Engineering Chemistry

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Module 1. Phase Rule

Lesson 1. Phase rule and its application to one component system

1.1 INTRODUCTION OF PHASE RULE

The phase rule is a generalization given by Willard Gibbs (1874), which seeks to explain the equilibria existing in heterogeneous system. It may be stated as: "provided the equilibrium between any number of phases is not influenced by gravity, or electrical, or magnetic forces or by surface action and only by temperature, pressure and concentration, then the number of degrees of freedom (F) of the system is related to number of components (C) and of phases (P) by the phase rule equation for any system at equilibrium at a definite temperature and pressure.

$$F = C - P + 2$$

This rule, if properly applied, has no exception.

Explanation of terms:

1.2.1 Phase: A phase is defined as "an homogeneous, physically distinct and mechanically separable portion of system, which is separated from other such parts of the system by definite boundary surface". For Example:

- At freezing point, water consists of three phase :

$$\text{Ice}_{(s)} \rightleftharpoons \text{Water}_{(l)} \rightleftharpoons \text{Water vapour}_{(g)}$$

- A gaseous mixture, being thoroughly miscible in all proportion, will constitute one phase only. Thus, a mixture of N_2 and H_2 forms phase only.
- If two liquids are immiscible (i.e., benzene and water), they will form two separate phase only.
- If two liquids are miscible (i.e., alcohol and water), they will form one liquid phase only.
- A solution of a substance in a solvent consists of phase only, e. g, glucose solution in water.
- Each solid mark up a separate phase, except in the case of solid solution, e. g, many forms of sulphur can exist together, but these are all separate phases.
- A heterogeneous mixture like :

$$CaCO3_{(s)} \rightleftharpoons CaO_{(s)} + CO_{2\,(g)}$$

Consists of three phases (i.e., two solids and one gasous). Similarly, in the equilibrium reaction,

$$Fe_{(s)} + H_2O \rightleftharpoons FeO_{(s)} + H_{2(g)}$$

There are two solid phases, Fe and FeO and one gaseous phase consisting of $H_2O_{(g)}$ and $H_{2(g)}$. Thus, three phases exists in equilibrium.

- A homogeneous solid solution of a salt constitutes a single phase. Thus, Mohr's [$FeSO_4\ (NH_4)_2SO_46H_2O$] solution constitutes a single phase, although it consists of $FeSO_4\ (NH_4)\ SO_4$, and H_2O.

1.2.2 Component: by the term component is meant "the smallest number of independent variable constituents, taking part in state of equilibrium, by mean of which the composition of each phase can be expressed in the form of chemical equation". For example:

i. In the water system,

$$\text{Ice}_{(s)} \rightleftharpoons \text{Water}_{(l)} \rightleftharpoons \text{vapour}_{(g)}$$

The chemical composition of all the three phases is H_2O. Hence, it is one component system.

ii. the sulphur system consists of four phases, rhombic, monoclinic, liquid and vapour, the chemical composition of all phases is S. hence, it is one component system.

iii. In the dissociation of NH_4CI in a closed vessel,

$$NH_4CI_{(g)} \rightleftharpoons NH_4CI_{(g)} \rightleftharpoons NH_{3(g)}+HCI_{(g)}$$

The proportions of NH_3 and HCl are equivalent and hence, the composition of both phases (solid and gaseous) can be expressed in terms of NH_4CI alone. Hence, the number of component is one. However, if NH_3 or HCl is in excess, the system become a two component system .

iv. A system of saturated solution of NaCI consists of solid salt, salt solution and water vapour. The chemical composition of all the three phases can be expressed in terms of NaCI and H_2O. Hence, it is a two component system.

v. In the thermal decomposition of $CaCO_3$

$$CaCO_{3(s)} \rightleftharpoons CaO_{(s)} + CO_{2(g)}$$

The composition of each of the three phases can be expressed in terms of at least any two of the independently variable constituents, $CaCO_3$, Cao and CO_2. Suppose $CaCO_3$ and CaO are chosen as the two components, the composition of different phases is represented as follows:

Phase: $CaCO_3 = CaCO_3 + 0\ CaO$

Phase: $CaO = 0\ CaCO_3 + CaO$

Phase: $CO_2 = CaCO_3 - CaO$

Thus, it is two component systems.

vi. In the dissociation reaction,

$$CuSO_45H_2O_{(s)} \rightleftharpoons CuSO_{4.}3H_2O_{(s)} + 2H_2O_{(g)}$$

The composition of each phase can be represented by the simplest component, $CuSO_4$ and H_2O

Hence, it is two component systems.

vii. In the equilibrium, $Fe_{(s)} + H_2O_{(g)} \rightleftharpoons FeO_{(s)} + H_{2(g)}$, the minimum components required the composition phase is three. Evidently, it is a three component system.

Number of component of a system may alternatively be defined as the number of chemical constituents of the system minus the number of equations relating to these constituents in an equilibrium state. For example:

1. Dissociation of $KClO_3$ in a closed vessel: following equilibrium exists :

$$KClO_{3(s)} \rightleftharpoons 2KCl_{(s)} + 3O_{2\,(g)}$$

No. of constituents = 3

Now

$$K_{eq} = \frac{[KCl]2[O2]3}{[KClO3]2} = [O_2]^3$$

No. of equations relating the concentration of constituents =1.

Hence, number of components = 3-1 = 2 i.e., it is a two component system.

2. Dissociation of NH_4Cl:

i. Only NH_4Cl is heated in a closed vessel. The equilibrium existing is: $NH_4Cl_{(s)} \rightleftharpoons NH_{3(g)} + HCl_{(g)}$

$$[NH_3] = [HCl]$$

Also $K_{eq} = \frac{[NH3][HCl]}{[NH4Cl]} = [NH_3][HCl]$

Because the active mass of $NH_4Cl_{(s)}$ is constant.

Now number of components, C

= No. of constituent –[No, of equations relating to concentration of constituents]

= 3(NH_4CL, NH_3 and HCl) – 2 = I, i.e. it is a single component system :

ii. When NH4Cl is heated in a closed vessel along with NH3 or HCl, At equilibrium:

Keq = [NH3][HCl] ……………..(i)

But [NH3] ≠ [HCl] …………(ii)

Only one equation (i) relates the concentrations of constituents

No. of component, (C) = 3 -1 = 2, i.e. under the above conditions, the system has two components

1.2.3 Degree of freedom or variance: By the term "degree of freedom is meant by" the minimum number of independently variable factors, such as temperature, pressure and composition of the phases, which must be arbitrarily specified in order to represent perfectly the condition of a system. For example

i. In case of water system, Ice$_{(s)}$ $\rightleftharpoons$ Water$_{(l)}$ $\rightleftharpoons$ Vapour$_{(g)}$, if all the three phases are present in equilibrium, then no condition need to be specified, as the three phases can be in equilibrium only at particular temperature and pressure. If condition (e.g. Temperature or pressure is altered, three phases will not remain in equilibrium and one of the phase disappears.

ii. For a system consisting of water n in contact with its vapour,

Water$_{(l)}$ $\rightleftharpoons$ Vapour$_{(g)}$

We must state either the temperature or pressure to define it completely. Hence, degree of freedom is one or system is univariant.

iii. For a system consisting of water vapour phase only, we must the values of both the temperature and pressure in order to describe the system completely. Hence, the system is bivariant or has two degrees of freedom.

iv. For a system consisting of ,

NaCl$_{(s)}$ $\rightleftharpoons$ NaCl $_{(aq)}$ $\rightleftharpoons$ water vapour $_{(g)}$.

We must state either the temperature or pressure, because the saturation solubility is fixed at a particular temperature or pressure. Hence, the system is univariant

v. For a gaseous mixture of N_2 and H_2, we must state both the pressure and temperature, because if pressure and temperature are fixed, the volume automatically becomes definite. Hence, for a gaseous system, two factors must be stated in order to define it completely and thus, it has two degree of freedom (or bivariant system).

1.2.4 Merits of phases rule:

1. It is applicable to both physical and chemical equilibria.
2. It require no information regarding molecular/ micro-structure, since it is applicable to macroscopic system.
3. It is a convenient method of classifying equilibrium states in terms of phases, components and degrees of freedom.
4. It helps us to predict the behaviour of a system, under different sets of variables.
5. It indicates that different systems with same degree of freedom behave similarly.
6. It does not take into cognizance of either the nature or quantities of component present in the system.
7. It helps in deciding whether under a given set of condition:

a. various substances would exist together in equilibrium or

b. some of the substances present would be interconverted or

c. some of the substances present would be eliminated .

1.2.5 Limitation of phase rule:

1. It can be applied only for system in equilibrium. Consequently, consequently, it is of little value in case of very slow equilibrium state attaining system.

2. It applies only to a single equilibrium system: and provided no information regarding any other possible equilibria in the system.

3. It requires utmost care in deciding the number of phases existing in an equilibrium sate, since it considers only the number of phases, rather than their amounts. Thus, even if a trace of the phase is present, it accounts towards the total number of phases.

4. It conditions that all phases of the system must be present simultaneously, under the identical conditions of temperature and pressure.

5. It conditions that solid and liquid phases must not be in finely –divided state; otherwise deviations occurs.

1.3 DERIVATION OF PHASE RULE

Consider a heterogeneous system having P phases and C components. Now according to definition the degree of freedom (F) of the system is minimum of independent variables which must be fixed arbitrarily to define the system completely. But the number of these variables is equal to the total number of variable minus the number of relations between them at equilibrium, since each relation diminishes the number of independent variables by one.

Now let us calculate the total number of independent variables:

i. Temperature: At equilibrium, temperature of every phase is same, so there is only one temperature variable for the entire system.

ii. Pressure: At equilibrium , each phase has the same pressure, so there is only one pressure variable for the entire system.

iii.Concentration : Concentration of each components is generally expressed in terms of mole fractions. As a rule, the number of composition variables required for each phase are (C-1), since the composition of all components may be expressed by stating the mole fraction of all except one of the components. For example, it there are two components A and B in one phase and if we know the concentration. (or mole fraction) of one (say A), the concentration of other (i.e,,B) can be automatically found, because the sum is always unity. Thus, if mole fraction of A is 0.4, that of B is known to be 1-0.4 or 0.6. Similarly, if we have three components and if the composition of two is known that of the third can be found out. Thus, if we have C components, we must know the concentration of C-1 component. So for P phases the total composition variable are p (C – 1).

Hence .Total number of variables

= 1(for temperature) + 1(for pressure) + P (C – 1) (for composition)

$= P (C – 1) + 2$

Now let us calculate the number of relations at equilibrium. We know that for a system in a thermodynamic equilibrium, the chemical potential (u), which is related to concentration of component in all the particular component I, we have at equilibrium :

$$[\mu_i]_\alpha = [\mu_i]_\beta = [\mu_i]_\gamma$$

Consequently, there are two equilibrium relationships for each component if there are 3 phases. Hence, for P phases, the number of such relationships for each component are (P -1),

Consequently, for C components, such relationships will be C (P – 1),

iv. Degree of freedom , F = Total number of independent variables

No. of relationships between these variables

$= [P(C-1)+2] – [C(P-1)]$

$$= C – P + 2.$$

This is nothing but mathematical statement of phase rule.

1.3.1 PHASE RULE FOR CHEMICAL REACTION EQUILIBRIUM

In a chemical reaction , various reactant with one another forming products. Consequently, the phase equilibrium become rather complicated due to simultaneous presence of reactants and products. Let N_e be the total number of chemical substances present in the overall system at equilibrium and r be the number of reactants, then the component term C of the phase rule equation is replaced by (Ne – r), i.e,,,

$$C = N_e – r$$

Hence, phase rule equation becomes :

$$F = C – P + 2 = (N_e – r) – p + 2.$$

Illustration: let us consider the reaction oxygen with carbon producing a mixture of carbon monoxide and carbon dioxide. Thus :

$$C_{(s)} + O_{2\,(g)} \text{ ----------à } CO_2$$

$$C_{(s)} + \tfrac{1}{2} O_{2\,(g)} \text{ -----------------à } CO_{(g)}$$

No. of phases at equilibrium (P)

= Solid phase due to carbon + Gaseous phase due to CO2+ CO + O2

= 1 + 1 = 2

No. of reactants ® = Carbon + oxygen

= 1 + 1 = 2

No. of chemical substances present at equilibrium (N_e)

$$= \text{Carbon} + CO_2 + CO + O_2$$

$$= 1 + 1 + 1 + 1 = 4$$

1. Degree of freedom (F) = $(N_e - r) - p + 2 = (4 - 2) - 2 + 2 = 2$

1.3.2 WATER SYSTEM

The water system consists of three phases , viz., ice, water and water vapour.

$$\text{Ice}_{(s)} \rightleftharpoons \text{Water}_{(I)} \rightleftharpoons \text{Water vapour}_{(g)}$$

Since H_2O is the only chemical compound involved, therefore, it is single or one-component system . From the phase rule, when C =1,

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

i.e, the degree of freedom depends on the number of phases present at equilibrium. Three different case are possible :

(i) $P = 1$; $F = 2$ (bivariant system)

(ii) $P = 2$; $F = 1$ (univariant system)

(iii) $P = 3$; $F = 0$ (invariant system)

From the above , it is clear that for any one-component system , the maximum number of degrees of freedom is two. Therefore, such a system can be represented completely by a two-dimensional

Diagram. The most convenient variable are the pressure and the temperature. The water system is shown in Fig. 1 The diagram consists of :

1. Areas : AOB. AOC and BOC are the fields of existence of vapour, liquid and ice phase respectively Within these single-phase areas, the system in bivariant , because to locate any point in an area, temperature as well as pressure co-ordinates need to be know.. This also following from phase rule equation : $F = 3 - P = 3 - 1 = 2$.

2. **Boundary lines:** separating the areas are lines OA, OB and OC, connecting the point at which two phases can co-exist in equilibrium. In order to locate any point on a particular line, either temperature or pressure co-ordinate should be known, because for fixed value of one co-ordinate, the second is automatically fixed, In other words, any point on boundary lines has one degree of freedom or is univariant. This also follows from phase rule equation : $F = 3 - P = 3 - 2 = 1$.

The curve OA, dividing the liquid from the vapour region, is called vapour pressure curve of liquid water or vaporization curve. At any given temperature, there is one and only one pressure at which water vapour is in equilibrium with liquid water. Similarly , at any given pressure, there is one temperature at which water vapour is in equilibrium with liquid water. In other words, the system is univariant. i.e,, has one degree of freedom. The curve OA has a natural upper limit at +374 C. which is the critical-point, beyond which the phase merges into vapour phase and they are no longer distinguishable from each other.

The curve OB is the sublimation curve of ice. It gives the conditions under which water vapour is in equilibrium with solid ice. The point B has a natural limit at -273^{o}C, beyond which the two phases merge into each other.

The curve OC , which divies the solid –ice region from the liquid – water region, is called melting curve, because it indicates how the melting temperature of ice or the freezing tempereature of water varies with the pressure. The slope of OC towards the pressure axis shows that the melting point of ice is decreased by increasing pressure.

3. Triple point: The three curves OA, OB, and OC meet at O, at which solid, liquid and vapour are simultaneously at equilibrium. This point at 273.16 k is called a triple – point. Since three phases co-exist, the system is invariant (F=3-3=0). In other words, there is no degree of freedom at O, i.e., neither pressure nor temperature can be altered, even slightly, without causing the disappearance of one of the phase.

4.Metastable curve OA': As water does not always freeze at 0oC, so if the vessel containing water and vapour is perfectly clean and free from dust, it is possible to super – cool water several degrees below its freezing point 0. The dotted curve OA', a continuation of vaporization curve AO, represents the pressure curve of super cooled water. This curve represents a metastable system. On slight disturbance, the super cooled water at once changes to solid ice. It may be noted that metastable vapour pressure of supper cooledh water is higher than the vapour pressure of ice.

5 Polymorphism:

Timman and Bridgman showed that water under high pressure (upto 5 X10^{3} atm), exists in six other forms, besides ordinary ice (called ice I), which are stable under different conditions of temperature and pressure. These polymeric forms of ice (called ice I to ice VII) differ in crystalline structure, density and other physical properties. Consequently, each of these polymeric ice form constitutes a separate bphse. The equilibria between different polymeric forms of ice are represented in fig.-1.2 . It may be pointed that ice IV has not been shown in the diagram, since it has been isolated. From the diagram, it is evident that:

1. Regions I,II,III,V,VI and VII indicate stability of ice in these regions
2. Except ice II, all other forms of ice can coexist withj water.
3. Melting point of ordinary ice I is lowered by the increase of pressure and it falls to about -22oC at a pressure of 2040 atm. Further, pressure increase results in transformation of ice I to ice III, whose melting point is raised by the increase of pressure.
4. The ice II can be obtained from ice I,II or V.
5. It is possible to obtain not only the ordinary triple point O for ice – water – vapour equilibrium, but also other triple points (C,D,E,F and G). At these point, three phases can coexist, Viz. (a) three form of ice, or (b) two forms of ice and liquid water. All these triple points are invariant (F=0).
6. Not more than three phases cannot exist in equilibrium, because:

P =4 (let),C=1 F=C-P +2 = 1- 4+2 = -1

Negative value of F has no meaning.

7. At a high pressure, the melting point of ice is considerably raised and ice VII melt at 190 ^{o}C at a pressure of 40000 atm. This is an astonishing fact.

Lesson 2. Phase rule and its application to two component system

2.1 Phase rule for two component systems:

In a two component system, when P=2, degree of freedom+ (F) has the highest value

F= C-P+2 = 2-1+12 =3. Since the maximum number of degrees of freedom in a two-component system is three, so the phase behaviour of binary system may be represented by a three dimensional diagram of pressure temperature and composition.

A solid liquid equilibrium of an alloy has practically no gas phase and the effect of pressure is small on this type of equilibrium. Therefore, experiments are usually, conducted under atmospheric pressure. Thus keeping the pressure constant of a system in which vapour phase is not considered, is known as condensed system. It will reduce the degrees of freedom of the system by one and for such a system the phase rule becomes

F = C – P +1

This is known as the reduced (condensed) phase rule having two variables solid liquid equilibria are represented on temperature composition diagrams.

2.1.2 THERMAL ANALYSIS

The shape of the freezing point curves for any system especially those involving metals can be determined by thermal analysis a method involving study of the cooling curves of various compositions of systems during solidification. The form of the cooling curve indicates the composition of the solid. The principle of the method can be understood from the following considerations

1. When a pure substance in the fused or liquid state is allowed to cool slowly and the temperature noted at definite time, the graphic representation of the rate of cooling will be continuous curve (fig.7a) . When the freezing point is reached and the solid makes it appearances, it is indicated by a break in the continuity of the cooling curve and the temperature will remain constant until is completely solidified. Thereafter, the fall in the temperature will again become continuous. FIGURE

2. If a mixture of two solids in the fused state be cooled slowly and the cooling curve is obtained in a similar manner. We likewise obtain a continuous cooling curve, so long as the mixture (solution) is in the liquid state. When a solid phase begins to form, the rate of cooling abruptly alters and the cooling curve exhibits a break. However, the temperature dose not remained constant, as in the previous case of cooling of the pure substance. They temperature decreases continuously, but at a different rate and if the mixture forms an eutectic, the fall of temperature continues, till the eutectic point is reached. The system now becomes in variant from the point of the view of the phase rule and the temperature remains content, until solidification is complete. (see Fig -7b page -403) there after the fall of the temperature becomes uniform but the rate of fall is quite different than the previous one.

From the cooling curve for any mixture of a definite composition, it is possible to obtain its freezing point and eutectic point.

1. The freezing point varies with the composition of the system, but the eutectic point remains constant for given system.
2. The nearer the composition of the system to the eutectic, the shorter is the portion bc and the more prolonged is the halt cd.
3. If the mixture coincides with the eutectic composition, the curve shows no break corresponding to bc, but the break appears only at the eutectic point, c.
4. If the cooling curve of a series of a alloys of known compositions are worked out and their freezing point are noted, by plotting freezing point against composition, T-C curve is obtained for the alloy system. However, in order to complete the diagram it is necessary to the freezing point s of the pure components also.
5. Now the cooling curve of an alloy of the same metals, but of unknown composition is determined and its freezing point located in the T – C diagram. The composition corresponding to this freezing point yields the composition of the alloy.
6. The thermal analysis procedure can be used to derive the phase diagram of any two component system

2.1.3 Construction of phase diagram:

The thermal analysis method (i.e. by studying the cooling rates) can be used to construct the phase diagram of a binary alloy system. It involves the study of temperature – time curves of the various compositions of alloy system during solidification. From theser curves, it is possible to detect the temperatures at which transformation and transitions occure. Let us illustrate it to determine the phase diagram for the binary alloy system of bismuth (Bi) – cadmium (Cd).

Method:

prepar a number of mixtures of Bi and Cd ranging in composition 100% Bi to 100% Cd. These mixtures are spaced at 10% interval and of equal eight. Place each of these mixtures separately in fireclay or graphite crucible and then melt in an electric furnace in an inert atmosphere of nitrogen. After melting and thorough agitation, a thermocouple is inserted in each melt and the furnace is allowed to cool slowly. Temperature and time reading are taken, until the charge in the crucible is completely solidified. Then prepare the plots of temperature versus time for each mixture. Figure-8 shows a set of cooling curves obtained for various compositions of Bi-Cd mixtures.

Explanation of cooling curves:

when a body is cooled slowly and uniformly, a smooth cooling curve is obtained, till the temperature approaches that of room. However when some transformation (or transition) that liberates heat occur during cooling, the slope of the curve is reduced suddenly. The nature of the reduction depends on the degree of freedom (F) of the system. A single phase (p=1) with F=2 exhibits a continuous curve, but when a phase appears, the degree of freedom (F) is reduced to one and the heat liberated by the formation of the new phase results in the discontinuity in the curve, due to the change of slope for the cooling of one phase to a lesser slope corresponding to the cooling of two phases. Again, when the third phase appears, F=0, the temperature of the system must remain constant, until one of the phases disappears. This in-turn results in a flat portion on the cooling curve. Finally, when solidification is complete, thesystem regains a degree of freedom, thereby the cooling curves once again exhibit continuous variation of temperature versus time.

In the light of the above facts:

1. Abreak (or arrest) in a cooling curve indicates the appearance of second phase, usually the separation of a solid from the melt, and
2. A horizontal portion in a cooling curve indicates the existence of three phases. With these consideration in mind we can conclude from the cooling curve in Fig. That the arrests indicated by t_i signifies the appearance of a second phase in the system and the horizontal portions results from the existence of three phases. In the system under consideration, solid phase are pure Bi and pure Cd, so the horizontal portions indicate the simultaneous occurrence of these solid plus melt. It may be noted that in curves (a) and (h) the horizontal portions are due to two phases.

Construction of equilibrium diagram:

From the cooling curves, the initial solidification temperatures (t_i) and final solidification temperature (t_f) for various concentrations are plotted on a temperature – concentration diagram. Smooth curves drawn through all the t_i and t_f to yield the phase diagram shown in Figure -9 in this diagram:

1. ABC represents the initial freezing point, while DBE represent the final freezing points of metals of various compositions
2. Curve AB indicates the temperatures at which Bi begins to separate from the various concentrations of melt. This line may be looked as the solubility curve of Bi in molten Cd.
3. Curve BC indicates the temperatures at which Cd begins to separate from the various concentration of melt. This line may be looked as the solubility curve of Cd in molten Bi.
4. Point A 9271oC) and C (321oC) represent the freezing (or melting) point of Bi and Cd respectively.
5. Point B (144oC) represents the solution is saturated with respects to both solids.

2.2 EUTECTIC SYSTEM

A binary system consisting of two substances, which are miscible in all proportion in the liquid phase, but which do not react chemically, is known as the eutectic (easy to melt) system, e.g. a mixture of lead and silver comprises of such a system.

Eutectic Mixture is a solid solution of two or more substances having the lowest freezing point of all the possible mixture of the components. This is taken advantage of in alloys of low melting point which are generally eutectic mixtures.

Eutectic point: Two or more solid substances capable of forming solid solutions with each other tave the property of lowering each other's freezing point; and the minimum freezing point attainable corresponding to the eutectic mixture is termed the eutectic point (means lowest melting point).

Components (m.p., °C)		Eutectic composition	Eutectic Temperature
Ag (960°)	Cu (1083°)	71.8 % Ag	778 °C
Pb (327°)	Ag (961°)	97.4 % Pb	303 °C
Bi (271°)	Cd (321°)	60.0 % Bi	144 °C
Cd (323°)	Zn (419°)	67.0 % Zn	270 °C
Zn (419°)	Al (659°)	95.6 % Zn	381 °c

Application of eutectics: Low-melting alloy are used in safety devices (e.g. as pluge in automobiles), fire-sprinklers device in boilers). By suitable choice of metals, very low melting alloys can be obtained e.g. wood's metal (alloy containing 50% Bi, 25 % Pb, 12.5 % Cd and 12.5 % Cd) melts at 65 °C only.

2.3 SAFTY FUSES AND SOLDERS

Safety Fuse is a protective device containing a piece of low melting alloy that melts under heat produced either by excess heating or by an excess current in the circuit , thereby, breaking the circuit. Main objectives of using safety fuses are (i) protection of the equipment by excessive heating or electric current, and (ii) to avoid the chances of accidents.

Examples:

1. Pressure cooker, used for cooking domestic food items, is provided with a safety fuse made of an alloy, having a definite composition and definite eutectic temperature. Below its eutectic temperature, the alloy exists in the solid form; while above the eutectic temperature it melts to liquid form. Consequently, whenever the cooker is heated above the eutectic temperature due to some reason, the safety fuse melts, thereby avoiding any chace of accident due to overheating of cooker. From these discussions, it is clear that the melting point of the fuse used must be lower than safety limit temperature of the equipment itself.

2. Safety Fuses (as plugs) are employed in buildings to protect them against any fire the hazards. When a building catches fire, the heat melts fusible alloy and water rushes out from the pipe. This controls the fire automatically.

3. Fuses are also used for protecting the cable in an electric circuit against damage from any excusive current than normal. The safety fuse (in the form of fuse wire) can carry normal working current safely, without heating, but when current is exceeded than the normal value, it gets heated upto the melting point of fuse alloy, thereby the circuit gets broken. In this way fuse protects the wires in the circuit from over – heating.

4. Safety fuse in the form of plug is fitted in steam boiling in order to avoid any accident caused, due to blockage of high pressure steam in the boiler. Whenever, steam pressure exceeds the

limiting value of pressure, safety plug gets over – heated and melts, thereby permitting excessive steam to escape out of the boiler.

Important safety fuse making alloys:

a. Wood metal contains Bi (50%), Pb(25%), Sn(12.5%) and Cd(12.5%). It meets at 70 ^{o}C and used for making fire – alarms, automatic sprinklers, safety plugs in cookers, milk pot, electric fuses and boiler fuses.

b. Rose metal contains Bi(50%), Pb(28%) and Sn (22%). It melts at 89 ^{o}C and used for making fire – alarms, electric fuse wires and in automobile sprinklers.

c. Fuse wires for 1.small currents are made of Pb-Sn alloy, 2. high currents are made of Pb,Sn,Zn,Sb,Cu,Al etc.

2.4 SOLDERS:

are various readily fusible alloys which are applied to the point between metal object to unite them closely and without heating the objects to the melting point. The capability of a solder to join the metal objects closely and intimately depends on the surface alloy formation between the solder and metal objects being joined. The selection of solder for a particular joining purpose depends on the melting point of alloy at which the solder form close and intimate surface alloy with the metal objects to be joined. Solders usually contain Pb and Sn as main components.

Lesson 3. Fuels and its classification

3.1 INTRODUCTION

This section briefly describes the main features of fuels. Energy from the Sun is converted into chemical energy by photosynthesis. But, as we know, when we burn dried plants or wood, producing energy in the form of heat and light, we are releasing the Sun's energy originally stored in that plant or in that wood through photosynthesis. We know that, in most of the world today, wood is not the main source of fuel. We generally use natural gas or oil in our homes, and we use mainly oil and coal to heat the water to produce the steam to drive the turbines for our huge power generation systems.

These fuels - coal, oil, and natural gas - are often referred to as fossil fuels. The various types of fuels (like liquid, solid and gaseous fuels) that are available depend on various factors such as costs, availability, storage, handling, pollution and landed boilers, furnaces and other combustion equipments.

The knowledge of the fuel properties helps in selecting the right fuel for the right purpose and for the efficient use of the fuel. Laboratory tests are generally used for assessing the nature and quality of fuels.

Fuel when burnt produces heat. Thus, the substances classified as fuel must necessarily contain one or several of the combustible elements: carbon, hydrogen, sulphur, etc. In the process of combustion, the chemical energy of fuel is converted into heat energy. To utilize the energy of fuel in most usable form, it is required to transform the fuel from its one state to another, i.e. from solid to liquid or gaseous state, liquid to gaseous state, or from its chemical energy to some other form of energy via single or many stages. In this way, the energy of fuels can be utilized more effectively and efficiently for various purposes.

Fuel is any material that stores potential energy in a form that can be practicably released and used as heat energy. The concept originally applied solely to those materials storing energy in the form of chemical energy that could be released through combustion, but the concept has since been also applied to other sources of heat energy such as nuclear energy (via nuclear fission or nuclear fusion), as well as releases of chemical energy through non-combustion oxidation (such as in cellular biology or in fuel cells). The heat energy released by many fuels is harnessed into mechanical energy via an engine. Other times the heat itself is valued for warmth, cooking, or industrial processes, as well as the illumination that comes with combustion. Fuels are also used in the cells of organisms in a process known as cellular respiration, where organic molecules are oxidized to release un-usable energy. Hydrocarbons are by far the most common source of fuel used by humans, but other substances, including radioactive metals, are also utilized. Fuels are contrasted with other methods of storing potential energy, such as those that directly release electrical energy (such as batteries and capacitors) or mechanical energy (such as flywheels, springs, compressed air, or water in a reservoir).

3.2 TYPE OF FUELS

The fuel can be classified into three type's mainly liquid, solid, and gaseous on the bases of their physical state.

