

Fig. 1.1 The phase diagram of water system.

is been found true. Actually, for any given temperature, there exists one and only one vapour pressure. Similarly, for each vapour pressure, the system can maintain one and only one temperature.

At point D, the vapour pressure of water equals to the atmospheric pressure. The corresponding temperature shown on the phase diagram (i.e., 100°C) represents the boiling point of water.

The curve OA terminates at point A where the temperature is 374°C and the corresponding pressure is 218 atm. At this point the liquid water and vapour are indistinguishable and the system has only one phase. This point is called the **critical point**.

The slope of the curve OA is positive i.e., the vapour pressure of water increase with temperature. It is also predicted by the Clausius-Clapeyron equation as

$$\frac{dP}{dT} = \frac{\Delta H_V}{T(V_g - V_l)} = +ve \quad [\because V_g > V_l]$$

where  $\Delta H_V$  = change in molar heat of vaporization  
 $V_g$  = molar volume of water vapours  
 $V_l$  = molar volume of water (liquid)  
 $T$  = boiling point of water.

$$\text{On integrating, we get } \log \frac{P_2}{P_1} = \frac{\Delta H_V}{2.303R} = \left[ \frac{T_2 - T_1}{T_1 T_2} \right]$$

where  $P_1$  and  $P_2$  are the vapour pressures at temperatures  $T_1$  and  $T_2$  respectively.

(ii) **Curve OB**: It is called the **sublimation curve** of ice and gives the vapour pressure of solid ice at different temperatures. Along this curve, the two phases - ice and vapour are together in equilibrium. The component is again 1. Thus, along this curve, we have  $C = 1$  and  $P = 2$ .

According to the phase rule,

$$F = C - P + 2 = 1 - 2 + 2 = 1$$

Hence, it is also a **univariant system**. We need to specify either temperature or pressure to define the system. This is also in accordance to the experimental observations. In a system consisting of ice and vapour in equilibrium, there exists one and only one pressure for a particular temperature. Similarly, the system can maintain one and only one temperature for a particular pressure.

The lower end of curve OB extends to absolute zero ( $-273^{\circ}\text{C}$ ) where no vapour exists.

Here the slope of the curve OB is positive and also predicted by the Clausius-Clapeyron equation as

$$\frac{dP}{dT} = \frac{\Delta H_s}{T(V_g - V_s)} = +\text{ve}$$

where  $\Delta H_s$  = change in molar heat of sublimation.

On integrating, we get

$$\log \frac{P_2}{P_1} = \frac{\Delta H_s}{2.303 R} = \left[ \frac{T_2 - T_1}{T_1 T_2} \right]$$

(iii) **Curve OC**: It is called the **fusion curve** of ice and represents the effect of pressure on the melting point of ice. Along this curve, water and ice exist together in equilibrium. Along the curve OC, we have two phases (ice and water) in equilibrium and one component ( $\text{H}_2\text{O}$ ) i.e.  $P = 2$  and  $C = 1$ .

Therefore, according to the phase rule,

$$F = C - P + 2 = 1 - 2 + 2 = 1$$

Thus, the system is **univariant**. It is in accordance to the experimental observations that pressure and temperature, only one factor is sufficient to be fixed in order to define the system. The other factor gets automatically fixed. For example, at 1 atm pressure and water can be in equilibrium only at  $0^{\circ}\text{C}$ , which is the normal melting point of water.

**The curve OC is inclined towards the pressure axis i.e., towards left.** The slope of the curve indicates that the melting point of ice decreases with increase in the pressure. The curve also indicates that the melting of ice proceeds with a decrease in volume. In accordance to the Le-Chatelier's principle\*. Thus, when pressure is increased on the system in water equilibrium, the equilibrium shifts in the direction that involves a decrease in volume i.e. some ice changes into water. The melting of ice takes latent heat from the system. Consequently, the temperature i.e. the melting point of ice gets lowered. The curve ends at the 1 atm line at point E which corresponds to  $0^{\circ}\text{C}$ . This is the normal melting point of water.

**Le-Chatelier's principle\*** It states that whenever a constraint is applied on a system at constant pressure, the system behaves in such a way so as to counteract the constraint.

The slope of the curve is negative i.e., the melting point of ice is lowered by increase of pressure. It is also predicted by Clausius-Clapeyron equation as

$$\frac{dP}{dT} = \frac{\Delta H_f}{T(V_l - V_s)} = -\text{ve}$$

$\therefore V_s > V_l$

here  $\Delta H_f$  = change in molar heat of fusion.

As the  $\frac{dP}{dT}$  is negative, to counter effect this the curve OC is sloping towards pressure axis.

**Note :** The freezing point of water is lowered by  $0.0075^{\circ}\text{C}$  increase by 1 atmospheric pressure.

## 2. Metastable Equilibrium (Supercooled water/vapour system)

When water is cooled with due care, sometimes it becomes possible to cool it below its freezing point (melting point of ice) without the separation of ice i.e. water remains in the liquid state even below its freezing point. Water in this state is called **super cooled water** and can be kept as such for some time by carefully eliminating the ice particles or any other solid phase. Under these circumstances, the vapour pressure curve of liquid water i.e. AO continues in the same direction even below the point O and the dotted line curve OA' is obtained. Thus, the curve OA' may be regarded as the prolongation of the curve AO. The curve OA' represents the supercooled water vapour equilibrium which is usually referred to as **metastable equilibrium**.

The supercooled water is metastable. As soon as the system is slightly disturbed or a small particle of ice is brought in contact with it, it changes into ice. It is to be noted that the curve OA' lies above the curve OB. This indicates that the metastable supercooled water-vapour system has a higher vapour pressure than the stable ice-vapour system.

## 3. Point O (Triple Point)

In the phase diagram of the water system, the three curves OA, OB and OC meet at the point O. At this point, all the three phases i.e. ice, water and vapour exist together in equilibrium. The point where three phases coexist in equilibrium is called a **triple point**. Hence, point O is a triple point. It corresponds to a temperature of  $0.0075^{\circ}\text{C}$  and a pressure of 4.58 mm.

At point O, we have three phases and one component i.e.  $C = 1$  and  $P = 3$  according to the phase rule,

$$F = C - P + 2 = 1 - 3 + 2 = 0$$

Thus, the system at point O is **non-varient**. This implies that neither temperature nor pressure needs to be specified to define the system at this point. Alternatively, neither temperature nor pressure can be changed without changing the system. This prediction is in accordance to the observed facts. We need not to specify either temperature or pressure to define the ice  $\rightleftharpoons$  water  $\rightleftharpoons$  vapour equilibrium. The three phases can exist in equilibrium only at  $0.0075^{\circ}\text{C}$  and 4.58 mm. If either temperature or pressure is changed, one phase will disappear and the system will change. For example, if temperature is increased, ice will melt and only two phases i.e. water and vapour will be left.

## 4. Areas

The regions between the curves are referred to as **areas**. The phase diagram of the system consists of three areas - BOC, COA and AOB. Each area consists of a single phase and

$$F' = C - P + 1$$

(where  $F'$  represents the number of remaining degrees of freedom of the system)  
This phase rule known as the **Reduced phase rule** and the equation is known as **Reduced phase rule equation**.

Note : When the two components are miscible in the liquid state, we have following three of two-component systems :

(i) **Simple eutectic systems** : In such systems, the two components although miscible in liquid state are not miscible in the solid state and form a eutectic mixture (Greek : eutectic meaning easy melting).

(ii) **Systems forming compounds with congruent melting points**: In this type of systems the two components form a stable compound which possess a **congruent melting point**

(iii) **Systems forming compounds with incongruent melting points** : In this type of systems, the two components form a compound which possesses an **incongruent melting point**.

### 1.6.1. Simple Eutectic Systems

A solid solution of two (or more) components having the lowest melting point (freezing point of all the possible mixture of the components is called an **eutectic mixture** and a binary mixture forming an eutectic mixture at a particular composition is called an **eutectic system**.

Note : In a simple eutectic system, the two components are completely miscible in the liquid state but they do not form any inter-component compound. Therefore, the remain immiscible in solid state and separate out as solid phases when the solution is cooled. The system has minimum freezing point at a particular composition. Lead-silver system is an important system of this type.

#### Lead-silver system

In the liquid state both lead and silver are completely miscible and form a homogeneous solution. They do not react chemically and therefore do not form any inter-component compound. However, they are not miscible in the solid state. therefore, when a lead-silver solution is subjected to cooling, either silver or lead (depending upon the composition) separates out as the solid phase.

The melting point of pure lead is  $327^\circ\text{C}$ . It is lowered by addition of silver. Similarly, melting point of pure silver is  $961^\circ\text{C}$ . It is lowered by addition of lead.

Since it is solid-liquid equilibrium system which does not have gaseous phase is called **condensed system**. Since the pressure does not have any effect on this type of equilibrium hence the degree of freedom for such a system will be reduced by one. Here the reduced phase rule,

$$F' = C - P + 1 \text{ is applicable.}$$

The lead-silver system has four possible phases :

- (i) Solid silver
- (ii) Solid lead
- (iii) Solution of molten silver and lead
- (iv) Vapour

The phase diagram of the lead-silver system is shown in fig. 1.4.

### Salient Features of Phase diagram of Lead Silver System

#### 1. Curves

(i) **Curve AC** : It is the freezing point curve of silver and shows the variation of melting point (freezing point) of silver on addition of molten lead. All along this curve – the silver which is added goes into solution while the separation of solid Pb takes place, solid Pb is in equilibrium with liquid melt (i.e., solution of Ag in liquid Pb) of varying composition and two

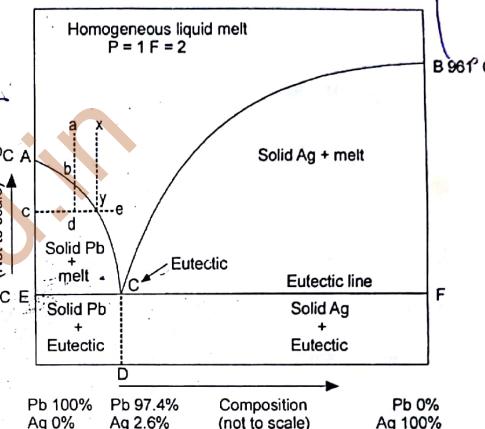


Fig. 1.4 Phase diagram of the Lead Silver System.

Solid Pb  $\longrightarrow$  Solution of Ag in liquid Pb

$$F' = C - P + 1 = 2 - 2 + 1 = 1$$

The system is **univariant** along this curve.

(ii) **Curve BC** : It represents the melting point or freezing point curve of Ag by addition of small amount of Pb. The melting point of Ag gets lowered gradually by the addition of lead to it. All along this curve – the Pb which is added goes into solution while the separation of solid Ag takes place, solid Ag is in equilibrium with liquid melt. (i.e., solution of Pb in liquid Ag), of varying composition and two phase solid silver and liquid melt co-exist.

Solid Ag  $\longrightarrow$  Solution of Pb in liquid Ag

$$F' = C - P + 1 = 2 - 2 + 1 = 1$$

i.e., the system is **univariant** along this curve.

#### 2. Areas

(i) **Area above the curve ACB** : In this region only one phase i.e., liquid alloy (melt of Ag and Pb) co-exist.

$$F' = C - P + 1 = 2 - 1 + 1 = 2$$

i.e., the system is **bivariant** in this region (temperature and composition).

**Cooling of melt in the area above curve ACB :** When a melt of certain composition (say 'a') in the area above the curve ACB is allowed to cool, it follows Newton's cooling and represented as in fig. 1.5. 'pq' represents the cooling of liquid and corresponds to 'ab' in the phase diagram.

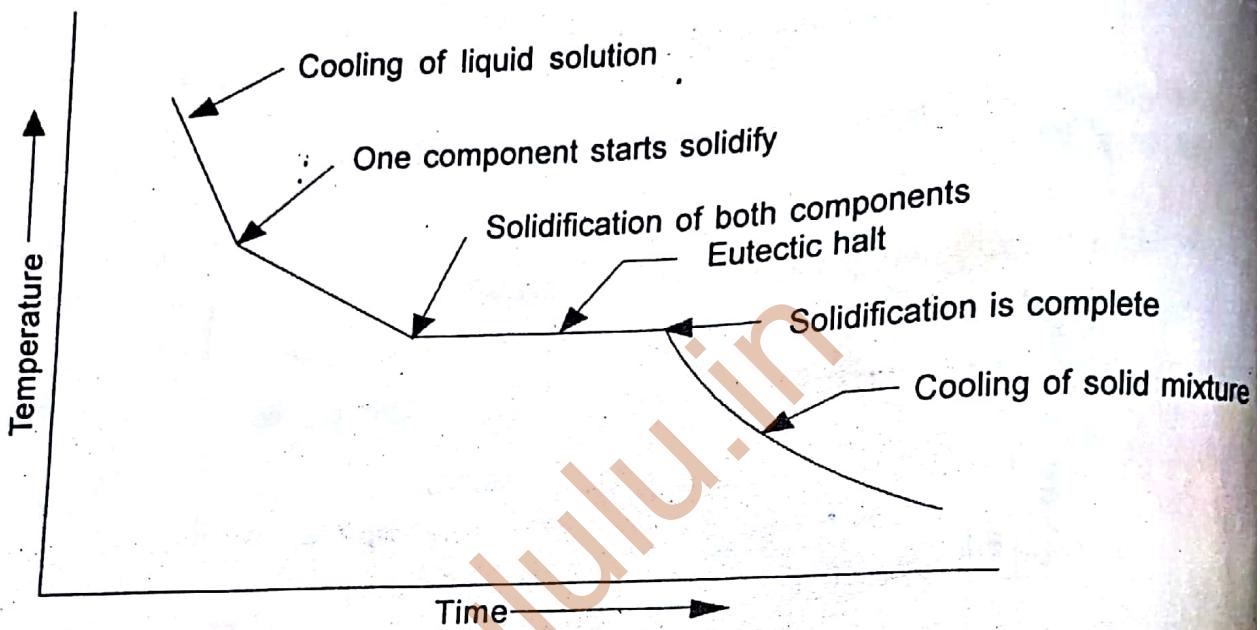


Fig. 1.5 Cooling curve of liquid melt.

Lead crystals start separating when point 'b' is reached and the rate of cooling changes due to latent heat of fusion of lead. It is represented by 'q' in the cooling curve. More and more lead goes on separating with the decrease in temperature from 'q' to 'r' in cooling curve. The melt goes on becoming more and more concentrated with respect to silver till the point 'C' is reached when both lead and silver start freezing out. At point 'C' in phase diagram lead and silver freeze out simultaneously. At this point, the composition of the melt is the same as that of the solid mixture of lead and silver. The liquid melt freezes out as if it was a pure compound. The whole of the melt freezes out at constant temperature, represented by a horizontal line 'rs' in the cooling curve. This constant temperature corresponds to point 'C' in phase diagram. This point 'C' is known as **eutectic point** (low melting) and the solid mixture is called **eutectic mixture** which has a characteristic composition for each system.

The eutectic though melts at a constant temperature, is not a chemical compound of lead and silver as :

- (i) Its composition does not correspond to any simple chemical formula.
- (ii) Its composition depends on temperature. Below point C only solid phase exists. The cooling of this solid eutectic is represented by a dotted line CD.
- (iii) **Area ACE :** In this area solid lead and liquid melt co-exists. The composition of liquid melt at any temperature, can be obtained from the curve AC. At point 'd' in this area, the composition of lead is in horizontal line passing through d, known as tie line. The amount of solid and the amount of saturated solution (melts) is given by the equation.

The phase diagram of the system is shown in fig. 1.7.

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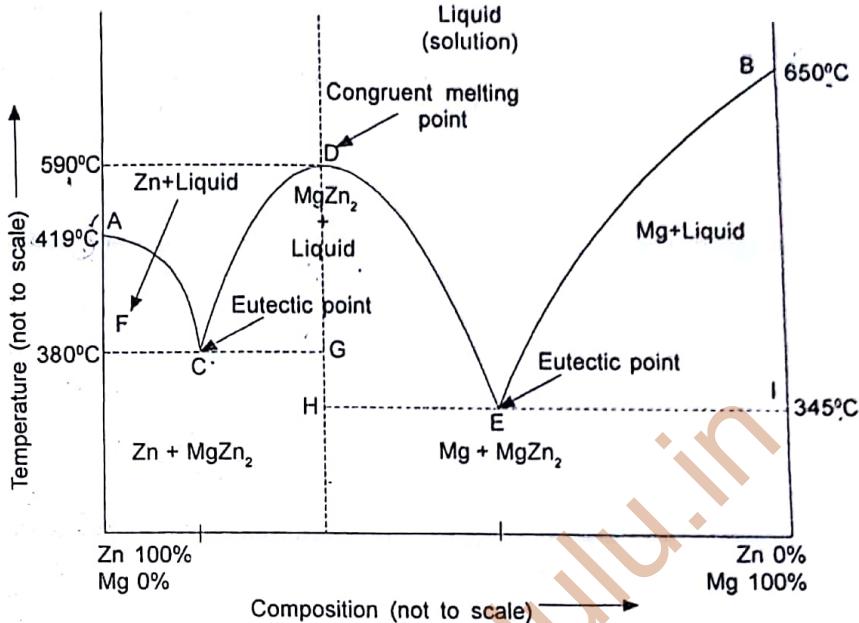


Fig. 1.7 The phase diagram of Zn-Mg system.

### Salient features of the phase diagram of Zn-Mg system

The phase diagram of this system may be considered as made up of two simple eutectic diagrams. The one on the left represents the eutectic system Zn-MgZn<sub>2</sub>, while the other on the right represents the eutectic system Mg-MgZn<sub>2</sub>.

#### 1. Curves

(i) **Curve AC** : This is the **freezing point curve of zinc** and shows that the melting point (freezing point) of zinc decreases on the addition of magnesium. The lowering in melting point continues till the point C is reached where a new phase, solid MgZn<sub>2</sub>, separates out.

The phases in equilibrium along AC are solid Zn and Zn-Mg solution (liquid).  
ince  
 $C = 2$  and  $P = 2$ ,

$$F' = C - P + 1 = 2 - 2 + 1 = 1 \text{ i.e., it is univariant system.}$$

(ii) **Curve CDE** : This curve has a maxima at point D which corresponds to the melting point of MgZn<sub>2</sub> (590°C).

The CD portion of the curve shows the increase of concentration of magnesium in the liquid with increase in its freezing point. At point D (the maxima), the composition of the liquid and that of the solid compound MgZn<sub>2</sub> becomes the same. Thus, the temperature corresponding to point D (590°C) represents the melting point of the compound MgZn<sub>2</sub>. Since at point D, MgZn<sub>2</sub> co-exists as solid and liquid having the same composition, the point D represents the **congruent melting point** of the system. The DE portion of the curve shows the lowering of the melting point of the system with increase in the percentage of magne-

sium. The curve terminates at point E which is an **eutectic point**.

Except at point D, the two phases - solid  $MgZn_2$  and the liquid exist in equilibrium in the curve CDE. Therefore, except at point D, the system is a two-phase ~~www.dudu.in~~ **univariant** system and is **univariant**.

(iii) **Curve BE** : It is the **freezing point curve of magnesium** and shows that the point of magnesium ( $650^\circ C$ ) gets lowered with the addition of zinc until the point reached. The two phases in equilibrium are solid magnesium and the liquid. The system is **univariant**.

## 2. Points

(i) **Point D (Congruent melting point)** : The point D is the **congruent melting point** of the system. The temperature corresponding to this point is  $590^\circ C$ .

At point D, the two-component Zn-Mg system reduces to a one-component system.

Thus at point D, we have  $C = 1$  ( $MgZn_2$ ) and  $P = 2$  (solid  $MgZn_2$  and liquid).

$$\text{Therefore, } F' = C - P + 1 = 1 - 2 + 1 = 0$$

Hence, the system is **invariant** at point D.

(ii) **Point C (Eutectic point)** : Point C represents an eutectic point and corresponds to a temperature of  $380^\circ C$  which is the minimum melting point of Zn-MgZn<sub>2</sub> system. At point, the three phases - solid Zn, solid MgZn<sub>2</sub> and liquid coexist in equilibrium.

Thus, at point C, we have  $C = 2$  and  $P = 3$

$$\text{Therefore, } F' = C - P + 1 = 2 - 3 + 1 = 0$$

Hence, the system is **invariant** at point C.

(iii) **Point E (Eutectic point)** : Point E represents another eutectic point of the system corresponds to a temperature of  $345^\circ C$  which is the minimum melting point of MgZn<sub>2</sub> system.

The three phase existing together in equilibrium at point E are solid Mg, solid MgZn<sub>2</sub> liquid. Since

$$C = 2 \text{ and } P = 3$$

Therefore

$$F' = C - P + 1 = 2 - 3 + 1 = 0$$

Hence, the system is **invariant** at point E.

## 3. Areas

(i) **Area ACF** : It consists of two phases zinc and liquid.]

Here,

$$P = 2, C = 2$$

$$F' = C - P + 1 = 2 - 2 + 1 = 1 \text{ i.e., the system is univariant}$$

(ii) **Area DCG** : It consists of two phases  $MgZn_2$  and liquid.

Here,

$$P = 2, C = 2$$

$$F' = 1$$

i.e., the system is **univariant**.

(iii) **Area HDE** : It consists of two phases  $MgZn_2$  and liquid.

Here,

$$P = 2, C = 2$$

$$F' = 1$$

i.e., the system is **univariant**.

**Area BEI** : It consists of two phases Mg and liquid.

$$P = 2, C = 2$$

$F' = 1$  i.e., the system is **univariant**.

(v) **Area below FCG** : It consists of two phases Zn and  $MgZn_2$ .

$$P = 2, C = 2$$

$F' = 1$  i.e., the system is **univariant**.

(vi) **Area below HEI** : It consists of two phases Mg and  $MgZn_2$ .

$$P = 2, C = 2$$

$F' = 1$  i.e., the system is **univariant**.

(vii) **Area above ACD** : It consists of only one phase that is liquid. In this area liquid Zn and  $MgZn_2$  co-exist.

$$P = 1, C = 2$$

$F' = 2 - 1 + 1 = 2$  i.e., the system **bivariant**.

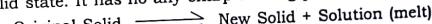
(viii) **Area above DEB** : It consists of only one phase that is liquid Mg and liquid  $MgZn_2$ .

$$P = 1, C = 2$$

$F' = 2$  i.e., the system **bivariant**.

## 3.3. Systems with Incongruent Melting Points

A system (compound) is said to be possess incongruent melting point, if it decomposes A system (compound) is said to be possess incongruent melting point, if it decomposes which below its melting point and forms a new solid phase and a solution having different position from solid state. It has no any sharp melting point.



The decomposition at this temperature is known as **transition reaction or meritecic peritectic reaction** and the temperature (the incongruent melting point) is known as **inversion temperature or meritecic or peritectic temperature**. In such type of systems components undergo in chemical combination and forms a new compound which is stable and on heating it decomposes much below its melting point to form a new solid and solution or melt.

### Sodium Sulphate - Water System

The phase diagram for  $Na_2SO_4 - H_2O$  system is shown in fig. 1.8.

Ident features of phase diagram of  $Na_2SO_4 - H_2O$  system

The sodium sulphate - water system forms two hydrate, i.e.

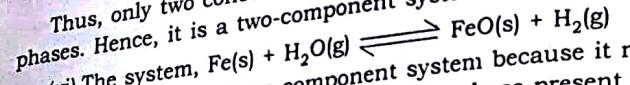
(i) Decahydrate-  $Na_2SO_4 \cdot 10H_2O$  and (ii) Heptahydrate-  $Na_2SO_4 \cdot 7H_2O$ .

Both these hydrates have different incongruent melting points.

Sodium sulphate also exists in two crystalline forms, namely rhombic and monoclinic. The remaining phase and solid ice, solution and vapour. All the investigations were made atmospheric pressure therefore vapour phase is ignored. Now  $Na_2SO_4 \cdot H_2O$  is a six phase denoted system.

Phase	Components
$\text{CaCO}_3(s)$	$\text{CaCO}_3 + \text{OCO}_2$
$\text{CaO}(s)$	$\text{CaCO}_3 - \text{CO}_2$
$\text{CO}_2(g)$	$\text{OCaCO}_3 + \text{CO}_2$

Thus, only two constituents are sufficient to represent the composition of all the phases. Hence, it is a two-component system.



is a three-phase and three-component system because it requires three constituents  $\text{Fe}$ ,  $\text{H}_2\text{O}$  and  $\text{H}_2$  to express the composition of each phase present in the system.



is a three-phase and two component system. It requires two constituents  $\text{CuSO}_4$  and  $\text{H}_2\text{O}$  to express the composition of each phase of the system.

