high temperatures. Applications: wire drawing of titanium, in cutting fluids in machining of tough metals, for hypoid gears used in rear axle drive of cars.

**c. Hydrodynamic or fluid film or Thick-film lubrication:** In this, the moving/sliding surfaces are separated from each other by a bulk lubricant film (at least 10000A thick). This bulk lubricant film prevents direct surface to surface contact so that the small peaks and valleys do not interlock. This consequently reduces friction and prevents wear. Fluid film lubrication is shown in figure.

The small friction is only due to the internal resistance between the particles of the lubricant moving over each other. In such a system, friction depends on the thickness and viscosity of the lubricant and the relative velocity and area of the moving/sliding surfaces the co-efficient of friction is as low as 0.002 to 0.03 for fluid film lubricated system.
Q.No. 8. Explain properties of lubricants: a) Flash & fire point b) Cloud & pour point c) Viscosity and viscosity index d) Aniline point & Mechanical strength

**Answer:** A lubricant may thus be defined as a substance which reduces the friction when introduced between two surfaces.

**Functions of lubricants:**
1. It reduces the maintenance and running cost of the machine.
2. It reduces unsmooth relative motion of the moving surfaces.
3. It reduces the loss of energy in the form of heat that is it acts as a coolant.
4. It reduces waste of energy, so that efficiency of the machine is increased.
5. It reduces surface deformation, because the direct contact between the moving surfaces is avoided.
6. It reduces the expansion of metals by local frictional heat.
7. In some times, it acts as a seal, preventing the entry of dust and moisture between the moving surfaces.
8. It minimizes corrosion.

**Properties of lubricants**

1. **Flash and fire point:** The flash point of oil is the lowest temperature at which it gives off vapors that will ignite for a moment when a small flame is brought near it. The fire point of oil is the lowest temperature at which the vapors of the oil burn continuously for at least 5 seconds when a small flame is brought near it.
   The flash and fire points are used to indicate the fire hazards of petroleum products and evaporation losses under high temperature operations. Knowledge of flash and fire points in lubricating oil helps to take preventive measures against fire hazards.

2. **Cloud and pour point:** The cloud point of petroleum oil is the temperature at which solidifiable compounds, like paraffin wax, present in the oil begin to crystallize or separate from solution. The pour point of petroleum oil is the temperature at which the oil ceases to flow or pour. Cloud and pour points indicate the suitability of lubricants in cold conditions.

3. **Viscosity:** Viscosity is the property of a fluid that determines its resistance to flow. It is an indicator of flow ability of a lubricating oil, the lower the viscosity, greater the flow ability. If temperature increases viscosity of the lubricating oil decreases. And pressure increases, viscosity of the lubricating oil increases. **Viscosity index:** The rate at which the viscosity of oil changes with temperature is measured by an empirical number, known as the viscosity-index. A relatively small change in viscosity with temperature is indicated by high viscosity index. Whereas a low viscosity index shows a relatively large change in viscosity with temperature.

4. **Aniline point:** Aniline point is defined as “the minimum equilibrium solution temperature for equal volume of aniline and oil sample”. A lower aniline point of an oil means a higher percentage of aromatic hydrocarbons in it. Aromatic hydrocarbons have a tendency to dissolve natural rubber and certain types of synthetic rubbers. Thus good lubricating oil should have higher aniline point.
   Aniline point gives an indication of the possible deterioration of oil in contact with rubber sealing, packing, etc. Aromatic hydrocarbons have a tendency to dissolve natural rubber and certain types of synthetic rubbers. Consequently, low aromatic content in the lubricants is desirable. A higher aniline point means a higher percentage of paraffin hydrocarbons and hence a lower percentage of aromatic hydrocarbons.
   Aniline point is determined by mixing mechanically equal volumes of the oil sample and aniline is a tube. The mixture is heated, till homogeneous solution is obtained. Then the tube is allowed to cool at a controlled rate. The temperature at which the two phases (oil and aniline) separate out is recorded at the aniline point.

5. **Mechanical stability:** to judge the suitability of a KOH required under conditions of very high pressure, etc., different mechanical tests are carried out. One of such tests is “four-ball extreme-pressure lubricant test”,
in which the lubricant under-test is poured in a machine containing four balls. The lower three balls are stationary; while the upper ball is rotated. Load is gradually increased and the balls withdrawn and examined at specific intervals for scale formation, etc., on them. If the lubricant is satisfactory under the given load, the ball bearings after the best comes out clean. However, when the load is progressively increased, and if liberated heat welds the balls together, then the lubricant is said to have failed completely. Thus, this test enables us to determine the maximum load that can be carried safely by a lubricant.