3.2.1 LIQUID FUELS

Liquid fuels like furnace oil and LSHS (low sulphur heavy stock) are predominantly used in industrial applications. The various properties of liquid fuels are given below:

3.2.1.a DENSITY

Density is defined as the ratio of the mass of the fuel to the volume of the fuel at a reference temperature of 15°C. Density is measured by an instrument called a hydrometer. The knowledge of density is useful for quantitative calculations and assessing ignition qualities. The unit of density is kg/m^3.

3.2.1.b SPECIFIC GRAVITY

This is defined as the ratio of the weight of a given volume of oil to the weight of the same volume of water at a given temperature. The density of fuel, relative to water, is called specific gravity. The specific gravity of water is defined as one. Since specific gravity is a ratio, it has no units. The measurement of specific gravity is generally made by a hydrometer. Specific gravity is used in calculations involving weights and volumes. The specific gravity of various fuel oils is given in Table 3.1:

Table 3.1 Specific gravity of various fuel oils (adapted from Thermax India Ltd.).

Fuel	Oil L.D.O (Light Diesel Oil)	Furnace oil	L.S.H.S (Low Sulphur Heavy Stock)
Specific Gravity	0.85 - 0.87	0.89 - 0.95	0.88 - 0.98

3.2.1.c VISCOSITY

The viscosity of a fluid is a measure of its internal resistance to flow. Viscosity depends on the temperature and decreases as the temperature increases. Any numerical value for viscosity has no meaning unless the temperature is also specified. Viscosity is measured in Stokes / Centistokes. Sometimes viscosity is also quoted in Engler, Saybolt or Redwood. Each type of oil has its own temperature - viscosity relationship. The measurement of viscosity is made with an instrument called a Viscometer. Viscosity is the most important characteristic in the storage and use of fuel oil. It influences the degree of pre-heating required for handling, storage and satisfactory atomization. If the oil is too viscous, it may become difficult to pump, hard to light the burner, and difficult to handle. Poor atomization may result in the formation of carbon deposits on the burner tips or on the walls. Therefore pre-heating is necessary for proper atomization.

3.2.1.d FLASH POINT

The flash point of a fuel is the lowest temperature at which the fuel can be heated so that the vapour gives off flashes momentarily when an open flame is passed over it. The flash point for furnace oil is 66°C.

3.2.1.e POUR POINT

The pour point of a fuel is the lowest temperature at which it will pour or flow when cooled under prescribed conditions. It is a very rough indication of the lowest temperature at which fuel oil is ready to be pumped.

3.2.1.f SPECIFIC HEAT

Specific heat is the amount of calories needed to raise the temperature of 1 kg of oil by 1^0C. The unit of specific heat is kcal/kg^{0}C. It varies from 0.22 to 0.28 depending on the oil specific gravity. The specific heat determines how much steam or electrical energy it takes to heat the oil to a desired temperature. Light oils have a low specific heat, whereas heavier oils have a higher specific heat.

3.2.1.g CALORIFIC VALUE

The calorific value is the measurement of heat or energy produced, and is measured either as gross calorific value or net calorific value. The difference is determined by the latent heat of condensation of the water vapour produced during the combustion process. Gross calorific value (GCV) assumes all vapour produced during the combustion process is fully condensed. Net calorific value (NCV) assumes the water leaves with the combustion products without fully being condensed. Fuels should be compared based on the net calorific value. The calorific value of coal varies considerably depending on the ash, moisture content and the type of coal while calorific value of fuel oils is much more consistent. The typical GCVs of some of the commonly used liquid fuels are given below:

Table 3.2. Gross calorific values for different fuel oils (adapted from Thermax India Ltd.)

Fuel Oil	Gross Calorific Value (kCal/kg)
Kerosene	- 11,100
Diesel Oil	- 10,800
L.D.O	- 10,700
Furnace Oil	- 10,500
LSHS	- 10,600

3.2.1.h SULPHUR

The amount of sulphur in the fuel oil depends mainly on the source of the crude oil and to a lesser extent on the refining process. The normal sulphur content for the residual fuel oil (furnace oil) is in the order of 2 - 4 %. Typical figures for different fuel oils are shown in Table 3.3.

Table 3.3. Percentages of sulphur for different fuel oils (adapted from Thermax India Ltd.)

Fuel oil	Percentage of Sulphur
Kerosene	0.05 - 0.2
Diesel Oil	0.05 - 0.25
L.D.O	0.5 - 1.8
Furnace Oil	2.0 - 4.0
LSHS < 0.5	

The main disadvantage of sulphur is the risk of corrosion by sulphuric acid formed during and after combustion, and condensation in cool parts of the chimney or stack, air pre-heater and economizer.

3.2.1.i ASH CONTENT

The ash value is related to the inorganic material or salts in the fuel oil. The ash levels in distillate fuels are negligible. Residual fuels have higher ash levels. These salts may be compounds of sodium, vanadium, calcium, magnesium, silicon, iron, aluminium, nickel, etc. Typically, the ash value is in the range of 0.03 - 0.07 %. Excessive ash in liquid fuels can cause fouling deposits in the combustion equipment. Ash has an erosive effect on the burner tips, causes damage to the refractories at high temperatures and gives rise to high temperature corrosion and fouling of equipments.

3.2.1.j CARBON RESIDUE

Carbon residue indicates the tendency of oil to deposit a carbonaceous solid residue on a hot surface, such as a burner or injection nozzle, when its vaporizable constituents evaporate. Residual oil contains carbon residue of 1 percent or more.

3.2.1.k WATER CONTENT

The water content of furnace oil when it is supplied is normally very low because the product at refinery site is handled hot. An upper limit of 1% is specified as a standard.

Water may be present in free or emulsified form and can cause damage to the inside surfaces of the furnace during combustion especially if it contains dissolved salts. It can also cause spluttering of the flame at the burner tip, possibly extinguishing the flame, reducing the flame temperature or lengthening the flame.

3.2.1.1 STORAGE OF FUEL OIL

It can be potentially hazardous to store furnace oil in barrels. A better practice is to store it in cylindrical tanks, either above or below the ground. Furnace oil that is delivered may contain dust, water and other contaminants. The sizing of the storage tank facility is very important. A recommended storage size estimate is to provide for at least 10 days of normal consumption. Industrial heating fuel storage tanks are generally vertical mild steel tanks mounted above the ground. It is prudent for safety and environmental reasons to build bund walls around tanks to contain accidental spillages. As a certain amount of settlement of solids and sludge will occur in tanks over time, tanks should be cleaned at regular intervals: annually for heavy fuels and every two years for light fuels. Care should be taken when oil is decanted from the tanker to the storage tank. All leaks from joints, flanges and pipelines must be attended to at the earliest. Fuel oil should be free from possible contaminants such as dirt, sludge and water before it is fed to the combustion system.

3.2.2 SOLID FUEL (COAL)

3.2.2.a COAL CLASSIFICATION

Coal is classified into three major types; anthracite, bituminous, and lignite. However, there is no clear demarcation between them. Coal is further classified as semi-anthracite, semi-bituminous, and sub-bituminous. Anthracite is the oldest coal from a geological perspective. It is a hard coal composed mainly of carbon with little volatile content and practically no moisture. Lignite is the youngest coal from a geological perspective. It is a soft coal composed mainly of volatile matter and moisture content with low fixed carbon. Fixed carbon refers to carbon in its free state, not combined with other elements. Volatile matter refers to those combustible constituents of coal that vaporize when coal is heated. The common coals used in for example Indian industry are bituminous and sub-bituminous coal. The chemical composition of coal has a strong influence on its combustibility. The properties of coal are broadly classified as physical properties and chemical properties.

3.2.2.b PHYSICAL AND CHEMICAL PROPERTIES OF COAL

Physical properties of coal include the heating value, moisture content, volatile matter and ash. The chemical properties of coal refer to the various elemental chemical constituents such as carbon, hydrogen, oxygen, and sulphur.

3.2.2.c ANALYSIS OF COAL

There are two methods to analyze coal: ultimate analysis and proximate analysis. The ultimate analysis determines all coal component elements, solid or gaseous and the proximate analysis determines only the fixed carbon, volatile matter, moisture and ash percentages. The ultimate analysis is determined in a properly equipped laboratory by a skilled chemist, while proximate analysis can be determined with a simple apparatus. (It may be noted that proximate has no connection with the word “approximate”).

i. Measurement of moisture

The determination of moisture content is carried out by placing a sample of powdered raw coal of size 200- micron size in an uncovered crucible, which is placed in the oven kept at 108 +2 °C along with the lid. Then the sample is cooled to room temperature and weighed again. The loss in weight represents moisture.

ii. Measurement of volatile matter

A fresh sample of crushed coal is weighed, placed in a covered crucible, and heated in a furnace at 900 + 15 oC. The sample is cooled and weighed. Loss of weight represents moisture and volatile matter. The remainder is coke (fixed carbon and ash).

iii. Measurement of carbon and ash

The cover from the crucible used in the last test is removed and the crucible is heated over the Bunsen burner until all the carbon is burned. The residue is weighed, which is the incombustible ash. The difference in weight from the previous weighing is the fixed carbon. In actual practice Fixed Carbon or FC derived by subtracting from 100 the value of moisture, volatile matter and ash.

iv. Proximate analysis

The proximate analysis indicates the percentage by weight of fixed carbon, volatiles, ash, and moisture content in coal. The amounts of fixed carbon and volatile combustible matter directly contribute to the heating value of coal. Fixed carbon acts as a main heat generator during burning. High volatile matter content indicates easy ignition of fuel. The ash content is important in the design of the furnace grate, combustion volume, pollution control equipment and ash handling systems of a furnace.

v. Fixed carbon

Fixed carbon is the solid fuel left in the furnace after volatile matter is distilled off. It consists mostly of carbon but also contains some hydrogen, oxygen, sulphur and nitrogen not driven off with the gases. Fixed carbon gives a rough estimate of the heating value of coal.

vi. Volatile matter

Volatile matters are the methane, hydrocarbons, hydrogen and carbon monoxide, and incombustible gases like carbon dioxide and nitrogen found in coal. Thus the volatile matter is an index of the gaseous fuels present. A typical range of volatile matter is 20 to 35%. Volatile matter:

1. Proportionately increases flame length, and helps in easier ignition of coal
2. Sets minimum limit on the furnace height and volume
3. Influences secondary air requirement and distribution aspects
4. Influences secondary oil support

vii. Ash content

Ash is an impurity that will not burn. Typical range of ash is 5% to 40%. Ash-

1. Reduces handling and burning capacity.
2. Increases handling costs.
3. Affects combustion efficiency and boiler efficiency.
4. Causes clinkering and slagging.

viii. Moisture content

Moisture in coal must be transported, handled and stored. Since it replaces combustible matter, it decreases the heat content per kg of coal. Typical range is 0.5 to 10%. Moisture-

1. Increases heat loss, due to evaporation and superheating of vapour
2. Helps to a certain extent with binding fines

3. Aids radiation heat transfer

ix. Sulphur content

Typical range is 0.5 to 0.8% normally. Sulphur-

1. Affects clinkering and slagging tendencies
2. Corrodes chimney and other equipment such as air heaters and economizers
3. Limits exit flue gas temperature

x. The ultimate analysis indicates the various elemental chemical constituents such as carbon, hydrogen, oxygen, sulphur, etc. It is useful in determining the quantity of air required for combustion and the volume and composition of the combustion gases. This information is required for the calculation of flame temperature and the flue duct design etc.

3.2.4 STORAGE, HANDLING AND PREPARATION OF COAL

Uncertainty in the availability and transportation of fuel necessitates storage and subsequent handling. Storing coal has its own disadvantages like build-up of inventory, space constraints, deterioration in quality and potential fire hazards. Other minor losses associated with the storage of coal include oxidation, wind and carpet loss. A 1% oxidation of coal has the same effect as 1% ash in coal. Wind losses may account for nearly 0.5 – 1.0 % of the total loss. The main goal of good coal storage is to minimize carpet loss and the loss due to spontaneous combustion. Formation of a soft carpet, comprising of coal dust and soil, causes carpet loss. On the other hand, if the temperature gradually rises in a coal heap, then oxidation may lead to spontaneous combustion of coal stored. Carpet losses can be reduced by:

- Preparing a hard solid surface for coal to be stored
- Preparing standard storage bays of concrete and brick

In industry, coal handling methods range from manual and conveyor systems. It would be advisable to minimize the handling of coal so that further generation of fines and segregation effects are reduced. The preparation of coal prior to feeding into the boiler is an important step for achieving good combustion. Large and irregular lumps of coal may cause the following problems:

Poor combustion conditions and inadequate furnace temperature.

Higher excess air resulting in higher stack loss.

Increase of unburnts in the ash.

Low thermal efficiency.

3.2.3.1 GASEOUS FUEL

Gas fuels are the most convenient because they require the least amount of handling and are used in the simplest and most maintenance-free burner systems. Gas is delivered "on tap" via a distribution network and so is suited for areas with a high population or industrial density. However, large individual consumers do have gasholders and some produce their own gas.

3.2.3.1 TYPES OF GASEOUS FUEL

- The following is a list of the types of gaseous fuel:
- Fuels naturally found in nature:
- Natural gas
- Methane from coal mines
- Fuel gases made from solid fuel
- Gases derived from coal
- Gases derived from waste and biomass
- From other industrial processes (blast furnace gas)
- Gases made from petroleum
- Liquefied Petroleum gas (LPG)
- Refinery gases
- Gases from oil gasification
- Gases from some fermentation process

Gaseous fuels in common use are liquefied petroleum gases (LPG), Natural gas, producer gas, blast furnace gas, coke oven gas etc. The calorific value of gaseous fuel is expressed in Kilocalories per normal cubic meter (kCal/Nm^3) i.e. at normal temperature (20 ^{0}C) and pressure (760 mm Hg).

2.3.2 PROPERTIES OF GASEOUS FUELS

Since most gas combustion appliances cannot utilize the heat content of the water vapour, gross calorific value is of little interest. Fuel should be compared based on the net calorific value. This is especially true for natural gas, since increased hydrogen content results in high water formation during combustion.

2.3.3 LPG

LPG is a predominant mixture of propane and butane with a small percentage of unsaturated (Propylene and Butylene) and some lighter C2 as well as heavier C5 fractions. Also propane (C3H8), Propylene (C3H6), normal and iso-butane (C4H10) and Butylene (C4H8) are included in the range of LPG. LPG may be defined as those hydrocarbons, which are gaseous at normal atmospheric pressure, but may be condensed to the liquid state at normal temperature, by the application of moderate pressures. Although they are normally used as gases, they are stored and transported as liquids under pressure for convenience and ease of handling. Liquid LPG evaporates to produce about 250 times volume of gas.

LPG vapour is denser than air: butane is about twice as heavy as air and propane about one and a half times as heavy as air. Conseque ntly, the vapour may flow along the ground and into drains sinking to the lowest level of the surroundings and be ignited at a considerable distance from the source of leakage. In still air vapour will disperse slowly. Escape of even small quantities of the liquefied gas can give rise to large volumes of vapour / air mixture and thus cause considerable hazard. To aid in the detection of atmospheric leaks, all LPG's are required to be odorized. There should be adequate ground level ventilation where LPG is stored. For this very reason LPG cylinders should not be stored in cellars or basements, which have no ventilation at ground level.

2.3.4 NATURAL GAS

Methane is the main constituent of natural gas and accounting for about 95% of the total volume. Other components are: Ethane, Propane, Butane, Pentane, Nitrogen, Carbon Dioxide, and traces of other gases. Very small amounts of sulphur compounds are also present. Since methane is the largest component of natural gas, generally properties of methane are used when comparing the properties of natural gas to other fuels.

Natural gas is a high calorific value fuel requiring no storage facilities. It mixes with air readily and does not produce smoke or soot. It did not contains sulphur. It is lighter than air and disperses into air easily in case of leak.

Lesson 4. Fuels and its testing

4.1 Performance Evaluation of Fuels

This section explains the principles of combustion, how fuel performance can be evaluated using the stochiometric calculation of air requirement, the concept of excess air, and the draft system of exhaust gases.

Principles of Combustion:

Combustion process

Combustion refers to the rapid oxidation of fuel accompanied by the production of heat, or heat and light. Complete combustion of a fuel is possible only in the presence of an adequate supply of oxygen. Oxygen (O2) is one of the most common elements on earth making up 20.9% of our air. Rapid fuel oxidation results in large amounts of heat. Solid or liquid fuels must be changed to a gas before they will burn. Usually heat is required to change liquids or solids into gases. Fuel gases will burn in their normal state if enough air is present. Most of the 79% of air (that is not oxygen) is nitrogen, with traces of other elements. Nitrogen is considered to be a temperature reducing diluter that must be present to obtain the oxygen required for combustion. Nitrogen reduces combustion efficiency by absorbing heat from the combustion of fuels and diluting the flue gases. This reduces the heat available for transfer through the heat exchange surfaces. It also increases the volume of combustion by-products, which then have to travel through the heat exchanger and up the stack faster to allow the introduction of additional fuel-air mixture. This nitrogen also can combine with oxygen (particularly at high flame temperatures) to produce oxides of nitrogen (NOx), which are toxic pollutants. Carbon, hydrogen and sulphur in the fuel combine with oxygen in the air to form carbon dioxide, water vapour and sulphur dioxide, releasing 8,084 kcals, 28,922 kcals and 2,224 kcals of heat respectively. Under certain conditions, carbon may also combine with oxygen to form carbon monoxide, which results in the release of a smaller quantity of heat (2,430 kcals/kg of carbon). Carbon burned to CO2 will produce more heat per unit of fuel than when CO or smoke are produced.

Three T's of combustion

The objective of good combustion is to release all of the heat in the fuel. This is accomplished by controlling the "three T's" of combustion which are (1) Temperature high enough to ignite and maintain ignition of the fuel, (2) Turbulence or intimate mixing of the fuel and oxygen, and (3) Time, sufficient for complete combustion.

Commonly used fuels like natural gas and propane generally consist of carbon and hydrogen. Water vapour is a by-product of burning hydrogen. This removes heat from the flue gases, which would otherwise be available for more heat transfer.

Natural gas contains more hydrogen and less carbon per kg than fuel oils and as such produces more water vapour. Consequently, more heat will be carried away by exhaust while firing natural gas. Too much, or too little fuel with the available combustion air may potentially result in unburned fuel and carbon monoxide generation. A very specific amount of O_2 is needed for perfect combustion and some additional (excess) air is required for ensuring complete combustion. However, too much excess air will result in heat and efficiency losses. Not all of the fuel is converted to heat and absorbed by the steam generation equipment.

Usually all of the hydrogen in the fuel is burned and most boiler fuels, allowable with today's air pollution standards, contain little or no sulphur. So the main challenge in combustion efficiency is directed toward unburned carbon (in the ash or incompletely burned gas), which forms CO instead of CO_2.

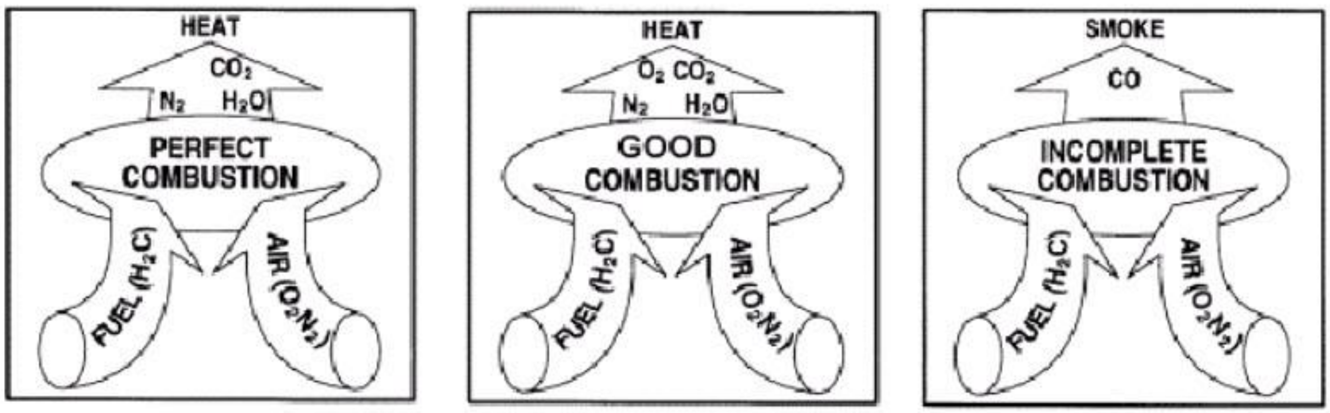


Figure 4.1. Perfect, good and incomplete combustion

(Bureau of Energy Efficiency, 2004)

Stochiometric Calculation of Air Requirement

Calculation of stochiometric air needed for combustion of furnace oil

For combustion air is needed. The amount of air needed can be calculated using the method given below.

The first step is to determine the composition of the furnace oil. Typical specifications of furnace oil from lab analysis is given below:

If we take these analysis data, and considering a sample of 100 kg of furnace oil, then the chemical reactions are as follows:

Element	**Molecular Weight (kg / kg mole)**
C	12
O_2	32
H_2	2
S	32
N_2	28
CO_2	44
SO_2	64
H_2O	18

$C + O_2 \rightarrow CO_2$

$H_2 + 1/2O_2 \rightarrow H_2O$

$S + O_2 \rightarrow SO_2$

Constituents of fuel

$C + O_2 \rightarrow CO_2$

$12 + 32 \rightarrow 44$

12 kg of carbon requires 32 kg of oxygen to form 44 kg of carbon dioxide therefore 1 kg of carbon requires 32/12 kg i.e 2.67 kg of oxygen

$(85.9)\ C + (85.9 \times 2.67)\ O2 \rightarrow 315.25\ CO_2$

$2H_2 + O_2 \rightarrow 2H_2O$

$4 + 32 \rightarrow 36$

4 kg of hydrogen requires 32 kg of oxygen to form 36 kg of water, therefore 1 kg of hydrogen requires 32/4 kg i.e. 8 kg of oxygen.

$(12)\ H_2 + (12 \times 8)\ O_2 \rightarrow (12 \times 9)\ H_2O$

$S + O_2 \rightarrow SO_2$

$32 + 32 \rightarrow 64$

32 kg of sulphur requires 32 kg of oxygen to form 64 kg of sulphur dioxide, therefore 1 kg of sulphur requires 32/32 kg i.e. 1 kg of oxygen

$(0.5)\ S + (0.5 \times 1)\ O_2 \rightarrow 1.0\ SO_2$

Total oxygen required = 325.57 kg

(229.07+96+0.5)

Oxygen already present in

100 kg fuel (given) = 0.7 kg

Additional oxygen required = 325.57 – 0.7

= 324.87 kg

Therefore quantity of dry air needed = (324.87) / 0.23

(air contains 23% oxygen by weight)

= 1412.45 kg of air

Theoretical air required = (1412.45) / 100

= 14.12 kg of air / kg of fuel

Therefore, in this example, for each kg of furnace oil burnt, 14.12 kg of air is required.

4.2 Calculation of theoretical CO_2 content in the flue gases

It is necessary to also calculate the CO_2 content in the flue gases, which then can be used to calculate the excess air in the flue gases. A certain amount of excess air is needed for complete combustion of furnace oils. However, too much excess air points to heat losses and too little excess air points to incomplete combustion. The CO_2 in flue gases can be calculated as follows:

Nitrogen in flue gas = 1412.45 – 324.87

= 1087.58 kg

Theoretical CO_2% in dry flue gas by volume is calculated as below:

Moles of CO_2 in flue gas = (314.97) / 44 = 7.16

Moles of N_2 in flue gas = (1087.58) / 28 = 38.84

Moles of SO_2 in flue gas = 1/64 = 0.016

Theoretical CO_2 % by Volume = (Moles of CO_2 x 100) / Total Moles (Dry)

= (7.16 x 100) / (7.16 + 38.84 + 0.016)

= 15.5%

4.3 Calculation of constituents of fuel gas with excess air

Now we know the theoretical air requirements and the theoretical CO_2 content of flue gases. The next step is to measure the actual CO_2 percentage in the flue gases. In the calculation below it is assumed that the measured %CO_2 in the flue gas is 10%.

% Excess air = [(Theoretical CO_2%/Actual CO_2) – 1] x 100

= [(15.5/10 – 1)] x 100

= 55%

Theoretical air required for 100kg of fuel burnt = 1412.45 kg

Total quantity of air supply required with 55% excess air = 1412.45 x 1.55

= 2189.30 kg

Excess air quantity (actual – theoretical excess air) = 2189.30 – 1412.45

= 776.85

O_2 (23%) = 776.85 x 0.23

= 178.68 kg

N_2 (77%) = 776.85 – 178.68

= 598.17 kg

The final constituents of flue gas with 55% excess air for every 100 kg fuel is as follows:

CO_2 = 314.97 kg

H_2O = 108.00 kg

SO_2 = 1 kg

O_2 = 178.68 kg

N_2 = 1685.75 kg (= 1087.58 in air + 598.17 in excess air)

4.4 Calculation of theoretical CO_2% in dry fuel gas by volume

Now that we have the constituents by weight, we can calculate the constituents on a volume basis as follows:

Moles of CO_2 in flue gas = 314.97 / 44 = 7.16

Moles of SO_2 in flue gas = 1/64 = 0.016

Moles of O_2 in flue gas = 178.68 / 32 = 5.58

Moles of N_2 in flue gas = 1685.75 / 28 = 60.20

Theoretical CO_2% by volume = (Moles of CO_2 x 100) / Total moles (dry)

= (7.16 x 100) / (7.16 + 0.016 + 5.58 + 60.20)

= 10%

Theoretical O_2% by volume = (5.58 x 100) / 72.956

= 7.5%

4.5 Concept of Excess Air

For optimum combustion, the real amount of combustion air must be greater than that required theoretically. Part of the stack gas consists of pure air, i.e. air that is simply heated to stack gas temperature and leaves the boiler through the stack. Chemical analysis of the gases is an objective method that helps to achieve finer air control. By measuring CO_2 or O_2 in flue gases (by continuous recording instruments or Orsat apparatus or some cheaper portable instruments) the excess air level and stack losses can be estimated. The excess air to be supplied depends on the type of fuel and the firing system.

A faster way to calculate the excess air is by using the figures 4.1 and 4.2, provided the percentage of CO_2 or O_2 in the flue gases have been measured

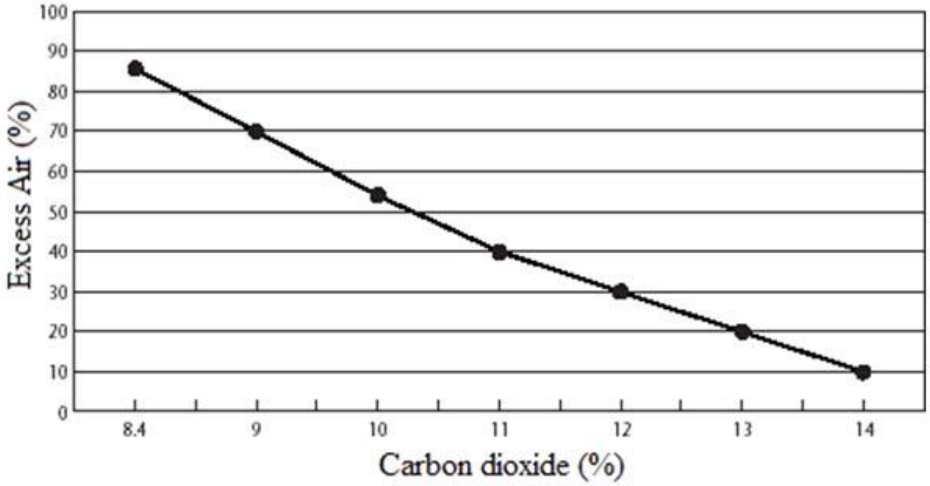


Figure 4.2 Relations between CO_2 & Excess Air

(Bureau of Energy Efficiency, 2004)

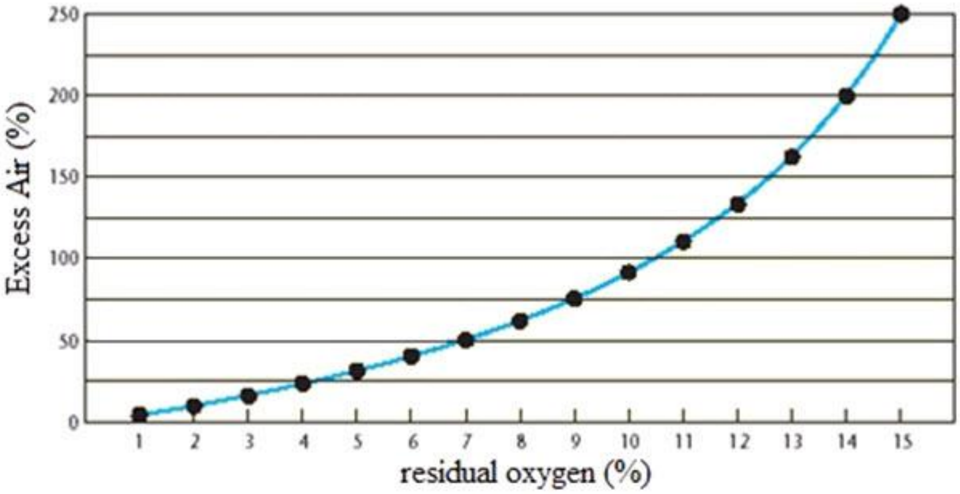


Figure 4.3 Relationship between residual oxygen and excess air

(Bureau of Energy Efficiency, 2004)

For optimum combustion of fuel oil the CO_2 or O_2 in flue gases should be maintained as follows:

CO_2 = 14.5–15 %

O_2 = 2–3 %

Draft System

The function of draft in a combustion system is to exhaust the products of combustion, i.e. flue gases, into the atmosphere. The draft can be classified into two types namely natural draft and mechanical draft.