#### 1.2.4 Degree of Freedom (F)

The degree of freedom of a system is defined as the minimum number of independent variable factors such as temperature, pressure and concentration which must be specified to define the system completely.

Degree of freedom of a system is also termed as variance. A system having no degrees of freedom (i.e.,  $F = 0$ ) is called a **non-varient system** or **invariant system**. The system having only one degree of freedom (i.e.,  $F = 1$ ) is termed as a **univariant** or a **monovariant system**. Similarly, a system having two degrees of freedom is referred to as a **bivariant system**.

Some common examples are:

(i) For a pure gas, the number of degrees of freedom is two (i.e.,  $F = 2$ ). This is because a pure gas satisfies the gas equation  $PV = RT$ . If the values of pressure ( $P$ ) and temperature ( $T$ ) are fixed, then the volume automatically gets fixed. In fact, if any two variables (out of  $V$  and  $T$ ) are specified, the third one gets specified by itself. Thus, such a system can be defined completely by specifying any two factors. Hence, it is a **bivariant system**.

(ii) For a mixture of gases, the number of degrees of freedom is three (i.e.,  $F = 3$ ). Such a system can be completely defined when the temperature, pressure and composition are specified. In this case, the remaining factor i.e. volume gets automatically fixed. For example, a gaseous mixture consisting of 60%  $\text{N}_2$  and 40%  $\text{O}_2$  at 25°C and 1 atm pressure is completely defined and does not require any other information for its description. Hence, it is a **trivariant system**.

(iii) The system water  $\rightleftharpoons$  water vapour has only one degree of freedom (i.e.,  $F = 1$ ). Such a system can be completely defined by specifying either temperature or pressure. This is because on fixing one factor (either temperature or pressure), the other gets automatically fixed. Hence, it is a **univariant system**.

(iv) The system ice  $\rightleftharpoons$  water  $\rightleftharpoons$  vapour has no degree of freedom (i.e.,  $F = 0$ ). This is because the three phases of water i.e. ice, liquid water and vapour can exist together in equilibrium only at a particular temperature and pressure (corresponding to the freezing point) and no factor is necessary to be specified to define the system. Hence, it is a **non-varient system**.

(v) For a saturated  $\text{NaCl}$  solution, the number of degrees of freedom is one (i.e.,  $F = 1$ ). This is because the system can be completely defined by specifying the temperature only. The other two factors i.e. composition and vapour pressure get automatically fixed when the temperature is fixed. Hence, it is a **univariant system**.

#### 2.5. Dynamic equilibrium

A system is said to be in state of true equilibrium under a given set of conditions if the same state can be realised by approach from either direction by following any possible procedure.

For example, the equilibrium exists between ice and water at 1 atm pressure and 273 K.



It is true equilibrium because it can be attained by partial melting of ice or by partial freezing of water.

#### Meta-stable equilibrium

A system is said to be in a state of metastable equilibrium under a given set of conditions if the state can be realised only from one direction by a careful change of conditions. For example, it is possible to cool water slowly and very carefully to 271 K (-2°C) or even lower temperature without the appearance of ice. Hence water at 271 K is said to be in a state of metastable equilibrium. Metastable state may be preserved, if the system is not disturbed by addition of solid phase or stirring etc. However, if stirring is done or if a small piece of ice is added, solidification sets in and a temperature rises to 0°C.

#### Criteria for Phase Equilibria

The temperature, pressure and chemical potential must be same throughout the system in the equilibrium. If we consider the equilibrium between two phases in an isolated system



If  $T_1$  and  $T_2$  are temperatures,  $P_1$  and  $P_2$  are pressures and  $\mu_1$  and  $\mu_2$  are chemical potentials then

at constant temperature,  $T_1 = T_2$  (Thermal equilibrium)

at constant pressure,  $P_1 = P_2$  (Mechanical equilibrium)

at constant composition,  $\mu_1 = \mu_2$  (Chemical equilibrium)

#### 3. DERIVATION OF THE PHASE RULE EQUATION

It is derived thermodynamically as :

Let us consider a heterogeneous system in equilibrium consisting of  $P$  number of phases and  $C$  number of components. Let the phase be denoted as  $\alpha, \beta, \gamma, \delta, \dots, P$  and the components as  $C_1, C_2, C_3, \dots, C$ . Let us assume that the system is chemically non-reacting. The system can be defined completely by specifying the following variables :

- (i) Temperature
- (ii) Pressure
- (iii) Composition of each phase

Composition of each phase can be specified by specifying the concentration of substance (component) in each phase. Since there are C component and P phases in the system, total number of concentration variables required to represent the composition of each phase will be CP. Thus in all, CP + 2 variables should be required to specify completely the system under consideration. They can be represented as

$$T, P, (x_1 \alpha; x_2, \alpha; \dots, x_C, \alpha), (x_1, \beta; x_2, \beta; \dots, x_C, \beta) \dots \dots (x_1, P; x_2, P \dots, x_C, P)$$

where  $x_i$ s are the composition of the  $i^{\text{th}}$  component.

In equation (1) all the variables are not independent due to the restrictions imposed by the equilibrium conditions. The conditions that must be satisfied for the system to be in equilibrium can be obtained as follows:

In each phase, the sum of the mole fractions must be equal to unity. Thus,

$$x_1, \alpha + x_2, \alpha + \dots + x_C, \alpha + x_1, \beta + x_2, \beta + \dots + x_C, \beta + \text{etc.} = 1$$

$$\text{i.e., } \sum_i x_i, P = 1 \quad (i = 1, 2, 3 \dots, C)$$

Since there are P phases present in the system, we shall have P equations of this type.

The various phases present in the system can remain in equilibrium only when the **chemical potential\*** of each component is the same in each phase, i.e.

$$\text{For component 1} \quad \mu_1, \alpha = \mu_1, \beta = \mu_1, \gamma = \dots = \mu_1, P$$

$$\text{For component 2} \quad \mu_2, \alpha = \mu_2, \beta = \mu_2, \gamma = \dots = \mu_2, P$$

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$$\text{For component C} \quad \mu_C, \alpha = \mu_C, \beta = \mu_C, \gamma = \dots = \mu_C, P$$

Total no. of equations in one row = P - 1

Total no. of rows = C

$\therefore$  Total no. of equations = C(P - 1)

Hence, the total number of restricting conditions = P + C (P - 1)

The number of degree of freedom,

$$F = \left( \begin{array}{l} \text{Total no. of variables required} \\ \text{to specify the state of the system} \end{array} \right) - \left( \begin{array}{l} \text{Number of restricting conditions imposed} \\ \text{by the interdependence of variables} \end{array} \right)$$

or

or

or

$$F = (CP + 2) - [P + C (P - 1)]$$

$$= CP + 2 - P - CP + C$$

$$F = C - P + 2$$

Equation (5) represents the **Gibbs phase rule equation**.

**Phase rule for a chemically reacting system :** Suppose the system under consideration

\* **Chemical Potential :** Chemical potential  $\mu_i$  of the  $i^{\text{th}}$  component in a mixture is defined as

$$\mu_i = \left( \frac{\partial G}{\partial n_i} \right)_{P, T, n_1, n_2, \dots}$$

where  $n_1, n_2, \dots$  etc. represent the number of moles.

# Chapter - 1

## Phase Rule

### 1. INTRODUCTION

In order to study heterogenous systems, a very important generalisation called **Phase rule** was given by **J.W. Gibbs** in 1876. It was deduced on the basis of the principles of thermodynamics. The phase rule is an important tool to predict the conditions necessary to be specified for a heterogeneous system to exhibit equilibrium. The rule is also able to predict qualitatively the effect of changing temperature, pressure, or concentration on a heterogeneous system in equilibrium.

### 2. TERMINOLOGY

#### 2.1. Statement of Phase Rule

The Gibbs phase rule can be stated as – *for heterogeneous system in equilibrium at a definite temperature and pressure, the number of degrees of freedom is greater than the difference in the number of components and the number of phases by two provided the equilibrium is not influenced by external effects such as gravity, electrical or magnetic forces, surface tension etc.*

Mathematically,

$$F = C - P + 2$$

where F is the number of degrees of freedom, C is the number of components and P represents the number of phase of the system.

**Note :** The phase rule is a very important generalisation and is free from exceptions. The law has the theoretical background of thermodynamics and can be applied universally to all heterogeneous systems.

#### 1.2.2. Phase (P)

A phase may be defined as *any homogeneous and physically distinct part of a system which is bounded by a surface and is mechanically separable from the other parts of the system is called a phase.*

When a system consists of only phase, it is termed as a **homogeneous system**. For example, a solution of NaCl in water. On the other hand, when a system consists of two or more phase, it is referred to as **heterogeneous system**. For example, a system consisting of CHCl<sub>3</sub> and water. It has two phase - water phase and CHCl<sub>3</sub> phase.

#### Required conditions for phase

1. It should be physically homogeneous.
2. In case of more than one phase, all phases must be separated from each other by surface of contact (interface) at equilibrium.
3. A dynamic equilibrium must be established between phases of the system through exchange of chemical species.

Some common example of the system consisting of one, two and three phases :

- (i) A system having only a pure liquid (no vapour in equilibrium) has only one phase i.e.

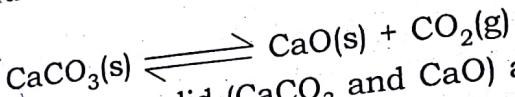
the liquid phase. Such a system is termed as a one-phase system and for such a system,  $P = 1$ . For example, a system consisting of only pure water is a one-phase system.

(ii) A system consisting of a liquid in equilibrium with its vapours has two phases, liquid phase and vapour phase. Such a system constitutes a two-phase system and for such a system,  $P = 2$ . For example, the system consisting of liquid water in equilibrium with its vapour consists of two phase-water phase and vapour phase.

(iii) A system containing ice, liquid water and water vapour in equilibrium constitutes a three-phases-ice phase, water phase and vapour phase. Hence it constitutes a three-phase system and for such a system,  $P = 3$ .

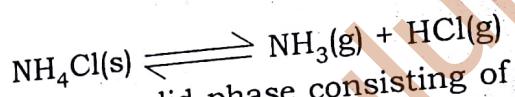
(iv) Each solid constitutes a separate phase, except in the case of solid solutions (alloys). Therefore, a system containing a mixture of several solids possesses several phases. For example, a system containing a mixture of rhombic sulphur and monoclinic sulphur is a two-phase system because it consists of two phase - rhombic sulphur phase and monoclinic sulphur phase.

(v) The decomposition of  $\text{CaCO}_3$  into  $\text{CaO}$  and  $\text{CO}_2$  in a closed vessel constitutes a two-phase system.



The system consists of two solid ( $\text{CaCO}_3$  and  $\text{CaO}$ ) and one gaseous ( $\text{CO}_2$ ) phases.

(vi) Decomposition of ammonium chloride in a closed container constitute a two-phase system.



In this case we have one solid phase consisting of solid  $\text{NH}_4\text{Cl}$  and one gaseous phase consisting of a mixture of  $\text{NH}_3$  and  $\text{HCl}$  gases.

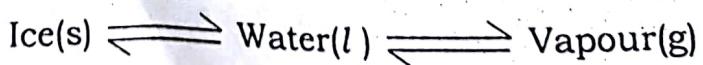
### 1.2.3. Components (C)

The number of components of a system is defined as the smallest number of independent variable constituents in terms of which the composition of each phase of a heterogeneous system can be expressed directly or in the form of a chemical equation.

The term component actually refers to a chemical constituent which is present in all phases of a heterogeneous system. For example, a system consisting of water only ( $P = 1$ , water phase) has only one component and that is  $\text{H}_2\text{O}$ , because the only chemical constituent present in the phase is water. Similarly, a system consisting of water and its vapour in equilibrium ( $P = 2$ , water phase and vapour phase) is also a one component system because the chemical constituent present in either of the two phases is  $\text{H}_2\text{O}$  only. On the other hand, a system consisting of a solution of sugar in water ( $P = 1$  i.e. solution phase) is a one component system because the solution phase present in the system consists of two constituents-water and sugar.

#### Some more examples:

(i) Let us consider the following system consisting of ice, water and vapour in equilibrium.



Obviously, the system consists of three phase-ice phases, water phase and vapour phase. The chemical substance present in each phase is  $\text{H}_2\text{O}$ . Therefore, the composition of each phase can be expressed as follows:

(i) The sulphur s

composition of c

(ii) A saturated

(iii) Hence, it is

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(h)

(i)

(j)

### 3.2. HARDNESS OF WATER

The characteristic property which prevents water from forming lather with soap is termed as **hardness of water**. It was originally defined as *the soap consuming capacity of a sample of water*.

Hard water contains soluble salts of calcium and magnesium. When soap comes in contact with hard water the calcium ion and magnesium ion present in hard water combines with soap and forms insoluble sticky precipitate. That's why hard water does not produce lather with soap. When all calcium ion and magnesium ion get consumed then hard water becomes soft and forms lather with soap.



where  $M^{2+} = Ca^{2+}$  or  $Mg^{2+}$

#### 3.2.1. Causes of Hardness of Water

Hardness of water is due to the presence of sulphate, chloride and bicarbonate of calcium or magnesium. These salts get dissolved in it when it passes over rocks or through the various underlying layers of earth.

#### 3.2.2. Types of Hardness of Water

There are two types :

(i) **Temporary hardness** : This is due to the presence of bicarbonates of calcium and magnesium dissolved in water. This hardness of water can very easily be removed simply by boiling the hard water.

(ii) **Permanent hardness** : This type of hardness is due to the presence of chlorides and sulphates of calcium and magnesium dissolved in water. This can not be removed easily.

**Note** : Now a days temporary and permanent hardness of water is replaced by alkaline and non-alkaline hardness

**Alkaline hardness (Carbonate hardness)** : When hardness of water is due to the presence of bicarbonate, carbonates and hydroxide of calcium and magnesium is called alkaline hardness or carbonate hardness.

**Non-alkaline hardness (Non-Carbonate hardness)** : The non-alkaline hardness is determined by the subtracting of alkaline hardness from the total hardness. Such type of hardness is due to the presence of sulphate, chloride etc. of calcium and magnesium.

#### 3.2.3. Expression of Hardness as Equivalents of Calcium Carbonate

Since a number of salts such as bicarbonate, sulphate and chloride of calcium and magnesium can cause hardness of water. For comparing the hardness of different sample of water it would be easier, if the hardness caused by different salts may be expressed in terms of single salt like  $CaCO_3$ .

##### **Reasons for choosing $CaCO_3$ as a standard for expressing the hardness**

- (i)  $CaCO_3$  is complete insoluble salt thus it can be easily precipitated during water treatment.

### 3.2.4. Units of Hardness

Hardness of a water sample can be expressed in following units.

1. **Parts per million (ppm)** : It is the parts of  $\text{CaCO}_3$  equivalent hardness per  $10^6$  parts of water. Thus, 1 ppm = 1 part of  $\text{CaCO}_3$  equivalent hardness present in 1 litre of water.
2. **Milligrams per litre (mg/L)** : It is the number of milligrams of  $\text{CaCO}_3$  equivalent hardness present in one litre of water. Thus,

$$1 \text{ mg/L} = 1 \text{ mg of } \text{CaCO}_3 \text{ equivalent hardness in 1 litre of water}$$

#### Relationship between ppm and mg/L :

$$\text{Mass of 1 litre of water} = 1 \text{ kg} = 1000 \text{ g} = 10^6 \text{ mg of water}$$

$$\begin{aligned}\therefore 1 \text{ mg/L} &= 1 \text{ mg of } \text{CaCO}_3 \text{ equivalent hardness in 1 litre of water} \\ &= 1 \text{ mg of } \text{CaCO}_3 \text{ equivalent hardness in } 10^6 \text{ mg of water} \\ &= 1 \text{ part of } \text{CaCO}_3 \text{ equivalent hardness in } 10^6 \text{ parts of water} \\ &= 1 \text{ ppm}\end{aligned}$$

$$\text{Hence, } 1 \text{ ppm} = 1 \text{ mg/L}$$

3. **Clark's Degree\* ( ${}^{\circ}\text{Cl}$ )** : It is the parts of  $\text{CaCO}_3$  equivalent hardness per 70,000 parts of water.

$$1 {}^{\circ}\text{Cl} = 1 \text{ part of } \text{CaCO}_3 \text{ hardness per 70,000 parts of water.}$$

4. **Degree French ( ${}^{\circ}\text{Fr}$ )** : It is the parts of  $\text{CaCO}_3$  equivalent hardness per  $10^5$  parts of water.

$$\text{Thus, } 1 {}^{\circ}\text{Fr} = 1 \text{ part of } \text{CaCO}_3 \text{ hardness per } 10^5 \text{ parts of water.}$$

#### Relationship Between Different units of Hardness

$$1 \text{ ppm} = 1 \text{ mg/L} = 0.1 {}^{\circ}\text{Fr} = 0.07 {}^{\circ}\text{Cl} = 0.07 \text{ grains per gallon}$$

$$1 \text{ mg/L} = 1 \text{ ppm} = 0.1 {}^{\circ}\text{Fr} = 0.07 {}^{\circ}\text{Cl} = 0.07 \text{ grains per gallon}$$

$$1 {}^{\circ}\text{F} = 10 \text{ ppm} = 10 \text{ mg/L} = 0.7 {}^{\circ}\text{Cl} = 0.7 \text{ grains per gallon}$$

$$1 {}^{\circ}\text{Cl} = 14.3 \text{ ppm} = 1.43 {}^{\circ}\text{Fr.} = 14.3 \text{ mg/L} = 1 \text{ grain per gallon}$$

$$1 \text{ grain per gallon} = 14.3 \text{ ppm} = 1.43 {}^{\circ}\text{Fr.} = 14.3 \text{ mg/L} = 1 {}^{\circ}\text{Cl}$$

**Example 3.1.** A water sample contains 140 mg of  $\text{Ca}(\text{HCO}_3)_2$  per litre. Calculate the hardness of water in terms of  $\text{CaCO}_3$  equivalent.

**Solution.** Mass of  $\text{Ca}(\text{HCO}_3)_2$  (w) = 140 mg/litre

Equivalent mass (E) of  $\text{Ca}(\text{HCO}_3)_2$  = 81

$$\text{Equivalent of } \text{CaCO}_3 = \frac{w \times 50}{E} = \frac{140 \times 50}{81} = 86.42 \text{ mg/litre. Ans.}$$

**Example 3.2.** A sample of water contains 220 mg of  $Mg^{2+}$  per litre. What is the hardness sample in terms of  $CaCO_3$  equivalent?

**Solution.** Mass of  $Mg^{2+}$  (w) = 220 mg/litre

Equivalent mass (E) of  $Mg^{2+}$  = 12

$$\text{Equivalent of } CaCO_3 = \frac{w \times 50}{E} = \frac{220 \times 50}{12} \\ = 916.67 \text{ gm/L. Ans.}$$

**Example 3.3.** A sample of water contains 18.6 mg/L of  $Mg(HCO_3)_2$ , 19.6 mg/L of  $MgCl_2$ , 22.8 mg/L of  $MgSO_4$  and 22.8 mg/L of  $CaCl_2$ . Calculate alkaline and non-alkaline and total hardness of water in terms of  $CaCO_3$  equivalent.

**Solution. (i)** Calculation of  $CaCO_3$  equivalent of hardness producing substances

Substances	Mass of the substance (w)	Equivalent mass of the substance (E)	$CaCO_3$ equivalent (w)
$Mg(HCO_3)_2$	18.6 mg/L	73	$\frac{18.6 \times 50}{73} = 12.74 \text{ mg/L}$
$MgCl_2$	19.6 mg/L	47.5	$\frac{19.6 \times 50}{47.5} = 20.63 \text{ mg/L}$
$MgSO_4$	24.4 mg/L	60	$\frac{24.4 \times 50}{60} = 20.33 \text{ mg/L}$
$CaCl_2$	22.8 mg/L	55.5	$\frac{22.8 \times 50}{55.5} = 20.54 \text{ mg/L}$

Hence, total hardness of water in terms of  $CaCO_3$  equivalent

$$= 12.74 + 20.63 + 20.33 + 20.54$$

$$= 74.24 \text{ mg/L}$$

**(ii) Calculation of alkaline, non-alkaline and total hardness of water sample**

The alkaline hardness (carbonate hardness) is due to the presence of bicarbonates and hydroxides of hardness producing metals.

$\therefore$  Alkaline hardness of the given sample

$$= Mg(HCO_3)_2 \text{ hardness}$$

$$= 12.74$$

$$= 12.74 \text{ mg/L equivalents of } CaCO_3.$$

The total hardness of the sample = 74.24 mg/L equivalents of  $CaCO_3$ .

Hence, Non-alkaline hardness =  $74.24 - 12.74 = 61.5 \text{ mg/L equivalents of } CaCO_3$ .

**Example 3.4.** A sample of water on analysis has been found to contain following in ppm

$Ca(HCO_3)_2 = 10.5$ ,  $Mg(HCO_3)_2 = 12.5$ ,  $CaCl_2 = 8.2$ ,  $MgSO_4 = 2.6$ . Calculate the temporary and permanent hardness.

Substances	Amount of the substance (w)	Equivalent mass of the substance (E)	$CaCO_3$ equivalent ( $\frac{W \times 50}{E}$ )
$Ca(HCO_3)_2$	10.5 ppm	81	$\frac{10.5 \times 50}{81} = 6.48 \text{ ppm}$
$Mg(HCO_3)_2$	12.5 ppm	73	$\frac{12.5 \times 50}{73} = 8.56 \text{ ppm}$
$CaCl_2$	8.2 ppm	55.5	$\frac{8.2 \times 50}{55.5} = 7.39 \text{ ppm}$
$MgSO_4$	2.6 ppm	60	$\frac{2.6 \times 50}{60} = 2.17 \text{ ppm}$

**(ii) Calculation of temporary and permanent hardness :**

$$\text{Temporary hardness} = Ca(HCO_3)_2 \text{ hardness} + Mg(HCO_3)_2 \text{ hardness} \\ = 6.48 + 8.56 = 15.04 \text{ ppm Ans.}$$

$$\text{Permanent hardness} = CaCl_2 \text{ hardness} + MgSO_4 \text{ hardness} \\ = 7.39 + 2.17 = 9.56 \text{ Ans.}$$

**Example 3.5.** 200 ml of a water sample contains 2.24 mg of  $CaSO_4$ , 1.14 mg of  $MgCl_2$  and 38 mg of  $Ca(HCO_3)_2$ . Calculate the total hardness of the sample in Clarke's degree.

**Solution. Calculation of  $CaCO_3$  equivalents in 200 ml sample :**

Substances	Amount of the substance (w)	Equivalent mass of the substance (E)	$CaCO_3$ equivalent in 200 ml sample
$CaSO_4$	2.24 mg	68	$\frac{2.24 \times 50}{68} = 1.65 \text{ mg}$
$MgCl_2$	1.14 mg	47.5	$\frac{1.14 \times 50}{47.5} = 1.2 \text{ mg}$
$Ca(HCO_3)_2$	2.88 mg	81	$\frac{2.88 \times 50}{81} = 1.78 \text{ mg}$

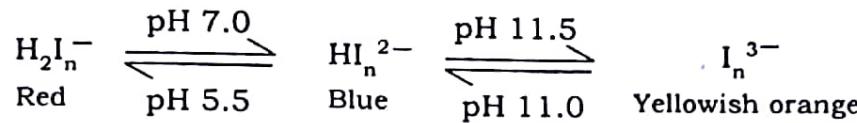
$\therefore$  Total hardness in 200 ml sample =  $1.65 + 1.2 + 1.78 = 4.63 \text{ mg equivalent of } CaCO_3$ .

$$\text{Total hardness of the sample } \frac{4.63}{200} \times 1000 = 23.15 \text{ mg/L equivalent of } CaCO_3. \\ = 23.15 \times 0.07 ^{\circ}Cl \\ = 1.62 ^{\circ}Cl \text{ equivalent of } CaCO_3. \text{ Ans.}$$

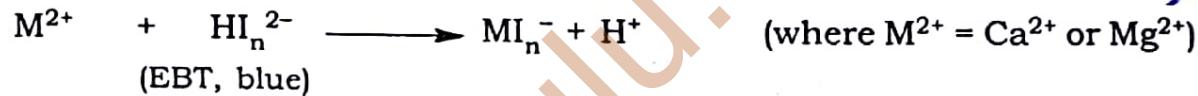
**Principle :** The total hardness (permanent as well as temporary) in water is determined titrating the water sample against standard ethylenediaminetetraacetic acid (EDTA<sup>+</sup>) solution in ammonia buffer solution having pH = 10 using eriochrome black-T (EBT<sup>+</sup>) as an indicator. The calcium and magnesium ion present in hard water forms stable complex with EDTA and less stable complex with eriochrome black-T solution.