Q.No.9. Write a note on lubricants with special reference to their classification, mode of action, examples and uses. (or ) Discuss the important functions of lubricants. Discuss solid & liquid lubricants

Answer: A lubricant may thus be defined as a substance which reduces the friction when introduced between two surfaces.

Functions of lubricants:
1. It reduces the maintenance and running cost of the machine.
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7. In some times, it acts as a seal, preventing the entry of dust and moisture between the moving surfaces.
8. It minimizes corrosion.

Classification of Lubricants:
Lubricants are classified on the basis of their physical state as follows
1. Liquid Lubricants or Lubricating Oils
2. Semi-Solid Lubricants or greases

1. Liquid Lubricants or Lubricating Oils: Lubricating oils reduce friction and wear between two moving metallic surfaces by providing a continuous fluid film in between the surfaces. A good lubricant must have the following characteristics.
   a. It must have high boiling point or low vapour pressure.
   b. Thermal stability and oxidation resistance must be high.
   c. It must also have adequate viscosity for particular operating conditions.
   d. The freezing point must be low.
   e. It must also have non-corrosive property lubricating oils are further sub-classified as
      a. Animal and Vegetable oils
      b. Petroleum oils or Mineral oils
      c. Blended oils or Additives for lubricating oils
      d. Synthetic lubricants

Animal and Vegetable oils: Animal and vegetable oils are glycosides of higher fatty acids. They have very good oiliness. However, they are costly, undergo oxidation very easily, and have a tendency to hydrolyze when it contact with moist air or water.

These oils undergo decomposition on heating without distilling, and hence they are “fixed oils”. They are used as additives to improve the oiliness of petroleum oils.

Petroleum oils or Mineral oils: They are obtained by fractional distillation of crude petroleum oils. The length of the hydrocarbon chain varies between $C_{12}$ to $C_{50}$. They are cheap and quite stable under operating conditions. They possess poor oiliness, the oiliness of which can be improved by the addition of higher molecular weight vegetable or animal oils. Crude liquid petroleum oil cannot be used as such, because they contain lot of impurities like wax. Asphalt, colored substances and other oxidisable impurities
**Blended oils or Additives for lubricating oils:** No single oil serves as the most suitable lubricant for many of the modern machineries. Specific additives are incorporated into petroleum oils to improve their characteristics. These oils are to improve their characteristics. These oils are called “blended oils” and give desired lubricating properties, required for particular machinery.

**Synthetic lubricants:** Mineral oils cannot be used effectively as they tend to get oxidized at very higher temperatures while wax separation will occur at very low temperatures. so, synthetic lubricants have been developed, which can meet the severe operating conditions such as in aircraft engines. The same lubricants may have to be in the temperature range of -50 °C to 250 °C. Polyglycol ethers, fluoro and chloro hydrocarbons, organophosphates and silicones are currently used as synthetic lubricants.

2. **Semi-Solid Lubricants or greases:** Grease is a semi solid lubricant obtained by thickening liquid lubricating oil through the addition of a metallic soap. The thickness is usually sodium or calcium or lithium soap.

   **Types of grease:**
   a. Soda-base grease
   b. Lime-base grease
   c. Lithium-soap grease
   d. Barium-soap grease
   e. Axle (Resin) grease

3. **Solid Lubricants:** Solid lubricants are used where
   - The operating temperature and load is too high.
   - Contaminations of lubricating oils or greases by the entry of dust or grit particles are avoided.
   - Combustible lubricants must be avoided.

Graphite and Molybdenum disulphide are the widely used solid lubricants.

- **Graphite:** It consists of a multitude of flat plates, which are held together by weak Vander Waals’s forces, so the force to shear the crystals parallel to the layers is low. It is used either in powder form or as suspension. When graphite is dispersed in oil, it is called ‘oil dag’ and when graphite is dispersed in water is called ‘aquadag’. It is ineffective at above 370 °C. It is used for lubricating internal combustion engines.

- **Molybdenum disulphide:** It has a sand-witch like structure in which a layer of molybdenum atoms. Lies between two layers of sulphur atoms. The weak Vander Waals forces, acting in between the layers, can be destroyed easily. MoS$_2$ can also be used as power or dispersions. It is effective up to 800 °C. It is used in wire-drawing dues.