Natural draft

Natural draft is the draft produced by a chimney alone. It is caused by the difference in weight between the column of hot gas inside the chimney and column of outside air of the same height and cross section. Being much lighter than outside air, chimney flue gas tends to rise, and the heavier outside air flows in through the ash pit to take its place. Draft is usually controlled by hand-operated dampers in the chimney and breeching connecting the boiler to the chimney. Here no fans or blowers are used. The products of combustion are discharged at such a height that it will not be a nuisance to the surrounding community.

Mechanical draft

It is draft artificially produced by fans. Three basic types of drafts that are applied are:

- **Balanced draft**: Forced-draft (F-D) fan (blower) pushes air into the furnace and an

induced draft (I-D) fan draws gases into the chimney thereby providing draft to remove the gases from the boiler. Here the pressure is maintained between 0.05 to 0.10 in. Of water gauge below atmospheric pressure in the case of boilers and slightly positive for reheating and heat treatment furnaces.

- **Induced draft:** An induced-draft fan draws enough draft for flow into the furnace, causing the products of combustion to discharge to atmosphere. Here the furnace is kept at a slight negative pressure below the atmospheric pressure so that combustion air flows through the system.
- **Forced draft**: The Forced draft system uses a fan to deliver the air to the furnace, forcing combustion products to flow through the unit and up the stack.

Energy Efficiency Opportunities

This section includes energy efficiency opportunities in Fuel Combustion:

Pre-heating of the Combustion Oil

The viscosity of furnace oil and LSHS (Low Sulphur Heavy Stock) increases with decreasing temperature, which makes it difficult to pump the oil. At low ambient temperatures (below 25 ^{0}C), furnace oil cannot be pumped easily. To avoid this, preheating of oil is accomplished in two ways:

- The entire tank may be preheated. In this form of bulk heating, steam coils are placed at the bottom of the tank, which is fully insulated;

- The oil can be heated as it flows out with an outflow heater. To reduce steam

requirements, it is advisable to insulate tanks where bulk heating is used.

Bulk heating may be necessary if flow rates are high enough to make outflow heaters of adequate capacity impractical, or when a fuel such as LSHS is used. In the case of outflow heating, only the oil, which leaves the tank, is heated to the pumping temperature. The outflow heater is essentially a heat exchanger with steam or electricity as the heating medium.

Temperature control of Combustion Oil

Thermostatic temperature control of the oil is necessary to prevent overheating, especially when oil flow is reduced or stopped. This is particularly important for electric heaters, since oil may get carbonized when there is no flow and the heater is on. Thermostats should be provided at a region where the oil flows freely into the suction pipe. The temperature at which oil can readily be pumped depends on the grade of oil being handled. Oil should never be stored at a temperature above that necessary for pumping as this leads to higher energy consumption.

Preparation of Solid Fuels

Sizing of coal

Proper coal sizing is one of the key measures to ensure efficient combustion. Proper coal sizing, with specific relevance to the type of firing system, helps towards even burning, reduced ash losses and better combustion efficiency. Coal is reduced in size by crushing and pulverizing. Pre-crushed coal can be economical for smaller units, especially stoker-fired units. In a coal handling system, crushing is limited to an upper size of 6 or 4mm. The devices most commonly used for crushing are the rotary breaker, the roll crusher and the hammer mill. It is necessary to screen the coal before crushing, so that only oversized coal is fed to the crusher. This helps to reduce power consumption in the crusher. Recommended practices in coal crushing are:

Incorporation of a screen to separate fines and small particles to avoid extra fine generation in crushing.

Incorporation of a magnetic separator to separate iron pieces in coal, which may damage the crusher.

Conditioning of coal

The fines in coal present problems in combustion on account of segregation effects. Segregation of fines from larger coal pieces can be reduced to a great extent by conditioning coal with water. Water helps fine particles to stick to the bigger lumps due to surface tension of the moisture, thus stopping fines from falling through grate bars or being carried away by the furnace draft. While tempering the coal, care should be taken to ensure that moisture addition is uniform and preferably done in a moving or falling stream of coal. If the percentage of fines in the coal is very high, wetting of coal can decrease the percentage of un burnt carbon and the excess air level required for combustion. The table below shows the extent of wetting, depending on the percentage of fines in coal.

Blending of coal

In the case of coal containing excessive fines, it is advisable to blend the predominantly lumped coal with lot of coal that contains excessive fines. Coal blending may thus help to limit the extent of fines in coal being fired to not more than 25%. Blending of different qualities of coal may also help to supply a uniform coal feed to the boiler.

4.4 Combustion Controls

Combustion controls assist the burner in regulation of fuel supply, air supply, (fuel to air ratio), and removal of gases of combustion to achieve optimum boiler efficiency. The amount of fuel supplied to the burner must be in proportion to the steam pressure and the quantity of steam required. The combustion controls are also necessary as safety device to ensure that the boiler operates safely.

Various types of combustion controls in use are:

On/Off control: The simplest control, ON/OFF control means that either the burner is firing at full rate or it is OFF. This type of control is limited to small boilers.

High/low/off control: Slightly more complex is HIGH/LOW/OFF system where the burner has two firing rates. The burner operates at slower firing rate and then switches to full firing as needed. Burners can also revert to the low firing position at reduced load. This control is fitted to medium sized boilers.

Modulating control: The modulating control operates on the principle of matching the steam pressure demand by altering the firing rate over the entire operating range of the boiler. Modulating motors use conventional mechanical linkage or electric valves to regulate the primary air, secondary air, and fuel supplied to the burner.

Full modulation means that boiler keeps firing, and fuel and air are carefully matched over the whole firing range to maximize thermal efficiency.

Biomass

Importance of Biomass

Prior to the industrial revolution, wood and agricultural residues are the primary source of energy for sectors like industry, transport and domestic. The transition took place from wood to coal and to oil and treated wood and agricultural residues as old fuels. Today, many fossil fuel based technologies have reached more advanced form of technological maturity, dependability access and efficiencies, incomparable to past few decades, thus only leaving more scope for conservation and search for new alternatives than changing the pattern of consumption and the domestic oil reserves are insufficient forcing import of oil and related products leading to pollution, global warming etc. The concerted efforts are required to identify new resources to put back the old fuel resources for meeting the requirements on large scale for local area energy demands. This helps in reducing the import of oil and naturally economics will recover. This kind of reversals is quite possible since the time is ripe and ideal to focus on utilization of biomass as a source of energy, food and fodder. Among various renewable energy sources, biomass offers a wide range of products to meet the present days' challenges. Unlike other forms of renewable energy sources, biomass offers a wide variety of bi-products similar to the fuels presently derived from fossils for other applications, where as the residues still offer their energy potential. So biomass is the best and dependable.

A practicable long term strategy helps us to store large quantities of energy in the form of biomass, whereas large investments are required to store solar energy or wind energy in batteries. However, such a large amount of solar energy can be stored in the form of biomass by the process called photosynthesis.

Exploiting Biomass as a Fuel

Over selling biomass as a source of fuel, may force us to utilize indiscriminately leading to an expensive concept of whole plant utilization. Most of the earth's fertile soil is made of biomass due to death and decay. This allows and supports the standing of crops and trees. To provide macro and micro-nutrients and organic constituents required for an active soil, the minimum required biomass must be left out returnable to the soil. If this requirement is not met, the starving soils will give no biomass to the generation to come. Hence, there is a need to postulate some restrictions based on benchmark studies and to recommend the quantities of biomass to be left for soils without fail. Hopefully, a regularity mechanism to monitor soil fertility and biomass as energy option helps sustainability.

Scope of Biomass Feed Stocks

Plant stores the solar energy in the form of fixed carbon achieved by the biochemical process called photosynthesis. This biochemical potential is stored by the plants in various forms at different stages of its growth. Based on the nature of these forms of availability, feed stocks can be classified as follows.

1 **Woody:** The wood can be made available from forests and energy plantations. Wood have high density is ideal for direct combustion, gasification and also for the production of ethanol and oils.

2 **Non-woody:** Small branches of trees, annually available agricultural residues like cotton stalk, maize, corn, pulses stalk, bagasse, tobacco etc terrestrial weeds like prosophis, lantana, parthenium and others.

Though bulk densities are low, well suited for gasification, direct combustion and for production of ethanol.

3 **Process residues:** The process residues like rice husk, coconut shells saw dust, coir pith, groundnut shells, cashew nut shells, etc. The bulk densities are reasonable with advantage of suitable material for gasification and direct burning.

4 **Aquatic plants:** Water hyacinth, lemma, algae, marsh reeds, sea weeds etc. subjected to anaerobic fermentation for biogas. Direct combustion and gasification have limited application due to high moisture content.

5 **Plants oils and fluids:** Agricultural crops like groundnut, soybean, sunflower, sesame etc. yield vegetable oils which are suitable for diesel substitution also. However, these oils are basically edible in nature. The residues viz., oil cakes offer the opportunity for producing appreciable amounts of biogas and the slurry is a good soil conditioner and manure. For eg. oils from Neem, pongamia, mahua, sal and the like produce oils, which are basically non-edible in nature. As on today, these oils are mostly used in sectors like pharmaceuticals, lubricants, dying and others. There are above 120 species classified under non-edible grade oil category both tree-born and crop based. These oils have very high value for substitution for diesel.

Biomass availability

The biomass available annually, was put to use only to an extent of 50% and remaining is wasted or lost. Dependence on forests for wood should be discouraged and to provide incentives of utilization for excess available crop residues for judicial application for thermal and power application.

The following various seven options available for the use of biomass

1. Direct combustion as cooking fuel or for the industrial usage
2. Charcoal production and utilization
3. Thermal power generation
4. Production of producer gas
5. Biogas production
6. Alcohol production and its utilization
7. Compaction of solid biomass in the form of briquettes and briquettes utilization

Advantages and Disadvantages

Biomass has both advantages as well as disadvantages in being used as an energy source which are enumerated below.

i. The biomass provides an effective low sulphur fuel.

ii. It provides an inexpensive and readily available source of energy, and

iii. Processing biomass materials for fuel reduce the environmental hazard.

The major problems or difficulties in utilizing biomass for solar energy conversion as well as a renewable source of energy are:

i. The relatively small percentage (less than 0.1%) of light energy is converted into biomass by plants.

ii. The relatively sparse and low concentration of biomass per unit area of land and water

iii. The scarcity of additional land suitable for growing plants.

iv. Scattered and seasonal availability of biomass

v. Their large volume and low bulk density associated with high moisture content that makes their collection and transport expensive and energy conversion relatively inefficient.

vi. The very abrasive nature due to silica cellulose structure causing high wear and tear in grinding machinery and fragile and porous nature of some agro industrial residues like rice husk makes them difficult to be stored in outdoor piles which become vulnerable to fire hazard and be air borne by the wind.

These methods are based on thermal, chemical and enzymatic conversion processes. In dry process, material is transformed under high temperature In wet process, Biological processes such as fermentation are involved.

Physical Processes / Mechanical Methods

This method is used to increase the bulk density of biomass material for easy transportation and storage and involves the following processes.

I. **Briquetting:** The briquetting is the process of making small size compressed block to get more surface area per unit weight of biomass by adding suitable binder. It includes the following process.

a) **Moisture removal**: The process involves the removal of moisture from contents to break down its elasticity to reduce its volume sufficiently.

b) **Densification:** The product is carried out at high pressure and temperature 1800C to get more homogeneous product after moisture is removed.

II. **Pelletization:** Fuel pellets or refused derived fuel (RDF) are small cubes mode from the solid waste/garbage and are used as a fuel for boilers to produce steam or electricity. Pelletization of the wood is carried out by compressing it in the forms of rods of small diameter 5-12 mm in the

extruder after removal of moisture 7-10%.

III. **Size Reduction:** Making small pieces by using shredding machines or Hammer mills.

Different types of dry processes

1. Combustion: Direct combustion is a complete oxidation process where liberation of heat is the primary objective. Burning of any substance in excess air whether it be solid, liquid or gas is termed as combustion. In combustion, a fuel is oxidized evolving heat and often light

$C+O_2 \rightarrow CO_2 + \text{Heat}$

The combustion of solid fuel occurs in stages. i.e. Actual combustion of organic residues is not a single process but a combination of processes occurring simultaneously.

Three overlapping phases can be identified as

1. Initial phase: Evaporation of moisture

2. Volatilization and burning of volatiles: Dry matter absorbs heat, drives off volatile gases by thermal decomposition of the fuel and burning of volatiles in the air occurs.

3. Final phase: Fixed carbon burns

At usual combustion temperature, the burning of hot solid residue is controlled by rate at which oxygen of the air diffuses to its surface. If the residue is cooled by the radiation of heat, combustion ceases.

Eg: Open chulas thermal efficiency : 3 – 4 %

Improved chulas thermal efficiency : 10 – 14%

Consumption of the fuel : 0.5 – 1 Kg /per person

Use: To produce steam for process use and for electricity.

2. Pyrolysis: Pyrolysis is defined as the destructive distillation of organic material heated to more than 200^0C in the absence of air/oxygen for several hours to produce combustible gases (H_2, CO, CH_4), other hydrocarbons, CO_2 and N_2, solid char, liquid tar and organic liquids. It is a non oxidative thermal process that results in gases, liquids and char. It is thermal degradation of cellulose. In practice, many processes allow a restricted admission of air for partial combustion to achieve the temperature required for pyrolysis. The temperature of pyrolysis, composition of biomass (C, H, N, O, S), retention period and heating rate in pyrolyser etc determine the nature and quantum of these products. The slow rate of heating, low temperature and adequate retention time tend to give high yields of char.

3. **Gasification**: It is a chemical change involve several chemical reactions which occur simultaneously at varying rates. The dry process is combustion of biomass in a controlled atmosphere. This is a gasification process involving the burning of biomass with a limited air supply at temperature above 1100^0C. The typical product is a mixture of $CO + H_2$ i.e. producer gas which is 1/10th of the petroleum gas. Useful for cooking, heating and electricity generation.

4. **Liquification:** The dry process of biomass conversion is hydro carbonization or liquification, which combines high temperature and pressure to produce oil or gas. These Fuels are same as that of petroleum and natural gas. But the operating cost and energy expenditure higher

Module 3. Colloids Classification, properties

Lesson 5. Colloids - I

5.1 INTRODCTION

Thomas Graham (1861) while doing his classical researches on liquid diffusion observed two classes of substances.

Solution of some substances could readily pass through animal and vegetable membranes. To this class belonged almost all inorganic acids, bases and salts and many organic compounds like urea, sugar etc. Graham called them crystalloid as most of them were crystalline.

The other class of substances are diffused very slowly in solution and the solution could not pass through the membrane, they were called colloids (from the Greek word Kolla meaning glue, which is a member of this class). Other members are starch, gelatin, albumin, proteins and other amorphous substances.

Graham's view has undergone changes since it has been seen that every substance can exhibit colloidal properties under suitable conditions. Thus we now define colloidal state as: a two phase heterogeneous system in which one phase is dispersed in a fine state of subdivision having diameter of 10^{-4} to 10^{-7} cm in another medium termed the continuous or dispersion medium. In a colloidal solution there exists a discontinuous phase called the dispersed phase and the continuous dispersion medium, and also a stabilizing agent which does not allow the dispersed phase to coalesce and settle.

5.2 CLASSIFICATION OF COLLOIDS

5.2.1 Classification based on dispersed phase and dispersion medium which may be either solid or liquid or gas and so the following types (Table 5.1) of colloids are formed

Table 5.1 Types of colloidal systems

Dispersion medium	Dispersed phase	Colloidal system	Examples
Gas	Liquid Solid	Liquid aerosol Solid aerosol	Mist, Fog, Cloud, Insecticide spray, Smoke, Fume
Liquid	Gas Liquid Solid	Foam Emulsion Sol	Foam, Froth, Whipped cream, Lemonade Milk, Cream, Mayonnaise, Glue, Paints, Starch paste, Milk of Magnesia, Gold sol, As_2O_3, S, FeO_3 or AgCl sol in water
Solid	Gas Liquid Solid	Solid foam Gel Solid sol	Pumice stone, bread dough, Lava, Styrene foam, Rubber. Curd, Jelly, Cheese, Butter, Shoe polish, Pearl ($CaCO_3$ with water). Gems, Alloys, Minerals

5.2.2 Classification based on affinity for solvent When there is a strong affinity between the dispersed phase and the dispersion medium the colloid is known as lyophilic colloid, while if there is no apparent affinity it is called lyophobic colloid. The main differences between these two classes of colloids are summarised below:

Lyophillic sol are stable. The particles may or may not migrate in an electrical field, and viscosity is much higher than that of the medium. They are reversible sols and are self-stabilized due to the strong attraction between two phases. They are self-stabilized due to the strong attraction between two phases. Surface tension is much lower than that of the medium. They are not easily precipitated by the addition of electrolytes. Starch gelatin, gum, albumin are lyophilic colloids which are not visible under ultramicroscope. They are prepared simply by direct dissolving.

Lyophobic sols are unstable compared to lyophillic sols. The particles are charged and hence move towards electrode in an electrical field. The viscosity is same as that of the medium. They are irreversible sols. They are much less stable, stabilizer is required for stabilization. Surface tension is same as that of the medium and is coagulated easily by adding electrolyte. Colloidal metals, metallic sulfides are lyophobic colloids, Visible under ultramicroscope and prepared by indirect methods

5.2.3. Classification based on nature of dispersed phase

i. Multimolecular colloids: When the dispersed phase consists of aggregates of atoms or molecules and the main attractive force between them is the van der Waals force of attraction. They are lyophobic in nature.

Examples: Gold sol and Sulfur sol.

ii. Macromolecular colloids: A large number of small molecules combine to form a giant molecule held by covalent bonds having a colloidal dimension are called macromolecular colloids. They are lyophilic and have gold numbers.

Examples: Proteins, Polysaccharides, Gums, Synthetic rubber, Nylon etc.

iii. Association colloids: On increasing concentration, the solute molecules or ions come closer to form aggregate spontaneously of colloidal dimensions, called micelles are associated colloids. Example: Soaps and synthetic detergents.

Sodium oleate forms micelles and contains a lyophobic group ($C_{17}H_{33}^+$) and a lyophilic group (-COONa), the hydrocarbon portion inside the micelle, while the ionised groups are at the surface. They move freely in an electric field and the solution has high conductivity. The minimum concentration at which the micellization begins is called the critical micellization concentration (cmc). These colloids play very important role in solubilizing solvent repellant substances, such as water insoluble dyes are solubilized in soap solutions.

5.3 PREPARATION OF COLLOIDAL SOLUTIONS

The main methods of preparation of colloidal solutions are

5.3.1. Condensation method

5.3.2. Dispersion method

5.3.1 . Condensation Method: In this method, a large number of particles of molecular size are allowed to coalesce or condense to form bigger particle of colloidal dimension. The various processes used are:

i. By exchange of solvent: Sulfur or phosphorus is not directly soluble in water. If an alcohol solution of S or P is poured into water, colloidal solution of S or P is formed.

ii. By changing physical state: Hg or S sols are produced by allowing their vapours to pass through cold water. Ammonium citrate is added to stabilize the solution.

iii. By controlled condensation: Prussian blue sol is obtained by precipitating it in presence of a protective colloidal system like starch.

iv. Chemical methods: (a) by double decomposition, colloidal solution of arsenious sulfide is made by passing H_2S gas, through a suspension of As_2O_3in water, until saturation

$As_2O_3 + 3H_2S \longrightarrow As_2S_3 + 3H_2O$.

Sols of insoluble inorganic salts are prepared in this way

b. By reduction: Colloidal solutions of metals such as Ag, Au, Pt in water can be prepared by reducing aqueous solution of their salts by reductants like formaldehyde, carbon monoxide, hydrazine etc

Thus gold sol is obtained by treating a solution of gold chloride with formaldehyde

(0.3 %).

$2AuCl_3 + 3HCHO + 3H_2O$ à 2 Au(sol) + 3HCOOH + 6HCl

The liberated acid is neutralized by $K_2CO_3$to stabilize the sol.

c. By hydrolysis: Colloidal solutions of many oxides and hydroxides of iron, aluminium can be prepared by this method. On adding a freshly prepared saturated solution of $FeCl_3$ dropwise on boiling water, hydrolysis of $FeCl_3$ takes place with the formation of deep red colloidal sol of ferric hydroxide.

$FeCl_3 + 3H_2O$ à $Fe(OH)_3$ (sol) + 3HCl

d. By oxidation: Sulfur sol is prepared by passing H_2S through a solution of SO_2 in wate until the smell of SO_2 is removed. The solution on boiling with satrated NaCl solution precipitates out S, on filtration, which is washed free of Cl^- and finally dissolves on further addition of water.

5.3.2. Dispersion method: In this method, the bigger or large particles are broken down to colloidal dimension and dispersing them in a medium to form colloidal solution. The methods used are:

i. By mechanical dispersion: Many substances of large size are ground and dispersed in a medium to get a coarse suspension which is then passed through a colloid mill, which is essentially two metal discs rotating in opposite directions at high speed with a very narrow clearance

The space in between the metal discs breaks down the particles to colloidal size. Black ink, paints, varnishes, ointments dyestuffs are prepared by this method

ii. Bredig's arc method or electro dispersion: (Figure 5.1) Colloidal solution of metals like Au, Ag, Cu, Pb, Pt etc. are obtained by this method. An electric current is passed through water containing traces of alkali, when an electric arc is produced between the tips of two closely placed electrodes of these metals. The heat of the spark converts the ends of the metal rods to form vapours of metal which immediately condense to give metal colloids. The trace of alkali stabilizes the colloidal solution and finally the solution is cooled by cooling mixture.

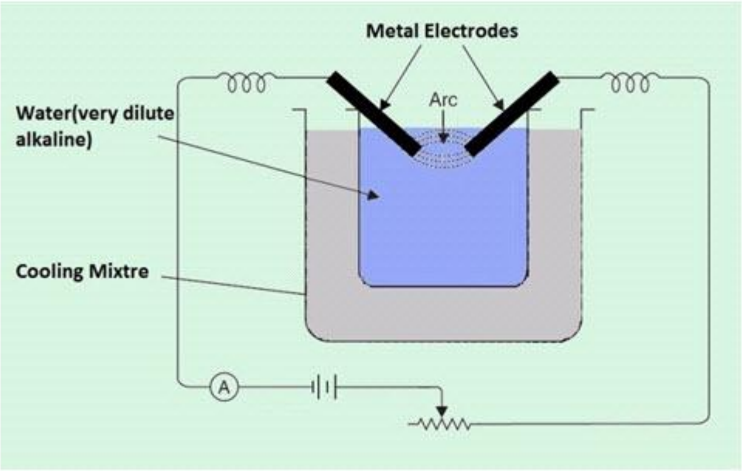


Fig. 5.1 Bredig's arc method

iii. Mechanical dispersion method: (Fig. 5.2) this technique consists of finely pulverising the substances to be dispersed in the medium, which constitutes the dispersion phase. This coarse suspension is then passed through colloid-mill which mechanically grinds the coarse particles. The colloid-mill consists of two discs made of metal, which rotates in opposite direction at a very high speed. The clearance between the discs is very small that apparently determines the size of the colloidal particle. The coarse particles which come in between the two rotating discs get teared to smaller colloidal particles, which are finally stabilized by addition of a suitable protective colloid.

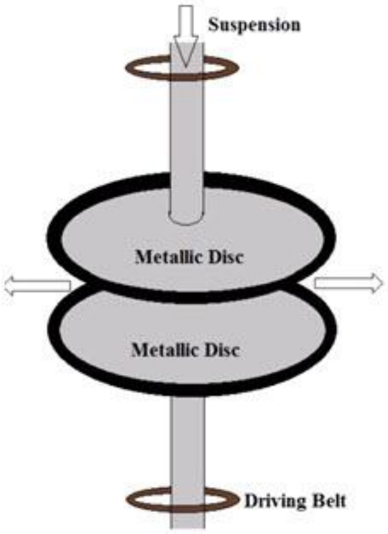


Fig.5.2 Colloidal Mill

iv. Peptization: A freshly prepared precipitate such as AgCl, $Fe(OH)_3$, $Al(OH)_3$ etc can be converted into colloidal state by the addition of small amount of a foreign electrolyte solution. The foreign electrolyte is known as the peptizing agent and the process is called peptization.

a. Thus freshly precipitated $Fe(OH)_3$, if shaken with a dilute solution of $FeCl_3$, would

give rise to ferric oxide sol.

$Fe(OH)_3\ (s) + \quad Fe^{3+} \rightarrow Fe(OH)_3 \,.\, Fe^{3+}$

Precipitate Peptizing agent (Sol/Colloid)

b. Freshly precipitated AgCl can be peptized by shaking with a dilute aq sol. of $AgNO_3$

$AgCl(s) + \quad Ag^+ \rightarrow AgCl \,.\, Ag^+$

Precipitat Peptizing agent (Sol/Colloid)

c. $Al(OH)_3 \quad + \quad H^+ \rightarrow Al(OH)_3 \,.\, H^+$

Precipitate Peptizing agent (Colloid)

Though there is no rule, but it is common that the peptizing agent which are most effective contains a common ion with the precipitate forming colloid.

Dispersion is also sometimes carried out by the use of an atomiser e.g., in the dispersion of a liquid in a gas.

5.4 PURIFICATION OF COLLOIDAL SOLUTIONS

The colloidal solutions prepared by the above methods contain several impurities of electrolytes and other soluble substances. So, they become unstable. Hence, it is essential to purify these colloidal sols. The following methods are commonly used for purification.

i. Dialysis. The semi-permeable membranes like cellophane parchment paper, animal membrane have pore sizes which allow the free passage of only the dissolved molecules or ions of a true solution but retains the bigger colloidal particles. Thus, the process of separation of crystalloids from colloids by diffusion through the animal or vegetable membrane is called Dialysis. The sol to be purified is taken in a parchment or cellophane bag, which is partly immersed in water or the dispersion medium. The crystalloids from the sol move out through the cellophane while some amount of water or solvent from outside may enter the bag. The solvent is renewed from time to time. The process is allowed to continue until most of the ions are eventually removed and the retained colloid gets stabilized. In certain sols such as Al_2O_3 hydrosol, the disperse phase is too small to be retained by cellophane and hence the system needs controlled heating whereby the particles grow bigger in size.

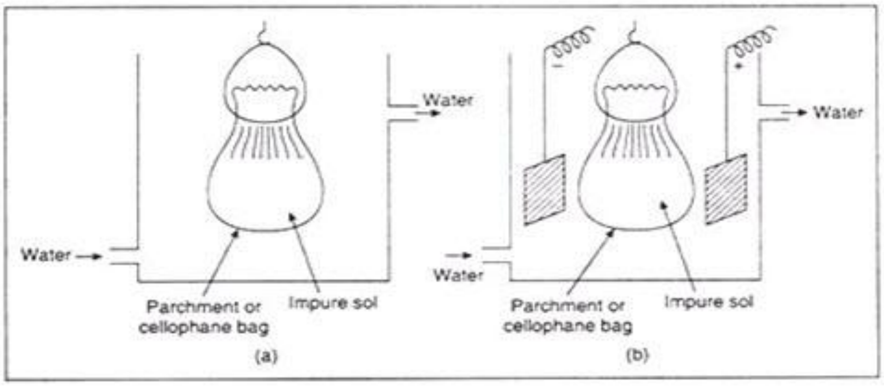


Fig. 5.3. Dialysis

To accelerate this slow process of purification and also to achieve a higher degree of purity the dialysis is carried out in a direct current electric field, and the process is called electrodialysis. Electrodialysis is of no use in separating non-electrolytic impurities.

ii. Ultra-filtration. Colloidal particles can pass through ordinary filter papers. But when ordinary filter paper is impregnated with a solution of gelatin or collodion and hardened by formaldehyde the pores become smaller, so that colloidal particles cannot pass through it. Such a filter paper is called ultrafilter paper. The sol when poured over the ultrafilter, electrolytes can pass through, but the colloidal particles are retained and form a slime over it. The slime when brought in contact with water, disperses freely and forms colloidal solution. This process of purifying colloids from the crystalloids using ultrafilters is called ultrafiltration.

By using impregnating solutions of different concentration graded ultrafilters can be prepared which is capable of separating impurities of different sizes.

Lesson 6. Colloids - II

6.1 PROPERTIES OF COLLOIDAL SOLUTIONS

Colloidal solutions possess some characteristic properties. Important ones are described below:

6.2.1 PHYSICAL PROPERTIES

a. Colloidal systems are heterogeneous, intermediate between true solution and suspension and contain two phases, dispersed phase and dispersion medium.

b. Colour. Colour and appearance depend on the size, shape, refractive index and some other properties of the dispersed phase. Gold sol of very fine particles is red and of coarser particles is blue in colour; sulfur sols may be colorless to faint and deep yellow in reflected light and reddish in transmitted light.

c.Shape. Although the most common shape of the particles are spherical; but highly asymmetrical shape is also found. Vanadium pentoxide particles are rod-shaped, RBCs (red blood corpuscles) normally are double concave plates and give red color, but in sickle-cell anaemia they become new-moon shaped. Colloidal particles are readily filterable through ordinary filter paper.

d. Adsorption. Generally colloidal particles are either positively or negatively charged, so they attach to a variety of molecules on their surfaces. This property of colloid has been utilized in dyeing fabrics where the fabrics are first treated with colloidal suspension which adsorbs dye.

6.2.2 COLLIGATIVE PROPERTIES.

High molecular weight is the characteristic of colloidal particles and hence in a solution, the number of moles present is very low. Colligative properties like osmotic pressure, depression of freezing point, lowering of vapour pressure depend on the molarity of the solution and hence these values are very low for colloidal solution.

6.2.3 MECHANICAL PROPERTIES

a. Brownian movement. Robert Brown, an English botanist, in 1927, observed under a microscope that pollen grains dispersed in water executed a ceaseless random motion. This random zigzag motion is also executed by all colloidal particles, including colloidal particles suspended in a gaseous medium, independent of their nature, smaller particles executing a more rapid and brisk motion than the larger ones. This perpetual zigzag motion is called Brownian motion. This motion is described by Perrin as .they go and come, stop, start again, mount, descent, remount again, without in the least tending towards immobility.