Sodium salt of EDTA ionises in water to give two Na<sup>+</sup> and a strong chelating agent. It is hexadentate ligand and represented by H<sub>2</sub>Y<sup>2-</sup>. It forms complexes with bivalent cations (Ca<sup>2+</sup>, Mg<sup>2+</sup> etc.) or higher valent cations. The complexes with hardness causing divalent ions are stable in alkaline medium (pH 8-10).

The eriochrome black-T has two ionisable phenolic hydrogen atoms and for simplicity is presented by Na<sup>+</sup>H<sub>2</sub>I<sub>n</sub><sup>-</sup>



The calcium and magnesium ion present in hard water combine with the indicator eriochrome black-T at pH 9-10 to form less stable wine red complex.



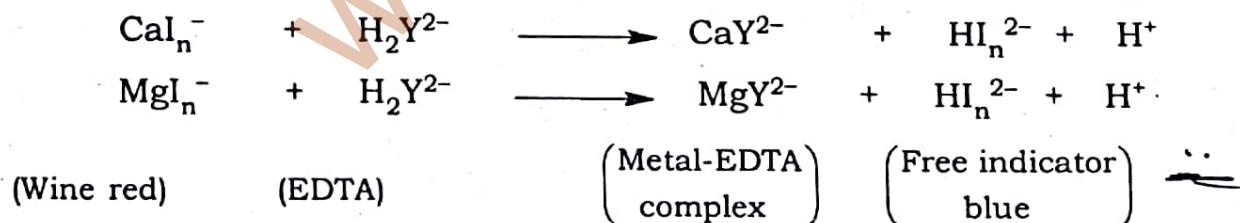
Magnesium ion produces wine red colour with the indicator.

When EDTA is added, the free Ca<sup>2+</sup> and Mg<sup>2+</sup> forms a stable complex of metal-EDTA.

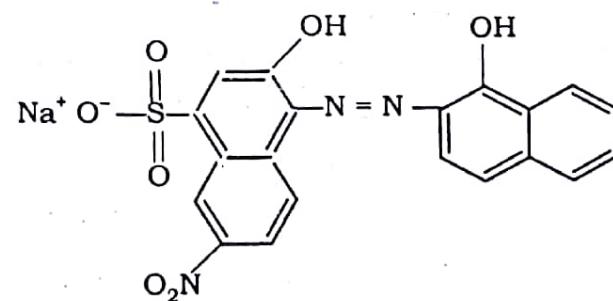
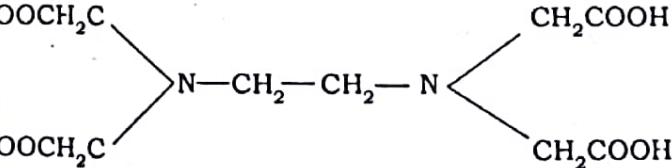


Mg-EDTA complex is less stable than Ca-EDTA complex but more stable than Mg-indicator complex.

When all Ca<sup>2+</sup> and Mg<sup>2+</sup> ions get complexed with EDTA then further addition of EDTA sets free the metal ion from metal indicator complex and form more stable complex.



#### Chemical structures of EDTA and EBT -



Sodium 4 - (1-hydroxy-2-naphthylazo)

-3-hydroxy-7-nitronaphthalene-1-sulphonate.

**Permanent hardness**

Total volume of water sample after boiling =  $z$  ml

And volume of EDTA solution used =  $V_3$  ml

1 ml of EDTA solution =  $\frac{x}{V_1}$  mg of  $\text{CaCO}_3$

$V_3$  ml of EDTA solution =  $\frac{x}{V_1} \times V_3$  mg of  $\text{CaCO}_3$

$z$  ml of water sample =  $\frac{x}{V_1} \times V_3$  mg of  $\text{CaCO}_3$

1000 ml water sample =  $\frac{x}{V_1} \times \frac{V_3}{z} \times 1000$  mg of  $\text{CaCO}_3$

Permanent Hardness =  $\frac{x}{V_1} \times \frac{V_3}{z} \times 1000$  ppm

Temporary Hardness = Total hardness - Permanent hardness

**Example 3.6.** 100 ml of a water sample requires 20 ml  $\frac{N}{100}$  EDTA when titrated using

$\text{Cl}^- - \text{NH}_4\text{OH}$  buffer and EBT indicator. Calculate the hardness of the sample.

Solution. Number of gram equivalents of EDTA used by 100 ml sample.

$$= \frac{\text{Normality} \times \text{Volume}}{1000} = \frac{\frac{1}{100} \times 20}{1000} = 2.0 \times 10^{-4}$$

Number of gram moles of EDTA consumed

$$= \frac{20 \times 10^{-4}}{2} = 1.0 \times 10^{-4}$$

Since, 1 gram mole of EDTA  $\equiv 10^5$  mg of  $\text{CaCO}_3$

$1.0 \times 10^{-4}$  gram moles of EDTA  $= 10^5 \times 1.0 \times 10^{-4} = 10$  mg of  $\text{CaCO}_3$

Since, total hardness of the sample  $= \frac{10}{100} \times 1000$

$$= 100 \text{ mg/L of } \text{CaCO}_3 \text{ Ans.}$$

**Example 3.7.** 100 ml of a hard water sample require 22.5 ml of 0.01M EDTA with  $\text{Cl}^- - \text{NH}_4\text{OH}$  buffer and EBT indicator. Another 100 ml of the sample is boiled for about half hour and after filtering the precipitate, the volume of the filtrate is made to 100 ml again by addition of distilled water. 20 ml of this boiled sample require only 4 ml of 0.01 M EDTA to titrate. Calculate the temporary and permanent hardness of the sample.

or permanent hardness

1 ml EDTA required for  $\frac{30}{25}$  mg CaCO<sub>3</sub>

12 ml EDTA required for  $\frac{30}{25} \times 12$  mg CaCO<sub>3</sub>

100 ml H<sub>2</sub>O contains  $\frac{30}{25} \times 12$  mg CaCO<sub>3</sub>

1000 ml H<sub>2</sub>O contains =  $\frac{30 \times 12 \times 1000}{25 \times 100}$

$$= 144 \text{ mg CaCO}_3$$

Permanent hardness = 144 ppm.

Temporary (carbonate) hardness

= Total hardness - permanent (non-carbonate) hardness

$$= 72 \text{ ppm. Ans.}$$

#### 4. ALKALINITY OF WATER

The alkalinity of water refers to the total amount of those substances present in water which tend to increase the concentration of OH<sup>-</sup> ions, either on account of dissociation in water or due to hydrolysis.

The alkalinity of natural water may be due to any of the following factors.

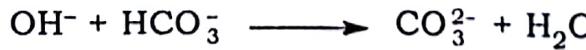
(i) **Presence of HCO<sub>3</sub><sup>-</sup>, HSiO<sub>3</sub><sup>-</sup>, SiO<sub>3</sub><sup>2-</sup> etc. ions :** The presence of ions such as HCO<sub>3</sub><sup>-</sup>, SiO<sub>3</sub><sup>-</sup>, SiO<sub>3</sub><sup>2-</sup> etc. ions cause alkalinity because they act as Bronsted and Lowry acids and have a tendency of take H<sup>+</sup> ions from water. As a result concentration of OH<sup>-</sup> ions in water increases. CO<sub>3</sub><sup>2-</sup> ions sometimes also produce alkalinity.

(ii) **Presence of salts of weak organic acids :** The salts of weak organic acids, known as umates, undergo hydrolysis and consume H<sup>+</sup> ions of water leading to an increase in the concentration of OH<sup>-</sup> ions.

(iii) **Presence of buffer forming salts :** Salts of certain weak acids such as borates and ilicates induce buffer capacity in water and resist the lowering of pH. This causes alkalinity in water. The alkalinity of a sample of water may be due to

- (i) hydroxides only;
- (ii) carbonates only;
- (iii) bicarbonates only;
- (iv) both hydroxides and carbonates;
- (v) both carbonates and bicarbonates.

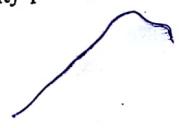
**Note :** The possibility of hydroxides and bicarbonates existing together in water is ruled out because they combine with each other to form carbonate.



### 3.4.1 Classification of Alkalinity

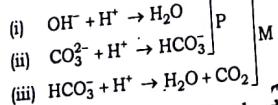
Depending upon the nature of alkalinity producing anion, the alkalinity may be classified into -

- Bicarbonate alkalinity
- Carbonate alkalinity
- Hydroxide alkalinity



### 3.4.2 Determination of Alkalinity

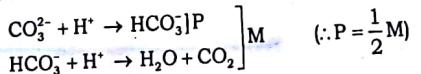
**Principle :** The type and extent of alkalinity of a sample of water can be determined by titrimetric method. An aliquot of the sample is titrated against a standard acid phenolphthalein and methyl orange as indicators. The reactions involved are as follows:



The volume of the standard acid used upto **Phenolphthalein end point P** marks completion of reactions (i) and (ii), whereas the total volume of the standard acid used from the beginning upto the **methyl orange end point M** corresponds to the completion of reactions (i), (ii) and (iii).

**Conclusions :** From the above, following conclusions may be drawn.

- When  $P = 0$ , both  $\text{OH}^-$  and  $\text{CO}_3^{2-}$  are absent: In such a case, the alkalinity is due to presence of bicarbonates only. Thus, alkalinity due to  $\text{HCO}_3^- = M$ .
- When  $P = M$ , the sample consists of only  $\text{OH}^-$  ions: Thus, alkalinity due to  $\text{OH}^-$
- When  $P = \frac{1}{2}M$ , the sample consists of only  $\text{CO}_3^{2-}$  ions: This is because, the reaction will take place as follows :



Thus, alkalinity due to  $\text{CO}_3^{2-} = 2P = M$ .

- When  $P > \frac{1}{2}M$ , the sample consists of  $\text{OH}^-$  ions in addition to  $\text{CO}_3^{2-}$  ions.

In this case,

$$\text{Alkalinity due to } \text{CO}_3^{2-} = 2(M - P)$$

$$\text{Alkalinity due to } \text{OH}^- = M - 2(M - P) = 2P - M.$$

- When  $P < \frac{1}{2}M$ , the sample consists of  $\text{HCO}_3^-$  ions in addition to  $\text{CO}_3^{2-}$  ions:

In this case

$$\text{Alkalinity due to } \text{CO}_3^{2-} = 2P$$

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alkalinity due to  $\text{HCO}_3^- = M - 2P$ .

These conclusions have been summarised in the following table

#### Summary of Calculation of Alkalinity of Water by Titrimetric Method

Results of titration to Phenolphthalein end point P, and methyl orange end point M	$\text{OH}^-$	$\text{CO}_3^{2-}$	$\text{HCO}_3^-$
(i) $P = 0$	0	0	$M$
(ii) $P = M$	$P = M$	0	0
(iii) $P = \frac{1}{2}M$	0	$2P$	0
(iv) $P > \frac{1}{2}M$	$2P - M$	$2(M - P)$	0
(v) $P < \frac{1}{2}M$	0	$2P$	$M - 2P$

Note : Alkalinity of a water sample is usually expressed in terms of parts per million (ppm) of  $\text{CaCO}_3$ .

**Procedure :** A known volume of water sample is titrated against standard acid ( $\text{H}_2\text{SO}_4$ ) by using phenolphthalein indicator. The end point is detected by disappearance of pink colour. The volume of acid consumed is noted. Now the titrated water sample is again titrated against the same standard acid ( $\text{H}_2\text{SO}_4$ ) by using methyl orange indicator. The end point is detected by appearance of red colour. The volume of acid consumed is noted.

**Calculations :** Let volume of water sample for titration =  $V$  ml  
Strength of acid solution =  $N$  / 50

$$\begin{aligned} \text{Volume of acid used in case of phenolphthalein indicator} &= A \\ \text{Volume of acid used in case of methyl orange indicator} &= B \\ \text{For phenolphthalein indicator } N_1 V_1 &= N_2 V_2 \\ (\text{Water}) &(\text{Acid}) \end{aligned}$$

$$N_1 \times V = \frac{N}{50} \times A$$

$$N_1 = \frac{1}{50} \times \frac{A}{V}$$

$$N_1 \times \text{Eq.wt.} = \frac{1 \times A}{50 \times V} \times 50$$

( $\because$  Eq. wt. of  $\text{CaCO}_3 = 50$ )

$$\therefore \text{Phenolphthalein alkalinity} = \frac{1 \times A \times 50 \times 1000}{50 \times V} \text{ ppm in terms of eq. wt. of } \text{CaCO}_3$$

## Suggested Limits of Tolerance (in mg/L) for Boiler Feed Water

Pressure (psi)	0 - 150	150 - 250	250 - 400	Over 400
Bicarbonates	50	30	5	0
Carbonates	200	100	40	20
Hydroxides	50	40	30	15
Total hardness ( $\text{CaCO}_3$ )	80	40	10	2
Total solids	3000-500	2500-500	1500-100	50
Dissolved oxygen	1.4	0.14	0.0	0.0
Turbidity	20	10	5	1
Colour	80	40	5	2
Hydrogensulphide	5	3	0	0
Sulphate - carbonate ratio	1 : 1	2 : 1	3 : 1	3 : 1
Aluminium oxide	5	0.5	0.05	0.01
Silica	40	40	5	1
pH value (min.)	8.0	8.4	9.0	9.6

### 3.5.3. Sludge and Scale formation

When hard water is boiled in the boiler to generate the steam, the dissolved salt starts separating in order to their solubilities after the saturation point. The least soluble salts separate out first and the precipitate forms as a layer inside the boiler. When precipitation of dissolved salts take place inside the boiler in the form of soft, slimy and non-adherent layer, it is called 'sludge' and if the precipitation takes place in the form of hard adhering coating inside the boiler walls, it is called 'scale'.

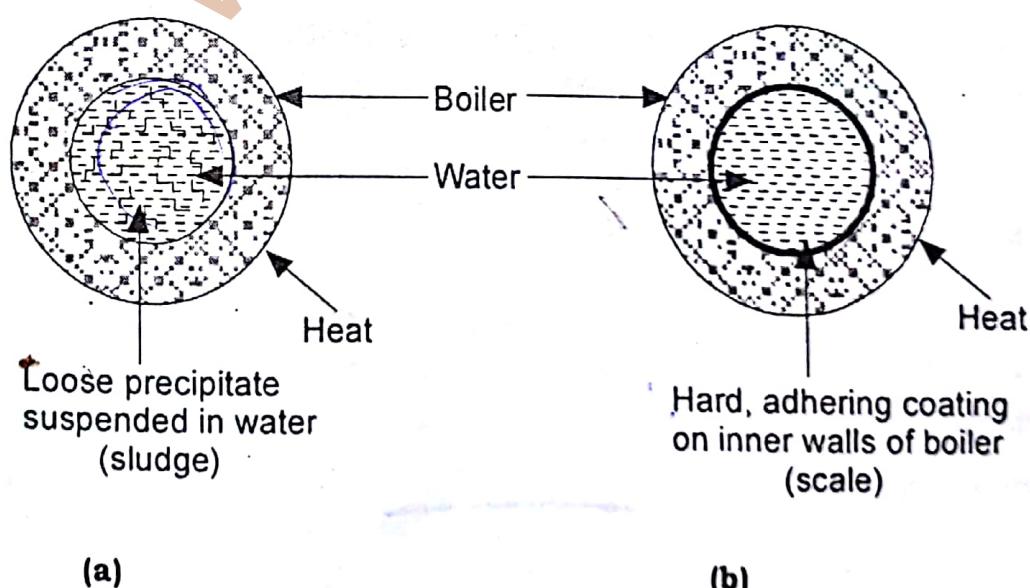


Fig. 3.1 (a) Sludge formation in boilers (b) Scale formation in boilers

o expansion and water suddenly comes in contact with overheated iron plates. This causes the formation of large amount of steam suddenly. This results high pressure and explosion may occur.

(iii) Bagging : The distortion of boiler material is called bagging. Due to overheating the rapid reaction may take place between water and iron at high temperature in the boiler.



It cause the distortion of boiler materials. At high temperature corrosion may takes place.

(iv) Decrease in efficiency : Due to deposition of scales in boilers valve and pipes, it may be chocked and hence efficiency of boiler is decreased.

**Removal of Scales** : (i) These are removed by scrapper or hard brush.

(ii) These can be removed by thermal shocks i.e., heating the boiler and suddenly cooling with cold water.

(iii) These can be removed by dissolving in some suitable chemicals.  $\text{CaCO}_3$  scales can be dissolved in 5-10% diluted HCl. Similarly, calcium ions can be removed by EDTA solution.

**Prevention of Scale Formations** : The scale formation may be minimized by:

1. External treatment : It includes the water softening techniques like lime soda process, zeolite process or demineralized (ion exchange process).

2. Internal treatment : In this treatment suitable chemicals are added to the boiler containing hard water. The scales are either precipitated or converted into soluble complexes. This process is also known as "sequestration" and the chemical which is added is called "sequestering agent".

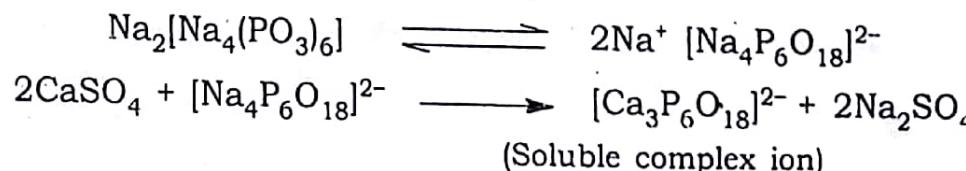
### Important conditioning methods

(i) Phosphate Conditioning : Phosphate conditioning is generally applicable for avoiding the scale formation in high-pressure boilers. Sodium phosphate is added to the hard water in boiler. It reacts with calcium chloride and magnesium chloride to form soft sludge of calcium phosphate and magnesium phosphate respectively. These soft sludges can be removed by blow-down operation.



**Note** : For this conditioning we use generally sodium dihydrogenphosphate  $\text{NaH}_2\text{PO}_4$  (acidic), sodiumhydrogenphosphate  $\text{Na}_2\text{HPO}_4$  (weakly alkaline), trisodiumphosphate  $\text{Na}_3\text{PO}_4$  (alkaline) and sodium pyrophosphate  $\text{Na}_4\text{P}_2\text{O}_7$ .

(ii) Calgon conditioning : Calgon is sodium hexametaphosphate  $\text{Na}_2[\text{Na}_4(\text{PO}_3)_6]$ . Calgon is added to the boiler water. It forms soluble complex compound with  $\text{CaSO}_4$  and hence prevents from the formation of scale and sludge.



### 3.5.5. Priming and Foaming

#### Priming

When water is boiled rapidly in a boiler, the steam formed may sometimes be associated with small droplets of water. The steam associated with small water droplets is called **steam**. The process of formation of wet steam is called **priming**.

**Causes of priming :** (i) By the presence of large amounts of dissolved solids such as sulphates and chlorides.

(ii) By very high water level, high steam velocity and sudden steam demand which leads to sudden boiling.

(iii) The improper designing of boiler.

**Prevention of priming :** (i) By using mechanical steam purifiers;

(ii) Keeping the low water level.

(iii) Avoiding rapid changes in steam rate;

(iv) Efficient softening and filtration of boiler feed water; and

(v) A proper designing of boiler.

#### Foaming

The formation of persistent foam or bubbles at the surface of water in the boiler is called **foaming**.

**Causes of foaming :** (i) By the presence of oil and grease in water. These substances greatly reduce the surface tension of water in boiler and causes foaming.

(ii) The presence of finely divided sludge particles may also cause foaming.

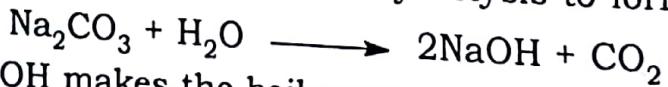
**Prevention of foaming :** (i) By removing oil, grease and finely divided sludge from the boiler feed water by the addition of coagulants such as ferrous sulphate, aluminate etc.;

(ii) Adding antifoaming chemicals such as castor oil.

### 3.5.6. Caustic Embrittlement

Caustic embrittlement is a particular type of boiler corrosion caused by the use of alkaline water in the boiler. It may be defined as, the formation of irregular intergranular on the boiler metal particularly at points of high local stress by the use of highly alkaline water in the boiler is called caustic embrittlement.

**Cause of caustic embrittlement :** Caustic embrittlement is more common when the water operates at high pressures and boiler feed water contains dissolved  $\text{Na}_2\text{CO}_3$  as impurities. At high pressures, sodium carbonate undergoes hydrolysis to form sodium hydroxide.



The formation of NaOH makes the boiler water caustic. The caustic water flows minute hair cracks (like bends, joints, rivets etc.) inside the boiler by capillary action. As water evaporates and the concentration of dissolved NaOH increases progressively, the highly concentrated NaOH solution attacks the metal.

13.	Lead	0.10 mg/L	No relaxation	-	0.10 mg/L
14.	Chloride	250 mg/L	1000 mg/L	200 mg/L	1000 mg/L
15.	Sulphate	200 mg/L	400 mg/L	200 mg/L	400 mg/L
16.	Nitrate	45 mg/L	45 mg/L	20 mg/L	-
17.	Flouride	1.0 mg/L	1.5 mg/L	1.0 mg/L	1.5 mg/L
18.	Mineral oil	0.01 mg/L	0.03 mg/L	-	-
19.	Aluminium	0.03 mg/L	0.2 mg/L	-	-
20.	Alkalinity	200 mg/L	600 mg/L	-	-
21.	Pathogenic micro-organism (Coliform)	-	-	-	1 coliform per 100 ml

\* Nephelometric turbidity unit.

\*\* Jacson turbidity unit.

#### 4.1.2. Potable Water

Water, which is safe to drink is known as potable water.

##### Characteristics of Potable water

- (i) It should be colourless, odourless, and transparent.
- (ii) It should be free from hardness, suspended particles and pathogenic micro-organisms.
- (iii) It should be neither too hard nor too soft. The recommended hardness is about 300 mg/L as  $\text{CaCO}_3$  equivalent.
- (iv) The turbidity should not exceed 10 ppm.
- (v) Its pH value should be about 7.0 – 8.0.
- (vi) It should be free from harmful dissolved solids like compounds of arsenic or lead etc. and harmful dissolved gases like  $\text{H}_2\text{S}$ ,  $\text{SO}_2$  etc.
- (vii) The total dissolved solids (TDS) should be less than 500 ppm.

**Note :** Pure soft water is plumbo-solvent i.e., it attacks lead used in plumbing. For health point of view some minerals and ions must be present in water. Drinking water possess about 60-70 ppm hardness. It is firm and suitable for health.

#### 4.2. TREATMENT OF WATER FOR DOMESTIC USE

The natural water obtained from river, canals etc. does not satisfy the characteristics of potable water. Hence in order to make natural water suitable for municipal supply, several treatment processes are necessary to be done.

##### 1. Screening

The raw water is allow to passes through screens having large number of holes. The floating matters are retained by them and only water is passed through the holes.

##### 2. Sedimentation

It is the process by which water is allow to stand in a big tank for sometimes in order to facilitate the setting down of the coarse suspended particles under the action of gravity is called sedimentation.

The water is then drawn off from the bottom under the action of gravity. The clear water is then drawn off.

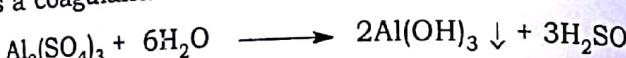
**Note :** Sedimentation is a very slow process and may take hours or even days. It is not a complete removal of suspended particles. Plain sedimentation usually removes 70 to 75% of the suspended particles.

### 3. Coagulation

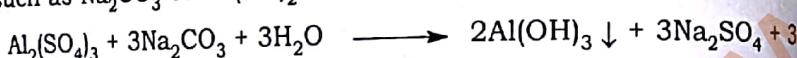
Coagulation is the process by which the fine suspended and colloidal particles from the water by the addition of suitable chemicals (coagulants). When fine clay colloidal particles are present in water, they do not get settle down by ordinary sedimentation because colloidal particles have some charges which repel each other. Due to repulsion they do not combine to form a large size. But when coagulants are added they neutralize the charges on colloidal particles. The chargeless particles now stick to one another and combines to form larger molecules, which get settled down by gravitational force.