**Q.10. Write a short note on superconductors and mention its applications.**

**SUPERCONDUCTORS:**
Superconductivity was invented by Kamerlingh Onnes in 1911 during his experiments on electrical resistivity of metals and alloys at sufficiently low temperatures. With decrease in temperature, the electrical resistivity of many metals decreases. The phenomenon in which the electrical resistivity of the materials suddenly falls to nearly zero when it is cooled to a very low temperature is known as ‘superconductivity’ and materials under this condition is called ‘superconductor’. 

**Preparation of 1:2:3 or YBa$_2$Cu$_3$O$_{7-x}$ superconductor:**
Two methods are adopted for the preparation of superconductor. They are
1. Ceramic method &
2. Microwave method.

1. **Ceramic method:** The ceramic method involves heating together of two or more solids to get the desired product. For the preparation of, a mixture of (0.750gm), Ba$_2$C$_3$ (2.62 gm) and CHO (1.58 gm) are grinded into paste in a mortar. The mix is heated in a porcelain crucible kept in a furnace at 920 – 930°C for about 12 yours. Then the mixture is allowed to cool gradually. The crucible is removed when the temperature reaches
to 100°C. When the crucible reaches room temperature the sample is taken out. This sample possesses the superconductivity at liquid N2 temperature. Its composition is YBa$_2$Cu$_3$O$_{7-X}$.

**Disadvantages:** Very high temperature is required for the process. Some times the product may not be homogeneous. It is very slow and time consuming process.

2. **Microwave method:** By using microwaves, the superconductor YBa$_2$Cu$_3$O$_{7-X}$ can be prepared in just 2 hours. During the reaction, nitrogen oxides are removed safely in a modified microwave oven.

A stoichiometric proportion of reaction mixture of and Ba(NO$_3$)$_2$CuO is placed in a microwave oven. The mixture is subjected to microwave radiation of 500 W for 5 minutes. After regrinding, the mixture is exposed for 15 minutes to radiation at 130 – 500 W. finally, the mixture is again ground and exposed to radiation for another 25 minutes.

In this method, the microwave was coupled to copper oxide. This non-stoichiometric oxide is heated by microwave radiation. For example, just 5 gm CuO exposed to radiation of 500 W for 30 seconds attains a temperature of 1074 K.

**Advantages:**
- Reaction time is greatly reduced.
- The problem with cracking is minimized since heating is from inside, not absorbed from outside as in ceramic method.

**Limitations:**
- Temperatures are very high.
- Chemical in homogeneity cannot be overcome.

**Properties of superconductors:**
- Superconductors offer more resistivity than other elements at room temperature.
- Critical temperature of superconductor is lower when a small amount of impurity is added to it.
- During phase change of materials from normal state to superconducting state, the thermal expansion and elastic properties remain unchanged.
- In superconducting state, all electromagnetic effects disappear. The materials become diamagnetic.
- When a strong magnetic field is applied to a superconductor below its critical temperature, the superconductivity is destroyed.

**Applications of superconductors:**
- Some superconductors act as excellent catalysts for industrial processes. For example, YBa$_2$Cu$_3$O$_{7-X}$ and related cuprates act as catalysts in oxidation or dehydrogenation reactions.
- La$_{2-x}$Sr$_x$CuO$_4$ is a good sensor for alcohol vapours. On contact with certain gases, the electrical resistivity of superconductor changes sharply.
- Because of their speed of operation and efficiency, they replace the conventional doped metallic conductors and alloy conductors in electronic circuits. Super clips made of superconductors for computers. These can function 1000 times faster than silicon clips.
- Superconducting magnets capable of generating high fields with low power consumption are being employed in scientific tests and research equipments.
- Because of their small size and less energy consumption, superconductors are used in magneto-hydrodynamic power generators to maintain plasma.
- Superconductors are used in magnetic resonance imaging (MRI) in the field of medicine as a diagnostic tool. Based on the production of cross – sectional images, any abnormalities in body tissues and organs can be detected. Magnetic resonance spectroscopy is used in the chemical analysis of body tissues.
- Superconducting cables can be used to transmit electric power over long distances without resistive losses.
- High efficiently separating machines are built using superconducting magnets, which are also used to separate tumour cells from healthy cell by high gradient magnetic separation method.
ix. They can be used as a memory or storage device in computers, since the current can flow without any change in its value with time in a superconductor.

x. In Japan, superconducting magnets have been used to levitate an experimental train above its track and can drive it at a great speed of 500 km/h with minimum expenditure of energy. A similar magnetic propulsion system may be used to launch satellites into orbits directly from the earth without the use of rockets.

xi. Using superconducting elements, one can built up an extremely fast and large scale computer in compact size. It consumes less than 0.5 W powers.