The true cause of Brownian movement was suggested by Wiener in 1863 as molecular collision of colloidal particles with liquid molecules. The colloidal particles are constantly hit from all sides of the surrounding molecules. The colloidal particles after impact with solvent molecule move in a straight line until its speed and direction are not altered by another impact. The intensity of Brownian motion is less with increase in size of the colloidal particles and also with the increase in viscosity of medium.

Brownian motion also increases with increase in temperature. Large particles do not show Brownian movement.

b. Diffusion. In a colloidal solution, colloidal particles move from a region of higher concentration to a region of lower concentration until uniformity is attained. But the diffusion process is slower than diffusion in true solution due to higher mass and lower speed of colloidal particles. Diffusion is used to separate colloidal particles of different size.

c. Sedimentation. Colloidal particles constantly exhibit Brownian motion and remain suspended in solution, thereby stabilizing the colloidal solution. Larger colloidal particles settle slowly by the effect of gravity and is called sedimentation. Svedberg increased the rate of sedimentation with centrifugal sedimentation by employing a high-speed centifuge called ultracentrifuge. In this machine sedimentation is effected under enormous centrifugal force of rotation.

6.2.4 **OPTICAL PROPERTIES OR TYNDALL EFFECT**

When a beam of light is passed through a colloidal solution, the path of light becomes illuminated due to the scattering of light by the colloidal particles. This phenomenon is called Tyndall effect, which does not happen for true solution. These colloidal particles can be viewed through a microscope placed at right angles to the path of light and is called the ultramicroscope. The phenomenon of Tyndall effect can be explained by the scattering of light by the colloidal particles. The particles absorb the incident light energy, becomes self-luminous and scatter this absorbed light. The intensity of the scattered light depends on the difference between the refractive indices of particle and medium.

Tyndall effect was first studied by Zeigmondy in 1903 and this effect can be applied for viewing the colloidal particles quantitatively.

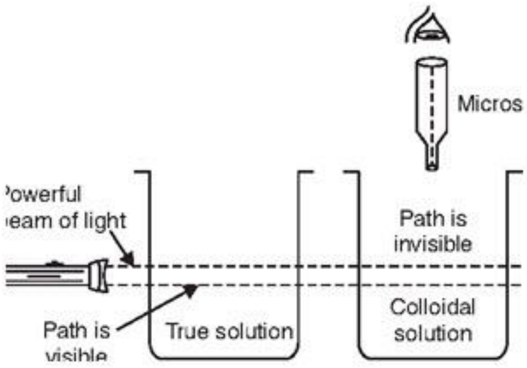


Fig. 6.1 Tyndall effect exhibited by a colloidal solution.

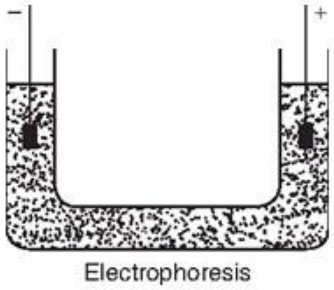


Fig. 6.2 Electrophoresis

6.2.5 ELECTRICAL PROPERTIES

- Electrophoresis. Lyophilic and lyophobic colloid particles are either positively or negatively charged. In a U-tube, containing a colloidal solution, when a potential gradient is applied the colloidal particles move towards oppositely charged electrode. After reaching the electrode, they lose their charge and coagulate there. The movement of the colloidal particles in an electric field is called electrophoresis. When the negatively charged particles like CdS, As_2S_3 metallic sols, organic sols move towards cathode, the phenomenon is called cataphoresis. Positively charged particles are $Fe(OH)_3$, $Al(OH)_3$, basic dyes etc. The speed of the colloidal particle under the potential gradient of 1 volt/cm is called electrophoretic mobility.

- Electro-osmosis. When electric current is passed through a colloidal solution such that the dispersed phase is prevented from movement, the dispersion medium begins to move in the electric field. This phenomenon is called electro-osmosis.

- Isoelectric Point. The colloidal sols of protein are either positively or negatively charged in acidic or alkaline solution and hence when electrolysed in a medium, pH of the medium will dictate the migration of the colloidal particle to any electrode. Hence the pH of the dispersion medium at which the dispersed particles are neutral and hence they do not migrate when subjected to an electric field is called isoelectric point. The isoelectric point of protein depends on pH and ionic strength in the medium. Proteins are least soluble in isoelectric point and hence coagulate at isoelectric point.

6.3 COAGULATION OF COLLOIDS

- Colloid particles are electrically charged, so they repel each other and become stable. When the charge is neutralised, the particles approach each other to form aggregates and settle down. The precipitation of colloidal solution is called coagulation or flocculation. This can be achieved by

- Adding oppositely charged: Two oppositely charged colloidal solutions when mixed, mutual coagulation of the two sols takes place.

- Electrophoresis: In electrophoresis the electrically charged colloidal particles migrate towards the oppositely charged electrode and finally coagulate.

- Adding electrolytes: By addition of oppositely charged ion i.e., by adding electrolytes the charges of the colloidal particles are neutralised and precipitated. Coagulating power of an ion increases with the increasing valency of the coagulating ion. The higher the valency of the ion, greater is the coagulating power this is known as Schulze-Hardy law. Thus, the coagulating power increases in the series

$Na^+ < Ba^{+2} < Al^{3+}$ or $Cl^- < SO_4^{2-} < PO_4^{3-}$.

Generally, the coagulating power of trivalent ion is 500 - 1000 times greater than bivalent ion which is 100-500 times greater than monovalent ion.

6.4 PROTECTION OF COLLOID

- The stability of colloids can be achieved by any of the following:

- Electrical charge. All the colloidal particles of a colloidal solution bear similar charges and hence they repel each other. This mutual repulsion prevents them from coalescing and coagulating.

- Solvation. Colloidal particles are surrounded by a layer of solvent molecules which resists the dispersed phases from forming large aggregates and coagulate. Thus, the solvent layer forms a protective envelope. These sols are very stable.

- Protective agents. Protective agents are added to some colloidal systems, which get adsorbed on the surface of the colloidal particles and by coating them prevents coagulation.

- Protective colloids. Lyophilic colloids are much more stable than the lyophobic colloids.since the former are extensively solvated. When a lyophilic colloid is added to a lyophobic colloid, the latter becomes more stable even to the action of electrolytes. The process by which lyophilic colloid protects the lyophobic sol is called protection and the lyophilic colloid is called the protective colloid. Thus, if a little albumin (lyophilic colloid) is added to a gold sol (lyophobic sol), the former acts as protective colloid and prevents coagulation of the latter even against addition of high concentration of an electrolyte, like NaCl. This protection is due to the formation of a protective thin layer surrounding the particles of the lyophobic colloid, through which the oppositely charged ion of the electrolyte cannot penetrate to neutralize the charge for coagulation. Zsigmondy introduced the term gold number to measure the protective power of lyophilic colloids. It is defined as the minimum weight in mg of a protective colloid, which when added to one ml of standard gold sol (containing 0.0053 to 0.0058 % gold) containing also 1 ml of 10 % NaCl solution to just prevent its coagulation. This is indicated by the change of colour from red to blue. The smaller the gold number the greater is the protective power of lyophilic colloid.

Table 6.1 Gold numbers

Protective colloid	Gold number
Gelatin	0.005 to 0.015
Casein	0.01 to 0.02
Albumin	0.1 to 0.2
Gum	0.1 to 0.2
Starch	10 to 15
Sodium oleate	0.40
Haemoglobin	0.003 to 0.07

6.5 EMULSION AND GEL

Emulsions are colloidal systems in which both dispersed phase and dispersion medium are liquids (immiscible). The familiar examples are milk, which consists of liquid fat dispersed in water (oil in water type); butter, which consists of water dispersed in liquid fat (water in oil type).

Emulsions are prepared merely by shaking one liquid with the other, and hence they are not stable and easily separate into two immiscible layers. Emulsions are stabilized by adding a third substance (emulsifier) as stabilizer. This substance forms a thin layer around the dispersed phase thereby preventing it from coalescing and coagulating. The emulsifier also decreases the surface tension of the two liquids.

Albumin, casein, gum, agar-agar, soaps and detergents are the common emulsifiers. Emulsifiers are selected according to the type of emulsion, e.g., soaps of alkali metals, gelatin etc. are more soluble in aqueous phase, hence they are used as stabilizers for oil-in-water-type of emulsion whereas heavy metal soaps of palmitic and oleic acid are soluble in fat and hence used in water-in-oil-type emulsion.

Emulsions have properties similar to those of lyophobic colloids like Tyndall effect, Brownian movement etc.

Gel: Many lyophilic sol and few lyophobic sol when coagulated under certain conditions form semi-solid mass. Such a product is called gel and the process is called gelation, e.g., jam, jelly, cheese, curd etc. This is formed by entrapment of the dispersion medium inside the loose network of the dispersed particle. Gels have high viscosity and swell if placed in the dispersion medium and some shrink in volume.

Gel formation is utilized for preparation of shoe polish, cheap soaps, curds, jellies, solid fuel of alcohol with calcium oxalate.

Reversible colloid. When a colloid can be reversibly converted from a sol to gel and vice versa, it is called a reversible colloid, e.g., solution of gelatin can be reconverted into sol by heating. Other colloids which cannot be reversibly transformed are called irreversible colloid, e.g., normal Au colloid.

Zeta potential. In lyophobic colloids, particles are of similar charge, which do not allow the particles to come closer and coalesce and hence bring stability to the system.

The charge is embedded in the colloidal particle and an equivalent amount of opposite charge remains outside and these two layers form a double layer. A part of this opposite charge is fixed on the particle and another part is mobile and distributed throughout the medium.

Hence, there is a potential difference between the particle and the medium. This potential is called the zeta potential which is responsible for the stability of the colloid.

6.6 APPLICATION OF COLLOIDS

1. **Purification of water**. Impure water is treated with alum. Al^{3+} ions of alum precipitate negatively charged clay particles, bacteria, colloidal particles and the impurities.

2. **Purification of polluted air**. Suspended particles, smoke etc., polluted air. Smoke is negatively charged colloidal suspension consisting of carbon particles. Air is passed through Cottrell precipitator where the charge is neutralised and carbon settles down while the hot air passes out through chimney.

3. **Removal of dirt from sewage**. Sewage contains charged dirt particles, which is passed through tanks fitted with oppositely charged electrodes. By neutralizing the charge, dirt is coagulated.

4. **Leather tanning**. The raw material skin is positively charged colloidal system, which is treated with negatively charged colloidal solution of tannin, whereby mutual coagulation of oppositely charged colloids takes place.

5. **Laundry**. Soaps in water form colloidal solution, which adsorb greasy materials, dirt by emulsion formation and remove dirt from clothes.

6. **Medicine**. Colloidal system of medicines are better assimilated. Blood coagulation is effected with alum or $FeCl_3$.

7. **Cosmetics**. Different types of colloidal systems and emulsion are used in cosmetics.
8. **Analysis**. Noble metals are detected by formation of their colloidal solutions and observing their colours.
9. **Artificial rains** are made by throwing charged sand on clouds.
10. **Delta formation**. Negatively charged sand particles of the river water Sand Na^+, K^+, Ca^{2+} present in the sea water are responsible for the deposition of colloidal particles where river meets sea.

Module 4. Corrosion Causes, type and methods of prevention

Lesson 7. Corrosion and ais classification

7.1 INTRODCTION

Except noble metals (Au and Pt) most other metals exist in nature in combined forms as their sulphide, oxides, silicates, carbonates etc. These are reduced to their metallic states from their ores, during their extraction processes. During extracting of metals, considerable amount of energy is required. Consequently, isolated pure metals can be regarded in exited state then their corresponding ores, and they have a natural tendency to revert back to combined state. Hence, when metals are put in to use in various forms, they are exposed to environment, the exposed metal surfaces begin to decay in to more stable compounds more or less rapidly. When they come in contact with gaseous and/or liquid environment. In other words, destruction or deterioration of metal starts at the surface. This type of the metallic destruction may be due to direct chemical attack or by electrochemical attack.

Any process of destruction and consequent loss of solid metallic materials, through an unwonted chemical or electro chemical attack by its environment, starting at its surface, is called **corrosions**. Thus corrosion is a process "reverse of extraction of metals".

The mos familiar examples of corrosion are rusting of iron, when expose to the atmospheric conditions. During this, a layer of reddish scale and powder of oxide (Fe_3O_4) is formed, the iron becomes weak. Another common example is formation of green film of basic carbonate ($CuCO_3 + Cu(OH)_2$) on the surface of copper, when expose to moist air containing carbon dioxide.

Gravidity of corrosion problem; the process of corrosion is slow and occurs only at metal surfaces, but the lows incurred due to corrosion, are enormous weast or destruction of machines, equipments and different type of metallic products. Losses occurring, due to corrosion cannot be measured in turns of the cost of metals alone, but the high cost of fabrication into equipments- machine tools structure should be considered.

7.2 CLASSIFICATION OF CORROSION

It is convenient to classify the corrosion by the forms in which it manifests itself, the bases of this classification being the appearance of the corroded metal. Each form can be identified by mere visual observation. In most cases the naked eye is sufficient, but sometimes magnification is helpful or required. Valuable information for the solution of a corrosion problem can often be obtained through careful observation of the corroded test specimens or failed equipment. Examination before cleaning is particularly desirable.

Some of the eight forms of corrosion are unique, but all of them are more or less inter -related. The eight forms are: 1. Uniform or general attack, 2. Galvanic or two metal corrosion, 3. Crevice corrosion, 4. Pitting, 5. Intergranular corrosion, 6. Selective leaching or parting, 7. Erosion corrosion, 8. Stress corrosion . This listing is arbitrary but covered practically all corrosion failure and problems. The forms are not listed in any particular order of importance.

Below, the eight forms of the corrosion are discussed in terms of their characteristics, mechanism and preventive measures. Hydrogen damage, though not a form of corrosion, often occurs indirectly as a result of corrosive attack.

7.2.1UNIFORM ATTACK

Uniform attack is the most common form of corrosion. It is normally characterized by a chemical or electrochemical reaction that proceeds uniformly over the entire exposed surface or over a large area. The metal becomes thinner and eventually fails. For example, a piece of steel or zinc immersed in dilute sulphuric acid will normally dissolve at a uniform rate over its entire surface. A sheet iron roof will show essentially the same degree of rusting over its entire outside surface.

Uniform attack, or general overall corrosion, represents the greatest destruction of metal on a tonnage basis. This form of corrosion, however, is not of too great concern from the technical stand point, because the life of equipment can be accurately estimated on the basis of comparatively simple tests. Merely immersing specimens in the fluid involved is often sufficient. Uniform attack can be prevented or reduced by (1) proper materials, including coatings, (2) inhibitors, or (3) cathodic protection. These expedients, which can be used singly or in combination. Most of the other forms of corrosion are insidious in nature and are considerably more difficult to predict. They are also localized; attack is limited to specific areas or parts of a structure. As a result, they tend to cause unexpected or premature failures of plants, machines or tools.

7.2.2 GALVANIC CORROSION

A potential difference usually exists between two dissimilar metals when they are immersed in a corrosive or conductive solution. If these metals are placed in contact (electrically connected), this potential difference produced electron flow between them. Corrosion of the less corrosion resistant metal is usually increased and attack of the more resistant material is decreased, as compared with the behaviour of these metals when they are not in contact. The less resistant metal becomes anodic and the more resistant metal cathodic. Usually the cathode or cathodic metal corrode very little or not at all in this type of couple. Because of the electric currents and dissimilar metals involved, this form of corrosion is called galvanic or two metals corrosion. It is electrochemical corrosion, but we shall restrict the term galvanic to dissimilar metal effects for purposes of clarity.

The driving force for current and corrosion is the potential developed between the two metals. The so called dry cell battery is a good example of this point. The carbon electrode acts as a noble or corrosion resistant metal – the cathode- and the Zinc as the anode, which corrode. The moist paste between the electrodes is the conductive (and corrosive) environment that carries the current. Magnesium may also be used as the anodic material or outer case.

7.2.3 CREVICE CORROSION

Intensive localized corrosion frequently occurs within crevices and to other shielded areas on metal surfaces exposed to corrosives. This type of attack is sally associated with small volumes of stagnant solution cased by holes, gasket surfaces, lap joints, surface deposits, and crevices under bolt and rivet heads. As a result, this form of corrosion is called crevice corrosion or sometimes, deposit or gasket corrosion.

7.2.4 PITTING:

Pitting is a form of extremely localized attack that results in holes in the metal. These holes may be small or large in diameter, but in most cases they aree relatively small. Pits are sometimes isolated or so close together that they look like a rough surface. Generally a pit may be described as a cavity or hole with the surface diameter about the same as or less than the depth. Pitting is one of the most destructive and insidious forms of corrosion it causes equipment to fail because of perforation with only a small percent weight loss of the entire structure. It is often difficult to detect pits because of their small size and because the pits are often covered with corrosion products. In addition, it is difficult to measure quantitatively and compare the extent of pitting because of the varying depths and numbers of pits that may occur under identical conditions. Pitting is also difficult to predict by laboratory test. Sometime the pits require a long time to show up in actual service. Pitting is particularly vicious because it is a localized and intense form of corrosion, and failures often occur with extreme suddenness.

7.2.5 INTERGRANULAR CORROSION

The more reactive nature of grain boundaries effect is of little or no consequence in most applications of uses of metals. If a metal corrodes, uniform attack results since grain boundaries are usually only slightly more reactive then the matrix. However under certain conditions, grain interfaces are very reactive and intergranular corrosion results. Localized attack at an adjacent to grain boundaries, with relatively little corrosion of the grains is intergranular corrosion. The alloy disintegrates and / or loses its strength. Intergranular corrosion can be impurity at the grain boundaries, enrichment of one of the alloying elements or depletion of one of these elements in the grain boundary areas. Small amount of iron in aluminium, where in the solubility of iron is low, have been shown to segregate in the grain boundaries and cause intergranular corrosion. It has been shown that based on surface tension considerations the zinc content of a brass is higher at the grain boundaries. Depletion of chromium in the grain boundary region results in intergranular corrosion of stainless steel.

7.2.6 SELECTIVE LEACHING

Selective leaching is the removal of one element from a solid alloy by corrosion processes the most common examples is the selective removal of zinc in brass alloy (Dezincification). Similar process occur in other alloy systems in which aluminium, iron, cobalt, chromium and other elements are removed. Selective leaching is the general term that describes the processes, and its use precludes the creation of terms such as dealluminiumification, decobaltification etc. Parting is a metallurgical term that is some time applied but selectively leaching is proffered.

7.2.7 EROSION CORROSION

Erosion corrosion is the acceleration or increase in rate of deterioration or attack on a metal because of relative movement between a corrosive fluid and the metal surface. This movement is quiet rapid, and mechanical wear effects or abrasion are involved. Metal is removed from the surface as dissolved iron, or it forms solid corrosion products that are mechanically swept from the metal surfaces. Sometimes movement of the environment decreases corrosion, practically when localized at attack occurs under stagnant conditions, but this is not erosion corrosion because deterioration is not increased. Erosion corrosion is characterized in appearance by grooves, gullies, waves, rounded holes, and valleys and usually exhibits a directional pattern. For example: heat exchanger tube handling water, failure because of erosion corrosion occurs in relatively short time and they are unexpected largely because evaluation corrosion tests were run under static conditions or because the erosion effects were not considered. Most metals and alloy are susceptible to erosion corrosion damage. Many depend upon the development of surface film of some sort (passivity) for resistance to corrosion. Examples are aluminium, lead, and stainless steels. Erosion corrosion results when these protective surfaces are damaged or worn and the metal and alloy are attacked at a rapid rate. Metals that are soft and readily damaged or worn mechanically, such as copper and lead are quiet susceptible to erosion corrosion.

7.2.8 STRESS CORROSION

Stress corrosion cracking (SCC) refers to cracking caused by the simultaneous presence of tensile stress and specific corrosive medium. Many investigators have classified all cracking failures occurring in corrosive medium as stress corrosion cracking, including failures due to hydrogen embrittlement. These two types of cracking failures respond differently to environmental variables. To illustrate cathodic protection is an effective method of preventing stress corrosion cracking where as it rapidly accelerates hydrogen – emrittlement effects. Hence the importance of considering stress corrosion cracking and hydrogen embrittlement as separate phenomena is obvious. For this reason two cracking phenomena are considered. During stress corrosion cracking the metal or alloy is virtually attacked over most of its surface, while fine cracks progress through it. This cracking phenomenon has serious consequences since it can occur at stresses within the range of typical design stresses. The stresses required for stress corrosion cracking are compared with the total range of strength capability for type 304 stainless steel.

Lesson 8. Prevention methods of corrosion

The most common method of preventing corrosion is the selection of the proper materials for a particular corrosive service. Since this is the most important method of preventing corrosion damage. Stainless steel is the generic name for a series alloys containing chromium and nickel, together with other alloy additions. Stainless steels have widespread application in resisting corrosion, but it should be remembered that they do not resist all corrosives. In fact, under certain conditions, such as chloride-containing medium and stressed structures, stainless steels are less resistant than ordinary structural steel. Stainless alloys are more susceptible to localized corrosion such as intergranular corrosion, stress-corrosion cracking, and pitting attack than ordinary structural steels. Many stainless steel alloys are magnetic, and many of the cast austenitic stainless steels show some ferromagnetic properties. There is no correlation between magnetic susceptibility and corrosion resistance. Under certain conditions many of the magnetic stainless steels are superior to the nonmagnetic varieties.

In many instances, cheaper materials or more resistant materials are available. For nitric acid service, the stainless steels are usually considered first, as these have excellent resistance. Tin or tin coatings are almost always chosen as a container or piping material for very pure distilled water. For many years, tantalum has been considered and used as an ultimate corrosion-resistant material. Tantalum is resistant to most acids at all concentrations and temperatures and is generally used under conditions, where minimal corrosion is required, such as implants in the human body. Glass and tantalum are resistant to virtually all mediums except hydrofluoric acid and caustic solutions. There are some general, rules that may be applied to the resistance of metals and alloys. For reducing or non-oxidizing environments, such as air-free acids and aqueous solutions, nickel, copper, and their alloys are frequently employed. For oxidizing conditions, chromium containing alloys are used. For extremely powerful oxidizing conditions, titanium and its alloys have shown superior resistance.

8.1 METAL PURIFICATION

The corrosion resistance of a pure metal is usually better than that of one containing impurities or small amounts of other elements. However, pure metals are usually expensive and are relatively soft and weak. In general, this category is used in relatively few cases which are more or less special. Aluminium is a good example because it is not expensive in a fairly pure state 99.5% plus. The commercially pure metal is used for handling hydrogen peroxide, where the presence of other elements may cause decomposition because of catalytic effects. In another case, localized attack of aluminium equipment occurred because of segregation of impurity iron in the alloy. Reduction of the maximum iron content, agreeable to both producer and user eliminated the localized attack and satisfactory performance of the equipment was obtained without added cost of material. Another example is arc-melted zirconium, which is more corrosion resistant than induction-melted zirconium because of more impurities in the latter. This is a special case in an atomic-energy application where a little corrosion is too much.

8.2 NON METAL

This category involves solid non-metallic construction and also sheet linings or coverings of substantial thickness (to differentiate from paint coatings). The five general classes of non-metallic are:

1. natural and synthetic rubbers
2. plastics
3. ceramics
4. carbon and graphite

5. wood

In general, rubbers and plastics, as compared with metals and alloys, are much weaker, softer, more resistant to chloride ions and hydrochloric acid, less resistant to strong sulphuric acid and oxidizing acids such as nitric, less resistant to solvents, and have relatively low temperature limitations (75 to 90°C). Ceramics possess excellent corrosion and high-temperature resistance, with the main disadvantages being brittleness and lower tensile strength. Carbons show good corrosion resistance, electric and heat conductivity, but they are fragile. Wood is attacked by aggressive environments. Rubber linings for tanks, lines, fans, filters, scrubbers, etc. This manual contains sections on rubbers used, selection, testing, and design, and fabrication, preparation of equipment to be lined, processing, inspection, acceptance, maintenance, chemical resistance and cost factors. Good and bad practices are described. Hard and soft natural rubbers, polychloroprene and butyl rubbers are included.

8.3 ALTERATION OF THE ENVIRONMENT

8.3.1 Changing Mediums altering the environment provides a versatile means for reducing corrosion. Typical changes in the medium that are often employed are (1) lowering temperature, (2) decreasing velocity, (3) removing oxygen or oxidizers, and (4) changing concentration. In many cases, these changes can significantly reduce corrosion, but they must be done with care. The effects produced by these changes vary depending on the particular system.

8.3.2 Lowering temperature: This usually causes a pronounced decrease in corrosion rate. However, under some conditions, temperature changes have little effect on corrosion rate. In other cases, increasing temperature decreases attack. This phenomenon occurs as hot, fresh or salt water is raised to the boiling point and is the result of the decrease in oxygen solubility with temperature. Boiling sea water is therefore less corrosive than hot sea water (e.g., 65°F).

8.3.3 Decreasing velocity: This is often used as a practical method of corrosion control. Velocity generally increases corrosive attack, although there are some important exceptions. Metals and alloys that passivate, such as stainless steels, generally have better resistance to flowing mediums than stagnant solutions. Very high velocities should be always avoided where possible, because of erosion-corrosion effects.

8.3.4 Removing oxygen or oxidizers: This is a very old corrosion control technique. Boiler feed water was de-aerated by passing it through a large mass of scrap steel. In modern practice this is accomplished by vacuum treatment, inert gas sparging, or through the use of oxygen scavengers. Hydrochloric acid that has contacted steel during its manufacture or storage contains ferric chloride as an oxidizer impurity. This impure acid, termed muriatic acid in commerce rapidly corrodes nickel-molybdenum alloys, whereas these materials possess excellent resistance in pure hydrochloric acid. Although de-aeration finds widespread application, it is not recommended for active-passive metals or alloys. These materials require oxidizers to form and maintain their protective films and usually possess poor resistance to reducing or non-oxidizing environments.

8.3.5 Changing concentration: Decreasing corrosive concentration is usually elective. In many processes, the presence of a corrosive is accidental. For example, corrosion by the water coolant in nuclear reactors is reduced by eliminating chloride ions. Many acids such as sulphuric and phosphoric are virtually inert at high concentrations at moderate temperatures. In these cases, corrosion can be reduced by increasing acid concentration.

No discussion of corrosion control would be complete without mentioning the magic devices or water conditioning gadgets that have been and continue to be widely sold for purposes of controlling water corrosion. These gadgets are usually promoted on the basis that they will stop corrosion, prevent scaling, destroy bacteria, and improve taste and odour, or reduce water hardness. Some manufacturers make all of the above claims for their product. In every case, the device is based on some pseudoscientific principle, is simply constructed, quite expensive, and totally worthless. Several of them consist merely of a pipe coupling that looks identical to those available in any hardware store.

Magic devices should not be confused with the water-softening, water-treating and cathodic protection apparatus and systems sold by reputable manufacturers. The worthless device is easily spotted by a number of clues:

(1) it is based on a questionable or a "secret" new principle. (2) The advertising contains an excessive number of testimonials. (3) The promotion makes no mention of any limitations the device will work in any kind of water and protect any size system. (4) The device is always sold with a complete guarantee.

8.4 INHIBITORS:

An inhibitor is a substance that, when added in small concentrations to an environment, decreases the corrosion rate. An inhibitor can be considered as a retarding catalyst. There are numerous inhibitor types and compositions. Most inhibitors have been developed by empirical experimentation, and many inhibitors are proprietary in nature and thus their composition is not disclosed. Inhibition is not completely understood because of these reasons, but it is possible to classify inhibitors according to their mechanism and composition.

Adsorption-type inhibitors: These represent the largest class of inhibiting substances. In general, these are organic compounds which adsorb on the metal surface and suppress metal dissolution and reduction reactions. In most cases, it appears that adsorption inhibitors affect both the anodic and cathodic processes, although in many cases the effect is unequal. Typical of this class of inhibitors are the organic amines.

8.5 CATHODIC AND ANODIC PROTECTION

8.5.1 Cathodic Protection

Cathodic protection was employed before the science of electrochemistry had been developed. The principles of cathodic protection may explained by considering the corrosion of a typical metal M in an acid environment. Electrochemical reactions occurring are the dissolution of the metal and the evolution of hydrogen gas;

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

$$2H^{+} + 2e \rightarrow H_2$$

Cathodic protection is achieved by supplying electrons to the metal structure to be protected. Examination of above equations indicates that addition of electrons to the structure will tend to suppress metal dissolution and increase the rate of hydrogen evolution. If current is considered to flow from (+) to (-), as in conventional electrical theory, then a structure is protected if current enters it from the electrolyte. Conversely, accelerated corrosion occurs if current passes from the metal to the electrolyte. This current convention has been adopted in cathodic protection technology and is used here for consistency.

There are two ways to cathodically protect a structure : (1) by an external power supply or, (2) by appropriate galvanic coupling. An external dc power supply is connected to an underground tank, and the negative terminal of the power supply is connected to the tank, and the positive to an inert anode such as graphite. The electric leads to the tank and the inert electrode are carefully insulated to prevent current leakage. The anode is usually surrounded by backfill consisting of coke breeze, gypsum or bentonite, which improves electric contact between the anode and the surrounding soil. Current passes to the metallic structure, and corrosion is suppressed.

Cathodic protection by galvanic coupling: Magnesium is anodic with respect to steel and corrodes preferentially when galvanically coupled. The anode in this case is called a sacrificial anode since it is consumed during the protection of the steel structure. Cathodic protection using sacrificial anodes can also be used to protect buried pipelines. The anodes are spaced along the pipe to ensure uniform current distribution. Protective currents are usually determined empirically. Aggressive corrosives such as hot acids require prohibitively high currents, whereas much lower currents are needed to protect steel in less severe environments. For example, in certain very acidic soils, 10 to 15 mA is often needed to reduce the corrosion of steel structures to tolerable levels. Also, pipes with organic coatings require much lower currents since the only areas requiring protection are defects in the protective layer. In such cases, trial-and-error adjustments of anode size or applied current can be made until satisfactory protection is achieved. A more accurate and less time-consuming approach is to measure the potential of the protected structure with a suitable reference electrode.