#### Useful coagulants

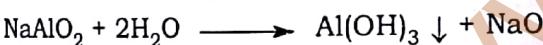
(i) **Aluminium sulphate** : It is the most common coagulating agent and is used as filter alum  $[Al_2(SO_4)_3]$ , or as alum  $[K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O]$ . It hydrolyses in water to give  $Al(OH)_3$  which acts as a coagulant.



In order to render the  $Al(OH)_3$  filterable and to neutralise the  $H_2SO_4$  produced during hydrolysis, some alkali should be present. If water possesses a little or no natural alkali such as  $Na_2CO_3$  or  $Ca(OH)_2$  is added.

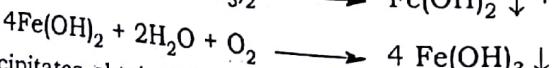
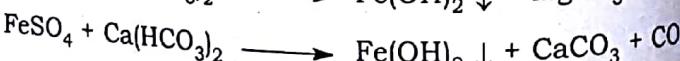
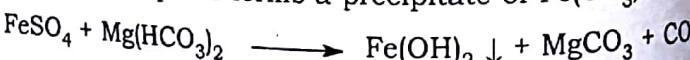


(ii) **Sodium Aluminate ( $NaAlO_2$ )** : It is used for treating water having low pH (i.e.,  $pH < 7$ ). It is also used along with  $Al_2(SO_4)_3$  for the treatment of water in which there is no natural alkali.



**Note :** Aluminium hydroxide thus produced acts as coagulant.

(iii) **Ferrous Sulphate ( $FeSO_4 \cdot 7H_2O$ )** : Ferrous sulphate is widely used as a coagulant in alkaline water (i.e.,  $pH > 8.0$ ). If alkalinity is not present in water then sufficient lime is also added. Ferrous sulphate forms a precipitate of  $Fe(OH)_3$ .



**Note :** The precipitates obtained by using suitable coagulants in water get settled down by sedimentation.

### Filtration

is the process by which the colloidal particles, suspended matter etc. and some micro-organisms are removed by passing water through a porous material consisting of a fine bed of sand and other granular materials. The porous material used is called **filtering medium** and the apparatus used for filtration is called a **filter**.

There are two types of filters, i.e., (i) **Gravity type filter** and (ii) **Pressure type filter**. Gravity type filter is also classified on the basis of their efficiency as **slow sand filters** and **rapid sand filter**.

**Slow sand filter:** The filtering medium in sand filter consists of 3 layers, fig. 4.1. The top layer consists of fine sand and is thick layer. The middle layer consists of coarse sand and the bottom layer consists of gravels. The filter is provided with an inlet for sedimented water and an outlet drain channel at the bottom for exit of filtered water. The sedimented water enters the filter and is uniformly distributed over the fine sand bed. The filtration gets start and impurities are retained by the filtering medium. Filtered water comes out from the outlet.

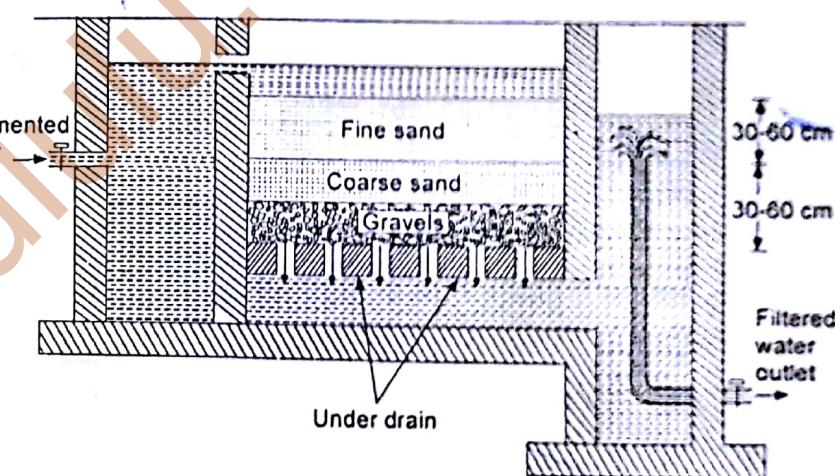


Fig. 4.1 Sand Filter.

During filtration the sand pores get clogged, due to retention of impurities in the pores. As a result the rate of filtration becomes slow. At this stage, about 2-3 cm of the top fine sand is scrapped off and replaced with clean and fresh sand. The filter is ready to reuse. The discarded sand is washed with water and dried for reuse at the time of next scrapping operation.

### Disinfection or Sterilization of water

Disinfection of water means the removal of micro-organisms (bacteria, virus etc.) from water. The filtered water may contain pathogenic bacteria and other micro-organisms. These are very harmful and make the water unfit for domestic use. Hence it is necessary to remove the micro-organisms and pathogenic bacteria from water. **The process of destroying of pathogenic bacteria and other micro-organisms is called disinfection and the agents used for this purpose are called disinfectants.**

After reaching the minima (i.e., the point C) the added chlorine does not take part in chemical reaction. As a result the amount of residual chlorine is increased by adding the amount of chlorine and is represented by curve CD. The point 'C' is known as '**break-point chlorination**' at which free residual chlorine begins to appear. Hence for effectively killing the micro-organisms, sufficient amount of chlorine (minima of the curve i.e., point 'C') must be added.

**Note :** Break-point chlorination helps in eliminating disagreeable odour and bad taste in water.

**Advantages and Significance:** (i) It indicates the complete destruction of organic compounds, which are present in water.

(ii) It completely destroys all the pathogenic bacteria.

(iii) It helps to calculate the just sufficient amount of chlorine for adding in water.

(iv) It prevents the growth of any weeds in water.

(v) It also signifies complete decomposition of  $\text{NH}_3$ , removal of colouring materials and improvements of taste and odour of the water sample.

### 4.3. SOFTENING OF WATER

Water plays very important role in industry and domestic purpose. The natural water contains several types of dissolved solid so it is necessary to remove the dissolved solid, which causes hardness of water. *Softening of water is the process of removing the hardness of water.*

#### 4.3.1. Methods for softening of water

1. Lime-soda process
2. Zeolite process (Permutit process)
3. Demineralization process (Ion exchange process)

##### 1. Lime soda process

**Principal:** When lime  $[\text{Ca}(\text{OH})_2]$  and soda  $(\text{Na}_2\text{CO}_3)$  are added to hard water, the soluble calcium and magnesium salts present in hard water are converted into insoluble compounds like  $\text{CaCO}_3$ ,  $\text{Mg}(\text{OH})_2$  etc. which are separated as precipitate by filtration.

**Functions of lime  $[\text{Ca}(\text{OH})_2]$  :** Lime is very effective to remove the temporary hardness, permanent magnesium hardness, dissolved iron and aluminium salts, free mineral acids, dissolved  $\text{CO}_2$  and  $\text{H}_2\text{S}$  in water. Reactions involved are:

###### (i) Removal of temporary calcium and magnesium hardness

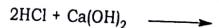
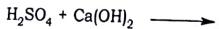
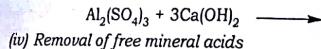


###### (ii) Removal of permanent magnesium hardness

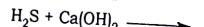
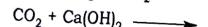


###### (iii) Removal of dissolved iron and aluminium salts

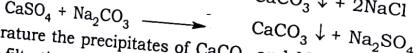
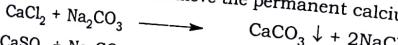




(v) Removal of dissolved  $\text{CO}_2$  and  $\text{H}_2\text{S}$



**Functions of Soda  $[\text{Na}_2\text{CO}_3]$ :** When lime is used to remove the hardness or acids, etc. It has been found that permanent calcium hardness  $\text{CaCl}_2$  and  $\text{CaSO}_4$  is reduced in water. Soda is very effective to remove the permanent calcium hardness as follows:



At room temperature the precipitates of  $\text{CaCO}_3$  and  $\text{Mg}(\text{OH})_2$  are fine and do not settle down easily, so the filtration becomes difficult. These fine particles may take part in clogging and corrosion in the pipes and boiler tubes. These drawbacks of the process may be improved by:

- thorough mixing of chemicals and water,
- allowing proper time for the completion of reactions,
- the use of accelerators such as active charcoal, and
- the use of coagulants such as alum or  $\text{NaAlO}_2$ .

**Process :** Lime-soda process can be carried out both at room temperature as well as high temperature ( $90\text{--}100^\circ\text{C}$ ) and is known as **cold lime-soda process** and **hot lime-soda process** respectively.

#### Cold lime-soda process

In this process a calculated amount of lime and soda are mixed with water at room temperature. Small amount of coagulant like alum, aluminium sulphate, sodium aluminate etc. are also added. The coagulant help the finely divided precipitates formed in the process to flocculate. Sodium aluminate also helps in the removal of silica and oil, if present in the water.

**Method :** A calculated amount of lime and soda are mixed with raw water along with a small amount of a coagulant. This mixture is fed from the top of the inner vertical circular chamber, fig. 4.3. The inner chamber is fitted with a vertical rotating shaft carrying a number of paddles. When the raw water and chemicals flow down, there is a vigorous stirring and continuous mixing takes place. Here chemical reactions take place and hard water is converted into soft water. The insoluble precipitate form a heavy sludge which comes out from the outlet from time to time at the bottom of apparatus. The softened water comes out of the outer co-axial chamber and rises upwards. It passes through a filtering media (usually made of wood fibres) to ensure complete removal of the sludge. Filtered softer water finally comes out continuously through the outlet at the top.

**Note :** Softened water containing a residual hardness of about 50-60 ppm.

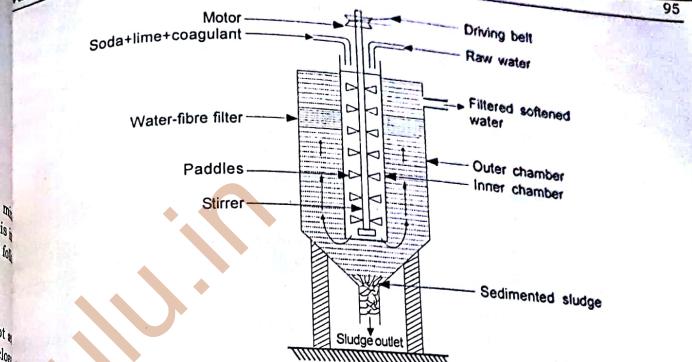


Fig. 4.3 Cold lime soda water softener.

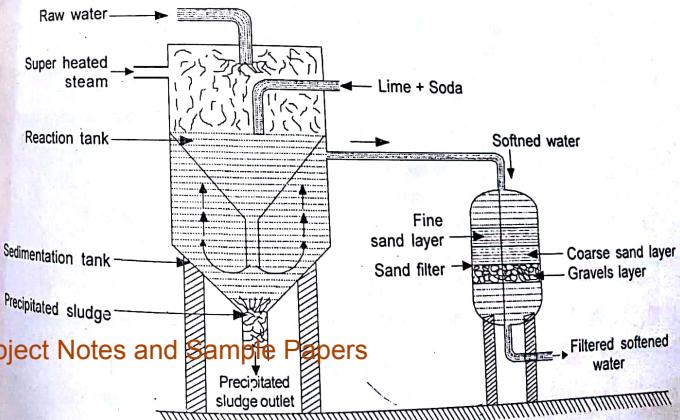
#### Hot lime-soda process

In this process water is treated with softening chemicals at a temperature of  $90^\circ\text{--}100^\circ\text{C}$ .

**Method :** A typical hot lime-soda water softening plant (fig. 4.4) consists of

(i) a reaction tank, (ii) a conical sedimentation vessel and (iii) a sand filter.

Raw water is fed from the top of the reaction tank where it is thoroughly mixed with the



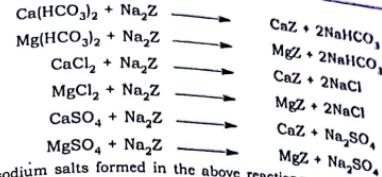
$$= 17575000 \text{ mg}$$

$$= 17.575 \text{ Kg.}$$

(III) Calculation of Soda requirement :

Soda required for  $\text{Ca}^{2+}$ ,  $\text{Ca}^{2+}$  introduced during the removal of  $\text{Mg}^{2+}$  by lime  
 $(\text{Mg}^{2+} + \text{Ca}(\text{OH})_2 \rightarrow \text{Mg}(\text{OH})_2 + \text{Ca}^{2+})$  and  $\text{FeSO}_4$ . Moreover, one equivalent of  $\text{CO}_3^{2-}$  introduced during the reaction of 1 equivalents of  $\text{HCO}_3^{2-}$  with lime may be considered equivalent to 1 equivalent of soda ( $2\text{HCO}_3^{-} + \text{Ca}(\text{OH})_2 \rightarrow \text{CO}_3^{2-} + \text{CaCO}_3 + \text{H}_2\text{O}$ ). Hence required for the treatment of 50,000 litres of water

$$\begin{aligned} &= \frac{106}{100} \times \left[ \frac{\text{Ca}^{2+} + \text{Mg}^{2+} + \text{FeSO}_4 \cdot 7\text{H}_2\text{O} - \text{HCO}_3^{-}}{\text{as CaCO}_3 \text{ equivalents}} \right] \times \text{Volume of water} \\ &= \frac{106}{100} \times [200 + 150 + 25 - 200] \times 50,000 \\ &= \frac{106}{100} \times 175 \times 50,000 \\ &= 9275000 \text{ mg.} \\ &= 9.275 \text{ kg Ans.} \end{aligned}$$



Note : The sodium salts formed in the above reactions remain dissolved in the softened water and do not cause any hardness.

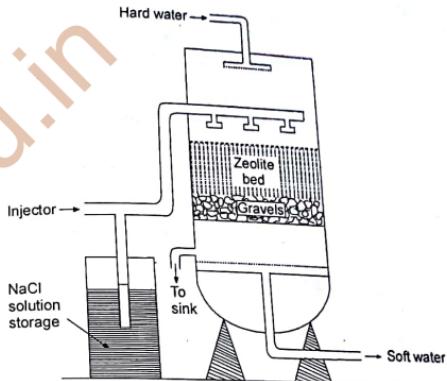


Fig. 4.5 Zeolite water softner.

## 2. Zeolite Process (Permutit process)

Zeolite process or Permutit process is an ion-exchange-technique, widely used to soften water. The process makes use of certain complex inorganic salts called **zeolites\*** which possess the property of exchanging the hardness producing ions such as  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$  etc. with those ions which do not cause hardness, e.g.,  $\text{Na}^+$  ions.

### Types of Zeolites

(i) **Natural zeolites**. These are non porous, amorphous and durable, e.g.,

Natrolite ( $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{SiO}_2 \cdot 2\text{H}_2\text{O}$ ) and Laumontite ( $\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 4\text{SiO}_2 \cdot 4\text{H}_2\text{O}$ ).

(ii) **Synthetic zeolites** : These are generally porous in nature and possess gel structures. They are prepared by heating together  $\text{Na}_2\text{CO}_3$ ,  $\text{Al}_2\text{O}_3$  and  $\text{SiO}_2$ . For example synthetic zeolite has higher exchange capacity than natural zeolite. Sodium zeolite ( $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot x\text{SiO}_2 \cdot y\text{H}_2\text{O}$  ( $x = 2 - 10$  and  $y = 2 - 6$ )) are important synthetic zeolites commonly known as **permutit**.

**Note** : Sodium zeolite is represented by  $\text{Na}_2\text{Z}$  for simplicity, where 'Z' stands for the insoluble radical framework.

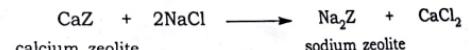
**Process** : The zeolite (permutit) is loosely packed over a layer of coarse sand in a tank shown in fig. 4.5. Hard water is allowed to percolate through it.

The hard water percolates through the permutit the  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  present in hard water replaced by the action of sodium zeolite. As

\* Zeolites are naturally occurring hydrated sodium aluminosilicate minerals ( $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot x\text{SiO}_2 \cdot y\text{H}_2\text{O}$ ),  $x = 2-10$  and  $y = 2-6$ .

**regeneration**. After working continuously about 10-12 hours the sodium zeolite gets completely exhausted due to the conversion of sodium zeolite into calcium zeolite and magnesium zeolite. Hence it is necessary to regenerate it.

The regeneration of zeolite is done by percolating a 10% brine ( $\text{NaCl}$ ) solution through the exhausted zeolite. This operation converts calcium and magnesium zeolites back into sodium zeolite as



After this treatment, the packing is washed with water to remove the chlorides of

5 L NaCl contain =  $100 \times 5 = 500$  gm

the amount of substance (W) = 500 gm  
equivalent mass of NaCl (E) = 58.5

equivalent of  $\text{CaCO}_3$  =  $\frac{W \times 50}{E} = \frac{500 \times 5}{58.5} = 427.35$  g  $\text{CaCO}_3$

10,000 L water = 427.35 gm  $\text{CaCO}_3$

1 L water =  $\frac{427.35 \times 1,000}{10,000} = 42.735$  ppm. Ans.

**Example 4.5.** A zeolite softener was 90% exhausted by removing the hardness completely when 1,00,000 litres of hard water sample passed through it. The exhausted zeolite bed required 150 lt of 30% NaCl solution for its complete regeneration. Calculate the hardness of water.

**Sol.** 150 lt of 30% NaCl solution required =  $150 \times 30 = 4500$  g NaCl

$$W = 4,500 \text{ g}, E = 58.5$$

equivalent of  $\text{CaCO}_3$  =  $\frac{W \times 50}{E} = \frac{4,500 \times 50}{58.5} = 3,846$  g  $\text{CaCO}_3$

1,00,000 lit water =  $3,846 \times 1,000 \times \frac{100}{90}$  g  $\text{CaCO}_3$

1 lit water =  $\frac{3,846 \times 1,000 \times 1000}{90 \times 1,00,000} = \frac{3,846}{90} = 42.73$  ppm. Ans.

### 3. Demineralization process

It is also known as **ion exchange process** or **deionization process**. Demineralization is the process of complete removal of all ions (cations and anions) present in water by using ion-exchange resins.\*

The two important demineralisation processes are discussed below –

#### Ion-Exchange process

In ion-exchange process, the ions present in water are removed by some complex organic compounds known as resins. Resins act as ion-exchangers and remove all minerals from hard water. They remove all cations and anions (except  $\text{H}^+$  and  $\text{OH}^-$  ions) from hard water and make it completely demineralised.

The resins used for exchanging all the ions present in hard water in this process are of following two types :

(i) **Cation exchange resins** : This type of resins exchange cations present in hard water with  $\text{H}^+$  ions. They possess acidic groups such as — COOH or —  $\text{SO}_3\text{H}$  groups.

**Ion exchange resins** consists of cross-linked, long chain organic polymer. Generally polystyrene vinylbenzene (PS-DVB), polymethacrylic acid-divinylbenzene or phenol-formaldehyde polymer are used as ion exchange resin

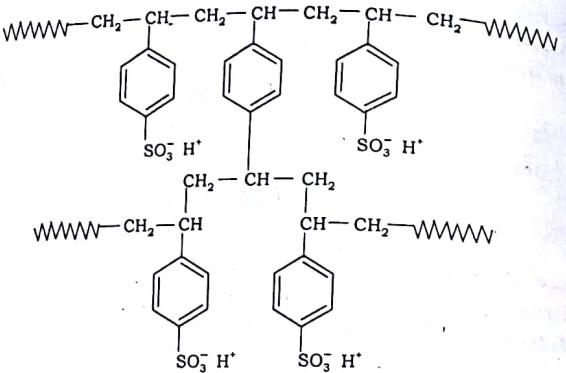


Fig. 4.6 A cation exchange resin.

The cation exchange resins are mainly *carboxylated or sulphonated styrene-divinylbenzene copolymers*. The structure of a cation exchange resin containing  $-SO_3H$  groups can be represented as shown in fig. 4.6. Example : Amberlite IR-120, Dowex-50.

**Note :** (i) In general, a cation exchange resin represented as RH where R represents the network for simplicity.

(ii) Resins containing  $-SO_3H$  group are more acidic than those containing  $-COOH$  group.

(ii) **Anion exchange resins :** This type of resins exchange anions present in hard water with  $OH^-$ . They possess basic groups such as  $OH^-$  or  $NH_2^-$  group. The cation exchange resins mainly *styrene-divinylbenzene or amine-formaldehyde copolymers containing amino or quaternary ammonium etc. groups*.

Example : Amberlite-400, Dowex-3.

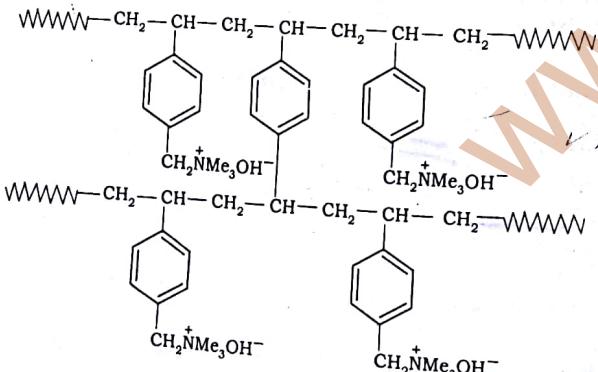


Fig. 4.7 An anion exchange resin

**Note :** (i) In general, an anion exchange resin represented as R'OH where R'-represents the resin network for simplicity.

(ii) Resin containing quaternary ammonium salts are strongly basic than those containing  $-NH_2$  or  $-NH-NH_2$  group.

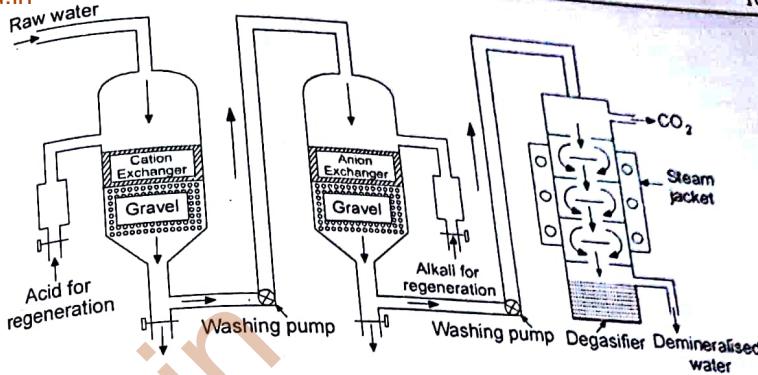
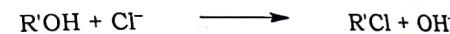


Fig. 4.8 Demineralization of water by ion exchange resins.

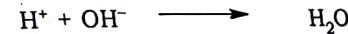
**Process :** Cation exchanger and anion exchanger both are interconnected with a pipe as shown in Fig. 4.8. The water is passed through first cation exchange resin. The  $Ca^{2+}$  and  $Mg^{2+}$  in water get exchanged by  $H^+$  from cation exchanger as follows :



Then the treated hard water is passed through anion exchanger resin columns where anions like  $SO_4^{2-}$ ,  $Cl^-$  etc. present in hard water are replaced by  $OH^-$  ions from resins as:

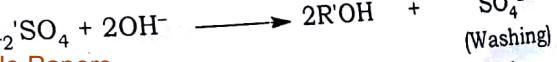
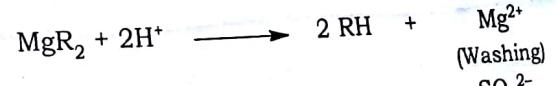
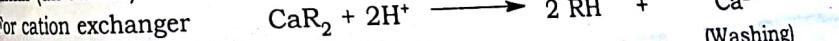


The released  $H^+$  from cation exchanger treatment and  $OH^-$  from anion exchanger treatment get combined to produce water.



It is called deionized water because it is free from cations and anions.

**Regeneration of resins :** The continuous use of resins exhaust them after some time. Therefore, they must be regenerated. The exchanger is regenerated by first back washing and then by passing a solution of appropriate ion. Then cation exchangers is regenerated by passing suitable acids ( $2\% HCl$  or  $H_2SO_4$ ) and anion exchanger is regenerated by passing an alkali (dil NaOH) solution.



## 4.1. Methods of Desalination of Water

- 1. Distillation,
- 4. Electrodialysis, and
- 2. Freezing,
- 3. Reverse Osmosis.