8.5.2 Anodic Protection

In contrast to cathodic protection, anodic protection is relatively new. This technique was developed using electrode kinetics principles. Anodic protection is based on the formation of a protective film on metals by externally applied anodic currents. It appears that the application of anodic current to a structure should tend to increase the dissolution rate of a metal and decrease the rate of hydrogen evolution. This usually does occur except for metals with active-passive transitions such as nickel, iron, chromium, titanium, and their alloys. If carefully controlled anodic currents are applied to these materials, they are passivated and the rate of metal dissolution is decreased. To anodically protect a structure, a device called a potentiostat is required. A potentiostat is an electronic device that maintains a metal at a constant potential with respect to a reference electrode. The potentiostat has three terminals, one connected to the tank, another to an auxiliary cathode (a platinum or platinum-clad electrode), and the third to a reference electrode (calomel cell). In operation, the potentiostat maintains a constant potential between the tank and the reference electrode. The optimum potential for protection is determined by electrochemical measurements. Anodic protection can decrease corrosion rate substantially.

8.6 ORGANIC COATINGS

These involve a relatively thin barrier between substrate material and the environment. Paints, varnishes, lacquers, and similar coatings protect more metal on a tonnage basis than any other method for combating corrosion. Exterior surfaces are most familiar, but inner coatings or linings are also widely utilized. These coatings should not be used where the environment would rapidly attack the substrate material.

Aside from proper application, the three main factors to consider for organic coatings, are (1) surface preparation, (2) priming coat, and (3) selection of top coat. If the metal surface is not properly prepared, the paint may peel off because of poor bonding. If the primer does not have good adherence or is not compatible with the top coat, early failure occurs. If the first two factors are wrong, the system will fail regardless of the top coat used. Poor paint performance is, in most cases, due to poor application and surface preparation.

Surface preparation involves surface roughening to obtain mechanical bonding (teeth) as well as removal of dirt, rust, mill scale, oil, grease, welding flux, crayon marks, wax, and other impurities. In other words a clean, rough surface is needed. The best method is to grit-blast or sandblast the steel surface. Other methods are pickling and other types of chemical treatments, scraping, wire brushing, flame cleaning (heat with torch and scrape off dirt and scale), chiselling, and chipping. Pinholes in welds and sharp edges should be ground out to ensure contact between the paint and the metal. Other chemical methods are solvent degreasing, hot or cold alkali treatments, phosphatising, chromate treatment and electro chemical treatments such as anodizing and cathodic cleaning.

Module 5. Water Hardness

Lesson 9. Water Treatment

9.1 INTRODCTION

Water is nature's most wonderful, abundant and useful compound. Of the many essential elements for the existence of human beings, animals and plants (wiz. air, water, food, shelter, etc.), water is rated to be of the greatest importance. Without food, human call survives for a number of days, but water is such an essential thing that without it one cannot survive.

Water is not only essential for the lives of animals and plants, but also occupies a unique position in industries. Probably, its most important use as an engineering material is in the 'steam generation '. Water is also used a coolant in power and chemical plants. In addition to it, water is widely used in other fields such as production of steel, rayon, paper, atomic energy, textiles, chemicals, ice, and for air-conditioning, drinking, bathing, sanitary, washing, irrigation, fire-fighting, etc.

9.2 SOURCES OF WATER:

9.2.1 Surface waters:

(i). Rain water is probably the purest form of natural water, since it is obtained as a result of evaporation from the surface water. However, during the journey downwards through the atmosphere, it dissolves a considerable amount of industrial gases (like CO_2, SO_2, NO_2, etc.) and suspended solid particles, both of organic and inorganic origin.

(ii). River water: Rivers are fed by rain and spring waters. Water from these sources flow over the surface of land, dissolves the soluble minerals of the soil and finally falls in rivers. In general, the greater the contact that water has with the soil, or the more soluble the minerals of the soils with which it has come in contact, the greater is the amount of dissolved impurities in river water. River water thus contains dissolved minerals of the soil such as chlorides, sulphates, bicarbonates of sodium, calcium, magnesium and iron. River water also contains the organic matter, derived from the decomposition of plants, and small particles of sand and rock suspension. Thus, river water contains considerable amounts of dissolved as well as suspended impurities.

(iii). Lake water has a more constant chemical composition. It, usually, contains much lesser amount of dissolved minerals than well water, but quantity of organic matter present in it is quite high.

(iv). Sea water is the most impure form of the water. Rivers join sea and throw in the impurities carried by them. Moreover, continuous evaporation of water from the surface of sea makes sea water continuously richer in dissolved impurities. Sea water contains, on an average, about 3.5% of dissolved salts, out of which about 2.6% is sodium chloride. Other salts present are sulphates of sodium; bicarbonates of potassium magnesium and calcium; bromides of potassium and magnesium and a number of other compounds.

Surface water, generally, contains suspended matter, which often contains the disease–producing (or pathogenic) bacteria's. Hence, such waters as such are not considered to be safe for human consumption.

9.2.2 Underground waters: A part of the rain water, which reaches the surface of the earth, percolates into the earth. As this water journeys downwards, it comes in contact with a number of mineral salts present in the soil and dissolves some of them. Water continues its downwards journey, till it meet a hard rock, when it retreads upwards and it may even come out in the form of 'spring'.

9.2.3 Spring and well water (or underground water), in general, is clearer in appearance due to the filtering action of the soil, but contain more of dissolved salts. Thus, water from these sources contains more hardness. Usually, underground water is of high organic purity.

9.3 CHARACTERISTICS IMPARTED BY IMPURITIES IN WATER

The natural water is, usually, contaminated by different types of impurities. The characteristic and consequent effects of impurities on the quality of water are discussed under the following three heads:

9.3.1 Physical impurities:

(a) Color in water is caused by metallic substances like salts of iron, manganese, humus materials, tannins, peat, algae, weeds, protozoa, industrial effluents (from paper and pulp, textile, tanneries, etc). Actually, color in water is due to dissolved substances and substances present as fine colloids. The change in color of water is not harmful, unless it is associated with any chemical of toxic nature. Variations in color of water from the same source (say a river) with time often serves as indices of quality of water. Usually, yellowish tinge indicates the presence of chromium and appreciable amount of organic matter. Yellowish-red color indicates the presence of iron; while red-brown color indicates the presence of peaty matter.

(b) Turbidity is due to the colloidal, extremely fine suspension such as clay, slit, finely divided matters (organic and inorganic) micro-organisms like plankton, etc. Turbidity expresses the optical properties of water containing insoluble substances, which scatter light rather than to transmit in straight lines. The turbidity depends not only on the quantity of insoluble substances, but also on their size, shape and refractive index. Turbidity in water can be eliminated by sedimentation, followed by coagulation, filtration, etc.

(c) Taste is, usually, interlinked directly with odor. However, in some waste water, taste is not accompanied by odor. Thus, presence of dissolved mineral in water produces taste, but not odor. For example;

(i) Bitter taste can be due to the presence of iron, aluminum, manganese, sulphate or excess of lime.

(ii) Soapy taste can be due to the presence of large amount of sodium bicarbonate.

(iii) Brackish taste is due to the presence of unusual amount of salts.

(iv) Palatable taste is due to the presence of dissolved gases (CO_2) and minerals (like nitrates) in water.

(d) Odor in water is undesirable for domestic as well as industrial purposes. Disagreeable odor in water may be caused by the presence of living organisms, decaying vegetation including algae, bacteria, fungi and weeds. The receiving water may be offensive where heavy pollution is caused by sewage/industrial effluents. The most common disagreeable odor in water bodies is due to presence of small quantity of sulphides. The causes of odor in polluted rivers are;

(i) Presence of inorganic and organic compounds of N, S and P and the putrefaction of proteins and other organic materials present in sewage;

(ii) Industrial effluents containing organic substances such as alcohols, aldehydes, phenols, esters, ketones, etc. flowing into the water bodies.

Besides these : (i) presence of algae in water bodies impart a strong grassy odor, due to the liberation of traces of essential oils from their bodies, (ii) growth of iron and sulphur bacteria may produce offensive odors, (iii) presence of colloidal vegetable matter in surface-water evolves a faint flavor, called 'peaty' odor, (iv) clay and sand in finely divided state impart a faint earthy odor, (v) improper bituminous coating on cast iron main pipes may give off a tarry odor to water which passes through it, (vi) a faint odor is imparted to water passing through new iron or galvanized. This odor is due to the impure hydrogen.

9.3.2 Chemical impurities in water includes: (1) inorganic and organic chemicals (some are toxic immature) released from dyes, paints, and vanishes, drugs, insecticides, pesticides, detergent, pulp and textiles, industries, canneries, etc. All these pollute water bodies, (2) acids discharged in water by DDT, high explosives, battery, industries, etc. The use of this type of contaminated water causes harmful effects on health of human-beings.

(a) Acidity is not any specific pollutant and it simply determines the power to neutralize hydroxyl ions and is, usually, expressed in terms of ppm (or mg/L) of calcium carbonate equivalent. Surface waters and ground waters attain acidity from industrial wastes like acid, mine, drainage, pickling liquors, etc. Usually, acidity is caused by the presence of free CO_2, mineral acids (e.g., H_2SO_4) and weakly dissociated acids. Mineral acids are released when iron and aluminum salts hydrolyze.

(b) Gases: (i) All natural waters contain dissolved atmosphere CO_2. Its solubility depends upon temperature, pressure and dissolved mineral content of water. Also polluted waters acquire CO_2 from the biological oxidation of organic matter. It's presence in water is of no significance.

(ii) Concentration of dissolved atmospheric O_2 in waters depends on temperature, pressure and salt content in water. Dissolved O_2 in industrial waters is nuisance, since it induces corrosion reactions. On the other hand, dissolved O_2 in water is essential to the life of aquatic organisms such as fishes.

(iii) Dissolved NH_3 in water arises from the decomposition (aerobic or anaerobic) of nitrogenous organic matter. Polluted waters and sewages contain nitrogen in the form of nitrogenous organic compounds and urea, which are partially converted into NH_3.

(c) Mineral matters have origin from rocks and industrial effluents. These include mineral acids, Ca^{2+}, Mg^{2+}, Na^+, K^+, Fe^{2+}, CO_3^{2-}, Mn^{2+}, $HC0_3^-$, Cl^-, SO_4^{2-}, $N0_3^-$, F^-, SiO_2 etc. However, from industrial point of view, alkalinity and hardness are important.

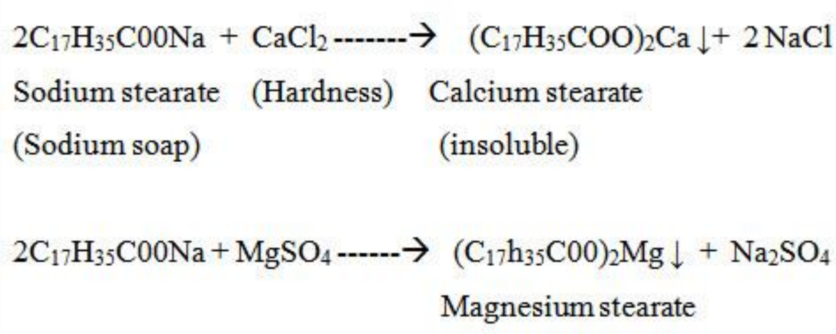
(3) Biological impurities are algae, pathogenic bacteria, fungi, viruses, pathogens, parasite worms, etc. The source of this contamination is discharge of domestic and sewage wastes, excreta (from man, animals and birds) etc.

(a) Micro-organisms are, usually; abundant in surface waters, but their count is often quite low or even nil in deep-well waters. The commonest type of micro-organisms from the point of treatment are algae, fungi and bacteria, which often form 'slime ', thereby causing fouling as well as corrosion. The slime so-formed clogs the spray nozzles and screens of the circulating pumps in air-conditioning and other industrial plants. The growth of micro-organisms takes place at temperature between 20-35^{o}C. In order to control the micro-organisms, chemical treatment like chlorination is done.

(b) Water bodies in water includes: (i) bacteria, organisms inhabitation the bottom sludge, and (ii) organisms and planktons developed at the water surface. These are inhabitated by different group of worms like flat worms, hair worms tiny round worms, rotifers, etc. Usually, most worms are parasite in nature and these water bodies are not only harmful to fishes, but also to human health.

9.4 HARDNESS OF WATER

Hardness in water is that characteristic, which prevents the lathering of soap. This is due to presence in water of certain salts of calcium, magnesium and other heavy metals dissolved in it. A sample of hard water, when treated with soap (sodium or potassium salt of higher fatty acid like oleic, palmitic or stearic) does not produce lather, but on the other hand forms a white scum or precipitate. This precipitate is formed, due to the formation of insoluble soaps of calcium and magnesium. Typical reactions of soap (sodium stearate) with calcium chloride and magnesium sulphate are depicted as follows:

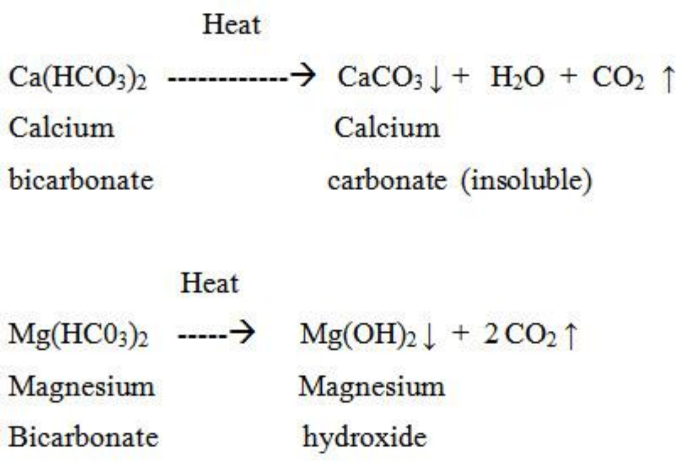


$$\underset{\text{Sodium stearate (Sodium soap)}}{2C_{17}H_{35}C00Na} + \underset{\text{(Hardness)}}{CaCl_2} \dashrightarrow \underset{\text{Calcium stearate (insoluble)}}{(C_{17}H_{35}COO)_2Ca\downarrow} + 2\,NaCl$$

$$2C_{17}H_{35}C00Na + MgSO_4 \dashrightarrow \underset{\text{Magnesium stearate}}{(C_{17}h_{35}C00)_2Mg\downarrow} + Na_2SO_4$$

Thus, water which does not produce lather with soap solution readily, but forms a white curd, is called hard water. On the other hand, water which lathers easily on shaking with soap solution, is called soft water. Such water, consequently, does not contain dissolved calcium and magnesium salts in it.

(1) Temporary or carbonate hardness is caused by the presence of dissolved bicarbonates of calcium, magnesium and other heavy metals and the carbonate of iron. Temporary hardness is mostly destroyed by mere boiling of water, when bicarbonates are decomposed, yielding insoluble carbonates or hydroxides, which are deposited as a crust at the bottom of vessel. Thus;



$$\underset{\text{Calcium bicarbonate}}{Ca(HCO_3)_2} \xrightarrow{\text{Heat}} \underset{\text{Calcium carbonate (insoluble)}}{CaCO_3\downarrow} + H_2O + CO_2\uparrow$$

$$\underset{\text{Magnesium Bicarbonate}}{Mg(HC0_3)_2} \xrightarrow{\text{Heat}} \underset{\text{Magnesium hydroxide}}{Mg(OH)_2\downarrow} + 2\,CO_2\uparrow$$

(2) Permanent or non-carbonate hardness is due to the presence of chlorides and sulphates of calcium, magnesium, iron and other heavy metals. Unlike temporary hardness, permanent hardness is not destroyed on boiling.

9.5 EQUIVALENTS OF CALCIUM CARBONATE

The concentration of hardness as well as non-hardness constituting ions are, usually expressed in terms of equivalent amount of $CaCO_3$, since this mode pemlits the multiplication and division of concentration, when required. The choice of $CaCO_3$ in particular is due to its molecular weight is 100 (equivalent weight = 50) and moreover, it is the most insoluble salt that can be precipitated during water treatment.

The equivalents of $CaC0_3$,

$$= \frac{[\text{Mass of hardness producing-substance}] \times [\text{Chemical equivalent of } CaCO_3]}{\text{Chemical equivalent of hardness-producing substance}}$$

$$= \frac{\text{Mass of hardness-producing substance} \times 50}{\text{Chemical equivalent of hardness-producing substance}}$$

9.6 UNITS OF HARDNESS

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

(2) Milligrams per liter (mg/L) are the number of milligrams of $CaCO_3$ equivalent hardness present per liter of water. Thus;

1 mg/L = 1 mg of $CaCO_3$ eq. hardness of 1 L of water

But 1 L of water weighs

= 1 kg = 1,000 g = 1,000 x 1,000 mg = 10^6 mg.

$\therefore$ 1mg/L = 1 mg of $CaCO_3$ eq. per 10^6 mg of water.

= 1 part of $CaCO_3$ eq. per 10^6 parts of water = 1 ppm

(3) Clarke's degree (^{o}CI) is number of grains (l/7000 1b) of $CaCO_3$ equivalent hardness per gallon(10lb) of water. Or it is parts of $CaCO_3$ equivalent hardness per 70,000 parts of water. Thus:

l^{o} Clarke = 1 grain of $CaC0_3$ eq. hardness per gallon of water.

1^{o} CI= 1 part of $CaC0_3$ eq. hardness per 70,000 parts of water.

(4) Degree French (^{o}Fr) is the parts of $CaCO_3$ equivalent hardness per 10^5 parts of water. Thus:

1^{o} Fr = 1 part of $CaCO_3$ hardness eq. per 10^5 parts of water.

(5) Mille equivalent per liter (meq/L) is the number of mill equivalents of hardness present per liter. Thus;

1 meq/L = 1 meq of $CaCO_3$ per L of water

= 10^{-3} x 50 g of $CaCO_3$ eq. per liter

= 50 mg of $CaCO_3$ eq. per liter

= 50 mg/L of $CaCO_3$ eq. = 50 ppm.

Relationship between various units of hardness:

1 ppm = 1 mg/L = 0.1° Fr = 0.07'°Cl = 0.02 meq/L

1 mg/L =1 ppm = 0.1° Fr = 0.1° Fr = 0.02 meq/L

1° Cl = 1.433° Fr = 14.3 ppm = 14.3 mg/L = 0.286 meq/L

1° Fr = 10 ppm =10 mg/L =0.07° Cl = 0.2 meq/L

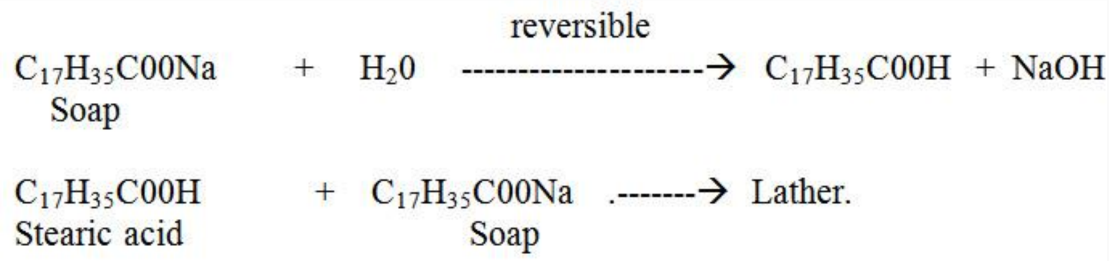
1meq/L = 50 mg/L =50ppm = 5° Fr = 0.35° Cl

Lesson 10. Disadvantages of hard Water

10.0 DISADVANTAGES OF HARD WATER

10.1.1 In domestic use:

(i) Washing: Hard water, when used for washing purposes, does not lather freely with soap. On the other hand, it produces sticky precipitates of calcium and magnesium soaps. The formation of such insoluble, sticky precipitated continues, till all calcium and magnesium salts present in water are precipitated. After that, the soap (e.g., sodium stearate) gives lather with water. Thus;



$$\underset{\text{Soap}}{C_{17}H_{35}C00Na} + H_20 \xrightarrow{\text{reversible}} C_{17}H_{35}C00H + NaOH$$

$$\underset{\text{Stearic acid}}{C_{17}H_{35}C00H} + \underset{\text{Soap}}{C_{17}H_{35}C00Na} \longrightarrow \text{Lather.}$$

This causes wastage of soap being used. Moreover, the sticky precipitate (of calcium and magnesium soaps) adheres on the fabric/cloth giving spots and streaks. Also presence of iron salts may cause staining of cloth.

(ii) Bathing: Hard water does not lather freely with soap solution, but produces sticky scum on the bath-tub and body. Thus, the cleansing quality of soap is depressed and a lot of it is wasted.

(iii) Cooking: Due to the presence of dissolved hardness-producing salts, the boiling point of water is elevated. Consequently, more fuel and time are required for cooking certain foods such as pulses, beans and peas do not cook soft in hard water. Also tea or coffee, prepared in hard water, has an unpleasant taste and muddy-looking extract. Moreover, the dissolved salts are deposited as carbonates on the inner walls of the water heating utensils.

(iv)Drinking: Hard water causes bad effect on our digestive system. Moreover, the possibility of forming calcium oxalate crystals in urinary tracks is increased.

10.1.2 Industrial use: (i) Textile industry: Hard water causes much of the soap (used in washing yarn, fabric etc.) to go as waste, because hard water cannot produce good quality of lather. Moreover, precipitated of calcium and magnesium soaps adhere to the fabrics. These fabrics, when dyed latter on, do not produce exact shades of color. Iron and manganese salts-containing water may cause colored spots on fabrics, thereby spoiling their beauty.

(ii) Sugar industry: Water containing sulphates, nitrates, alkali carbonated, etc., if used in sugar refining, causes difficulties in the crystallization of sugar. Moreover, the sugar so-produced may be deliquescent.

(iii) Dyeing industry: The dissolved calcium, magnesium and iron salts in hard water may react with costly dyes, forming undesirable precipitated, which yields impure shades and give spots on the fabrics being dyed.

(iv) Paper industry: Calcium and magnesium salts tend to react with chemicals and other materials employed to provide a smooth and glossy (i.e., shining) finish to paper. Moreover, iron salts may even affect the color of the paper being produced.

(v) Laundry: Hard water, if used in laundry, causes much of the soap used in washing to go as waste. Iron salts may even cause coloration of the clothes.

(vi) Concrete making: Water containing chlorides and sulphates, if used for concrete making, affects the hydration of cement and the final strength of the hardened concrete.

(vii) Pharmaceutical industry: Hard water, if used for preparing pharmaceutical products (like drugs, injections, ointments, etc.) may produce certain undesirable products in them.

10.1.3 In steam generation in boilers: For steam generation, boilers are almost invariably employed. If the hard water is fed directly to the boilers, there arise many troubles such as: (i) scale and sludge formation, (ii) corrosion,(iii) priming and foaming and (iv) caustic embrittlement.

10.2 SOFTENING METHODS

Water used for industrial purposes (such as for steam generation) should be sufficiently pure. It should, therefore, be freed from hardness-producing salts before put to use. The process of removing hardness-producing salts from water, is known as softening of water. In industry, main three methods employed for water softening. Like;

10.2.1 Lime-soda process: In this method, the soluble calcium and magnesium salts in water are chemically converted into insoluble compounds, by adding calculated amounts of lime ($Ca(OH)_2$) and soda (Na_2CO_3). Calcium carbonate ($CaCO_3$) and Magnesium hydroxide ($Mg(OH)_2$) are precipitated and are filtered off.

10.2.1.1 Cold lime-soda process: In this method, calculated quantity of chemical (lime and soda) is mixed with water at room temperature. At room temperature, the precipitates formed are finally divided, so they do not settle down easily and con not be filtered easily. It is essential to add small amount of coagulants which hydrolyze to flocculent, gelatinous precipitate of aluminum hydroxide, and entraps the fine precipitates. Use of sodium aluminates as coagulant also helps the removal of silica as well as oil, if present in water. Cold L-S process provides water, containing a residual hardness of 50 to 60 ppm.

$$NaAIO_2 + 2H_2O \text{ ---------}\rightarrow NaOH + AI(OH)_3$$
$$AI_2(SO_4)_3 + 3Ca(HCO_3)_2 \text{ --------}\rightarrow 2AI(OH)_3 + 3CaSO_4 + 6CO_2$$

Method: Raw water and calculated quantities of chemicals (lime + soda + coagulant) are fed from the top into the inner vertical circular chamber, fitted with a vertical rotating shaft carrying a number of paddles. As the raw water and chemicals flow down, there is a vigorous stirring and continuous mixing, whereby softening of water takes place. As the softened water comes into the outer co-axial chamber, it rises upwards. The heavy sludge (or precipitated flock settles down in the outer chamber by the time the softened water reaches up. The softened water then passes through a filtering media (usually made of wood fibers) to ensure complete removal of sludge. Filtered soft water finally flows out continuously through the outlet at the top. Sludge settling at the bottom of the outer chamber is drawn off occasionally.

10.2.1.2 Hot lime-soda process involves in treating water with softening chemicals at a temperature of 80 to 150 ^{0}C. Since hot process is operated at a temperature close to the boiling point of the solution, so :

(i) the reaction proceeds faster.

(ii) the softening capacity of hot process is increased to many fold.

(iii) the precipitate and sludge formed settle down rapidly and hence, no coagulants are needed.

(iv) much of the dissolved gases (such as CO_2 and air) driven out of the water

(v) viscosity of softened water is lower, so filtration of water becomes much easier.

This in-turn increases the filtering capacity of filters.

(vi) hot lime-soda process produces water of comparatively lower residual hardness of 15 to 30 ppm.

Advantages of Lime-Soda process :

(i) it is very economical.

(ii) if this process is combined with sedimentation with coagulation, lesser amounts of coagulants shall be needed.

(iii) The process increases the pH value of the treated-water; thereby corrosion of the distribution pipes is reduced.

(iv) Besides the removal of hardness, the quantity of minerals in the water is reduced.

(v) To certain extent, iron and manganese are also removed from the water.

(vi) Due to alkaline nature of treated-water, amount of pathogenic bacteria in water is considerably reduced.

Disadvantage of Lime-Soda process:

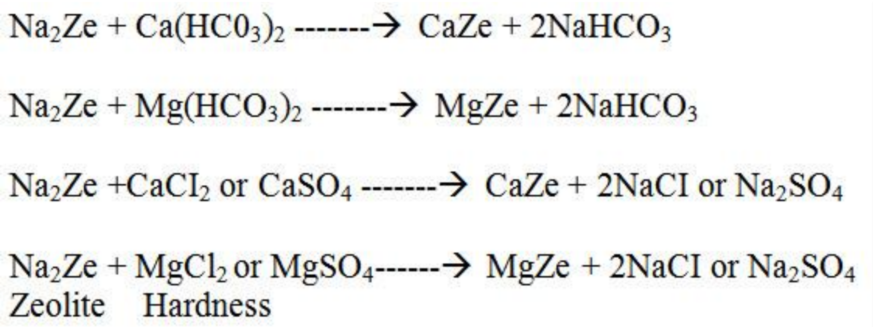
(i) For efficient and economical softening, careful operation and skilled supervision in required.

(ii) Disposal of large amounts of sludge (insoluble precipitate) poses a problem. However, the sludge may be disposed off in raising low-lying areas of the city.

(iii) This can remove hardness only up to 15 ppm, which is not good for boilers.

10.2.2 Zeolite or pemutits process : Chemical structure of sodium zeolite may be represented as : $Na_2O.Al_20_3.xSiO_2.yH_2O$ where x = 2-10 and y = 2-6. Zeolite is hydrated sodium alumino silicate, capable of exchanging reversibly its sodium ions for hardness-producing ions in water. Zeolites are also known as permutits. Zeolites are of typo types : (a) Natural zeolites are non-porous. For example, natrolite, $Na_2O.Al_3OS_4SiO_2.2H_2O$. (b) Synthetic zeolites are porous and possess gel structure. They are prepared by heating together china clay, feldspar and soda ash. Such zeolites possess higher exchange capacity per unit weight than natural zeolites.

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



$Na_2Ze + Ca(HC0_3)_2$ -------→ $CaZe + 2NaHCO_3$

$Na_2Ze + Mg(HCO_3)_2$ -------→ $MgZe + 2NaHCO_3$

$Na_2Ze + CaCI_2$ or $CaSO_4$ -------→ $CaZe + 2NaCI$ or Na_2SO_4

$Na_2Ze + MgCl_2$ or $MgSO_4$------→ $MgZe + 2NaCI$ or Na_2SO_4
Zeolite Hardness

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

$CaZe$ or $MgZe + 2NaCI$ -----> $Na_2Ze + CaCI_2$ or $MgCl_2$

The washings containing $CaCl_2$ and $MgCl_2$ are led to drain and the regenerated zeolite bed thus-obtained is used again for softening purpose.

Limitation of zeolite process:

(i) if the supply of water is turbid, the suspended matte must be removed (by coagulation, filtration, etc.), before the water is admitted to the zeolite bed; otherwise the turbidity will clog the pores of zeolite bed, thereby making it inactive.

(ii) if water contains large quantities of coloured ions such as Mn^{2+} and Fe^{2+}, they must be removed first, because these ions produce manganese and iron zeolites, which cannot be easily regenerated.

(iii) Mineral acids, if present in water, destroy the zeolite bed and, therefore, they must be neutralized with soda, before admitting the water to the zeolite softening plant.

Advantages of zeolite process:

(i) it removes the hardness almost completely and water of about 10 ppm hardness is produced.

(ii) The equipment used is compact, occupying a small space.

(iii) No impurities are precipitated, so there is no danger of sludge formation in the treated-water at a later stage.

(iv) The process automatically adjusts itself for variation in hardness of incoming water.

(v) it is quite clean.

(vi) it requires less time for softening.