### 1. Distillation

Brackish water may be purified by distillation of salty water into pure water on a large scale but it is very costly and not very common on a large scale.

### 2. Freezing

When salty water (brackish water) is allowed to freeze the ice crystals are separated from salt. It is washed and melted into pure water. The yield is satisfactory but the cost of production is high on a large scale.

### 3. By Electrodialysis

It is an efficient method for desalination of saline water.

**Principle :** It is based on the fact that when direct electric current is applied to saline water by using **electrodes** and **ion selective permeable membranes\***, the ions present in saline water migrate towards oppositely charged electrodes and water gets purified.

**Process :** The process is carried out in a special type of cell called **electrodialysis cell** shown in fig. 4.10. It consists of a large number of paired sets of ion-selective membranes.

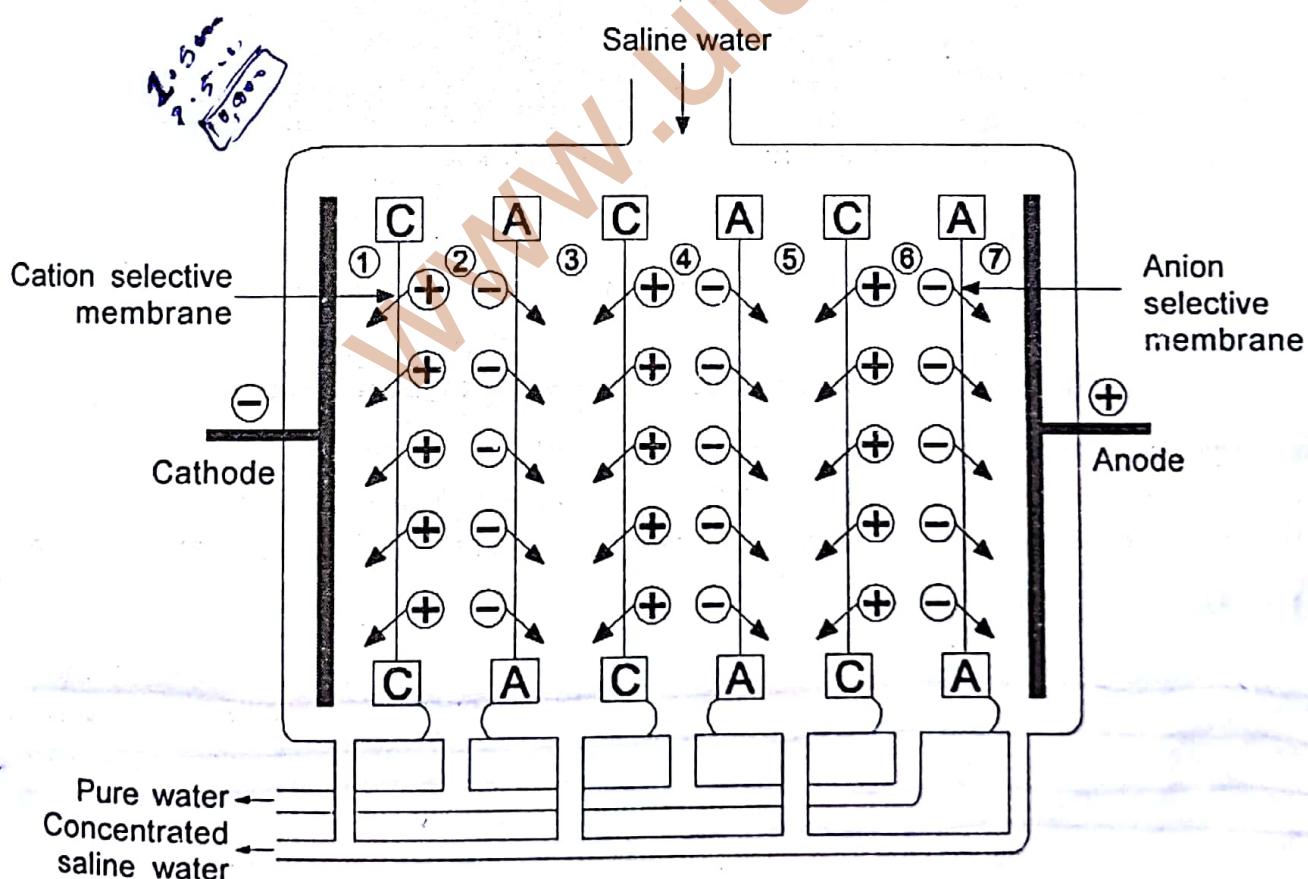


Fig. 4.10 Electrodialysis of saline water.

\***Ion selective permeable membrane** is that which allow to pass either cation or anion not both.

Saline water under a pressure of about  $5.6 \text{ kg/m}^2$  is introduced from the top of the direction of flow of water. The ions start moving towards the oppositely charged through the membranes. On account of this, the concentration of ions in alternate compartments, 2, 4, 6 etc. decreases, while the concentration of ions in alternate compartments 1, 3, 5, 7 etc. goes on increasing. Thus water collected from compartments 2, 4, 6 etc. while that collected from compartments 1, 3, 5, 7 etc. is more concentrated saline water.

In general, the movement of ions of saline water through the ion selective membrane takes place as, Fig. 4.11

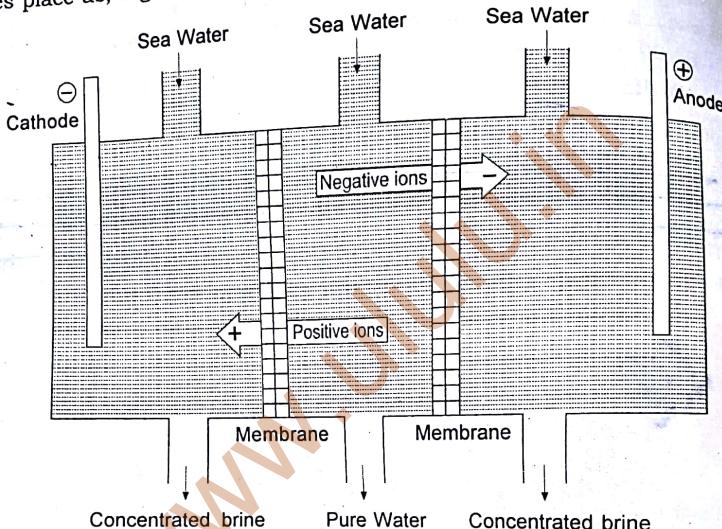


Fig. 4.11 The movement of the ions of saline water.

- Advantages of the process :**
- (i) It is economical.
  - (ii) It is convenient and may be applied at room temperature.
  - (iii) It is most compact in size and requires only electricity for operating.

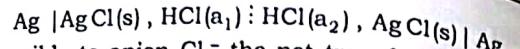
#### 4. By Reverse Osmosis

When two solutions having different concentrations are separated by a semipermeable membrane then flow of solvent takes place from lower concentration to the higher concentration until the concentration becomes equal on the both sides. This phenomenon is called osmosis and driving force is called the osmotic pressure. If a hydrostatic pressure is applied in excess of osmotic pressure, on the highly concentrated side then the flow of solvent gets reverse. It is called reverse osmosis. Thus, the pure water is separated from its contaminants by reverse osmosis. The membrane filtration is also known as super filtration or hyper-filtration. The technique is very useful in sea-coast areas. The out sketching line diagram of this tec

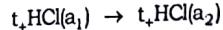
Principle :  
concentrated solution to the

Pro  
cell, fig  
perme  
Revers

Ac  
mole  
(i)



where electrodes are reversible to anion  $\text{Cl}^-$ , the net transfer is given by



The E.M.F. of such a cell is given by

$$E_{\text{Cell}} = \frac{2.303RT}{F} t_+ \log_{10} \frac{a_1}{a_2} \quad \dots(4)$$

Hence in both the cases, whether the electrodes are reversible to cation or anion, E.M.F. of the cell depends upon the transport number of the ion other than to which electrode is reversible. Therefore, such cells are used in the determination of transport number of the ions.

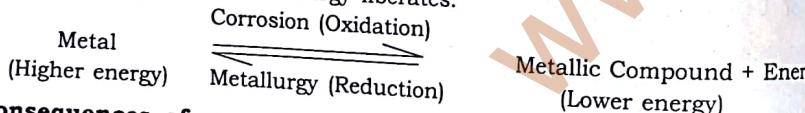
## 5.2. CORROSION

Corrosion is a chemical or electrochemical phenomenon. It may be defined as gradual disintegration or deterioration of a metal by the chemical or electrochemical action of environment is called corrosion. The extent of corrosion depends upon the nature of the metal and environment.

### 5.2.1 Causes of corrosion

It has been found that most metals (exceptions-noble metals like Au, Pt, Ir etc.) exist in their combined forms like oxides, carbonates, sulphates etc. In combined form they have lower energy. The pure or isolated metals have high energy so they are thermodynamically unstable. Due to this reason metals have tendency to acquire the thermodynamic stability i.e. lower energy. For this, metals easily undergo in interaction with the environment either chemically or electrochemically to form a stable compound by the process of corrosion.

Hence we can say that corrosion is an oxidation process in which metallic compound having lower energy is formed and energy liberates.



### 5.2.2 Consequences of corrosion

Although corrosion is a slow and undesirable process, yet the losses caused by it are substantial. Some of the important economical and social consequences of corrosion are:

(i) Corrosion involves the gradual eating away of metals and therefore it leads to the deterioration of machines and equipments. This reduces their efficiency. It may also lead to the failure of machines and consequently the shutdown of the plants.

(ii) The costs involved in adopting the preventive measures to check corrosion are substantial. The repairing and replacement of corroded parts are also quite expensive. This adds to the cost of production and consequently the cost of production is higher.

(iii) On account of corrosion, the products obtained may be contaminated and may lead to several problems including health hazards.

(iv) Corrosion may also pose problems to the safe operation of a plant. It may lead to an explosion, collapse of construction due to sudden failure or fire hazard.

(v) Corrosion may also create pollution problem due to escaping of harmful corrosion products from a corroded machine into the atmosphere.

## 5.3 TYPES OF CORROSION

On the basis of nature of corrodent, on the basis of the appearance of the corroded metal or on the basis of mechanism of corrosion, there are following types :

### 5.3.1. Dry Corrosion (Chemical Corrosion)

The corrosion caused by the direct chemical action of atmospheric gases such as  $\text{CO}_2$ ,  $\text{SO}_2$ ,  $\text{O}_2$ ,  $\text{H}_2\text{S}$ ,  $\text{Cl}_2$  etc. or anhydrous liquids on the metal surfaces is called dry corrosion.

#### Types of Dry Corrosion

(i) Oxidation corrosion

(ii) Corrosion by other gases

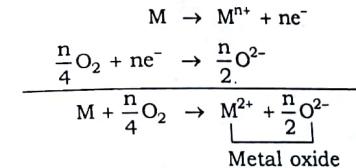
(iii) Liquid metal corrosion

(i) Oxidation corrosion

When corrosion takes place by direct action of oxygen on metal, is called oxidation corrosion.

It occurs usually at ordinary temperatures and in the absence of moisture. For example, alkali metals and alkaline earth metals undergo corrosion by this process.

**Mechanism :** When a metal is exposed to air it gets oxidized by losing its valence electrons and reduction of oxygen takes place, as



(Loss of electrons by metal)

(Gain of electrons by oxygen)

On account of the above electron transfer reactions, a metal oxide scale is formed at the metal surface. This scale acts as a barrier and tends to prevent the underlying metal atoms to come in contact with oxygen. Further oxidation can take place only when either the underlying metal gets diffused outwards through the scale to the surface, or oxygen gets penetrated inwards through the scale. Thus, once the metal surface is covered with a monolayer of oxide film, the growth of the oxide film takes place perpendicular to the metal surface and this results in the formation of a thick oxide film. The formation of oxide film is shown in Fig. 5.3.

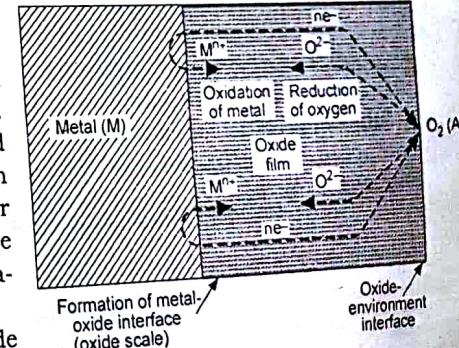


Fig. 5.3 Mechanism of Oxidation corrosion.

corrosion is due to -  
 (a) a dissolution of solid in liquid metal or  
 (b) penetration of liquid metal into solid metal.  
 For example, in nuclear reactor sodium metal acts as coolant it leads to corrosion of cadmium.

### 5.3.2 Wet Corrosion (Electrochemical Corrosion)

The corrosion involving the flow of electrons from a particular part of the metal surface called anodic area towards some other part called cathodic area through a conducting solution is called electrochemical corrosion or wet corrosion.

**Conditions for wet corrosion :** (i) When a conducting liquid with varying amount of oxygen is in contact with a metal.

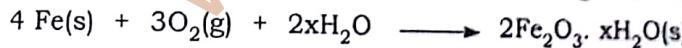
(ii) When two dissimilar metals or alloys are in contact with each other in the presence of a conducting medium (aqueous solution, moisture etc.)

When a metal in contact with a solution consists of anodic and cathodic areas or parts at its surface, electrons begin to flow from the anodic areas to the cathodic areas and thus the setting up of several galvanic cells occurs at the surface. At an anodic area, the metal undergoes oxidation by releasing electrons. These liberated electrons travel towards a cathodic area through the conducting solution. At the cathodic area, the dissolved constituent of the conducting solution take electrons and undergo reduction to form non-metallic ions such as  $O^{2-}$ ,  $OH^-$  etc. The oxidised metal in the anodic area then combines with these non-metallic ions to form the corrosion products. Thus, the metal continues to get corroded.

### Rusting of Iron

Rusting of iron is a specific case of corrosion. When an iron piece is exposed to moist air, it gets covered with a reddish brown coating is formed on the iron surface. This reddish brown layer is called **rust** and the phenomenon is known as **rusting**. The exact composition of rust depends upon the atmospheric conditions which are responsible for rusting. It mainly consists of hydrated ferric oxide,  $Fe_2O_3 \cdot xH_2O$ .

The formation of rust can be described by the following reaction :



**Note :** The layer of rust is porous so the inside layer of iron metal further undergoes corrosion. In this way the process of corrosion of iron metal continues till it is completely oxidised.

**Factors which govern rusting :** The rusting of iron is caused and governed by -

- (i) Presence of air
- (ii) Presence of moisture
- (iii) Presence of  $CO_2$
- (iv) Presence of impurities in metals
- (v) Presence of electrolytic impurities in water

### MECHANISM OF ELECTROCHEMICAL CORROSION Electrochemical Theory of Corrosion)

To explain the Phenomenon of electrochemical corrosion various theories have been

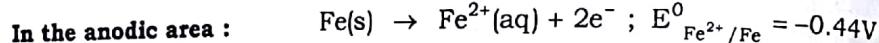
proposed. The electrochemical theory provides a satisfactory explanation to the proposed theory.

According to the theory, corrosion is mainly due to a difference in the behaviour of different parts of the surface of the metal.

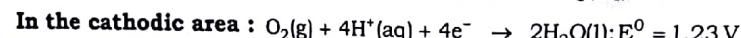
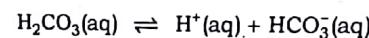
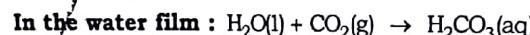
The mechanism of corrosion as explained by electrochemical theory can be understood by taking the example of rusting of iron.

**Mechanism of Rusting of Iron:** According to the electrochemical theory, the non-uniform parts of iron surface behave like miniature galvanic cells in the presence of water containing dissolved oxygen and carbon dioxide. One part of the surface acts as anode while some other part acts as cathode. The electrons thus begin to flow from the anodic area to the cathodic area.

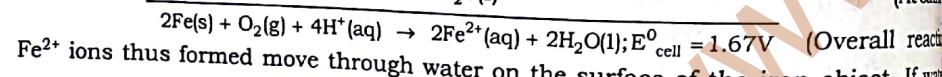
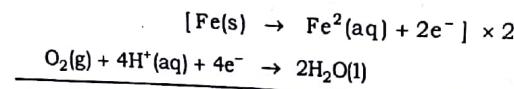
In the anodic area, oxidation occurs and iron atoms get oxidised to  $\text{Fe}^{2+}$  ions.



The electrons thus released move through the metal to the cathodic area. In the cathodic area, electrons reduce the oxygen in the presence of  $\text{H}^+$  ions.  $\text{H}^+$  ions are formed in the film due to the dissociation of  $\text{H}_2\text{CO}_3$  which is formed on account of the dissolution of water. Thus,



Thus, the overall cell reaction that takes place in a miniature galvanic cell on the surface of iron can be obtained as follows.



$\text{Fe}^{2+}$  ions thus formed move through water on the surface of the iron object. If we

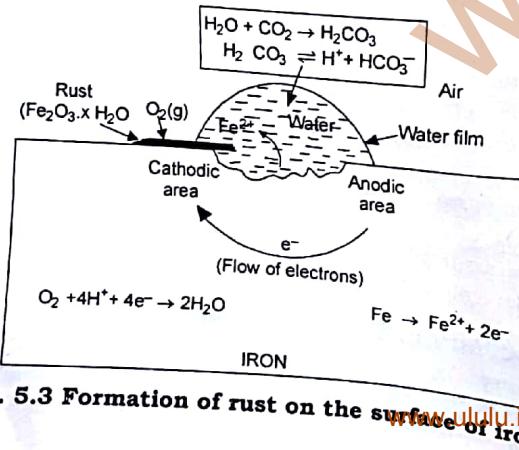
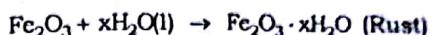
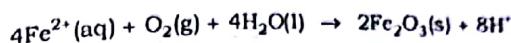


Fig. 5.3 Formation of rust on the surface of iron.

contains electrolytes e.g.  $\text{NaCl}$ ,  $\text{MgCl}_2$  etc., more current is carried in the miniature cell and corrosion takes place at a greater rate. The  $\text{Fe}^{2+}$  ions formed in the overall reaction in a miniature cell get further oxidised to  $\text{Fe}^{3+}$  ions by atmospheric oxygen and combine with atmospheric oxygen and moisture to form hydrated iron (III) oxide ( $\text{Fe}_2\text{O}_3 \cdot x\text{H}_2\text{O}$ ) which deposits on the surface of the object in the form of rust.



$\text{H}^+$  ions produced in the above reaction are utilised again in the process of rusting.

**Note :** (i) If iron contains impurities of less electropositive metals, the process of rusting gets accelerated because impurities set up a number of miniature galvanic cells.  
(ii) Very pure iron does not rust quickly.  
(iii) Presence of electrolytes in water also accelerates the process of rusting.

### 5.3.3 Galvanic Corrosion (Bimetallic Corrosion)

Galvanic corrosion occurs when two different metals either in direct contact or connected through an electrical conductor are exposed to a conducting solution. As a result, the less noble metal\* gets corroded.

For example, zinc ( $E^0 = -0.76\text{V}$ ) is less noble than copper ( $E^0 = +0.34\text{ V}$ ) as the former is placed higher in the electrochemical series. When the two metals either in direct contact or connected through a wire are exposed to a conducting solution, zinc being less noble undergoes corrosion, whereas copper being more noble remains protected (Fig. 5.5).

**Mechanism :** The galvanic corrosion is due to a difference in the electrode potentials of metals. The metal which has lower standard reduction potential act as anode, while that having a higher standard reduction potential acts as cathode and undergoes corrosion.

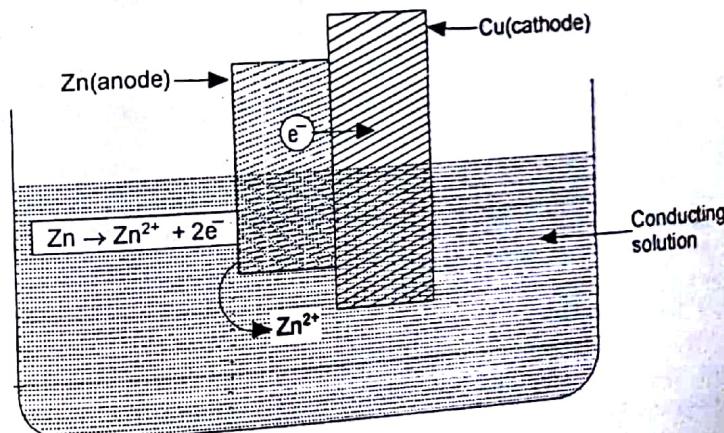


Fig. 5.5 Mechanism of Galvanic Corrosion.

**Noble metal :** The metal having a lower value of standard reduction potential or placed higher in the electrochemical series.

vibration, tapping, flexing etc. in the presence of a corrosive environment. This is common in alloy steels. The repeated cyclic stresses make specific regions of the metal less elastic which in turn become anodic with respect to the other regions of the metal. corrosion takes place in these specific regions leading to the formation of cracks.

### 5.3.8. Soil Corrosion

The presence of moisture, bacteria, other micro-organisms and electrolytes in soil responsible for causing underground or soil corrosion. When a buried or underground lines or cables passing from one type of soil to different soil, the change in the concentration of  $O_2$  takes place. Due to the differential aeration ( $O_2$  clay <  $O_2$  sand) of different soils, underground pipe lines get corroded. When the amount of free oxygen is less (water), microbial corrosion takes place because microbes can grow easily in this environment.

## 5.4 FACTORS AFFECTING CORROSION

The rate and extent of corrosion of a metal are mainly governed by two factors :

1. Nature of the metal and
2. Nature of the corroding environment

### 1. Nature of the Metal

The various factors which decide the nature of a metal from the view point of corrosion are as :

(i) **Purity of the metal** : The presence of impurities in metal or alloy enhances the rate of corrosion. Impurities present in the metal or alloy form minute electrochemical cells under suitable environmental conditions and undergo corrosion.

(ii) **Physical state of the metal** : The physical state of a metal is very important to decide the rate of corrosion. The rate of corrosion is appreciably influenced by –

(a) **Grain size of the metal** : The rate of corrosion increases with a decrease in the grain size. This is because smaller grains increase the solubility of the metal.

(b) **Orientation of crystals** : Orientation of crystals at the metal surface is also important. It is evident from fact that the rate of corrosion of copper ions is not uniform at all faces of a pure copper crystal.

(c) **Presence of stress** : As we have seen that areas under stress tend to be anodic and undergo corrosion even in case of pure metals.

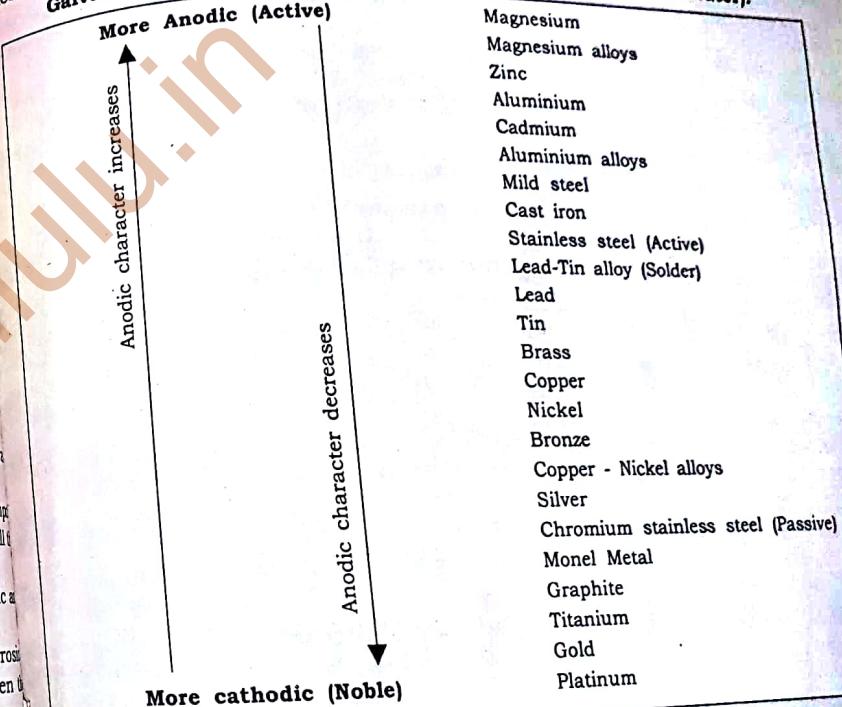
(iii) **Relative areas of the cathodic and anodic parts** : The rate and extent of corrosion increases with increase in the ratio of the areas of cathodic and anodic parts. When cathodic area is much larger as compared to the anodic area, corrosion is more severe, rapid and highly localised. This is because the great demand for electrons by a large cathodic area can be met by the anode of much smaller area only when it undergoes corrosion more briskly. Hence it may be concluded that in the absence of anodic polarisation, the extent and rate of corrosion of a metal are directly proportional to the ratio, cathodic area/anodic area.