(vii) it requires less skill for maintenance as well as operation.

Disadvantages of zeolite process:

(i) The treated-water contains more sodium salts than in lime-soda process.

(ii) The method only replaces Ca^{2+} and Mg^{2+} ions by Na^+ ions, but leaves all the acidic ions like HCO_3^- and CO_3^{2-} as such in the softened water. When such softened water (containing $NaHCO_3$, Na_2CO_3 etc.)

is used in boilers for steam generation, sodium bicarbonate decomposes producing CO_2, which causes corrosion ; and sodium carbonate hydrolysis to sodium hydroxide, which causes caustic embrittlement.

(iii) High turbidity water cannot be treated efficiently by this method, because fine impurities get deposited on the zeolite bed, thereby creating problem for its working.

10.2.3 Ion exchange or de-ionization or de-mineralization process : Ion-exchange resins are insoluble, cross-linked, long chain organic polymers with a microporous structure, and the "functional groups" attached to the chains are responsible for the ion-exchanging properties. Resins containing acidic functional groups (− C00H, − SO_3H etc.) are capable of exchanging their H^+ ions with other cations, which comes in their contact; whereas those containing basic functional groups (− NH_2 = NH as hydrochloride salt) are capable of exchanging their anions with other anions, which comes in their contact. The ion-exchange resins may be classified as:

(i) Cation exchange resins (RH^+) are mainly styrene-divinyl benzene copolymers, which on sulphonation or carboxylation, become capable to exchange their hydrogen ions with the cations in the water.

(ii) Anion exchange resins ($R'OH^-$) are styrene-divinyl benzene or amine formaldehyde copolymers, which contain amino or' quaternary ammonium or quaternary phosphonium or tertiary sulphonium groups as an integral part of the resin matrix. These, after treatment with dil. NaOH solution, become capable to exchange their OH^- anions with anions in water.

Process: The hard water is passed first through cation exchange column, which removes all the cations like Ca^{2+}, Mg^{2+}, etc. from it, and equivalent amount of H^+ ions are released from this column to water. Thus;

$2RH^+ + Ca^{2+}$ --------.> $R_2Ca^{2+} + 2H^+$

$2RH^+ + Mg^{2+}$ ------.> $R_2Mg^{2+} + 2H^+$

After cation exchange column, the hard water is passed through anion exchange column, which removes all the anions like SO_4^{2-}, Cl^-, etc. present in the water and equivalent amount of OH^- ions are released from this column to water. Thus:

$R'OH^- + Cl^-$ ---..------.> $R'Cl^- + OH^-$

$2R'OH^- + SO_4^{2-}$ ---..--> $R'_2SO_4^{2-} + 2OH^-$

$2R'OH^- + CO_3^{2-}$ ----.-> $R'_2CO_3^{2-} + 2OH^-$

H^+ and OH^- ions (released from cation exchange and anion exchange columns respectively) get combined to produce water molecule.

$H^+ + OH-$ --> H_2O

Thus, the water coming out from the exchanger is free from cations as well as anions. Ion-free water, is known as deionized or demineralised water.

Regeneration: When capacities of cation and anion exchangers to exchange H^+ and OH^- ions respectively are lost, they are then said to be exhausted. The exhausted cation exchange column is regenerated by passing a solution of dil. HCl or dil H_2SO_4. The regeneration can be represented as :

$R_2Ca^{2+} + 2H^+$ ----> $2RH^+ + Ca^{2+}$ (washing)

The column is washed with deionised water and washing (which contains Ca^{2+}, Mg^{2+}, etc. and Cl^- or SO_4^{2-} ions) is passed to sink or drain The exhausted anion exchange column is regenerated by passing a solution of dil. NaOH. The regeneration can be represented as :

$R'_2S0_4^{2-}$ + $2OH^-$ ---> $2R'OH^-$ + SO_4^{2-}(washing)

The column is washed with deionised water and washing (which contains Na^+ and SO_4^{2-} or Cl^- ions) is passed to silk or drain. The regenerated ion exchange resins are then used again.

Advantages:

(i) The process can be used to soften highly acidic or alkaline waters.

(ii) It produces water of very low hardness (say 2 ppm). So it is very good for treating water for use in high-pressure boilers.

Disadvantages:

(i) The equipment is costly and more expensive chemicals are needed.

(ii) If water contains turbidity, then the output of the process is reduced. The turbidity must be below 10 ppm. If it is more, it has to be removed first by coagulation and then by filtration.

Module 6. Scale and sludge formation in boilers, boiler corrosion

Lesson 11. Scale and sludge formation in boilers

In boilers, water evaporates continuously and the concentration of the dissolved salts increases progressively. When their concentrations reach saturation point, they are thrown out of water in the form of precipitates on the inner walls of the boiler. If the precipitation takes place in the form of loose and slimy precipitate, it is called sludge. On the other hand, if the precipitated matter forms a hard, adhering crust/coating on the inner walls of the boiler, it is called scale.

Sludge is a soft, loose and slimy precipitate formed within the comparatively colder portions of the boiler and collects in areas of the system, where the flow rate is slow or at bends. Sludge's are formed by substances which have greater solubility in hot water than in cold water, e.g., $MgCO_3$, $MgCl_2$, $CaCl_2$, $MgSO_4$, etc.

11.1 DISADVANTAGES OF SLUDGE FORMATION :

1. Sludges are poor conductor of heat, so they tend to waste a portion of heat generated.
2. If sludges are formed along with scales, then former gets entrapped in the latter and both get deposited as scales.
3. Excessive sludge formation disturbs the working of the boiler. It settles in the regions of poor water circulation such as pipe connection, plug opening, gauge-glass connection, thereby causing even choking of the pipes.

11.2 PREVENTION OF SLUDGE FORMATION :

(1) By using well softened water, (2) By frequently 'blow-down operation', i.e., drawing off a portion of the concentrated water. Scales are hard deposits, which stick very firmly to the inner surfaces of the boiler. Scales are difficult to remove, even with the help of hammer and chisel. Scales are the main source of troubles. Formation of scales may be due to;

(1) Decomposition of calcium bicarbonate

$$Ca(HCO_3)_2 \rightarrow \underset{\text{Scale}}{CaCO_3} \downarrow + H_2O + CO_2 \uparrow$$

However, scale composed chiefly of calcium carbonate is soft and is the main cause of scale formation in low-pressure boilers. But in high-pressure boilers, $CaCO_3$ is soluble.

$$CaCO_3 + H_2O \rightarrow Ca(OH_2)_2 \text{ (soluble)} + CO_2 \uparrow$$

11.3 DEPOSITION OF CALCIUM SULPHATE :

The solubility of calcium sulphate in water decreases with rise of temperature. Thus, solubility of $CaSO_4$ is 3,200 ppm at 15°C and it reduces to 55 ppm at 230°C and 27 ppm at 320°C. In other words, $CaSO_4$ is soluble in cold water, but almost completely insoluble in super-heated water. Consequently, $CaSO_4$ gets precipitated as hard scale on the heated portions of the boiler. This is the main cause of scales in high-pressure boilers. Calcium sulphate scale is quite adherent and difficult to remove even with the help of hammer and chisel.

(1) Hydrolysis of magnesium salts : Dissolved magnesium salts undergo hydrolysis (at prevailing high temperature inside the boilers) footing magnesium hydroxide precipitate, which forms a soft type of scale e.g.,

$$MgCl_2 + 2H_2O \rightarrow Mg(OH)_2\downarrow + 2HCl\uparrow$$

(2) Presence of silica (SiO_2), even present in small quantities, deposits as calcium silicate ($CaSiO_3$) and/ or magnesium silicate ($MgSiO_3$). These deposits stick very firmly on the inner side of the boiler surface and are very difficult to remove. One important source of silica in water is the sand filter

Disadvantages of scale formation :

(1) Wastage of fuel : Scales have a low thermal conductivity, so the rate of heat transfer from boiler to inside water is greatly decreased. In order to provide a steady supply of heat to water, excessive or over heating is carried out and this causes increase in fuel consumption. The wastage depends upon the thickness and the nature of scale :

thickness of scale (mm)	0.325	0.625	1.25	2.5	12
Wastage of fuel	10%	15%	50%	80%	150%

(2) Lowering of boiler safety : Due to scale formation, over-heating of boiler is to be done in order to maintain a constant supply of steam. The over-heating of the boiler tube makes the boiler material softer and weaker and this causes distortion of boiler tube and makes the boiler unsafe to bear the pressure of the steam, especially in high-pressure boilers.

(3) Decrease in efficiency : Scales may sometimes deposit in the valves and condensers of the boiler and choke them partially. Tills results in decrease in efficiency of boiler.

(4) Danger of explosion : When thick scales crack, due to uneven expansion, the water comes suddenly in contact with over-heated iron plates. This causes formation of a large amount of steam suddenly. So sudden high-pressure is developed, which may even cause explosion of the boiler.

Removal of scales : (i) With the help of scraper or piece of wood or wire brush, if they are loosely adhering. (ii) By giving thermal shocks (i.e., heating the boiler and then suddenly cooling with cold water), if they are brittle. (iii) By dissolving them by adding them chemicals, if they are adherent and hard. Thus, calcium carbonate scales can be dissolved by using 5-10% HCl. Calcium sulphate scales can be dissolved by adding EDTA (ethylene diamine tetra acetic acid), with which they form soluble complexes. (iv) By frequent blow-down operation, if the scales are loosely adhering.

11.4 PREVENTION OF SCALES FORMATION :

(1) External treatment includes efficient 'softening of water' (i.e. removing hardness producing constituents of water).

(2) Internal treatment : In this process (also called sequestration), an ion is prohibited to exhibit its original character by 'complexing' or converting it into other more soluble salt by adding appropriate reagent. An internal treatment is accomplished by adding a proper chemical to boiler water either : (a) to precipitate the scale forming impurities in the form of sludges, which can be removed by blow-down

operation, or (b) to convert them into compounds, which will stay in dissolved form in water and thus do not cause any harm.

Internal treatments methods are, generally, followed by 'blow-down operation', so that an accumulated sludge is removed. Important internal conditioning/treatment methods are;

(i) Colloidal conditioning : In low-pressure boilers, scale formation can be avoided by adding organic substances like kerosene, tannin, agar-agar (a gel), etc., which get coated over the forming precipitates, thereby yielding non-sticky and loose deposits, which can easily be removed by pre-determined blow-down operations.

(ii) Phosphate conditioning : In high-pressure boilers, scale formation can be avoided by adding sodium phosphate, which reacts with hardness of water forming non-adherent and easily removable, soft sludge of calcium and magnesium phosphates, which can be removed by blow - down operation, e.g.,

$$3CaCl_2 + 2Na_3PO_4 \rightarrow Ca_3(PO_4)_2 + 6\ NaCl$$

The main phosphates employed are : (a) NaH_2PO_4, sodium dihydrogen phosphate (acidic); (b) Na_2HPO_4, disodium hydrogen phosphate (weakly alkaline); (c) Na_3PO_4, trisodium phosphate (alkaline).

(iii) Carbonate conditioning : In low-pressure boilers, scale-formation can be avoided by adding sodium carbonate to boiler water, when $CaSO_4$ is converted into calcium carbonate in equilibrium.

$$CaSO_4 + Na_2CO_3 \rightarrow CaCO_3 + Na_2SO_4$$

Consequently, deposition of $CaSO_4$ as scale does not take place and calcium is precipitated as loose sludge of $CaCO_3$, which can be removed by blow-down operation.

(iv) Calgon conditioning involves in adding calgon [sodium hexameta phosphate $(NaPO_3)_6$ to boiler water. It prevents the scale and sludge formation by forming soluble complex compound with $CaSO_4$.

$$Na_2[Na_4(PO_3)_6] \rightarrow 2\ Na^+ + [Na_4P_6O_{18}]^{2-}$$

Calgon

$$2\ CaSO_4 + [Na_4P_6O_{18}]^{2-} \rightarrow [Ca_2P_6O_{18}]^{2-} + 2\ Na_2SO_4$$

Soluble complex ion

(v) Treatment with sodium aluminates ($NaAlO_2$) : Sodium aluminates gets hydrolyzed yielding NaOH and a gelatinous precipitate of aluminium hydroxide.

$$NaAlO_2 + 2H_2O \rightarrow NaOH + Al(OH)_3$$

Sodium meta-aluminate Gelatinous precipitation

The sodium hydroxide, so-formed, precipitates some of the magnesium as $Mg(OH)_2$,

$$MgCl_2 + 2NaOH \rightarrow Mg(OH)_2 + 2\ NaCI$$

The flocculent precipitate of $Mg(OH)_2$ plus $Al(OH)_3$, produced inside the boiler, entraps finely suspended and colloidal impurities, including oil drops and silica. The loose precipitate can be removed by pre-determined blow-down operation.

(vi) Electrical conditioning: Sealed glass bulbs, containing mercury connected to a battery, are set rotating in the boiler. When water boils, mercury bulbs emit electrical discharges, which prevents scale forming particles to adhere / stick together to form scale.

(vii) Radioactive conditioning: Tablets containing radioactive salts are placed inside the boiler water at a few points. The energy radiations emitted by these salts prevent scale formation.

(viii) Complex metric method involves addition of 1.5 % alkaline (pH = 8.5) solution of EDTA to feed-water. The EDTA binds to the scale-forming cations to form stable and soluble complex. As a result, the sludge and scale formation in boiler is prevented. Moreover, this treatment : (1) prevents the deposition of iron oxides in the boiler, (2) reduces the carryover of oxides with steam, and (3) protects the boiler units from corrosion by wet steam (steam containing liquid water).

11.5 CAUSTIC EMBRITTLEMENT:

Caustic embrittlement is a type of boiler corrosion, caused by using highly alkaline water in the boiler. During softening process by lime-soda process, free Na_2CO_3 is usually present in small proportion in the softened water. In high pressure boilers, Na_2CO_3 decomposes to give sodium hydroxide and carbon dioxide,

$$Na_2CO_3 + H_2O \rightarrow 2NaOH + CO_2$$

and this makes the boiler water basic ["caustic"]. The NaOH containing water flows into the minute hair-cracks, always present in the inner side of boiler, by capillary action. Here, water evaporates and the dissolved caustic soda concentration increases progressively. This caustic soda attacks the surrounding area, thereby dissolving iron of boiler as sodium ferroate this causes embrittlement of boiler parts, particularly stressed parts (like bends, joints, rivets, etc.), causing even failure of the boiler.

Caustic embrittlement can be avoided :

1. by using sodium phosphate as softening agent, instead of sodium carbonate ;
2. by adding tannin or lignin to boiler water, since these blocks the hair-cracks, thereby preventing infiltration of caustic soda solution in these;
3. by adding sodium sulphate to boiler water. Na_2SO_4 also blocks hair-cracks, thereby preventing infiltration of caustic soda solutions. It has been observed that caustic cracking can be prevented, if Na_2SO_4 is added to boiler water so that the ratio : $\frac{[\text{Na2SO4 concentrations}]}{[\text{NaOH concentration}]}$

is kept as 1:1:2:1 and 3:1 in boilers working respectively at pressures up to 10, 20 and above 20 atmospheres.

11.6 BOILER CORROSION

Boiler corrosion is decay of boiler material by a chemical or electro-chemical attack by its environment. Main reasons for boiler corrosion are:

(1) Dissolved oxygen : Water usually contains about 8 ml of dissolved oxygen per litre at room temperature. Dissolved oxygen in water, in presence of prevailing high temperature, attacks boiler material:

$$2\,Fe + 2H_2O + O_2 \rightarrow 2\,Fe(OH)_2$$

$$4\,Fe(OH)_2 + O_2 \rightarrow 2\,(Fe_2O_3.2H_2O)$$

Ferrous hydroxide Rust

Removal of dissolved oxygen :

(1) By adding calculated quantity of sodium sulphite or hydrazine or sodium sulphide. Thus;

$$2\,Na_2SO_3 + O_2 \rightarrow 2\,Na_2SO_4$$

$$N_2H_4 + O_2 \rightarrow N_2 + 2\,H_2O$$

Hydrazine

$$Na_2S + 2\,O_2 \rightarrow Na_2SO_4$$

(2) By mechanical de-aeration, i.e., water spraying in a perforated plate-fitted tower, heated from sides and connected to vacuum pump (see Fig. 2). High temperature, low pressure and large exposed surface (provided by perforated plates) reduces the dissolved oxygen in water

Flg. 2. Mechanical de-aeration of water

(2) Dissolved carbon dioxide : CO_2 is carbonic acid,

$$CO_2 + H_2O \rightarrow H_2CO_3$$

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

$$Mg(HCO_3)_2 \rightarrow MgCO_3 + H_2O + CO_2$$

Removal of CO_2 : (1) By adding calculated quantity of ammonia. Thus,

$$2NH_4OH + CO_2 \rightarrow (NH_4)_2CO_3 + H_2O$$

(2) By mechanical-aeration process along with oxygen.

(3) Acids from dissolved salts: Water containing dissolved magnesium salts liberate acids on hydrolysis, e.g.,

$$MgCl_2 + 2H_2O \rightarrow Mg(OH)_2 + 2HCl$$

The liberated acid reacts with iron (of the boiler) in chain like reactions producing HCI again and again. Thus

$$Fe + 2HCI \rightarrow FeCl_2 + H_2$$

$$FeCl_2 + 2H_2O \rightarrow Fe(OH)_2 + 2HCl$$

Consequently, presence of even a small amount of $MgCl_2$ will cause corrosion of iron to a large extent.

11.7 PRIMING AND FOAMING

When a boiler is steaming (i.e., producing steam) rapidly, some particles of the liquid water are carried along-with the steam. This process of 'wet steam' formation is called priming. Priming is caused by;

1. the presence of a large amount of dissolved solids;
2. high steam velocities,
3. sudden boiling ;

4. improper boiler design
5. sudden increase in steam-production rate.

Foaming is the production of persistent foam or bubbles in boilers, which do not break easily. Foaming is due to presence of substances like oils (which greatly reduce the surface tension of water).

Priming and foaming, usually, occur together. They are objectionable because; (i) dissolved salts in boiler water are carried by the wet steam to super-heater and turbine blades, where they get deposited as water evaporates. This deposit reduces their efficiency, (ii) dissolved salts may enter the parts of other machinery, where steam is being used, thereby decreasing the life of the machinery; (iii) actual height of the water column cannot be judged properly, thereby making the maintenance of the boiler pressure becomes difficult.

Priming can be avoided by: (i) fitting mechanical steam purifiers; (ii) avoiding rapid changing steaming rate; (iii) maintaining low water levels in boilers, and (iv) efficient softening and filtration of the boiler-feed water.

Foaming can be avoided by: (i) adding anti-foaming chemicals like castor oil, or (ii) removing oil from boiler water by adding compounds like sodium aluminates.

Lesson 12. Prevention methods of boiler corrosions

Prevention of corrosion in a boiler in standby condition is more difficult than in an operating boiler. The methods that may be followed to prevent or minimize deterioration of the internal surfaces of boilers from corrosion during inoperative periods. Two sets of conditions must be met: (1) The boiler must be held in readiness to operate at any time on short notice. This may be designated as intermittent standby. (2) The boiler will be continuously in-operative for an indefinite period of weeks or months. This is prolonged standby.

12.1.1 Intermittent stand by:

In general, the water level maintained in the boiler under these circumstances corresponds closely to that of operation, or reduced firing, the temperature is held closely to that of steaming temperature. Circulation, however, is very slight if at all.

During operation the boiler water is maintained uniformly in an alkaline state, and by its rapid circulation, segregation of any water containing oxygen is prevented. During the standby period, however, some loss of water occurs, slight leakage through the blow down valve, slight leakage which is replaced by feed water. If the feed water is sufficiently oxygen free and of suitable alkalinity (pH value), conditions leading to corrosion will not be developed. However, if the conditions are anything but ideal, delayed intermingling of boiler water and feed water due to lack of circulation or low alkalinity, oxygen rich water may form at the boiler surfaces and initiate corrosion. In the case of considerable length of time and of appreciable make up of feed water to replace losses, the boiler water alkalinity may completely disappear, and general corrosion will result.

No single rule can be given to assure correct conditions in the boiler. The regular boiler water tests must be made as carefully on these boilers as on the operating boilers. This is due to the fact that these boilers while in standby cannot be adjusted as easily as the operating boilers and as such, they can be severely damaged by water problems more easily. When testing multi-drum bent-tube boilers, it is very advantageous to take the samples from the rear drum when the boiler is in intermittent service.

If the alkalinity falls to low, it can be boosted by putting a small amount of alkali solution (preferably a caustic solution) directly into the boiler at the point of feed water entry with a pump or any other convenient manner.

In the cases where quantities of oxygen are dissolved in the feed water, a solution of sodium sulfite (Na_2SO_3) can be fed to the boiler by means of a pump either separately or in conjunction with the alkali solution. The minimum amount of residual sodium sulfate that should be maintained in the boiler is 100 ppm as a residual. The proper control of sodium sulfate as a residual in this type of storage should maintain the sodium sulfite from 100 ppm to 200 ppm. Remember that sodium sulfate is soluble in the boiler well above 1000 ppm, so over feed of sodium sulfate will not create a problem with deposition. Hence, it is better to have 150 ppm or 200 ppm of sodium sulfite residual than it is to try and stay close to the minimum level of 100 ppm.

If oxygen pitting and localized corrosion in separate sections of the boiler, then this is a display of typical corrosion due to feed water segregation. Should this occur, then the segregation of the feed water must be stopped. This can be done by intermingling feed water (either by boiler circulation, a circulating pump, or through an injection method). Additionally, the requirement for makeup water can be brought under control by stoppage of system leaks. Finally, if several boilers are subjected to intermittent use, they should be alternated in turn in operating service. This will stop the irregularities that may come about to one boiler that experiences extended standby conditions. This type of rotation prevents any one boiler from suffering from potential standby problems. On the other hand, do not alternate the boilers on a basis that is more frequent than every month, or you will experience problems from the heating and cooling of the boiler, which will result in tube leaks due to frequent expansion and contraction of the boiler tubes. The rules for treating a standby boiler are in large, the same as those for an operating boiler. The application of chemical treatment to a standby boiler must be as fully and more carefully performed.

12.1.2 Prolonged stand by

Two general procedures are available

1. The boiler may be emptied and dried out, and kept dry
2. The boiler may be filled completely with water

In this case the drums or the boiler body, whether a water tube or a fire tube boiler is being treated, are filled to the steam take off if the boiler is a water tube boiler or to the dry box if the boiler is a fire tube boiler.

12.2 DRAINING AND DRYING

This method will allow excellent protection from corrosion to the metal surfaces so long as there is no moisture present in the boiler. One method is to let the boiler open for free circulation of air after drying. Another method is to place a desiccant as silica gel in the boiler and the boiler is then closed up for drying. In either case, water leakage over, or sweating of the boiler metal surfaces must be protected against. Since this type of moisture is saturated with oxygen, its contact with metal surfaces will cause accelerated rates of corrosion. So long as the boiler metal surfaces remain free of moisture, no appreciable corrosion will occur.

Where a boiler has a super heater section, similar moisture free conditions will protect the drainable type of super heater. On the other hand, the lower bends of a non-drainable super heater may tend to collect moisture and as such, this condition will promote rapid attack on the metal surfaces. In order to protect the non-drainable type of super heater, you must blow, dry warm air trough each individual tube or element. To insure complete drying and elimination of any future condensation, a series of small heaters should be installed in the furnace at the lower extremities of the super heater section, equally spaced across its width. Maintenance of such a heating arrangement will insure internal and external dryness.

If the boiler's past history indicates that external sweating of the boiler tubes is a problem, then additional heater should be installed in the furnace at strategic locations in order to insure that the boiler tubes are maintained above the dew point. This concept must also include the super heater section if the boiler has a super heater. If you allow dew to form, then the purpose of layup is defeated, as the boiler tube metal will rapidly corrode both internally as well as externally. For extended dry standby, blanketing the super heater tubes with nitrogen should be considered. This method will dry out the metal in the tube and if maintained properly, it will help to maintain a moisture free atmosphere on the internal areas of the super heater tubes

12.3 BOILER FILLED WITH WATER

In this method, protection can be obtained for the boiler metal, if

1. Correct chemical conditions are maintained in the boiler water.
2. The boiler water is mixed adequately to maintain uniform Conditions throughout the boiler.
3. The boilers are completely filled with treated water as not to allow any boiler metal surfaces to come in contact with the air.

Sufficient caustic soda (or equivalent alkalinity builder) should be added to the boiler water in order to produce a hydroxyl (-OH) alkalinity of 350 to 600 ppm. In addition, sufficient sodium sulfite must be added to the boiler water to establish a sodium sulfite residual of 100 ppm. The mixing of the water in the boiler must be thorough so that correct chemical conditions can exist in every section of the boiler. Mixing of the boiler water can be accomplished by circulating water from one section of the boiler to another with the use of a pump, as in prolonged standby, the boiler is not fired off, and as such, cannot mix the boiler water by means of circulation through heating up the boiler. If the pump method is practical, additional chemicals can be trickled into the boiler as they are needed during the circulation procedure.

Some boiler water sludge will form during standby conditions and this must be treated for. The cleaner the boiler surface metal, the lower the potential for corrosion. Either a Polymeric sulfonated copolymer, carboxylated copolymer, polyacrylate or a combination of these dispersing agents should be fed at a rate that would be considered the mid range for the sludge dispersant during normal operating conditions. The mixing of these dispersing agents into the boiler water in order to insure a clean boiler is as important as the required use of the previously discussed treatment chemicals.

If the circulating pump method is not practical, then if mixing is required, the boiler will have to be accomplished through light steaming. In this case, the proper levels of treatment chemicals will have to be built up during the week prior to the boiler going off the line. If this is the method

to be used, then increase the chemical treatment levels to; 500 - 800 ppm, -OH alkalinity upto 200 ppm. Residual sodium sulfite and maximum mange meed for the sludge dispersant. This will supply the boiler water with sufficient treatment chemicals to maintain itself within the desired limits as the boiler sits and some boiler water is slowly lost.

Deaerated water should be used to fill the boilers that are going to be in standby service, whenever it is available.

A convenient method for keeping boiler full of water is to connect a small expansion tank to some connection at the top of the boiler. This tank is to be located above the boiler and is to be kept filled with chemically treated water. If the tank remains full, then the boiler will remain full. If the tank over flows, then the boiler is taking on water from some form of system leakage. It is convenient for maintaining the proper level of chemical treatment protection as well as acting as a level control indicator.

Module 7. Nuclear radiation, detectors and analytical application of radio active materials

Lesson 13. Radiation and radioactive materials

A number of elements such as Uranium and Radium are unstable. Their atomic nucleus breaks of its own accord to form to form a smaller atomic nucleus of another element. The protons and neutrons in the unstable nucleus regroup to give the new nucleus. This causes the release of excess particles and energy from the original nucleus, which we called radiation. The elements whose atomic nucleus emits radiation are said to be radioactive.

The spontaneous breaking down of the unstable atoms is termed radioactive disintegration or radioactive decay.The disintegration or decay of unstable atoms accompanied by emission of radiation is called Radio Activity.

13.1 TYPE OF RADIATION:

The radioactive radiation is of three types. Alpha (α), Beta (β) and gamma (γ) differ from each other in the nature and properties. (Figure)

13.1.1 Alpha (α) Rays:

They consist of stream of α- particles. By measurement of their e/m, Rutherford showed that they have a mass of 4 amu and charge of +2. They are Helium nuclei and may be represented as ${}^{4}_{2}\alpha$ or ${}^{4}_{2}He$. Tα particles are ejected from radioactive nuclei with very high velocity, about 16000 km/S. because of their charge and relatively large size α – particles have very little power of penetration through matter. They are stopped by sheet of paper, 0.01 mm thick Al foil or few centimeter of air. They cause intense ionization of a gas through which they passes. On account of their high velocity and attraction for electrons, α particle break away electron from gas molecules and convert them into positive ions.

13.1.2 Beta (β) Rays:

They are stream of β particles emitted by the nucleus from their deflection in electric and magnetic fields. Becquerel shows that β particles are identical with electrons. They have very small mass and charge of -1. A β particle is symbolized as ${}^{0}_{-1}\beta$ or ${}^{0}_{-1}e$. The velocity of β particles is around 160000 to 240000 km/S. their ionizing power is weak in comparison to α particle. β particles have 100 times more penetrating power as comparison to α - particles. This is because of their higher velocity and negligible mass. β particles can be stopped by about 1 cm thick sheet of Al or 1 meter of air.

13.1.3 Gamma (γ) Rays:

Unlike x and B rays they do not consist of particles of matters. γ rays are a form of electromagnetic radiation of shorter wavelength than X – rays. They could be thought of as high energy photon released by the nucleus during X and B emission. They have no mass or charge and may be symbolized as ${}^{0}_{0}\gamma$. γ rays travel with the velocity of light. Their ionization power is weak in comparison to α and β particles, because of their high velocity and non material nature γ Rays are most penetrating. They cannot be stopped by even by a 5 cm thick sheet of Lead.

13.2 DETECTION AND MEASUREMENT OF RADIOACTIVITY:

The radioactive radiation can be detected by numbers of methods. Few of them are Cloud Chamber, Bubbled chamber, Geiger –Muller Counter, Ionization chamber method and so on.

13.2.1 Cloud Chamber:

The chamber contains air saturated with water vapor. When the piston is lowered suddenly the gas expands and is super cooled. As β particles passes through the gas, ions are created along its path these ions provides nuclei upon which droplet of water condensed. The trail of cloud thus produced, marks the track of the particles. The track can be seen through the window above an immidiatly photographed. Similarly α or β particles form a trail of bubbles as they pass through liquid Hydrogen. The bubble chamber method gives batter photographs of the particles tracks.

13.2.2 Geiger Muler Counte:

It consists of cylindrical metal tube (Cathode) and central wire (anode). The tube is filled with Argon gas at reduced pressure (0.1 atm). A potential difference of about 1000 volts is applied across the electrode. When an α or β particles enters the tube through mica window, it ionizes the argon atom along its path. The Argon ion (Ar^+) is drown to the cathode and electron to the anode. Thus for a fraction of seconds a pulse of electric current flows through the electrodes and completes the circuit around. Each electrical pulse marks the entry of one α or β particle in to the tube and is recorded in an automatic counter. The number of such pulses registered by a radioactive material per min. gives the intensity of its radioactivity.

13.2.3 Ionization Chamber:

This is the simplest device used to measure the strength of radiation. An ionization chamber is fitted with two plates separated by air. When radiation passes through this chamber, it knocks electrons from gas molecules and positive ions are produced or formed. The freed electron migrates to the anode and positive ions to the cathodes. Thus a small current passes between the plates. This current can be measured with an ammeter and gives the strength of radiation that passes through the ionization chamber. In an ionization camber called Dosimeter, the total amount of electric charge passing between the plates in a given time is measured. This is proportional to the total amount of radiation that has gone through the chamber.

13.3 RADIOACTIVE DECAY:

According to the theory of Rutherford and Soddy, radioactivity is a nuclear property. The nucleus of a radioactive atom is unstable. It undergoes decay or disintrigration by spontaneous emission of an or β particle. This results in the change of proton neutron compassion of the nucleolus to form a more stable nucleolus. The original nucleolus is called parent the nucleolus and product is called daughter nucleolus.

$$\text{Uranium } {}^{238}{}_{92}\text{U} \rightarrow \text{Thorium } {}^{234}{}_{90}\text{Th}$$

There are two main type of decay: (i) α decay (ii)β decay

13.3.1 α Decay:

When a radioactive nucleolus decays by the emission of an α particle (α emission) from the nucleus, the process is termed α decay. An α particle has four units of atomic mass and two units of positive charge. If Z be the atomic number and M be the atomic mass of the parent nucleus, the daughter nucleus will have atomic mass = M- 4

Atomic number = Z-2

Thus an α emission reduces the atomic mass by 4 and atomic number by 2.

For example Radium decay by α emission to form a new element Radon

$$^{226}_{82}Ra \rightarrow {}^{222}_{86}Rn$$

13.3.2 β Decay:

When a radioactive nucleus decays by β particle emission (β emission), it is called β decay. A free β particle or electron does not exist as such in the nucleus. It is produced by the conversion of the neutron to a proton at the moment of the emission.

$$= P + e^-$$

This results in the increase of one positive charge on the nucleus. The loss of a β particle from the nucleus dose not altered its atomic mass. For a parent nucleus with atomic mass M and atomic number Z, the daughter nucleus will have

Atomic mass = M

Atomic number = Z + 1

Thus a β emission increases the atomic number by 1 with no change in atomic mass.

An example of B decay is the conversion of Lead (214) to Bismuth (214).

$$^{214}_{82}Pb - {}^{0}_{-1}\beta \rightarrow {}^{214}_{83}Bi$$

The Group Displacement Law:

It was stated by Fajans and Soddy in 1913, the position number of an element in a group of the periodic table corresponds to its atomic number. If the atomic number of a given element is changed, its group also changes accordingly. We know that an α particle emission decreases the atomic number of the parent element by 2 and a β particle emission increases the atomic number by 1. Thus in an α emission, the parent element will be displaced to a group two places to the left and in a β emmision, it will be displaced to a group one place to the right.

This is called the group displacement law a also known as Fajans – Soddy Displacement Law.

Module 8. Enzymes and their use in manufacturing of ethanol and acetic acid by fermentation methods

Lesson 14 Enzymes-I

Introduction

In this lesson, we will study about enzymes, their classification and characteristics.

18.2 Enzymes

Enzymes are biologic polymers which catalyze biochemical reactions. They are functional units of cell metabolism. Most of the enzymes are proteins. Measurement of activities of certain enzymes is an important tool in diagnosing diseases. Enzymes are important practical tools in medicine, chemical industry, food processing and agriculture.

18.3 Constituents of Enzymes

Almost all of the enzymes are proteins. Some enzymes (e.g. pancreatic ribonuclease) are made up of only polypeptides and contain no groups or atoms other than amino acid residues. Some enzymes require additional chemical component called cofactor. The cofactor can be of two types:-

1. Inorganic ions like Fe^{2+},Zn^{2+},Mg^{2+} etc.
2. Coenzyme: which is a complex organic group.

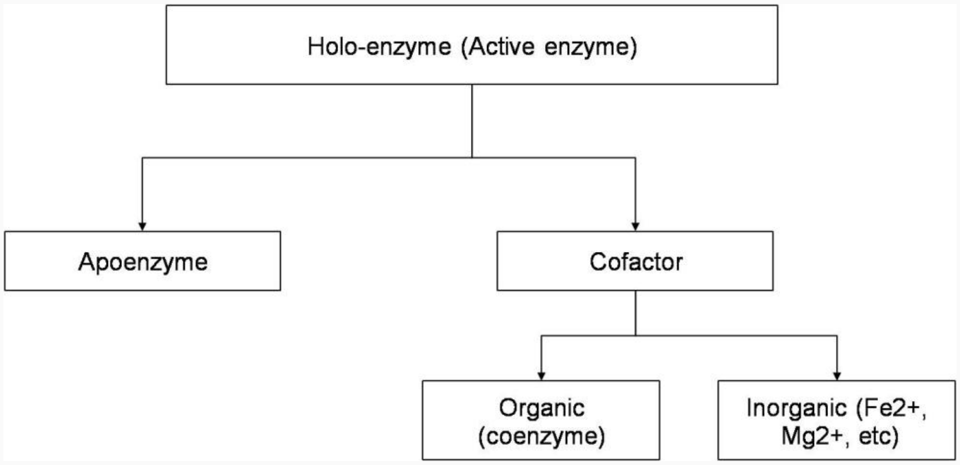


Figure 18.1 Figure showing constituents of enzyme molecules

There are some enzymes which require both coenzyme and metal ions for activity. In some enzymes, coenzymes or metal ions are loosely bound to the protein. In other enzymes it is tightly and permanently bound and is called prosthetic group. A complete catalytically active enzyme together which its coenzyme or metal ion is called holoenzyme. The protein part of an enzyme is known as apoenzyme. Coenzyme and metal ions are stable to heat while the protein part is unstable and denatured on heating.

In an enzyme, the inorganic part is essential for activity of some enzymes, while the coenzyme functions as carries of specific functional groups.

Table18.1 Some enzymes containing Inorganic elements as cofactors

Inorganic Part	**Enzyme**
Zn^{2+}	Alcohol dehydrogenase
Ni^{2+}	Urease
Mg^{2+}	Hexokinase
K+, Mg^{2+}	Pyruvate kinase

Table18.2 Coenzymes which function as carries of functional group

Coenzymes	**Group of atoms transferred**
Thiamine pyrophosphate	Aldehydes
Coenzyme A	Acyl groups
Pyridoxal Phosphate	Amino groups
Co enzyme B_{12}	H atoms and alkyl groups

18.4 Classification of Enzymes

Enzymes are classified into six major groups depending on the type of reactions they catalyze. The complete rules of nomenclature and classification can be found here.

Table18.3 International classification of enzymes

No.	Class	Type of reaction Catalyzed	Examples
1.	Oxidoreductases	Transfer of electrons	Alcohol dehydrogenase, peroxidases, catalases, etc
2.	Transferases	Transfer of groups.(e.g. methyl, NH_2)	Phosphorylases, transaminases, hexokinase, etc.
3	Hydrolases	Hydrolytic cleavage of C-C, C-N,C-O & some other bonds	α & β amylase, urease, etc
4.	Lysases	Addition of groups to double bond or cleavage of C-C, C-N, C-O & other bonds by elimination, resulting in formation of double bonds or rings.	Carboxylysases
5.	Isomarases	Geometric or structural changes within one molecules	Racemases, cis-trans isomerases, etc
6.	Ligases	Joining together of two molecules coupled with hydrolysis of diphosphate bond in ATP or similar molecules	Pyruvate carboxylase

18.5 Characteristics of Enzymes

18.5.1 Enzymes enhance rate of chemical reaction by lowering their activation energy.

Explanation:- During a chemical reaction the reactant molecules are first activated(their energy is increased). The difference in energy between activated state and initial state is known as activation energy. Once the molecules are activated they are converted to products. Enzymes lower the activation energy by providing an alternative path to reach that state. Thus in given time period more number of molecules reach the activation state and reaction is catalyzed.

18.5.2 The substrate concentration has significant effect on rate of enzyme catalyzed reactions and a quantitative relationship exist between the two.

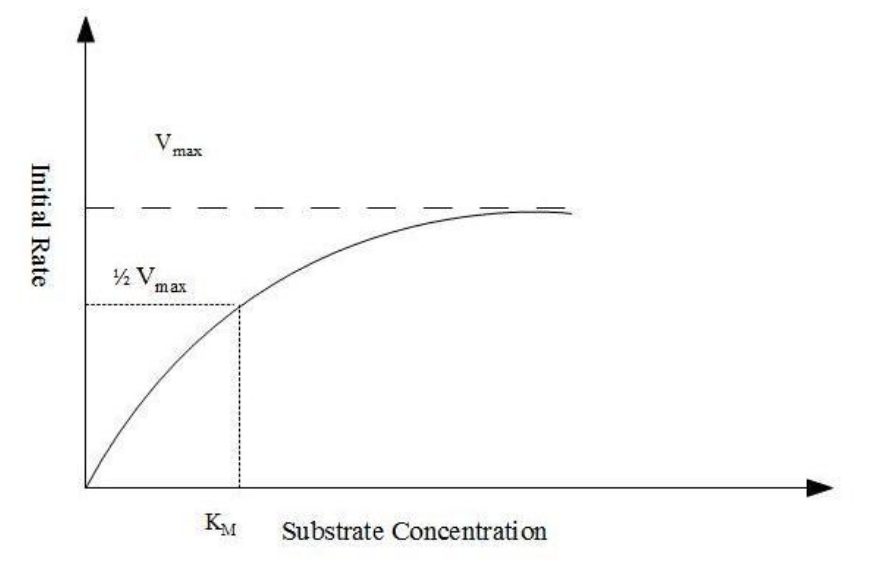


Figure 18.2 Figure showing effect of substrate concentration on initial rate of reaction

Explanation:- Consider a case where enzyme concentration is held constant. Also for simplicity consider that the enzyme acts on only on the substrate. If substrate concentration is low, the initial rate of reaction will also be low but it will increase as the former increases. As the substrate concentration increases, the increase in rate becomes smaller and smaller and approaches a constant value. At this rate the enzyme is saturated with the substrate. This phenomenon is known as the saturation effect exhibited by enzyme molecules.

If an enzyme acts on only one substrate, the relationship between initial rate of reaction and substrate concentration (known as Micheles-Menten equation) can be written as

$$Vo = \frac{V_{max}[S]}{[S] + K_M}$$

Where,

V_o = Initial rate at substrate concentration *[S]*

V_{max} = Maximum rate

K_M = Micheles-Menten constant

18.5.3 Enzymes have an optimum pH at which their activity is maximum.

For example, pepsin is an enzyme which is released in stomach and hydrolyses peptide bonds of proteins has its maximum activity at pH 1.5. The enzyme catalse has optimum pH 7.6.

18.5.4 The activity of enzyme can be determined quantitatively.

Explanation:- There are various methods of determining enzyme activity. By international agreements, 1.0 unit of enzyme activity is defined as that amount causing transformation of 1.0 micromole of a substrate per minute at 25°C under optimum conditions.

18.5.5 Enzymes are specific in their action.

Explanation:- some enzymes act on a a single substance and will not attack other closely related molecules. There are some enzymes which are broad in their action and will act on compounds having common structural feature.

18.5.6 Most enzymes can be inhibited by specific chemical reagents

Lesson 15 Enzymes-II

19.1 Introduction

In this lesson, we will study mechanism of enzyme action, enzyme kinetics, Michaelis-Menten equation and regulation of enzyme activity.

19.2 Mechanism of Enzyme activity

All enzymes contain at least one active site (a specific region of enzyme) which combines with substrate (reacting molecules). The binding of substrate and enzyme causes change in shape of substrate molecules which leads to formation of new bonds or breakage of old bonds which leads to formation of product molecules. The products are released from enzyme surface and the enzyme molecules can enter other reaction cycle. In this way a small number of enzymes molecules change a large number of reactant molecules to form products.

It is found that enzymes are specific towards substrates. This can be explained on the basis of lock and key model. Consider the enzyme molecule to be a 'lock' and substrate molecules its 'key'. We know that every lock and key combination is specific i.e. A lock can be opened only by a particular key. Similarly enzyme-substrate combination is specific. This happens because the shape of the active site of the enzyme and substrate are complimentary to each other similar to fitting of the puzzle pieces to form a complete picture as illustrated in figure no.19.1. This means that an enzyme molecule reacts with only one or very few similar compounds.

If a substrate molecule does not fit correctly to an enzyme, no reaction will take place as illustrated in Fig no.19.2

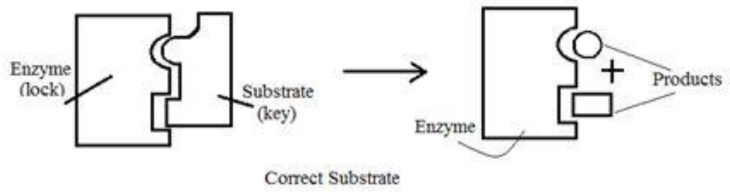


Figure 19.1 Figure showing combination of enzyme with correct substrate

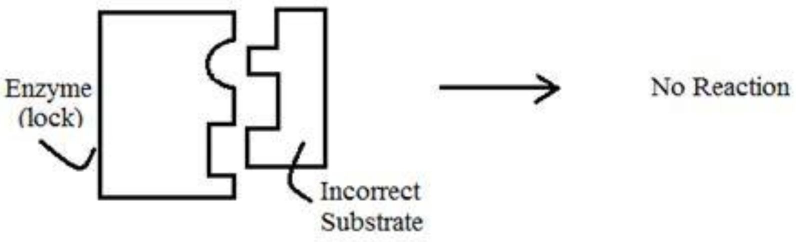


Figure 19.2 Figure showing combination of enzyme with incorrect substrate

19.3 Kinetics of enzyme action

Enzymes are catalysts. They enhance the rate of specific chemical reactions that would occur very slowly in absence of them. They do not change equilibrium point of a reaction nor are they used up or permanently changed by the reactions.

It is found that the substrate concentration has a great effect on initial rate of enzyme catalyzed reactions. All enzymes exhibit saturation effect as explained in section 18.5.2.

This led Victor Henri in 1903 to the conclusion that during enzyme catalyzed reactions, enzyme molecules combine with substrate molecules to form a complex. This idea was expanded into a general theory of enzyme action by Leonor Michaelis and Maud Menten in 1913.

19.4 Michaelis-Menten equation

There are two basic reactions involved in formation and breakdown of enzyme-substrate complex. The enzyme E first combines reversibly with substrate S to form an enzyme-substrate complex ES. This reaction is fast and reversible. The complex ES then breaks down in a second reaction to form product P and the enzyme E is regenerated. This reaction is also reversible but slower than the first reaction.

$$E + S \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} ES \qquad \text{Equation 1}$$

$$ES \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} E + P \qquad \text{Equation 2}$$

If $[E_t]$ represents total enzyme concentration (the sum of free and combined enzyme), [ES] is the concentration of the enzyme-substrate complex, then $[E_t]$-[ES] represents concentration of free or uncombined enzyme. Substrate concentration [S] is far greater than $[E_t]$, so the amount of S bound by E at any given time is negligible compared with total concentration of S.

The rate of formation of [ES] in Equation 1 is

Rate of formation $=k_1 ([E_t] - [ES])[S]$ --------- Equation 3

Where k_1 is the rate constant of forward reaction 1. The rate of formation of ES from E+P by reverse reaction of (2) is very small and can be neglected.

Rate of breakdown of ES is Rate of Breakdown = $k_{-1}(-1) [ES]+ k_2 [ES]$ -------------Equation 4

Where k_{-1} and k_2 are the rate constants for reverse of reaction (1) and reaction (2) respectively.

When rate of formation of ES is equal to its rate of breakdown, concentration of ES is constant and reaction is in steady state.

Thus, equating (3) and (4),

$k_1 ([E_t]- [ES])[S]=k_{-1}(-1) [ES]+ k_2 [ES]$ ---------------- Equation 5

This can be further solved as

$$k_1[E_t][S] - k_1[ES][S] = (k_{-1} + k_2)[ES]$$

$$k_1[E_t][S] = k_1[ES][S] + (k_{-1} + k_2)[ES]$$

$$k_1[E_t][S] = (k_1[S] + k_{-1} + k_2)[ES]$$

$$[ES] = \frac{k_1[E_t][S]}{k_1[S] + k_{-1} + k_2}$$

$$[ES] = \frac{[E_t][S]}{[S] + (k_2 + k_{-1})/k_1}$$

The initial velocity is determined by the rate of breakdown of ES in reaction (2) whose rate constant is k_2. Thus we have

$v_0 = k_2 [ES]$

Thus,

$$v_0 = \frac{k_2[E_t][S]}{[S] + (k_2 + k_{-1})/k_1}$$

Let, the Michaelis-Menten constant

and , the rate when all available enzyme is present as ES.

Substituting in above equation, we get,

$$v_0 = \frac{V_{max}[S]}{[S] + K_M}$$

This is the Miscaelis-Menten equation, the rate equation for one-substrate enzyme catalyzed reaction. It is a equation of the quantitative relationship between the initial velocity v_0, the maximum velocity V_{max}, and the initial substrate concentration, all related through the Michaleis-Menten constant K_M.

In the special case when the initial reaction rate is exactly one-half the maximum velocity

when,

$$v_0 = \frac{1}{2}V_{max}$$

$$\frac{V_{max}}{2} = \frac{V_{max}}{K_M + [S]}$$

Dividing by V_{max} and solving for K_M,

$$\frac{1}{2} = \frac{[S]}{K_M+[S]} \text{ or } K_M + [S] = 2[S] \quad \text{or} \quad K_M = [S] \quad \text{when, } v_0 = \frac{1}{2}V_{max}$$

when,

The Michaelis-Menten equation is basic to all aspects of kinetics of enzyme action. If we know K_M and V_{max}, we can calculate the reaction rate of an enzyme at any concentration of its substrate.

19.5 Regulation of enzyme activity

Enzymes are catalysts whose activity is regulated by the cell. There are two main reasons for this type of control

(1) All enzyme Action requires energy. A cell has limited store of energy. If an unnecessary enzyme action goes on continuing, the cell will be short of energy and will die.

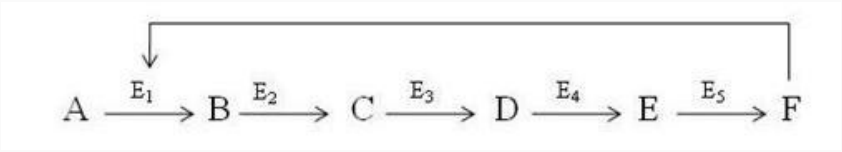
(2) Some of the products of the enzyme catalyzed reactions may be harmful to the cell. If the concentration of such products increases the cell may die.

Some of the mechanisms which exist for regulation of enzyme activity are as follows:

19.5.1 The simplest method is to produce the enzyme only when it is required. This mechanism is used by bacteria. The bacteria produce enzyme only when a substrate is available to it which it wants to degrade or when a particular product is desired.

19.5.2 Allosterism: Enzymes more than one binding site are called as allosterism enzymes. In such enzymes, one site will be for substrate molecule called as active site. The other site is called as effector binding site. When a molecule (called effector molecule) binds to this site, it changes the shape of active site so that its activity is either increased or decreased. If activity is increased it is called the positive allosterism and if the activity is decreased it is called negative allosterism.

19.5.3 Feedback inhibition: It regulates a chain of reaction involved in synthesis of biological molecules. Consider a sequence of reactions represented below



The starting material A is converted to B by enzyme E_1, B is converted to C by Enzyme E_2 and so on until final product F is generated. If F is no longer needed, then F will exert negative allosteric effect on enzyme E_1 and its activity will be decreased. Thus A will not be converted to B whole chain of relations will stop.

19.5.4 Zymogens: An enzyme in inactive form is called Zymogen or Proenzyme. It is produced away from where it is required. When it reaches its destination, it is converted to active form. E.g. the digestive enzymes pepsin, trypsin and chymotrypsin are very destructive in nature. These enzymes degrade protein to amino acids. If the enzymes are synthesized in active form, the cell will be killed. Thus the cells synthesize inactive forms called pepsinogen, trypsinogen and chymotrypsinnogen which are converted to the active forms in stomach, where they are required for digestion of proteins.

19.5.5 Protein Modification: In this mechanism a covalent group is added or removed from protein molecules of enzyme. This change in enzyme molecule either activates it or turns off its action. Generally, phosphoryl groups are added to or removed from amino acids serine, tyrosine or threonine in protein chain of enzyme.

19.5.6 Inhibition of enzyme activity by pH: Most enzymes are active only within a certain pH range. Making the solutions more basic or acidic causes denaturation of enzyme molecule in which its shape changes and as a result, the activity is lost because the enzyme substrate complex can no longer formed.

Lesson 16. Enzymes in Alcohol and Acetic Acid Fermentation

20.1 Introduction

In this lesson, we will study applications of enzymes in alcohol and acetic acid fermentation

20.2 Overview of Alcohol fermentation

Yeast and other microorganisms ferment glucose to ethanol and CO_2.The overall equation of alcoholic fermentation can be written as

$$\text{Glucose} + 2P_i + 2\text{ADP} \longrightarrow 2\ \text{Ethanol} + 2\ CO_2 + 2\text{ATP} + 2H_2O$$

Where, ATP stands for Adenosine triphosphate and ADP for Adenosine diphosphate. These serve as store house of energy in the cell.

The first 10reactions of this pathway is common to all organisms, and the pathway is known as Glycolysis or EMP pathway.

20.3 Glycolysis

In glycolysis, one Glucose molecules is degraded into 2 molecules of Pyruvate.

The 10 reactions of Glycolysis and brief explanation to the reactions are as follows

20.3.1 $$\text{Glucose} + \text{ADP} \longrightarrow \text{Glucose- 6-phosphate} + \text{ADP}$$

The D-Glucose molecule is phosphorylated to yield Glucose-6-phosphate by transfer of phosphate group from ATP to glucose. This reaction is catalyzed by enzyme Hexokinase. Hexokinase requires Mg^{2+} for functioning.

20.3.2 $$\text{Glucose-6-phosphate} \rightleftharpoons \text{Fructose-6-phosphate}$$

Glucose-6-phosphate is isomerized to Fructose-6-phosphate in reaction catalyzed by phosphoglucoisomerase. Phosphoglucoisomerase requires Mg^{2+} for functioning.

20.3.3 $$\text{Fructose-6-Phosphate} \longrightarrow \text{Fructose-1,6-biphosphate}$$

Fructose-6- phosphate is phosphorylated to fructose-1,6-biphosphate by transfer of a phosphate group from ATP molecule to fructose-6-phosphate. This reaction is catalyzed by Phosphofructokinase. This enzyme requires Mg^{2+} for functioning.

20.3.4 $$\text{Fructose-1,6-biphosphate} \rightleftharpoons \text{Glyceraldehyde-3-phosphate} + \text{Dihydroxy acetone phosphate}$$

Fructose-1,6-biphosphate is cleaved to yield Glyceraldehyde-3-phosphate and Dihydroxy acetone phosphate. This reaction is catalyzed by enzyme fructose diphosphate aldolase, which is abbreviated as aldolase. This enzyme requires Zn^{2+} for functioning.

20.3.5

$$\text{Dihydroxy acetone phosphate} \rightleftharpoons \text{Glyceraldehyde-3-phosphate}$$

Dihydroxy acetone phosphate is converted into Glyceraldehyde-3-phosphate in a reaction catalyzed by the enzyme triose phosphate isomerase.

20.3.6

$$2(\text{Glyceralsehyde-3-phosphate}) + 2NAD^+ + 2P^i \rightleftharpoons 2(\text{1,3-biphosphoglycerate}) + 2NADH + 2H^+$$

Glyceraldehyde-3- phosphate is oxidized to 1,3-biphosphoglycerate catalyzed by glyceraldehydes phosphate dehydrogenase.

20.3.7

$$2(\text{1,3-biphosphoglycerate}) + 2ADP \longrightarrow 2(\text{3-phosphoglycerate}) + 2ATP$$

The enzyme phosphoglycerate kinase transfers phosphate group from 1,3-biphosphoglycerate to ADP.

20.3.8

$$2(\text{3-phosphoglycerate}) \rightleftharpoons 2(\text{2-phosphoglycerate})$$

3-phosphoglyarete is converted to 2-phosphoglycerate by shift of phosphate group within the substrate molecule. This reaction is catalyzed by enzyme phosphoglycerate mutase. Mg^{2+} is essential for the enzyme action.

20.3.9

$$2(\text{2-phosphoglycerate}) \rightleftharpoons 2(\text{phosphoenol pyruvate}) + 2H_2O$$

2-phosphoglycerate is dehydrated to phosphoenol pyruvate. The enzyme enolase promotes reversible removal of water molecules. Enolase requires Mg^{2+} which makes complex with enzyme before substrate molecule can attach.

20.3.10

$$2(\text{phosphoenol pyruvate}) \longrightarrow 2(\text{pyruvate})$$

This reaction involves transfer of phosphate group from phosphoenol pyruvate to ADP catalyzed by pyruvate kinase. This enzyme requires K^+ and either Mg^{2+} or Mn^{2+} for functioning.

20.4 Reactions of alcohol fermentation

20.4.1

$$\text{Pyruvate} + H^+ \longrightarrow \text{Acetaldehyde} + CO_2$$

Pyruvate loses its carboxyl group by action of pyruvate decarboxylase. This enzyme requires Mg^{2+} and coenzyme thiamine pyrophosphate (Obtained from thiamine - vitamin B_1).

20.4.2

$$\text{Acetaldehyde} + NADH + H^+ \longrightarrow \text{Ethanol} + NAD^+$$

In this reaction acetaldehyde is reduced to ethanol through the action of alcohol dehydrogenase.

20.5 Acetic acid fermentation

Acetic acid is produced by different pathways by different bacteria. The bacteria of the genus *Acetobacter* oxidize ethanol to acetic acid.

$$C_2H_5OH + O_2 \longrightarrow CH_3COOH + H_2O$$

The anaerobic bacteria of the genus *Clostridium* or *Acetobacterium* convert glucose to acetic acid without producing ethanol. The pathway followed in propionobacteria is as follows

20.5.1

$$\text{Pyruvate} \longrightarrow \text{Acetyl CoA}$$

This reaction is catalyzed by the enzyme Pyruvateferredoxin oxidoreduuctase.

20.5.2

$$\text{Acetyl CoA} + P_i \longrightarrow CH_3\text{-}CO\text{-}PO_3^{2-}$$

Acetyl coenzyme A is converted to acetyl phosphate by the action of enzyme Phosphoacetyl transferase.

20.5.3

$$CH_3\text{-}CO\text{-}PO_3^{2-} + ADP \longrightarrow CH3COOH + ATP$$

Acetyl phosphate is converted to Acetic acid by the action of enzyme Acetate kinase. A phosphate group is transferred to ADP and one molecule of ATP is generated.

Module 9. Principles of Food Chemistry

Lesson 17 Carbohydrates

21.1 Introduction

Food Chemistry is a major aspect of food science. Food chemistry deals with composition and properties of food and chemical changes it undergoes during handling, processing and storage.

Chemically food consists of carbohydrates, proteins, lipids, vitamins, minerals, preservators, colouring and flavouring reagents of food. In this module we will learn more about them in details.

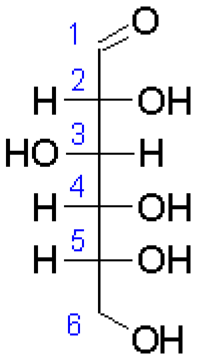
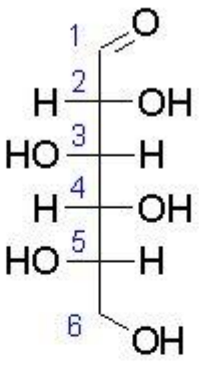
21.2 Carbohydrates

Carbohydrates are defined as polyhydroxy aldehydes or ketones and their derivatives. Their general formula can be represented as $C_x(H_2O)_y$. Carbohydrates are formed in plant cells from carbon dioxide and water in a process called as photosynthesis. Light energy is thus trapped in substances which provide energy to living beings. 1 g of carbohydrates provide 4 kcal energy. In human food, the sources of carbohydrates are cereals, roots, tubers, sugarcane and sugarbeet. Carbohydrates are named according to sources from which they are obtained e.g., fructose (fruit sugar), lactose (milk sugar), xylose (wood sugar) and cellulose (from cell membrane).

21.3 General properties of Carbohydrates

21.3.1 Most of the monosaccharides, disaccharides and lower polysaccharides are sweet in taste, whereas starch and cellulose are tasteless.

21.3.2 They exhibit stereoisomerism. Stereoisomers are compounds whose structural formula is same but arrangement of atoms in 3-Dimensional space is different. E.g., with respect to Carbon no. 5, Glucose has two forms, D-glucose and L-glucose.

	 L-Glucose
D-Glucose	

21.3.3 They exhibit optical activity. Optical activity is a phenomenon in which a molecule rotates plane of plain polarised light. If the molecule rotates the plane towards left, it is designated levo rotatory (- sign) and if the plane is rotated towards right, the molecule is designated dextro rotatory (+ sign). D-glucose rotates plane of plain polarised light towards right while L-fructose rotates it towards left.

21.3.4 The sugars in which free aldehyde or ketone groups are present can reduce Fehling's solution and Benedict's solution are called reducing sugars. The sugars in which free aldehyde or ketone groups are absent are called as non-reducing sugars. Glucose, fructose, lactose etc., are reducing sugars whereas sucrose is a non-reducing sugar.