(iv) **Over voltage** : Over voltage is the difference between the voltage which is actually required for occurring the electrode reaction and that expected theoretically. Since anodic areas having a smaller over voltage corrodes much faster as compared to that having higher over voltage under similar sets of conditions.

For example, when zinc is placed in 1N  $H_2SO_4$ , it undergoes corrosion forming a film along with the evolution of bubbles of hydrogen on the immersed metal surface. Inspite of high activity of zinc, the initial rate of reaction is quite slow due to high over voltage (about 0.70 V). However, the corrosion rate of zinc can be increased by adding a drop of  $CuSO_4$  solution. This is because on addition of  $CuSO_4$ , some copper deposits on zinc forming minute cathodes at which the hydrogen overvoltage is only 0.33V. Thus, reduction in overvoltage of the anodic metal accelerates its corrosion rate.

(v) **Position in galvanic series** : The metal or alloy which are placed at higher up in the series are more reactive and has greater tendency to undergo corrosion as shown in the table.

### Galvanic Series (Based on relative oxidation potentials in sea water).



(vi) **Nature of the oxide film** : In the presence of an aerated atmosphere, practically all metals undergo oxidation to different extents and get covered with a thin (measured in Angstroms) oxide film. In deciding the extent and rate of corrosion, Pilling-Bedworth ratio or specific volume ratio is an important. In case of alkali metals (Li, Na, K etc.) and alkaline earth metals (Mg, Ca, Sr, etc.), the volume of the oxide film formed on the surface is much lesser as compared to that of the metal consumed. Consequently, the oxide film formed is porous and allows free access of

# Lubrication and Lubricants

## INTRODUCTION

Lubricants are those type of substances which are used to reduce the frictional forces between two sliding surfaces, move together. It does not allow the direct contact between sliding surfaces. The process of decreasing the frictional forces between the sliding surfaces is called 'lubrication'.

Lubricants play very important role in machines, tools and many apparatus. The lubricants is not new to the modern civilisation. Archeological findings reveal that chariot drivers used lubricants and early as 1400 B.C. The first systematic study of friction and lubrication was made by **Leonardo da Vinci** (1452-1519) who discovered the fundamental principles of friction and lubrication. Later on in 1886, **Osborn Reynold** studied the nature of lubrication afforded by fluids. Now a days, different types of lubricants are available and being used in almost all the machines that we come across.

## 6.1. FRICTION AND WEAR

The main function of a lubricant is to minimise friction and wear between two bodies with their surface in contact to the maximum possible extent.

### 6.1.1. Friction

When two surfaces are come close to each other during motion, a resisting force comes into existence, which tends to retard their motion. The resisting force is known as frictional force. This phenomenon is termed as friction. It is a common phenomenon and occurs in all machines.

It has been established experimentally with the help of microscopic studies that material surfaces, no matter how smooth they are, are not smooth in two sense and contain many irregularities in the form of asperities (highest peaks) and valleys, fig. 6.1(a). When two such surfaces come in contact, the real contact between the two occurs only at a few number of asperities, fig. 6.1 (b). When the two surfaces are under load, deformation of the asperities takes place and the asperities get welded together to form flat junctions, fig. 6.1 (c).

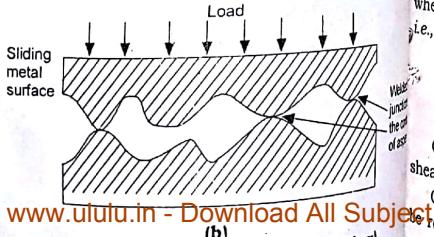
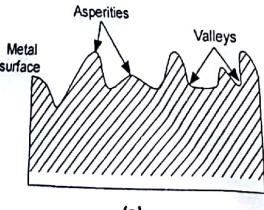


Fig. 6.1 (a) Valleys and Asperities on a metal surface (Magnified view),  
 (b) Welded flat junctions under high local load.

This leads to the formation of welded junctions at the point of contact of asperities which in true sense carry all the load between the two surfaces. Thus, the real area of contact is much smaller than the apparent area between the two surfaces.

**Classical laws of Friction :** According to classical theory of friction, the friction between two sliding surfaces in contact is governed by certain laws known as classical laws of friction. These laws are :

(i) The frictional force is directly proportional to the applied load on the surface.

**Exceptions :** very hard and very soft materials may not obey this law.

(ii) The frictional force is independent of apparent area of contact. This is because real area of contact is always smaller than the apparent area of contact between two surfaces.

**Exceptions :** When the metal surface is highly polished and finished to ideal conditions may not obey this law.

(iii) The coefficient of friction (frictional force) depends upon the nature of materials.

(iv) Static coefficient is always greater than the kinetic coefficient.

(v) The frictional force is independent of the sliding speed of surface up to an appreciable extent.

(vi) The coefficient of friction is directly proportional to mean shearing strength of the contact and inversely proportional to yield pressure of softer metal.

**Note :** There are a number of exceptions have been noticed by experience against these laws.

### Coefficient of Friction ( $f$ )

It has been observed that when two metallic surfaces are in contact with each other and are in motion then a frictional force is developed. Due to frictional force wearing and tearing of soft metal takes place hence a number of **asperities** and **valleys** are formed on the surface of metal. Due to these, the efficiency of machine is decreased. When lubricants are used between the metallic surfaces, this hinders the formation of asperities and reduce the frictional force as well as minimizes the wear and tear of metal.

When two sliding surfaces are in contact, the real area of contact, ( $A$ ) is smaller than apparent area and is represented as :

$$A = \frac{W}{P_m} \quad \Rightarrow \quad W = AP_m \quad \dots(1)$$

where  $W$  is the load applied and  $P_m$  is the yield pressure of softer metal.

For metal-metal contact,  $F = AS_m$  ... (2)  
 where  $F$  = force required to cause motion and  $S_m$  = mean shearing strength of the contacts i.e., metal junctions

The coefficient of friction,

$$f = \frac{F}{W} = \frac{S_m}{P_m} \quad \dots(3)$$

Coefficient of friction ( $f$ ) is independent of the real area of contact and is determined by shearing strength of a solid lubricant and the yield pressure.

Coefficient of friction ( $f$ ) must be as small as possible for effective lubrication and it may be reduced by lowering the shear strength or increasing the yield pressure.

**Note :** It has been found that solid lubricants have very low shear strength and coefficient of friction.

### 6.1.2. Wear

Due to the presence of asperities and valleys on the metal surfaces, the real area of contact is much smaller than the apparent area. This results in a tremendous increase in the magnitude of the applied load. An applied load of a few kilograms per square centimetre may create a pressure of several tonnes per square centimetre. During the movement of two surfaces in contact under an applied load, the asperities of the softer metal are picked up by the asperities of harder metal. Infact in due course of time, asperities of both metals are crushed and deformed plastically depending upon their hardness till the contact area is large enough to support the load. Thus, the movement of two surfaces in contact under an applied load, the asperities of both metals are picked up by the asperities of harder metal and in due course of time, asperities of both metals are crushed and deformed plastically depending upon their hardness till the contact area is large enough to support the load. The movement of two surfaces in contact always involves a loss of material from the surface and deformation of moving parts referred to as wear. It may be defined as *The progressive loss of substance from the surface of a body brought about by a mechanical action*.

**Note :** Wear is a general term and includes material losses due to several processes such as abrasion, scuffing, pitting, corrosion, galling etc.

## 6.2. LUBRICATION AND LUBRICANTS

The friction between sliding surfaces is not desirable for the efficient working of machine and should be minimised to the maximum possible extent. This has been achieved by the use of lubricants. The process of reducing friction by the use of a lubricant is known as lubrication.

### 6.2.1. Lubrication

Lubrication may be defined as *the reduction of friction and wear between two sliding or moving surfaces by the interposition of a lubricant between them.*

The reduction in the frictional force may be achieved in the following two ways:

(i) **Solid lubrication** : In this type of lubrication, the surfaces in contact are coated with a solid substance (lubricant), such as graphite.

(ii) **Fluid lubrication** : In this type of lubrication, a fluid film interposed between the rubbing surfaces which save them in coming in direct contact with each other and efficiently reduces the frictional resistances between them. This method is quite common in practice.

### 6.2.2. Lubricants

A lubricant may be defined as *any substance which when interposed between two sliding or moving surfaces reduces the friction and wear between them.*

A lubricant not only reduces the friction and wear between two sliding or moving surfaces but also serves several other functions.

**Important Functions of a Lubricant** (i) A lubricant avoids a direct contact between rubbing surfaces and therefore it reduces wear, tear and surface deformation.

- (ii) It reduces the cost of maintenance of the machines and tools.
- (iii) It reduces the loss of heat energy produced by frictional force between two rubbing surfaces. Hence, it acts as a **coolant**.
- (iv) It reduces the wastage of energy and thus increases the efficiency of a machine.
- (v) It does not allow the entry of moisture and dirt between the moving parts.
- (vi) It acts as a seal between the piston and cylinder wall and prevents the leakage of hot gases from the combustion chamber of an internal combustion engine.
- (vii) It washes and transports solid particles produced in combustion or wear.
- (viii) In chemical laboratory it is used in burettes, vacuum pumps, condensers etc.

### 6.2.3. MECHANISM OF LUBRICATION

There are three types of mechanism for lubrication.

1. Fluid film or Hydrodynamic lubrication
2. Thin film or Boundary lubrication
3. Extreme-pressure lubrication

#### 6.3.1. Fluid Film or Hydrodynamic Lubrication

Fluid film lubrication is done with liquid lubricants, [fig. 6.2.(a)]. The moving surfaces are separated from each other by a thick film of fluid ( $\sim 1000 \text{ \AA}$  thickness) so that the direct contact of two surfaces of metal or junctions may be minimized. Since thick film of lubricants ( $\sim 1000 \text{ \AA}$  thickness) are used, hence it is also known as **thick film lubrication**. As a result wearing and tearing of metals get minimized due to less friction. In such type of case the coefficient of friction is very low (0.001 to 0.03).

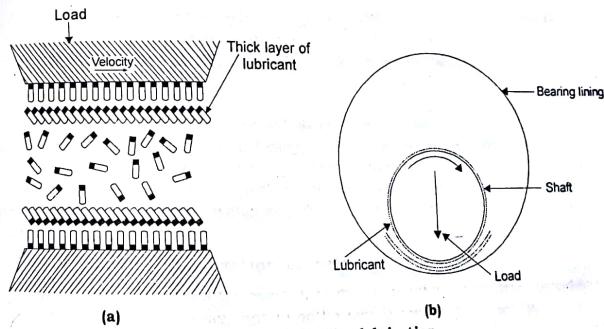


Fig. 6.2 Fluid film lubrication.

Hydrodynamic friction occurs in the case of a shaft running at a fair speed as well as in well-lubricated bearing with not very high load. In a general bearing, the film of lubrication oil covers the irregularities of shaft and the bearing surfaces and do not allow to come in

contact the metallic surfaces to each other [fig. 6.2(b)]. Such type of lubrication is used in delicate and light machines like watches, clocks, guns, sewing machines, scientific instruments etc.

### 6.3.2. Thin Film or Boundary Lubrication

It is not always possible to maintain a continuous fluid film between two sliding surface as required in hydrodynamic lubrication. Such a situation may arise in any of the following cases.

- (i) When a shaft comes into motion (action) from rest position.
- (ii) When the load is very high and speed is very slow.
- (iii) When the viscosity of lubricating oil is very low.

Under such conditions, a continuous fluid film cannot be maintained between the surfaces and lubrication can be achieved only if the lubricant is adsorbed on the rubbing surfaces either through physical or chemical forces. fig. 6.3. This separates the rubbing surfaces by a thin film of the lubricant and the surfaces come closer. Thus the lubricant maintains a **boundary film** between the two rubbing surfaces. The load is carried by the layers of the lubricant adsorbed on the two rubbing surfaces. This type of lubrication is referred to as **thin film lubrication** or **boundary lubrication**.

#### Important features of thin film lubrication

- (i) The conditions of boundary lubrication are not ideal but they can prevail at starting or stopping of machinery and also under high pressure and low speed of the system.
- (ii) The boundary lubrication does not depend much on the viscosity of the lubricant.
- (iii) The thin film is often disrupted due to the presence of asperities on the rubbing surfaces. Consequently, metal-to-metal contact may occur. This situation could be avoided by choosing a suitable lubricant which is capable of building up these layers as soon as they are disrupted.

(iv) The boundary lubrication is not effective in vacuum because vacuum removes the adsorbed layer. On the other hand, presence of air favours this type of lubrication by forming oxides which promote boundary binding.

(v) In boundary lubrication, the structure and chemical properties of the lubricant play a significant role and decide its effectiveness.

For the effective boundary lubrication, the molecule of the lubricant should have,

- (i) long chains hydrocarbon and lateral attraction between the chains,
- (ii) polar groups to promote spreading and orientation over the metallic surface at high pressure,

- (iii) active groups or atoms for forming chemical bonds with the metals or other surfaces.
- (iv) high viscosity index, good oiliness, low pour point.

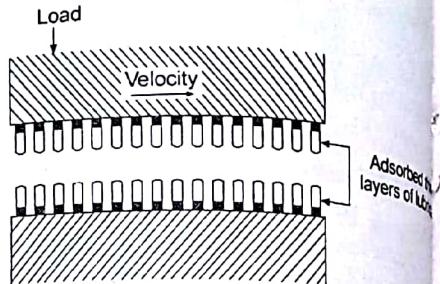


Fig. 6.3 Thin film lubrication.

[www.ululu.in](http://www.ululu.in) resistance to heat and oxidation.

(iv) On the basis of above properties the following types of lubricants are useful :

- (i) Mineral oils, which are thermally stable, mixed with fatty acids or fatty oils.
- (ii) Solid lubricants graphite or molybdenum disulphide as emulsion in oil.
- (iii) Vegetable and animal oils having greater oiliness than mineral oils.

### 6.3.3. Extreme Pressure Lubrication

When the sliding surfaces are under high speed and high pressure in a system (particularly in case of automobiles), excessive heat is generated which produces high local temperatures. The high local temperature thus produced at the rubbing surfaces change the physical and chemical characteristics of the lubricant due to decomposition. The lubricant may get evaporated also. Consequently, the lubricant becomes ineffective and fails to stick to the rubbing metal surfaces.

Thus the common lubricants fail to work under the conditions of high pressure and high speed. In order to provide effective lubrication under such conditions, certain special type of additives are added to the commonly used lubricants. The additives thus added are called **extreme pressure additives** and the lubrication involved is termed as **extreme pressure lubrication**. The commonly used extreme pressure additives are organic compounds containing chlorine (e.g., chlorinated esters) sulphur (e.g., sulphurised fats and oils), and phosphorus (e.g., tricresol phosphate).

The extreme pressure additives react with the metal surfaces under the conditions of high temperature to form solid surface films of corresponding metal chlorides, sulphide and phosphides. The solid surface films formed by them are more durable as they possess a greater shear strength. These films can withstand very high loads and high temperature due to their high melting points. Moreover, if the low shear strength films formed on the surfaces are broken by the rubbing action of moving parts, they are immediately replenished.

**Note :** Extreme pressure lubricants have great advantages. They are used as lubricants in wire drawing, machining of tough metals, etc.

#### Comparison between fluid film and thin film or boundary lubrication :

Fluid film lubrication	Thin film lubrication
1. The thickness of lubricating oil film is $> 1000 \text{ \AA}^{\circ}$ .	1. The thickness of lubricating oil film is $< 1000 \text{ \AA}^{\circ}$ .
2. These are used as such no metallic surfaces required for adsorption.	2. These are adsorbed by physical or chemical forces at the metallic surfaces.
3. Lubricants have less viscosity.	3. Lubricants have high oiliness.
4. The load applied is sufficient to keep apart the moving surfaces. Hence it is known as hydrodynamic lubrication.	4. The load applied is carried by the layers of adsorbed lubricants.
5. These are used in the machines working under light load and high speed.	5. These are used in the machines working under heavy load and low speed.
<b>For example</b> , watches, clocks, sewing machines and scientific instruments etc.	<b>For example</b> , rollers, gears, tractors, railway track joints etc.

## 6.4. CLASSIFICATION OF LUBRICANTS

Depending upon the physical state, lubricants can broadly be classified into :

1. Solid lubricants,
2. Semi-solid lubricants,
3. Liquid lubricants or lubricating oils

2. Semi-solid lubricants,
4. Emulsion lubricants

### 6.4.1. Solid Lubricants

Lubricants which exist in solid form are called solid lubricants. For example, graphite, molybdenum disulphide\*\*, soap stone, wax, mica, chalk etc. Recently some stearates

\* **Graphite** : It is very soapy to touch and non-inflammable. It does not oxidise in air below 300°C.

It satisfies the ideal requirements of solid lubricants and acts as an excellent solid lubricant. The lubricating action of graphite is due to its unique layer structure. The hexagonal sheets or layers of atoms, as shown in fig. The sheets are held together by weak van der Waals' forces and are separated by a distance of 3.4 Å. Due to weak van der Waals' forces, the sheets are not firmly attached and can slide over one another. This is why graphite is soft and possesses lubricating properties.

For lubrication purposes, graphite may be used in powdered form, as an aerosol from a freon pressurised container, as a paste in grease, or as liquid dispersion. A dispersion of graphite in water is called aquadag, whereas that in an oil is called oil dag. Oil dag is very useful in internal combustion engines, because it forms a film between the cylinder and piston rings to give a **tight-fit contact** which increases the compression of the air-fuel mixture. Aquadag is particularly useful in situations where a lubricant free from oil is needed.

**Uses of graphite as a lubricant** : (i) In air compressors, lathes, equipments used for processing foods and other machine shop operations. (ii) In conjunction with oil and grease, it is used in roll neck bearings, internal combustion engine assembly, automatic telephone equipments etc. (iii) A resin bonded dry film, used over chains and screw heads. (iv) As metal working lubricant, it is used for wire drawing, extrusion, press forging etc.

\*\* **Molybdenum disulphide** : Molybdenum sulphide ( $\text{MoS}_2$ ) has sandwich like structure, as shown in the fig., in which a layer of molybdenum atoms lie between two layers of sulphur atoms.

It has higher specific gravity than graphite, yet is slightly softer. It has a very low coefficient of friction and is stable in air upto 400°C.

**Uses of Molybdenum disulphide as lubricants** : (i) It is used as an additive to oils and greases in shaft bearings of jaw crushers, machine tool gearing, coal conveyer belt gear units etc. (ii) It is also used as resin bonded dry film in automobile steering ink assemblies, engine governor assemblies etc. (iii) It is also used as a working lubricant.

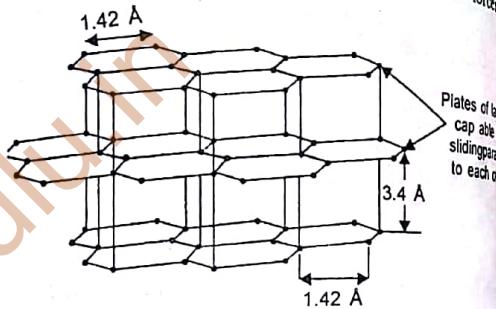


Fig. Structure of graphite

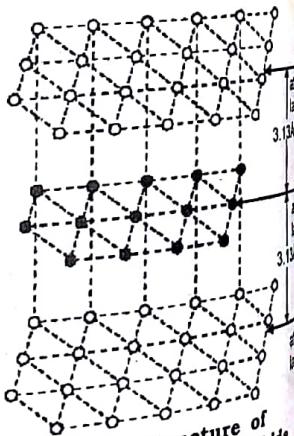


Fig. Structure of Molybdenum disulphide

6

**(i) Animal oils and vegetable oils :** Animal oils and vegetable oils having good oilness properties are obtained from the animal and vegetable kingdom contain glycerides of higher fatty acids. They were the most commonly used lubricants before the development of petroleum. For example, Animal oils - whale oil, seal oil, lard oil etc.

Vegetable oils - palm oil, mustard oil, olive oil, cotton-seed oil etc. Although animal and vegetable oils have good oilness property yet they have disadvantages :

- They are costly because their extraction is not simple.
- They undergo oxidation and lose lubricating properties.
- They hydrolyse in aqueous medium or in moist air.

Due to these limitations, vegetable and animal oils are rarely used as lubricants now. Instead, they are used as **blending agents** to improve the oiliness of other lubricants.

**(ii) Mineral oils (Petroleum oils) :** These are obtained by fractional distillation of petroleum at atmospheric pressure. They possess long hydrocarbon chains which contain 12 to 50 carbon atoms. The shorter chain oils possess lower viscosity as compared to those which possess longer chains.

Although they have poor oiliness but they are widely used as lubricants because they are cheap, stable and available in abundance.

**Note :** The oiliness is improved by the addition of high molecular weight compounds like acid, stearic acid etc.

**(iii) Blended oils (Compounded oils) :** Since a number of oils have poor oiliness hence no single oil is used as lubricant for many of the modern machines. A small quantity of some specific **additives\*** are added into the oils to improve their properties. The resultant oil is called **blended oil**.

#### 6.4.4. Emulsion lubricants

An emulsion is a two phase system of two immiscible liquids in which one liquid is dispersed in the other as dispersed phase. For example, a mixture of oil and water.

Emulsions are prepared by vigorously mixing of two immiscible liquids in the presence of a stabilizing substance known as emulsifier or emulsifying agent in ultrasonic waves.

Emulsions are important lubricant which are used in several machines like threading, milling etc.

##### \* Specific Additives

- Oiliness carrier — coconut oil, castor oil and fatty acids.
- Antioxidants (Inhibitors) — Aromatic phenolic or amino compounds.
- Antifoaming agents — Gycols and glycerol.
- Emulsifiers — sodium salts of sulphuric acid.
- Thickeners — polystyrene, polyesters etc.
- Viscosity index improvers — hexanol and other high molecular weight compounds.
- Extreme pressure additives — fatty esters or fatty acids, organic compounds containing sulphur or phosphorus or chlorine etc.
- Abrasion indicators — tricresylphosphate.
- Corrosion preventives — organic compound of phosphorous or antimony.

paraffinic base oils.

**9. Mechanical Stability :** A good lubricant must be great stable under very high pressure during different mechanical tests. It may be tested by 'four ball extreme pressure lubricant test' as in fig. 6.6

The experimental oil is poured in a machine containing four balls. The lower three balls are fix while the upper ball is rotated. The load is gradually increased and the balls are examined for scar formation at specific intervals. If the balls come out clean, the lubricant is satisfactory under the load. If the balls are welded together due to the formation of heat by increasing the load then the lubricants is not satisfactory.

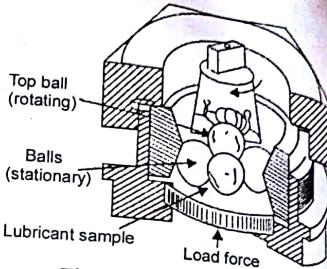


Fig. 6.6 Four ball extreme pressure test.

**10. Colour and Fluorescence :** Each type of lubricant has some specific colour or even colourless. Colour of a lubricant is very helpful to identify the lubricant. If the lubricant has not its own characteristics colour then it must contain impurities of contamination i.e., the lubricant is not fit for lubrication. The colour of lubricant is checked against a standard lubricant. Although it is not a sure test but is used widely.

The fluorescence is measured by a standard fluorometer. As mineral oils show fluorescence in reflected light whereas fixed oils do not, the fluorescence shown by an oil may be used to find any adulteration or difference in composition.

**11. Flash and Fire point :** The volatility and the tendency of a lubricating oil to burn is indicated in terms of flash and fire point.

**Flash point :** It is the minimum temperature at which the oil gives of sufficient vapour that ignite for a moment, when a flame of specific dimension is brought near to the surface of the oil under specified conditions.

**Fire point :** It is an extension of flash point and is defined as the minimum temperature at which it gives of sufficient vapour that burn continuously for at least five seconds when a flame of specific dimension is brought near to it under specified conditions.

**Note :** (i) In general, the fire point of an oil is nearly 5-10°C higher than the flash point for any lubricant.

(ii) A good lubricant should have flash point reasonably above the temperature, a machine attains during its working.

#### Determination of flash and fire point by Pensky-Marten's apparatus

The apparatus fig. 6.7 consists of

**(i) Oil cup :** It is a metallic cup with a mark to indicate the level of oil to be filled in it. The cup is provided with a thermometer, a stirrer, an inlet for air and an opening for introducing the test flame.

**(ii) Shutter :** It is provided at the top of the cup. It has a lever mechanism. When the

**Spontaneous Ignition Temperature (SIT).** It is the temperature at which ignition of an oil occurs without introducing of a flame, when an inflammable liquid is allowed to fall in drops into a hot metal crucible.

**Viscous-Static.** Such type of a lubricant can be prepared by adding appropriate amounts of suitable linear polymer or viscosity-index improver.

#### 14. Ash Content

The percentage of ash in a lubricant is very useful to determine the material that cause abrasion and wear. Ash content of a good lubricant should be less as much as possible. It is determined by heating strongly the known amount of lubricant in a weighed crucible in the presence of air. After cooling the weight of ash is calculated. The process is repeated so many times till the constant weight.

$$\text{Percentage of ash} = \frac{\text{Weight of ash}}{\text{Weight of lubricant}} \times 100$$

#### 15. Cloud point and Pour-point

These points indicate the suitability of lubricants in the machines working under temperature condition. They may be defined as, *when a lubricating oil is cooled in a standard apparatus at a specified rate, the temperature at which the oil first becomes cloudy or hazy appearance is called the cloud point and the temperature at which the oil just ceases to flow pour is called the pour point of the oil.*

**Note :** A good lubricant suitable for use in a machine working at low temperatures should possess low pour point, otherwise it will solidify at will cause a seizure.

**Solid point :** The highest temperature at which an oil does not move when the standard containing the oil is kept in a horizontal position for 5 seconds is called **solid point**.

The pour point of oil free from wax is called '**Viscosity pour point**'. For oil containing wax, pour point is the temperature at which crystallization of wax has gone to such an extent that the oil will stop flowing if cooled further. The temperature is called '**Wax pour point**'.

**Determination of cloud point and pour point :** The apparatus, fig. 6.10, consists of a flat-bottomed tube for taking lubricating oil. This tube is enclosed by an air-jacket. The air jacket is surrounded by freezing mixture (ice +  $\text{CaCl}_2$ ) contained in a jar. The flat tube is half filled with the experimental oil. A thermometer is placed in the oil. The oil gets start cooling and the temperature decrease slowly. At an interval of fall in temperature every  $1^\circ\text{C}$ , the tube is withdrawn from the air jacket for a moment (2-3 seconds) and examined and then replaced in ice-bath immediately. The temperature at which cloudiness is noted is recorded as the **cloud-point**. After this cooling is continued and the test tube is removed from the cooling bath after every  $3^\circ\text{C}$  fall of temperature and tilted to observe the flow or pour of oil. The temperature at which oil does not flow in the

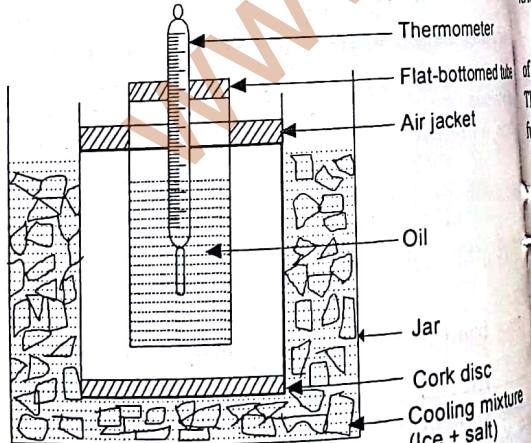


Fig. 6.10 Cloud point and pour point of an oil

tube, even when kept horizontal for 5 seconds, is recorded as the **pour point**.

#### 16. Aniline Point

Aniline point of a lubricating oil gives an indication of the tendency of the oil to undergo deterioration when it is in contact with rubber sealings, packing etc. It may be defined as the minimum temperature at which the equilibrium exists between equal volume of aniline and oil sample. Aniline is readily soluble in those type of lubricants which are rich in aromatic and naphthenic compounds.

**Note :** The aromatic hydrocarbons usually have a tendency to dissolve natural and certain types of synthetic rubbers. Hence, a good lubricant should possess a low aromatic content.

**Determination of Aniline Point :** The aniline point of an oil is determined by mixing mechanically equal volumes of aniline and the oil under examination till a homogeneous solution is obtained, fig. 6.11. The solution is cooled at a specific rate till the aniline and the oil phases separate out. The temperature at which the two phases just separate out corresponds to the aniline points of the oil.

**Mixed Aniline Point :** There are certain lubricants which have high aromatic contents. When these are mixed with equal volume of aniline, they form a homogeneous mixture but during cooling or solidification, separation of different phases may not be observed. For determination of such type of aniline points one volume of oil sample is mixed with two volumes of aniline and one volume of suitable solvent (diluent) like n-hexane or n-heptane. Addition of diluent lowers the miscibility of aniline with the sample. So with decrease in temperature, separation of phase can be easily observed. The equilibrium solution temperature observed under these conditions is known as **mixed aniline point**.

**Diesel Index :** The aniline point of an oil decreases with the increase in the percentage of its aromatic content. A diesel fuel with a high aniline point have low aromatic content. This gives an easy start to the engine and reduces knocking. The ignition quality of a diesel fuel is also reported in terms of **Diesel Index** which is related to the aniline point by

$$\text{Diesel Index} = \text{Aniline Point in } {}^{\circ}\text{F} \times \frac{\text{API gravity}}{100}$$

**Note :** For high-speed diesel fuel, the aniline point should be above  $160^\circ\text{F}$ .

#### 17. Neutralization Number :

The acidity or alkalinity of lubricating oil is usually expressed in terms of Neutralization Number. It represents either the total acid value or total base value.

During refining of the oils some free organic acids are always associated with the lubricating oil, so acidity is more common and is expressed in **acid value** or **acid number**. It may be defined as, the number of milligrams of KOH required to neutralize all the free acid present.

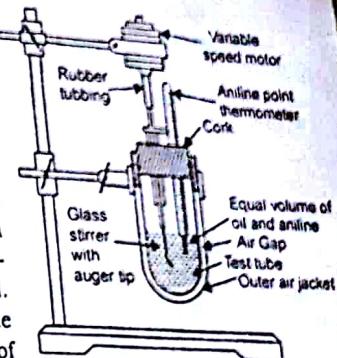


Fig. 6.11 Determination of an aniline point of an oil



# INTRODUCTION

Polymers are macromolecules of very high molecular masses, (Polymer- Greek; Poly = many, mer = unit). Such molecules occur in nature and can be synthesised in the laboratory. Cellulose, starch, proteins, rubber etc. are some common examples of naturally occurring polymers and synthetic fibres, plastics, rubber etc. are some common examples of synthetic polymers. These polymers find a variety of applications in our daily life. Infact, the age in which we are living today is the age of polymers because we cannot think of smooth running of life without polymers.

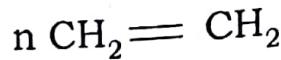
Polymers may be both of inorganic and organic nature. Important inorganic polymers\* are silicates, silicones, metaphosphoric acid  $(HPO_3)_n$  etc. However, the organic polymers, particularly the synthetic ones, are more important and are the chief products of modern chemical industry today.

## ORGANIC POLYMERS

### 1. Polymer and Polymerisation

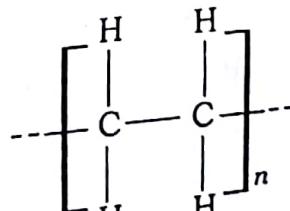
A polymer may be defined as - a polymer is a large molecule of very high molecular mass formed by the repeated combination of a very large number of one or more type of small molecules called monomers. The process by which monomer molecules combine together to form a polymer is called polymerisation. The repeating unit in the polymers is derived from monomers. These are linked together by covalent bonds.

W.H. Carothers, father of polymer chemistry succeeded in synthesising a large number of polymers by the polymerisation of small monomers. According to Carothers, polymerisation is a chemical combination of a number of similar or different molecules to form a single large molecule. For example, the polymer polyethylene is obtained by the chemical combination of a large number of ethylene molecule as :



Ethylene  
(monomer)

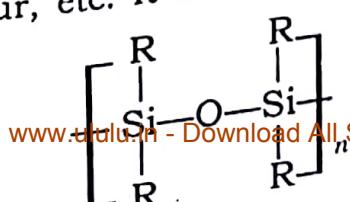
Polymerisation



Polyethylene (polymer)

$n = 800-1100$

**Inorganic polymers** : If the backbone of polymer is made of inorganic (other than carbon) atom oxygen, nitrogen, sulphur, etc. It is called inorganic polymers, e.g., silicones.



where  $R = \text{Alkyl}$  or halide groups

## 7.1.2. Repeat Units

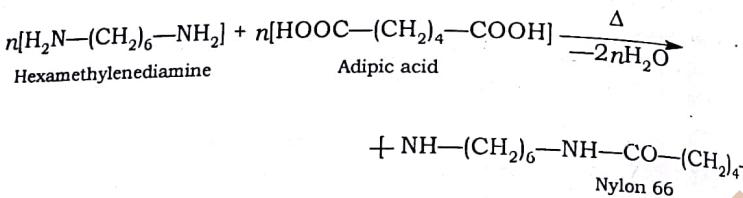
**7.1.2. Repeat Units**

Since, a polymer is formed by the repeated combination of a large number of monomer molecules. Therefore, the chain of a polymer molecule consists of a regular repetition of a particular unit derived from the monomer molecule. This unit is called the **repeat unit** and may be defined as, *the structural unit, which on repetition gives the entire chain of a polymer molecule is called the repeat unit of the polymer.* For example,

(i) The repeat unit in polyethylene is  $-\text{CH}_2-\text{CH}_2-$ . Hence, polyethylene can be represented as  $\text{+CH}_2-\text{CH}_2\text{+}_n$

sented as  $+ \text{CH}_2 - \text{CH}_2 +_n$

(ii) The repeat units in nylon - 66 are adipic acid and hexamethylenediamine. Hence nylon - 66 can be represented as



## **7.2. CLASSIFICATION OF POLYMERS AND POLYMERIZATION**

Polymers and polymerisation can be classified in several ways. Some important classes

1. Classification on the basis of nature of monomer units
  2. Classification on the basis of source of origin
  3. Classification on the basis of structure
  4. Classification on the basis of synthesis
  5. Classification on the basis of molecular forces.
  6. Classification on the basis of tacticity.

#### **7.2.1. Classification on the basis of nature of monomer units**

Depending upon the nature of monomer units, polymers can be classified into two:

**(i) Homopolymers :** The polymers obtained by the repeated combination of only one type monomer molecules are called **homopolymers**. For examples,

(a) Polyethylene,  $-\text{CH}_2-\text{CH}_2-$ <sub>n</sub> is a homopolymer of ethylene ( $\text{CH}_2 = \text{CH}_2$ )

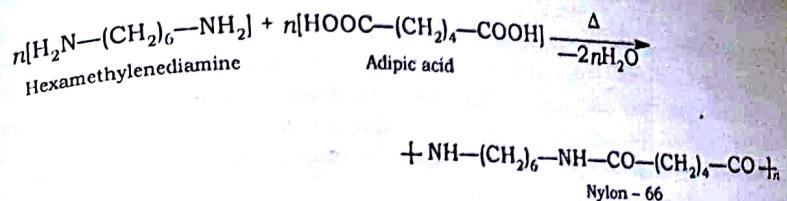
(b) Polyvinyl chloride (PVC),  $\text{+ CH}_2\text{---CH Cl}_n$  is a homopolymer of

v vinyl chloride ( $\text{CH}_2 = \text{CH} - \text{Cl}$ ).

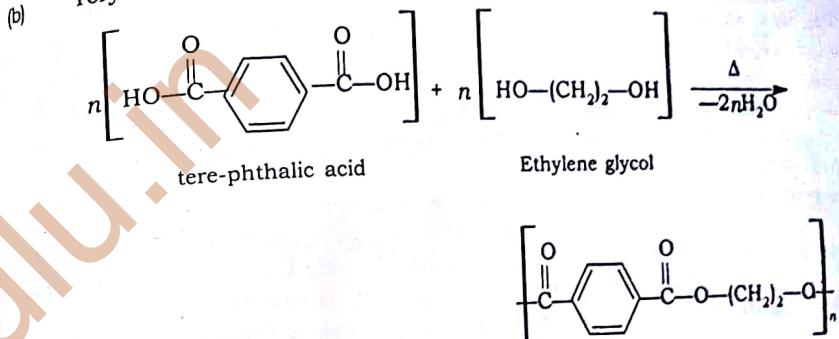
(ii) **Copolymers** : The polymers which are obtained by the repeated combination of two or more types of monomer units are called **copolymers**. For example, Download All Subject

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-66 is a copolymer of hexamethylenediamine and adipic acid.



Terylene is a copolymer of tere-phthalic acid and ethylene glycol.



Note: In a copolymer, the repeat unit is derived from two or more types of monomer units.

### **7.2.2. Classification of polymers on the basis of source of origin**

Depending upon the source of origin, polymers can broadly be classified into two categories.

depending upon the source of origin, poly-  
merized (i)天然的 (ii) Synthetic polymers

**Natural polymers\***: The polymers which occur in nature are called natural polymers. e.g., nucleic acids, natural rubber etc.

(ii) **Synthetic polymers** : The polymers which have been prepared in the laboratory are building blocks in animals. They are

**Natural polymers :** (a) **Proteins** : Proteins acts as building blocks of all living organisms. They are long chain polymers and may be cross-linked also. A protein molecule is composed of 20-1000 amino acids in a highly organised arrangement.

(b) **Cellulose** : It is the main structural material of plants. It consists of hundreds of  $\beta$ -D glucose units joined together through  $\beta$ -glycosidic linkage.

(c) **Starch** : It is the main food reserve of plants. It is a polymer of  $\alpha$ -D glucose. In a starch molecule, hundreds of  $\alpha$ -D glucose molecules are joined together through a particular type of linkage called  $\alpha$ -glycosidic linkage.

**Sugars** are present in the chromosomes of cell nuclei and control the various nucleotides and consists of base-sugars.

The bark of rubber

(d) Nucleic acids : Nucleic acids are present in hereditary characters. They are the polymers of various nucleotide units.

(e) **Natural Rubber**: Natural rubber is obtained from the latex of several trees. It is a polymer of 2-methyl-1, 3-butadiene which has the following structure:

synthetic routes are called synthetic polymers. These are also known as man-made polymers. For example, bakelite, rubber, PVC, polythene etc.

### 7.2.3. Classification of Polymers on the basis of structure

On the basis of structure, polymers can be classified into :

(i) **Linear Polymers** : The polymers in which the constituent monomeric units are joined together to form long straight chains are called linear polymers or straight chain polymers. In a linear polymer, the polymeric chains usually stack one over another and form a well packed structure, (fig. 7.1 a).

Due to the close packing of polymeric chains, linear polymers have high densities, high tensile strength and high melting point. For example, high density polythene.

(ii) **Branched chain polymers** : The polymers which consist of side chains (made of monomeric units) attached to the main chain (linear chain) are called branched chain polymers, (fig. 7.1 b).

Due to the presence of branching, branched chain polymer molecules are unable to pack themselves in a compact manner. This is why branched chain polymers have lower densities, melting points and tensile strength as compared to linear polymers. For example, low density polythene.

(iii) **Cross-linked polymers** : The polymers in which the adjacent polymeric chains link together through side chains to form a three-dimensional net work structure are called cross-linked polymers, (Fig. 7.1 c). Such polymers are also referred to as **network polymers**.

Due to the presence of cross-links, cross-linked polymers are hard, rigid and brittle. For example, bakelite, melamine formaldehyde resins, urea-formaldehyde resins etc.



(a)



(b)



(c)

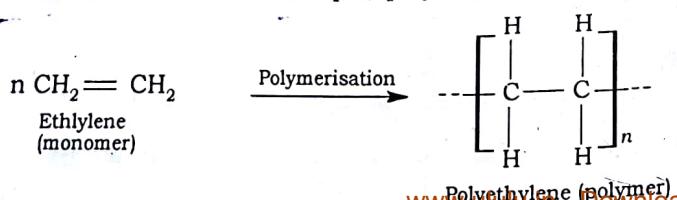
Fig. 7.1 (a) Linear Polymer, (b) Branched chain polymer, (c) Cross-linked polymer

### 7.2.4. Classification of Polymers and polymerisation on the basis of synthesis

Based on the synthesis of polymers, polymerisations may be of two types :

(i) Addition Polymerisation and (ii) Condensation Polymerisation

(i) **Addition Polymerisation and Addition Polymers** : When a large number of monomeric molecules add up together to form the polymer chain, the process is called addition polymerisation and the polymer formed is called addition polymer. The monomers involved in the process are unsaturated compounds, e.g., ethene. This type of polymerisation does not involve the elimination of small molecules like  $H_2O$ ,  $NH_3$ , alcohol etc. Therefore, the repeating unit is the same as the monomer unit. For example, polyethylene.

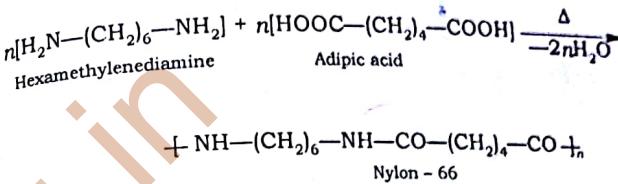


The process of addition polymerisation occurs through a chain mechanism via some active centre. These active centres could be free radicals, carbocations or carbanions.

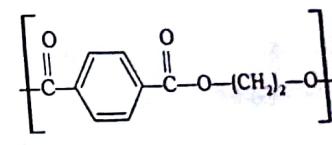
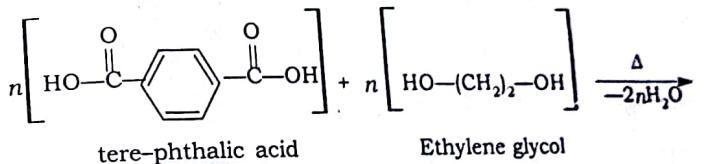
(ii) **Condensation Polymerisation and Condensation Polymers** : A polymer is formed by the combination of two or more similar or different molecules of monomeric units usually with the loss of small molecules like  $NH_3$ ,  $H_2O$ ,  $HCl$  etc., is called 'condensation polymer' and the process of polymerization is known as 'condensation polymerization'.

The basic requirements for these types of polymerization are the presence of some reactive functional groups like — OH, —COOH etc. in the monomeric units. For examples,

(i) Nylon-66 is a condensation polymer of hexamethylenediamine and adipic acid.



(ii) Terylene is a condensation polymer of tere-phthalic acid and ethylene glycol



Terylene (Dacron)

In several polymerisation process, it is difficult to ascertain whether the polymerisation has occurred through an addition or a condensation process. Therefore, in recent years, a more rational method for classifying polymers has been introduced. In this method, the polymers are classified on the basis of the mode of addition of monomer units to the growing chain. On the basis of this criterion, polymers can be classified into :

(i) Chain growth polymers and (ii) Step growth polymers

#### Chain Growth Polymers

Addition polymerization are also termed as chain growth polymerization because in addition polymerization process the chain growth take place. Thus, it is the type of polymers which are formed by the successive addition of monomer units to the growing chain through the generated reactive intermediate like free radical, carbocation or carbanion and the process is called chain growth polymerisation.

Note : Since each step involves the elimination of a water molecule, the repeating unit in notes 66 is not the same as the monomers forming it.

## Difference between Addition and Condensation Polymerization

Addition polymerization	Condensation polymerization
<ol style="list-style-type: none"> <li>It takes place only in monomers containing multiple bonds</li> <li>The concentration of monomer decreases steadily throughout reaction.</li> <li>Elimination of simple molecule does not take place.</li> <li>High molecular weight polymer is formed at once.</li> <li>Long reaction time give high yields but molecular weight of polymer is affected</li> <li>The product is generally a thermoplastic</li> </ol> <p>For examples, Polyethylene, polystyrene, polypropene, polyvinylchloride etc.</p>	<ol style="list-style-type: none"> <li>It takes place in monomers containing functional groups.</li> <li>The concentration of monomer disappears early in the reaction.</li> <li>Elimination of simple molecule like <math>H_2O</math>, <math>NH_3</math>, <math>HCl</math> etc. are essential.</li> <li>The molecular weight of polymer rises steadily throughout the reaction.</li> <li>Long reaction time are essential to obtain high molecular weights.</li> <li>The product may be either thermoplastic or thermosetting plastic.</li> </ol> <p>For example, Urea formaldhyade resin, bakelite etc.</p>

### 7.2.5. Classification of Polymers on the Basis of Molecular Forces

Polymers possess several unique mechanical properties such as tensile strength, elasticity, toughness etc. which make them highly useful for a variety of purposes. The unique mechanical properties of polymers are due to the accumulative effect of intermolecular forces like van der Waal's force, hydrogen bonding etc. along the long chains of the polymers. Longer the chain of a polymer, more intense is the effect of intermolecular forces. Therefore, from the view point of the mechanical properties and hence their applications, it is quite logical to classify polymers on the basis of molecular forces.

On the basis of the magnitude of intermolecular forces, polymers can be classified into

(i) **Elastomers** : The polymers in which the polymeric chains are held together by the weakest intermolecular forces are termed as **elastomers**.

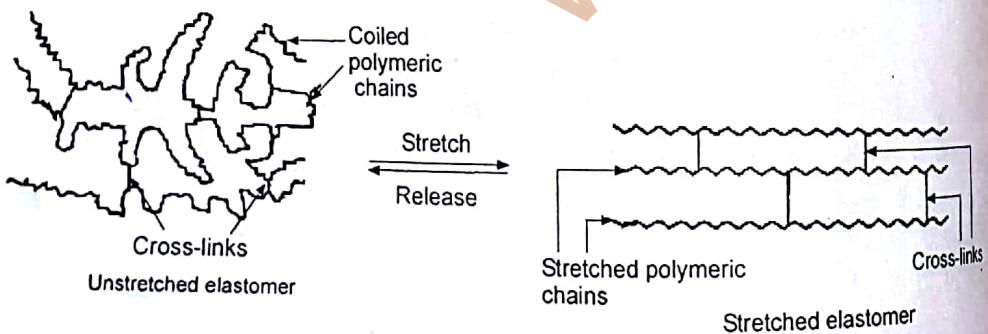


Fig. 7.2 The unstretched and stretched forms of an elastomer having cross-links

Due to weak intermolecular forces, the elastomers can be stretched by applying an external force. Such polymers consist of randomly coiled polymer chains. When a force is applied, the randomly coiled chains get opened up and the polymer gets stretched. In order to help the polymer to retract to its original position on the release of the applied force, a few cross-links are generally introduced between the polymer chains, fig. 7.2.

(ii) **Fibres** : The polymers consisting of strong intermolecular forces between the polymeric chains are called **fibres**.

The forces which hold the polymeric chains together in fibres are strong intermolecular forces such as hydrogen bonding, dipole-dipole interactions etc. Due to strong intermolecular forces, fibres possess high tensile strength and high modulus. The strong intermolecular forces also lead to the close packing of polymeric chains in them. This imparts a crystalline nature to them. This is why fibres have sharp melting points.

For example, (i) In nynol-66 (a polyamide) polymer, the polymeric chains are held together through hydrogen bonding.

(ii) Polyesters (e.g. terylene, dacron etc.) and polyacrylonitriles (e.g. orlon, acrilan etc.) consist of strong dipole-dipole interactions between the polymeric chains present in them.

(iii) **Thermoplastics** : The polymers in which the intermolecular forces of attraction are intermediary to those of elastomers and fibres are called **thermoplastics**.

Thermoplastics are linear polymers with no cross-linking between polymeric chains. Due to the presence of moderate (not very strong) intermolecular forces of attraction, thermoplastics soften on heating. At room temperature, they are quite hard but on heating they become soft and viscous. However, on cooling they again get hardened. As heating does not cause any cross-linking, they can easily be moulded by heating them. The process of heat softening, moulding and cooling can be repeated as many times as desired without affecting the mechanical properties of the polymer. Some common examples of thermoplastics are polythene, polypropylene, polyvinyl chloride (PVC), polystyrene, teflon etc.

**Plasticizers** : The workability of thermoplastics at relatively lower temperatures can be increased by the addition of certain organic compounds called **plasticizers**. Plasticizers help to soften thermoplastics at lower temperatures and thus make their moulding easier. Dialkyl phthalates (e.g. diethyl phthalate) and cresyl phosphates (e.g. tricresyl phosphate) are commonly used plasticizers. For example, polyvinyl chloride (a very tough thermoplastic) is usually made workable by the addition of dibutylphthalate which makes it soft and easily mouldable.

(iv) **Thermosetting polymers** : The polymers which on heating change irreversible into hard, rigid and infusible materials are called **thermosetting polymers**.

Thermosetting polymers are usually prepared by heating relatively low molecular mass semi-fluid polymers in a mould. On heating, they become infusible and form an insoluble hard mass. The hardening on heating is due to the formation of extensive cross-linking between different polymeric chains. This leads to the formation of a three dimensional network of bonds connecting the polymer chains. Since the three dimensional network structure is rigid and does not soften on heating, the thermosetting polymers can not be reprocessed.

For examples, phenol-formaldehyde (bakelite) resins, melamine-formaldehyde resins, urea-formaldehyde resins etc.

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Synthetic biopolymers are poly vinyl alcohol, polyacitic acid, poly vinyl esters, (PVA) polyglycolide (PGA), polylactide (LPLA) etc.

### Advantages of Biopolymerization

1. Biopolymers does not cause environmental pollution.
2. They are easily biodegradable without employing extra efforts.
3. They are obtained from natural and renewable resources.
4. They are metabolized in the body after their use.

### Drawbacks of Biopolymerization

1. Biopolymers are not very much thermally stable.
2. They possess less tensile strength.
3. They have complex structure that why their processing is difficult.

## 7.5. BIODEGRADABLE POLYMERS

Biodegradation of polymers is the decomposition or conversion of complex molecule into simpler units by photo degradation and by micro organisms. It is also defined as process of breaking the polymeric chain by enzymatic activities.

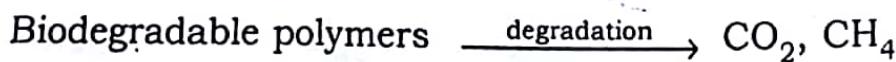
The extensive use of non biodegradable polymers increases the solid waste disposal problem, litter problem and hazards to marine life. This ultimately leads to the increasing environmental problem. Therefore there is a need for biodegradable polymers because these polymers are efficient options to minimise the solid waste and marine pollution. Moreover they do not require land fills for decomposition and gradually re enter in biogeochemical cycle ( $N_2$ ,  $H_2O$  and  $CO_2$  cycle).

### Uses of Biodegradable Polymers

- |                                 |   |                |
|---------------------------------|---|----------------|
| 1. Sutures for stitching wounds | : | PGA, LPGA, PDO |
| 2. Screws                       | : | LPLA, PGA      |
| 3. Pins and rods                | : | LPLA, DLPLA    |
| 4. Dental                       | : | DLPLA          |
| 5. Interference screws          | : | LPLA – DLPA    |

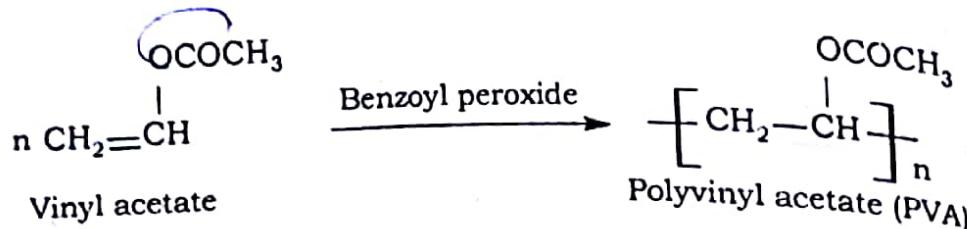
### Limitations Biodegradable Polymers

1. Biodegradable polymers are not recycled.
2. They are very expensive and not easily available.
3. They possess less mechanical strength.
4. Biodegradable polymers are precursors of green house gases ( $CO_2$ ,  $CH_4$ )



5. Increment of some advantageous properties in biodegradable polymers is not feasible

**Preparation :** It is prepared by the free radical addition polymerisation of vinyl acetate in the presence of benzoyl peroxide.



**Properties :** (i) Polyvinyl acetate is colourless, soft and sticky material.

(ii) It is resistant to atmospheric oxygen, water, mineral acids, alkalies and other chemicals.

(iii) It is soluble in organic solvents.

(iv) It is fairly resistant to heat but turns slightly yellow on prolonged storage above 120°C.

**Note :** (i) Articles formed from polyvinyl acetate are distorted even at room temperature under the influence of compressive and tensile forces. Therefore, it can not be used for moulding purposes.

(ii) Lower molecular weight polymers are brittle but become gum like when masticated. Therefore, it is used for making chewing gums.

**Uses :** (i) It is used in manufacture of adhesives, lacquers and water based emulsion paints (like latex paints)

(ii) It is used for bonding papers, leather, textiles etc.

(iii) It is used for making chewing gums, surgical dressings etc.

(iv) It is also used for the manufacture of vinylite, polyvinyl butyral, and polyvinyl alcohol.

### 7.6.2. Thermosets (Thermosetting Resins)

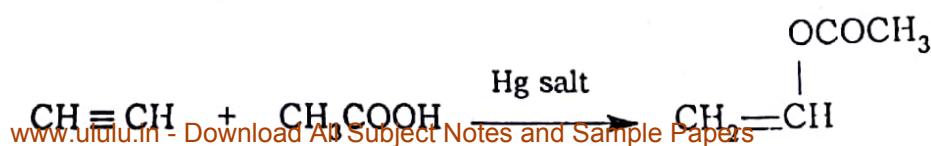
#### 1. Phenol-Formaldehyde Resins (PF Resins or Phenol Plastics)

Phenol-formaldehyde resins were first prepared by **Backeland**, an American chemist who gave them the name **bakelite**. They are condensation polymers.

**Preparation :** Phenol-formaldehyde resins are prepared by the reaction of phenol with formaldehyde in the presence of an acidic or a basic catalyst. The process may be carried out either in one stage or in two stages.

In **one-stage process**, a mixture of phenol and formaldehyde in the ratio of 1 : 1.25 and an alkaline catalyst are charged into resin kettle and allowed to react together. The process involves the formation of methylene bridges in ortho, para or both ortho and para positions. This results first in the formation of a linear polymer called **novolac** and then into a cross-linked polymer called **phenol-formaldehyde resin** or **bakelite**.

\* **vinyl acetate** : It is prepared by treating acetylene with acetic acid in the presence of a mercury salt.



$$\text{Novolac} \xrightarrow[\text{Heat}]{\text{Hexamethylenetetraamine}} \text{Bakelite (infusible)}$$

**Procedure :** A mixture of glacial acetic acid and phenol is taken in a beaker. A 40% aqueous solution of formaldehyde (formalin) is added with continue shaking. A few drops of concentrated HCl is added dropwise to this solution with constant stirring. A pink coloured mass of bakelite plastic is obtained. It is washed with distilled water, filtered and dried.

**Properties :** (i) Resins having high degree of polymerization are hard, rigid and infusible solid mass whereas resins having low degree of polymerizations are soft. Linking it is insoluble in almost all-organic solvents.

- (i) Due to cross-linking it is insoluble in all common organic solvents.
- (ii) It is scratch-resistant and water-resistant.
- (iii) It possesses excellent electrical insulating character.
- (iv) It resists non-oxidising acids, salts and many organic solvents but is attacked by alkalis due to the presence of free hydroxyl ( $-\text{OH}$ ) group in the structure.
- (v) It can withstand very high temperature.

**Uses.** (i) The main use of bakelite is in moulding applications. It is widely used in making telephone parts, cabinets for TV, radio and automobile parts.

(ii) It is used as adhesives for brake lining, grinding wheels etc.

(iii) Phenolic resins are used for impregnating paper, wood and other materials.

(iv) It is used in the manufacture of varnishes, paints and protective coatings.

(v) Bakelite is widely used for making electric insulators like switches, plugs, etc.

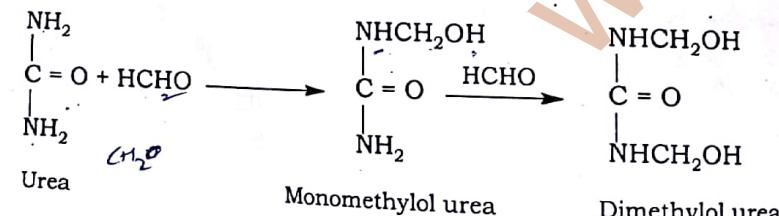
boards, heater handles etc.

(vi) It is used for making decorative laminates, walls coverings, etc.

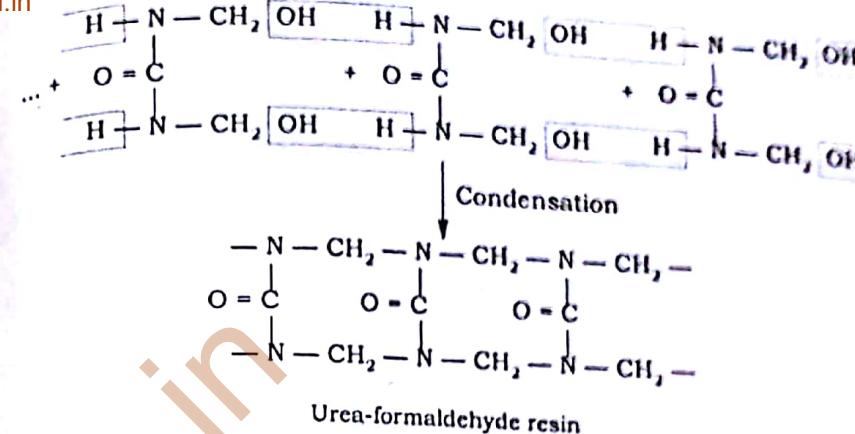
## **2. Urea-Formaldehyde (UF) Resins**

It is a condensation polymer of urea and formaldehyde.

**Preparation:** It is prepared by heating a mixture of urea and formaldehyde in the ratio of 2 : 1 in basic medium to 50°C in a stainless steel container. Urea and formaldehyde react to give monomethylol urea and dimethylol urea.



The dimethylol urea on condensation yield a cross-linked polymer called urea-formaldehyde resin.



**Procedure :** Urea is dissolved into 40% aqueous solution of formaldehyde (formalin) to get a saturated solution. Concentrated  $H_2SO_4$  is added dropwise with constant stirring. A white solid mass appears which is washed with distilled water and dried. The dried white solid mass is the cross-linked urea formaldehyde polymer.

**Properties :** (i) Urea-formaldehyde resins are clear and colourless hard materials.  
(ii) They are resistant to most of the solvents and greases.  
(iii) They are hard, abrasion resistant and stable to light.  
(iv) They can be synthesised in any desired colours by adding a proper pigment and Filler during synthesis.

(v) They are good electrical insulators and possess good chemical resistance.

**Uses :** (i) Urea formaldehyde resins are widely used in the manufacture of buttons, bottle caps, cosmetic container closures, household appliances, surgical items etc.

(iii) They are also used in the manufacture of enamels and other

- (iv) They are used in the manufacture of enamels and other surface coatings.
- (v) They are used in the paper industry to improve the wet strength of paper.
- (vi) They are used for the finishing of cotton textiles making them crease resistant, fire retardant and the control of shrinkage.

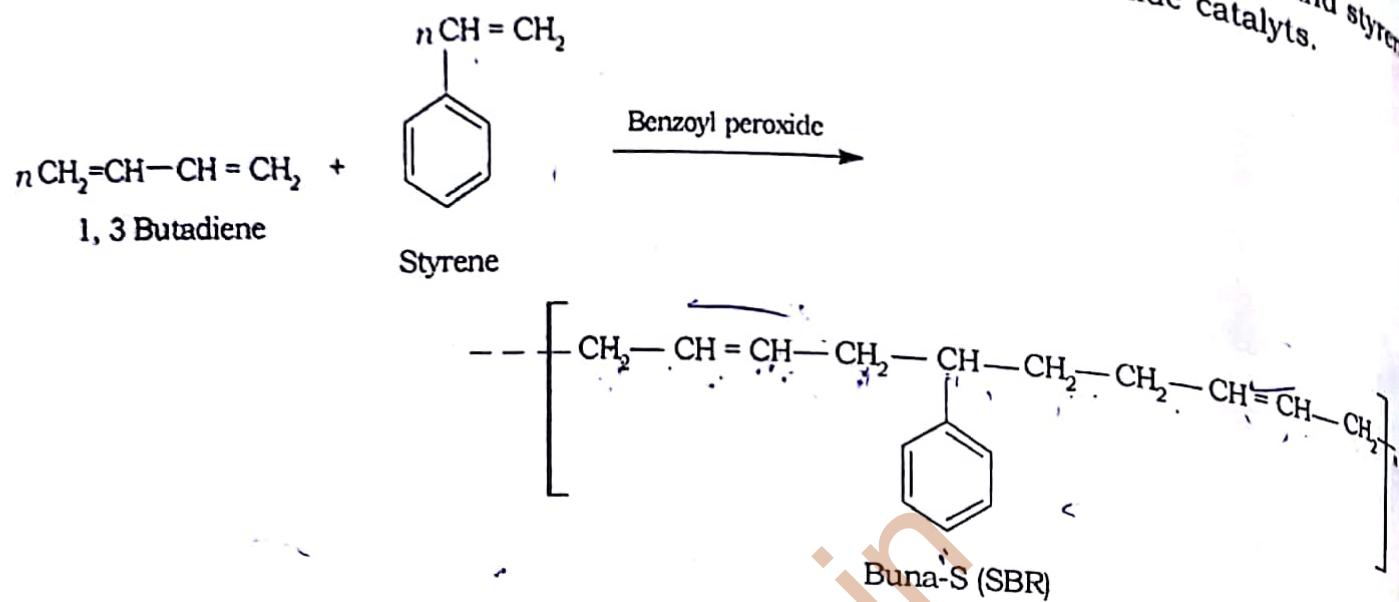
### 7.4.3 ELASTOMERS

An elastomer is a linear polymer having elastic properties like rubber. Elastomers can be stretched by applying an external force which retains the original size as soon as the external force is removed. They have been long flexible chains with weak intermolecular forces and sometimes cross-links across each other but the flexibility of the chain is preserved. For example, rubber, synthetic rubber etc.

**1 Styrene-butadiene rubber (SBR or Buna-S or GR-S)**

Styrene-butadiene rubber is a copolymer of butadiene and styrene in 3 : 1 ratio.

**Preparation :** It is prepared by the polymerization of a mixture of butadiene and styrene in 3 : 1 ratio in an emulsion system at 0°C in the presence of peroxide catalysts.



**Properties :** (i) It is also vulcanizable like natural rubber to give cross linked polymer.  
(ii) It swells in organic solvent and gets readily oxidized particularly in the presence of traces of ozone in the atmosphere.

(iii) It possesses high resilience, high load bearing capacity, high abrasion resistance and low oxidation resistance.

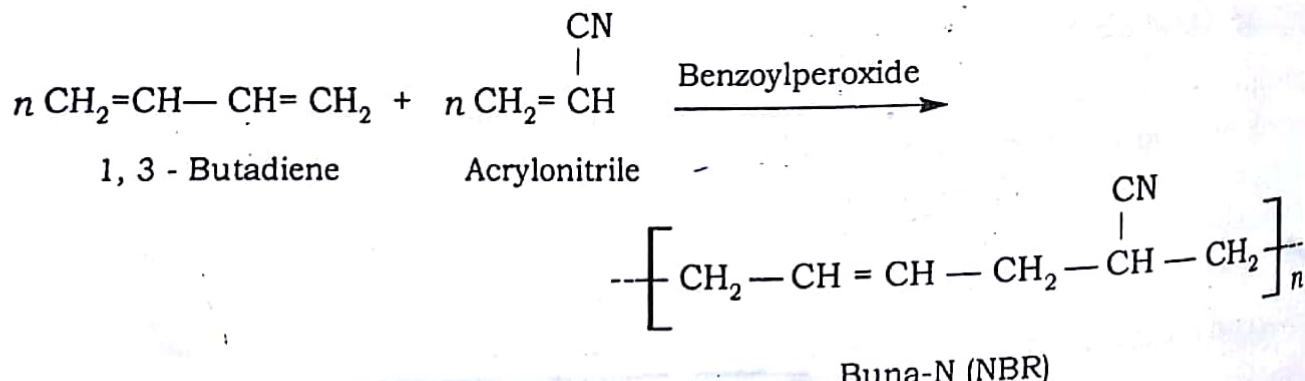
**Note :** Tensile strength and resistance to mechanical abrasion of the polymer can be increased by the emulsion polymerisation of butadiene and styrene at  $-18^{\circ}\text{C}$  to  $5^{\circ}\text{C}$  in the presence of an oxidation reduction system. The rubber thus obtained is called **cold rubber**.

**Uses :** (i) It is used in the manufacture of those mechanical goods which are required to possess greater resistance to mechanical abrasion e.g. motor tyres, shoe soles etc.  
(ii) It is also used in the manufacture of floor tiles, gaskets, cable insulations, foot carpet backing etc.

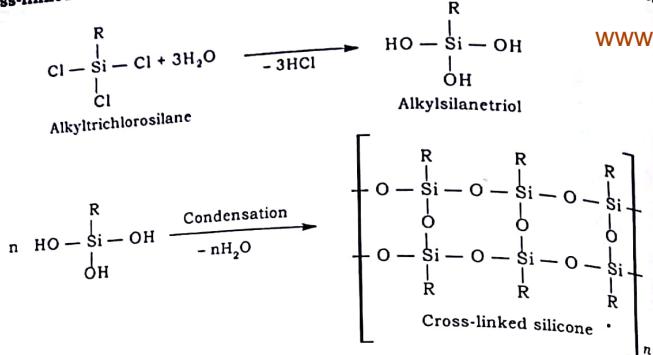
## 2. Nitrile rubber (Buna-N or GR-N or NBR)

It is a co-polymer of butadiene and acrylonitrile.

**Preparation :** It is prepared by the polymerization of butadiene and acrylonitrile in 3:1 ratio in an emulsion system.



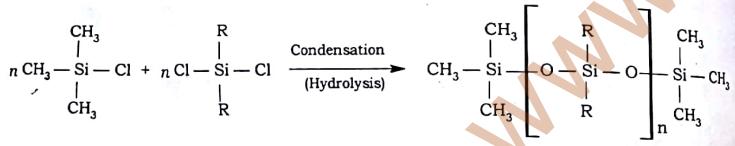
Cross-linked silicones are prepared by the hydrolysis of alkyl trichlorosilanes,  $\text{RSiCl}_3$



### Properties of silicones

- (i) The nature of a silicone polymer depends upon the length of the chain, extent of cross-linking and the size of alkyl or aryl groups present in it. Silicones having short chains (**lower silicones**) are oily liquids\*. Silicones having medium chains behave

\* **Silicone fluid :** Low molar mass straight chain polymers are obtained by the hydrolysis of dichlorosilanes. It is known as silicon fluid. For its preparation a small amount of trimethylchlorosilane is added to block the chain.



**Properties and uses :** (i) They have high viscosity index so they are used as hydraulic fluids.  
 (ii) They have excellent dielectric properties and are thermally stable and are useful in capacitors and small transformers.

- (iii) They can withstand high temperature so they are used in high temperature water baths.
- (iv) They are used in polishes for cars and furniture because dust and dirt particles remove easily from the coated surface.
- (v) They are nontoxic and possess antifoam properties so they are used to eliminate foam in petroleum oils.
- (vi) They are good lubricants at high temperature and high pressure so they are used in vacuum pumps, jet turbines etc.

- as viscous oils, jellies and greases\*, while those having long chains (**higher silicones**) behave as rubbery elastomers\*\* and resins.  
 They are water repellent and heat resistant. They are stable to heat atleast upto  $200^\circ\text{C}$  and are non-volatile on heating.  
 (iii) They are chemically inert.  
 (iv) The viscosity of silicone oils does not change much with temperature.  
 (v) They act as electrical insulators.  
**Uses of silicones :** (i) Silicones are used to form water-resistant coating on glass, clothes, paper, wood, wool etc.  
 (ii) They are used as lubricants over a wide range of temperature ( $-40^\circ\text{C}$  to  $200^\circ\text{C}$ ) because their viscosity is not affected much with rise or fall in temperature.  
 (iii) Silicone oils are used in high temperature oil baths.  
 (iv) Silicone rubbers are used as insulating material.  
 (v) They are also used in cosmetics and as antifoaming agents.

## 7.5 POLYMERIC COMPOSITES

A composites is a material made up of more than one components. A polymer belonging to a particular class has several properties or characteristics of its own class but may lack some important properties required for a particulars application. Hence to improve its properties the polymer may be mixed with some other polymers or non-polymeric materials. The resultant mixture is known as **polymeric composite**.

### Important polymeric composites

#### 7.5.1 Fibre reinforced plastics (FRP)

The strength of plastics can be greatly enhanced by reinforcing them with a high strength fibre material such as glass, graphite, alumina, boron, aromatic polyamides etc.

Fibre reinforced plastics are prepared by bonding a fibre material with a resin matrix (phenolic resins, silicone resins, epoxy resins, polyamides etc.) under heat and pressure. For example, fibre glass is prepared by reinforcing melamine or some other plastic matrix.

\* **Silicon Grease :** Silicon grease is the modified form of silicon fluids. It can be prepared by adding some fillers like silica, carbon black etc. to silicone oils or fluids.

**Properties and uses :** (i) Silicon greases are stable to a wide range of temperature from  $-100^\circ\text{C}$  to  $450^\circ\text{C}$ . So they are used in industries as a very effective lubricants.

- (ii) When treated with silica is used as electrical grease in car ignition systems.

(iii) Greases with lithium soap filler are used for ball-bearings, etc.

(iv) Greases with carbon black filler are used in high temperature conveyors and oven doors etc.

\*\* **Silicon Rubber :** These are polymers containing high molecular weight dimethylsilicon mixed with a filler usually finely divided  $\text{SiO}_2$  and a peroxide. Organic peroxide helps to form few bridges between linear chains,  $\text{SiO}_2$  reinforce the polysiloxane structure.

**Properties and uses :** (i) They are flexible at  $90-250^\circ\text{C}$  and are used in making tyres for fighter aircrafts.

- (ii) They are highly resistant to heat and are used in aircraft and insulating electrical parts.

[www.ululu.in](http://www.ululu.in) with spun fibres of borosilicate glass (known as E-glass).

The mechanical properties of fibre composites depend upon several factors like nature of fibre, fibre length, nature of matrix, percentage composition etc.

**Uses :** FRP have wide applications. They are used in space-crafts, aeroplanes, acid storage tanks etc.

### 7.5.2. Polymer blends

A polymer blend is a simple physical composition of two or more incomplete polymers. In the polymeric chains of a polymer blend the constituents are held together by Van der Waals force, hydrogen bonding etc.

Polymer blending is very useful to improve the properties of a polymer. It may help in protecting the particular polymer from degradation. For example :

(i) Polymethylmethacrylate (PMMA) undergoes degradation by  $\gamma$ -rays but the degradation is reduced by blending it with styrene acrylonitrile (copolymer).

(ii) Nylon-6 : polycarbonate blend is very tough and is used for making transparent containers and sports equipments.

### 7.5.3. Polymer alloys

When two or more compatible polymers chemically interact under a specific set of conditions the result mixture is called polymer alloy. The properties like mechanical strength, abrasion resistance etc. of polymer alloy is much better than the constituent polymers.

For example, ABS is a copolymer blend of polyacrylonitrile-styrene and butadiene-styrene rubber but ABS-polycarbonate alloys are typical polymer alloys. These have good mechanical strength and high work ability. They are used for making typewriters, helmets, electronic printers, food processors etc.

## EXERCISES

### Multiple Choice Questions

**Note :** Select the correct answer.

1. Which of the following is a step-growth polymer?
 

(a) Polyacrylonitrile	(b) Polyisoprene
(c) Nylon	(d) Polythene
2. Bakelite is obtained from phenol by reacting it with
 

(a) acetaldehyde	(b) acetal
(c) formaldehyde	(d) chlorobenzene
3. Which one of the following used to make 'non stick' cookware?
 

(a) PVC	(b) polystrene
(c) ethylene terephthalate	(d) polytetrafluoroethylene