21.4 Functions of Carbohydrates

21.4.1 They are a major part of total caloric intake.

21.4.2 Starch and glycogen serve as temporary stores of glucose.

21.4.3 Water insoluble carbohydrates are major components of cell wall in plant cells and cell membrane in animal cells.

21.4.4 Carbohydrates function as lubricants in skeletal joints and help the cells to stick with each other and remain in place.

21.5 Classification of carbohydrates

Carbohydrates are generally classified into monosaccharides (simple sugars), oligosaccharides (containing few sugar units) and polysaccharides (containing many sugar units).

21.5.1 Monosaccharides

Monosaccharides are sugar molecules containing short chain of carbon atoms, one aldehydic or ketonic group and hydroxyl groups attached to remaining Carbon atoms. If they contain aldehyde group, they are named as aldoses and if they contain ketone group they are named as ketoses. Depending on number of Carbon atoms, monosaccharides are named astrioses (3 C atoms), tetroses (4 C atoms), pentoses (5 C atoms), Hexoses (6 C atoms) and so on.

21.5.1.1 Important Monosaccharides

1. D-glucose or Dextose: It is the building block of starch and cellulose, source of energy for the animals.

2. Fructose: It is found in fruits and honey. Alongwith glucose, it is present in cane sugar (sucrose).

3. Galactose: It is not found in free state in foods but it is component of milk sugar (lactose) and agar-agar.

4. Arabinose and xylose : They are pentoses and found in plant gums.

21.5.1.2 Properties of monosaccharides

1. They are called as reducing sugars because they reduce Cu^{2+} and $Fe(CN)_6^{3+}$ ions.

2. The reducing sugars are oxidized to sugar acids. E.g., Glucose is oxidized to gluconic acid (monocarboxylic acid) and glucaric acid (dicarboxylic acid).

$$\underset{\text{glucose}}{HOCH_2.(CHOH)_4.CHO} \longrightarrow \underset{\text{gluconic acid}}{HOCH_2.(CHOH)_4.COOH}$$

$$\underset{\text{glucose}}{HOCH_2.(CHOH)_4.CHO} \longrightarrow \underset{\text{glucaric acid}}{HOOC.(CHOH)_4.COOH}$$

3. Reduction of monosaccharides yield sugar alcohols.

$$\underset{\text{glucose}}{HOCH_2.(CHOH)_4.CHO} \longrightarrow \underset{\text{sorbitol}}{HOCH_2.(CHOH)_4.CH_2OH}$$

21.5.1.3 Monosaccharide derivatives

These are sugar molecules in which one or more OH groups are replaced by other groups. They can be classified as

Amino sugars: The –OH group is replaced by $–NH_2$ group. E.g. glucosamine, sialic acid.

Deoxy sugars: In deoxy sugars, one –OH group is replaced by –H atom. L-Rhamonse and L-fucose are present in food polysaccharides. 2-deoxy D-ribose is constituent of DNA.

Glycosides: They are condensation products of sugar (glucose) with another molecule. If the second molecule is also a sugar, O-glycoside is formed. If the second molecule has amino group, product is N-glycoside and if the second molecule has thiol group, the product is S-glycoside.

21.5.2 Oligosaccharides

Oligosaccharides are formed by polymerisation of monosaccharide molecules by elimination of water molecules. Depending on number of monosaccharide units, oligosaccharides are classified as di-, tri-tetra-saccharides etc.The linkage between monosaccharide units in oligosaccharide units is glycosidic linkage.

21.5.2.1 Important oligosaccharides

Sucrose: It is most abundant in sugarcane and sugarbeet. It consists of one molecule of glucose and one molecule of fructose, joined together by glycosidic linkage between their anomeric –OH groups. Sucrose is thus non-reducing sugar.

Maltose: It is the intermediate product of starch hydrolysis. It consists of two molecules of glucose units with glycosidic linkage between anomeric C of one molecule and –OH molecule on C-4 of the other. Maltose is reducing sugar.

Lactose: It is found only in mammalian milk. It consists of one molecule of glucose and one molecule of galactose.

21.5.3 Polysaccharides

They are high molecular weight substancescomposed of large number of moosaccharide units combined to form one large polymer molecule. They may be straight chain or branched chain polymers.

21.5.3.1 Important Polysaccharides

Starch: It occurs in cereal grains, pulses, tubers, fruits etc. It is the major source of energy in diet of man. Starch is a polymer of glucose. Starch is a mixture of two substances, about 25% amylose (straight-chain polymer) and 75% amylopectin (branched chain polymer). Because of the structural differences between amylose and amylopectin, they exhibit different properties. Amylose contributes to gel-formation while amylopectin is responsible for thickness properties of foods containing starch.

Dextrin: It is the product of partial hydrolysis of starch. Their properties are intermediate between those of sugars and starch. They are produced when starch is subjected to dry heat. E.g. during toasting of bread.

Glycogen: Glucose is stored in the form of glycogen in animal tissues. It is mainly found in liver and muscles. It is similar in structure to amylopectin but is more branched than amylopectin.

Cellulose: It is a straight chain polymer of glucose molecules. The glycosidic linkages are different in cellulose and amylose. Cellulose is insoluble in water. It is not digested in human tract. Modified cellulose is used in food industries. Carboxymethyl cellulose is used in ice cream.

Pectic substances: They are constituents of plant cell wall. They are mixtures of polysaccharides formed from galactose, arabinose and galacturonic acid. Pectin, a water soluble component is present in fruits and forms gel with sugar and acid.

Gums: They are hydrophilic substances that give a viscous solution or dispersion when treated with hot or cold water. Starches, pectcic substances and derivatives of starch and cellulose are included in this category. They act as thickeners, moisture retainers, emulsion stabilizers, foam stabilizers, clarifying agents, etc. Important gums include Gum arabic (obtained from Acacia plant), Agar (obtained from red-brown algae) and algin (obtained from brown algae).

Lesson 18 Lipids

22.1 Introduction

Lipids are defined as substances which are insoluble in water but soluble in solvents of low polarity like chloroform, carbon tetrachloride and ether. This definition of lipids includes many different compounds like terpenes, steroids and fats. They are widely distributed in nature but are not found in free state. They occur in combined state with proteins (lipoprtoeins) or carbohydrates (glycolipids). The greatest amounts of fats present in foods are fats and phospholipids.

22.2 Functions of Lipids

22.2.1 They serve as fuel molecules. 1 gm of fat provides 9 kcal of energy.

22.2.2 Phospholipide and triglycerides are important to structure, composition and permeability of cell wall and cell membrane.

22.2.3 Lipoproteins help in transporting lipids in blood.

22.2.4 Skin waxes act as defense mechanism in avoiding thermal and physical shock.

22.2.5 Fats present in food help to carry fat soluble vitamins so that they are efficiently absorbed.

22.2.6 Fats serve as vitamins, emulsifiers and flavour and aroma compounds.

22.3 Classification of Lipids

Lipids are classified into two groups, simple lipids and compound lipids.

Simple lipids include fatty acids, fats and oils (triglycerides of fatty acids) and waxes (esters of fatty acids with long chain monohydroxy alcohols).

All other lipids like phospholipids, steroids, caretenoids etc. are included in compound lipids.

22.4 Fatty Acids

Fatty acids are long chain carboxylic acids having general formula $CH_3(CH_2)_nCOOH$. Most of the fatty acids contain even number of Carbon atoms because of the way in which they are synthesized in living beings. But few fatty acids are present which have odd number of Carbon atoms. Most of the fatty acids found in nature are linear, but few branched chain and cyclic fatty acids can also be found.

22.4.1 Saturated Fatty Acids

Straight chain fatty acids containing 2 to 80 Carbon atoms are known, but in food those having 4 to 24 Carbon atoms are present. The largest share is of fatty acids containing 16 & 18 Carbon atoms.

Table 22.1 Saturated fatty acids found in foods

No. of C atoms	Name	Structure
4	Butyric	$CH_3(CH_2)_2COOH$
5	Valeric	$CH_3(CH_2)_3COOH$
6	Caproic	$CH_3(CH_2)_4COOH$
8	Caprylic	$CH_3(CH_2)_6COOH$
10	Capric	$CH_3(CH_2)_8COOH$
12	Lauric	$CH_3(CH_2)_{10}COOH$
14	Myristic	$CH_3(CH_2)_{12}COOH$
16	Palmitic	$CH_3(CH_2)_{14}COOH$
18	Stearic	$CH_3(CH_2)_{16}COOH$
20	Arachidic	$CH_3(CH_2)_{18}COOH$
22	Behenic	$CH_3(CH_2)_{20}COOH$
24	Lignoceric	$CH_3(CH_2)_{22}COOH$

Fatty acids with Carbon atoms 4-10 are present mainly in milk fat, those having 12-24 Carbon atoms are present in vegetable and animal fats & fatty acids having greater than 24 Carbon atoms are found in waxes. In food, lauric, myristic, palmitic and stearic are the most common acids which are present.

22.4.2 Unsaturated fatty acids

Unsaturated fatty acids are fatty acids which contain double bonds between Carbon atoms. They are subdivided into two types MUFA (Mono-unsaturated fatty acid) and PUFA (poly-unsaturated fatty acid). Most of the naturally occuring unsaturated fatty acids are cis-isomers.

Table 22.2 Unsaturated fatty acids found in food

Common Name	IUPAC Name	Structure
Myristoleic	9-Tetradecenoic acid	$CH_3(CH_2)_3CH=CH(CH_2)_7COOH$
Palmitoleic	9-Hexadecenoic acid	$CH_3(CH_2)_5CH=CH(CH_2)_7COOH$
Oleic	9-Octadecenoic acid	$CH_3(CH_2)_7CH=CH(CH_2)_7COOH$
Linoleic	9,12-Octadecadienoic acid	$CH_3(CH_2)_4CH=CHCH_2CH=CH(CH_2)_7COOH$
Linolenic	9,12,15-Octadecatrienoic acid	$CH_3(CH_2CH=CH)_3(CH_2)_7COOH$
Arachidonic	5,8,11,14-Eicosatertaneoic acid	$CH_3(CH_2)_3(CH_2CH=CH)_4(CH_2)_3COOH$

Oleic Acid is commonly found in all fats. It is present upto a concentration of 75% in Olive oil. Linoelic acid is also commonly found and is present to an extent of 60-80 % in safflowerseed oil. Linolenic acid is found upto an extent of 50-60 % in linseed oil. Arachidonic acid is found in animal sources.

22.4.3 Essential Fatty Acids

Certain fatty acids like lineolic acid are necessary for maintaining healthy conditions of animals. In plants, these acids are formed from oleic acid, but animals lack necessary enzymes for their synthesis. Therefore, they must be supplied from the diet and are known as essential fatty acids.

22.5 Triglycerides:

Triglycerides are carboxylic esters derived from glycerol. Glycerol contains 3 –OH groups which can form ester linkage with fatty acids. If one –OH group is esterified, the compound is called monoglyceride, if two are esterified diglyceride and if all three are esterified, the compound is designated as triglyceride.

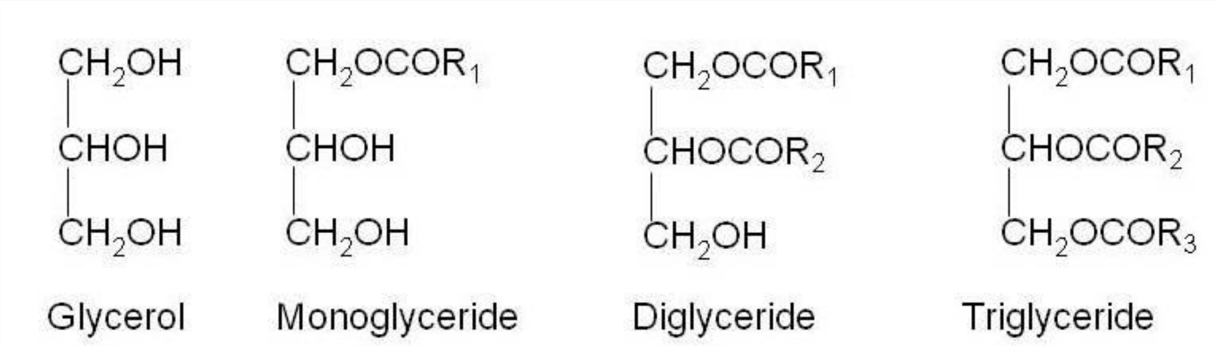


Figure 22.1 Structures of Glycerol, monoglycerides, diglycerides & triglycerides

22.6 Characteristics of lipids

Fats do not have sharp melting points because they are mixture of compounds. As unsaturation of fatty acids increases, the specific heat increases. Viscosity decreases with increasing unsaturation and increases with number of C atoms in fatty acid chain. Solid-liquid ratio can be found out by measuring density of fat. The refractive index increases with increasing unsaturation or with increasing no. of C atoms in fatty acid chain.

22.7 Rancidity

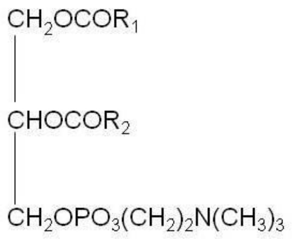
Lipids undergo chemical changes which lead to undesirable odour and flavour. This process is known as rancidity. Two reactions are responsible for rancidity – hydrolysis and oxidation.

Hydrolytic rancidity (lipolytic rancidity) is rancidity developed by hydrolysis reactions in which the lipids are hydrolyzed to yield glycerol and free fatty acids. These reactions can be catalyzed by acids, bases, enzymes or heat. If the reaction is catalyzed by base, salts of fatty acids are obtained and the reaction is known as saponification. Other catalysts release the acids in the free form. Hydrolytic rancidity is important for flavours of milk products, which are due to presence of fatty acids having even number of Carbon atoms, from 4 to 12. Lipolysis depresses the smoke point of cooking oils and as a result, cooking quality of fat is lost, because the foods fried in such oils absorb greater amounts of fat, and the frying quality is also degraded.

Oxidative rancidity is rancidity developed when fats react with oxygen in air, or oxygen producing products. In oxidative rancidity, a large number of intermediates are formed and compounds produced by their condensation are responsible for rancidity. This rancidity is catalyzed by heat, light, ionizing radiatioons and enzymes. This type of rancidity can be prevented by adding substances called anti-oxidants. They function by reacting with intermediates which lead to spoilage of foods.

22.8 Phospholipids

In phospholipids or phosphoglycerides, one of the terminal –OH groups in glycerol is esterified by phosphoric acid and the remaining two by fatty acids. The phosphoric acid is in turn esterified by other compounds like choline, ethanolamine, serine or inositols. Phospholipid containing choline is called lecithin. It is a very good emulsifier and present in egg yolk.



$$\begin{array}{l} CH_2OCOR_1 \\ | \\ CHOCOR_2 \\ | \\ CH_2OPO_3(CH_2)_2N(CH_3)_3 \end{array}$$

Phospholipids (Lecithin)

Figure 22.2 Structure of Phospholipid

Phospholipids are components of cell membrane, and influence its structure and function. They help in transporting other lipids in the blood.

Lesson 19 Proteins

23.1 Introduction

The name protein is derived from Greek word "proteios" which means first or prime or principal. They are so named because proteins are the main constituents of all living cells. All protein molecules have Nitrogen alongwith Carbon, Hydrogen and Oxygen in their molecules (unlike carbohydrates and lipids which are primarily made up of Carbon, Hydrogen and Oxygen). Some protein molecules contain small amounts of Sulphur, Phosphorous and minerals. Chemically proteins are polymers. They are polyamides of α-amino acids.

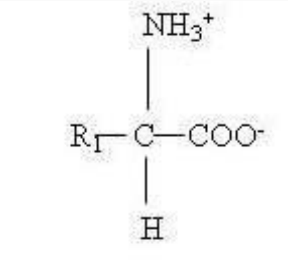
23.2 Biological Importance

Some proteins act as enzymes and hormones. Many important processes like growth, digestion, metabolism, excretion etc. are controlled by proteins. Proteins help in maintaining osmotic pressure and pH of body fluids. Some proteins act as natural defence agents. 1 gm of protein yields 4 kcal of energy. Proteins should provide 10-14% of total energy of the diet.

23.3 Amino Acids

Amino acids are the building blocks of protein molecules. There are 20 amino acids which are commonly found in proteins. A single protein molecule contains hundreds or thousands of amino acids. Thus, the number of protein molecules which can be formed from different permutations and combinations of the 20 amino acids is infinite.

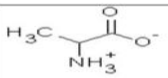
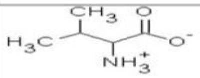
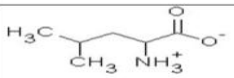
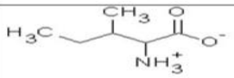
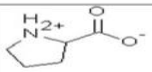
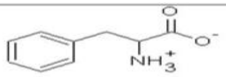
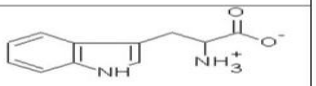
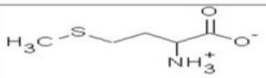
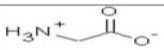
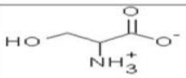
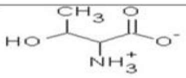
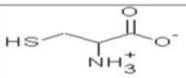
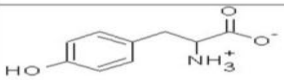
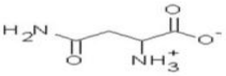
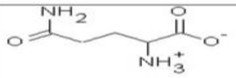
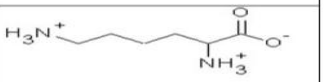
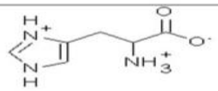
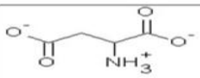
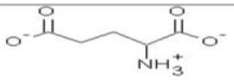
Amino acids contain two functional groups, basic amino ($-NH_2$) group and acidic ($-COOH$) group. The third group is known as the side chain and designated as ($-R$). The general structure of amino acid molecule is as follows:



$$R-\overset{NH_3^+}{\underset{H}{C}}-COO^-$$

23.3.1 Classification of Amino acids

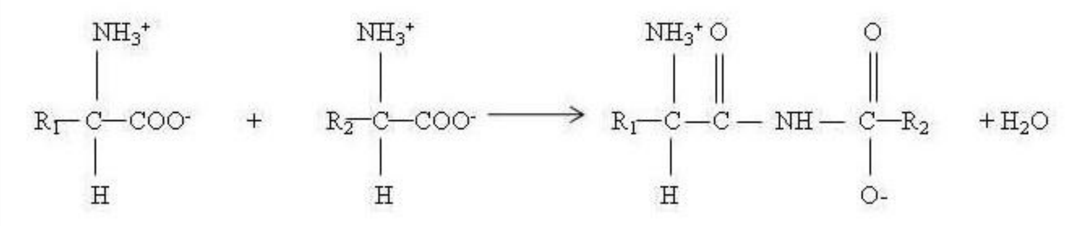
The amino group and carboxylic group are common to all acids, hence the amino acids can be classified on the basis of their R groups as shown in Table :

Name	Abbreviation	Structure
I. Amino acids containing Nonpolar R groups		
Alanine	Ala	
Valine	Val	
Leucine	Leu	
Isoleucine	Ile	
Proline	Pro	
Phenylalanine	Phe	
Tryptophan	Trp	
Methionine	Met	
II. Amino acids containing Polar R groups (uncharged)		
Glycine	Gly	
Serine	Ser	
Threonine	Thr	
Cysteine	Cys	
Tyrosine	Tyr	
Asparagine	Asn	
Glutamine	Gln	
III. Amino acids containing Positively charged R groups		
Lysine	Lys	
Arginine	Arg	
Histidine	His	
IV. Amino acids containing Negatively charged R groups		
Aspartic Acid	Asp	
Glutamic Acid	Glu	

All amino acids except glycine have a chiral Carbon atom (all four groups attached to this C atom are different) and can have D- and L- configurations. All the naturally occuring amino acids have L-configuration. All amino acids are ionized at neutral pH. Amino acids exhibit reactions of both amino and carboxylic acid groups.

23.4 Peptides

α-amino group of one amino acid reacts with carboxyl group of another, with loss of a water molecule to form a peptide bond between the two.



When 2-10 amino acids are joined together, resulting molecule is called as oligopeptide, with more than 10 amino acids it is called polypeptide and when the number of amino acids is more than about 100, it is called a protein.

23.5 Proteins

Proteins can be classified according to their composition into simpple proteins and conjugate proteins. After hydrolysis simple proteins yield only amino acids while conjugated proteins yield amino acids and inorganic or organic groups known as prosthetic groups. The simple proteins are further classified into Albumins, Globumins, Glutelins, Prolamines, Histones, Protamines, Sclero-proteins (albuminoids), etc.

23.5.1 Structure of Protein

The structure of protein molecules is considered at four levels – primary, secondary, tertiary and quaternary

23.5.1.1 Primary Structure

It is the way in which amino acids are sequentially attached in the polypeptide chains by covalent bonds. The sequence of amio acids in a protein molecule is unique and is responsible for many of its properties e.g., replacement of a single amino acid in a protein chain can render it inactive. The secondary and tertiary structures of a protein molecule depend to a large extent on primary structure. The primary structure can be foud out by repeated hydrolysis of protein molecule and analyzing the fragments obtained.

23.5.1.2 Secondary Structure

A peptide chain is not stable and folds itself under the influence of 3-dimensional nature of the bonds. The 3-dimensional manner in which relatively close members of the protein chain are arranged is referred to as secondary structure. The secondary structure of the protein depends upon structural characteristics of peptide bonds. The secondary structure can be found out by x-ray diffraction technique. The various types of secondary structures are α-helix, collagen helix, β-pleated sheets, etc.

23.5.1.3 Tertiary Structure

It defines specific 3-dimensional configuration of the protein molecule. This involves folding of repeating units of secondary structure. The folded portions are held together by hydrogen bonds, electrostatic attraction between oppositely charged groups, hydrophobic interactions and covalent disulphide linkages. In tertiary structure, all polar groups are at surface of the molecule and non-polar groups in the interior, which is the reason for their solubility in aqueous solutions.

23.5.1.4 Quaternary Structure

When a protein molecule contains only a single polypeptide chain, it has only three levels of structure (primary, secondary and tertiary). When a protein molecule has two or more polypeptide chains, the structure formed when individual polypeptide chains interact to form the protein molecule is known as quaternary structure. The bonding mechanism involved in holding the different polypeptide chains together are hydrogen bonds, electrostatic attraction and hydrophobic interactions.

23.5.2 Properties of Proteins

Protein molecules behave as electrolytes. Their solubility is affected by pH, ionic strength, temperature and dielectric properties of solvent. This property is used in isolation and purification of protein molecules.

Proteins can be hydrolyzed by acids, alkalies or enzymes. Acid or alkaline hydrolysis causes racemization of amino acids and loss of certain amino acids. Enzyme hydrolysis prevents destruction of amino acids.

Proteins are putrefied by microorganisms during which microbial proteases act on protein molecules resulting in destruction of amino acids leading to production of offensive odous and toxins, and changes in flavour and texture.

Proteins can be denatured. Denaturation is a process in which quaternary, tertiary or secondary structures are modified in such a way that the properties responsible for identity of the protein molecule are lost. Denaturation does not affect primary structure. Denaturation is reversible if mild agents are used. Some of the agents which cause denaturation are heat, stirring, shaking, high pressure, ultraviolet radiation, pH changes, detergents, etc.

Dry proteins have the ability to absorb water and can form a gel like structure.

Lesson 20. Food Flavors and Colors

24.1 Introduction

In this lesson we will learn more about food flavors and coloring compounds.

24.2 Flavors

Flavor is the sensation produced by a material taken in the mouth, perceived principally by the senses of taste and smell, and also by the general pain, tactile and tmperature receptors in the mouth. Flavor denotes the sum of the characteristics of the material which produces that sensation. Flavor is one of the three main sensory properties which help in deciding slection, acceptance and ingestion of food (the other two being appearance which includes colour, size shape, etc and kinesthetics which includes texture and consistency).

Flavor is composed of taste and odor. Other qualities like texture or temperature contribute to overall sensation of flavor. The main taetes are Salty (sodium chloride), Sweetness (sugar), Sourness (all acids like citric, tartaric etc), Bitterness (quinine), Umami (glutamic acid). The important odors are Camphoraceous (camphor), Pungent (formic acid), Etheral (chloroform), Floral (terpineol), Pepperminty (menthone), Musky (Androsan-3oc-ol), Putrid (skatole).

24.3 Flavor Compounds

Volatile compounds in food like aliphatic esters, aldehydes or ketones are responsible for aroma of foods. The important groups of flavoring compounds are as follows:

24.3.1 Flavonoids

They are responsible for flavor of fruits like orange, lemon. The peel of these fruits contain flavanone glycosides like Hesperidin (tasteless) and naringenin (bitter).

24.3.2 Terpenoids

They are omnipresent in plant foods. They contribute to flavor of citrus fruits and are major components of citrus oils. The major constituent of the essential oils is Limonene (about 90%).

24.2.3 Sulphur Compounds

Some volatile sulphur-containing compounds possess distinctive odours which contribute to aroma of many foods, e.g. the aroma of onion, garlic, cabbage, cauliflower, broccoli, etc. The compounds belong to class thioglucosides, isothiocyanates etc.

24.3.4 Other volatile flavor compounds

Foods can be classified into four groups in terms of volatile flavour. They are:

(1) Foods whose aroma is due to a single compound only. E.g., banana (isopentyl acetate), lemon (citral), almonds (benzaldehyde), etc.

(2) Foods whose aroma is due to mixture of small number of compounds, one of which is rhe major component. E.g., the major flavour imparting component of apple is 2-methyl butyrate and it contains four other components.

(3) Foods whose aroma can be reproduced with the help of a large number of compounds e.g., pinepple, walnut etc.

(4) Foods whose aroma cannot be reproduced by complex mixture of compounds e.g., strawberries, chocolate, etc.

The volatile compounds can be classified into following groups:

Carbonyl compounds: Acetaldehyde (butter), hexanal (apples), benzaldehyde (almonds, cherries), geranial (lemon), 2-3butanedione (butter, celery), etc

Acids: Acetic acid (vinegar), 2-methylbutyric acid (cranberries), etc

Esters: pentyl valerate (apple), methyl salicylate (grapes), pentyl acetate (banana), octyl acetate (orange), ethyl butyrate (strawberry), butyl acetate (strawberry), etc

Hydroxyl compounds: cis-3-hexen-1-ol (tomato, raspberry), 1-octen-3-ol (mushroom), phenol (some cheeses), eugenol (cloves), etc.

24.4 Types of flavors

The flavours can be broadly classified into three types

24.4.1 Developed flavor

Flavor compounds are formed during food processing and may originate from fractionation (manufacture of perfumes) and decomposition and other reactions of food components.

24.4.2 Processed flavor

Heating changes the flavor of many compounds, e.g., coffee, beans, peanuts, etc.

24.4.3 Added flavor

These are added to foods and are of two types

Essential oils or oleoresins or other extracts of aromatic plants, e.g., peppermint oil

Synthetic substances that may or may not occur in nature, e.g., benzaldehyde (almond), acetylmethylcarbinol (butter), citral (orange), eugenol (clove) limenone (lemon), vanillin (vanilla), etc.

24.5 Flavor Enhancement

24.5.1 Monosodium glutamate

It is prepared from wheat gluten, beet sugar waste and soy protein. It is also used in the form of protein hydrolysate derived from proteins. Wheat gluten, casein and soy flour are good sources of glutamic acid and are used to prepare protein hydrolysates.

The flavour of glutamate is unique and has no resemblance to flavour of other compounds. Glutamate causes a tingling feeling and persistency of tatse sensation. It provides a feeling of satisfaction. Presence of salt is required to produce glutamate effect. Monosodium glutamate improves the flavour of many food products and is widely used in processed foods like meat and poultry products, soups, vegetables and seafood.

24.5.2 Maltol

Maltol has the ability to enhance sweetness produced by sugars. Maltol is formed during roasting of malt, coffee, cacao and grains. It is also formed in the crust of bread during baking process and in dairy products that have been heated as a product of decomposition of casein-lactose system. Maltol has anti-oxidant properties. It increases storage life of coffee and roasted cereal products. Maltol is used as a flavour enhancer in chocolate, candies, ice cream, baked products, instant coffee and tea, liqueurs and flavourings.

24.6 Food Colors

Color plays a major role in deciding acceptance of food. It also serves as a criteria for quality of food. The characteristic color of raw food is due to natural pigments present in plant and animal materials. Sometimes artificial coloring matter is added to improve the color of processed foods. The natural pigments occuring in food products can be classified into following groups:

24.6.1 Chlorophylls

They are green pigments involved in photosynthesis in plants and some microorganisms. There are number of chlorophylls such as chlorophylls a,b,c and d, bacteriophylls a and b, and chlorobium chlorophylls. In food, only chlorophyll a and b, found in higher plants are important. Chlorophylls are complex molecules containing four pyrrole rings with a central Magnesium atom. In presence of an acid, the central magnesium of the chlorophylls is replaced by hydrogen. As a result the colour changes from gteen to dull brown.

24.6.2 Myoglobin and Haemoglobin

Myoglobin imparts red colour to fresh muscle. Haemoglobin imparts red colour to the blood. Both are complex proteins consisting of protein part called globin and non-protein part called haem. Haem is a porphyrin consisting of four pyrrole rings, at the centre of which is Iron atom in Fe^{2+} state. Myoglobin and haemoglobin complex with and transport Oxygen required for metabolic activity of the animal.

24.6.3 Anthocyanins

These pigments are responsible forr red, purple and blue colour of fruits, vegetables and flowers. These are water soluble pigments. Anthocyanins are polyphenols and are found linked with sugar molecules like glucose, rhamnose, galactose, xylose and arabinose.

24.6.4 Flavanoids

These pigments impart yellow colour and are present in all plants. They have structures similar to that of anthocyanins.

24.6.5 Tannins

They are complex mixtures of polymeric polyphenols. They impart colour ranging from colourless to yellow or brown. They contribute to astringency and enzymatic browning of foods.

24.6.6 Betalains

They are group of pigments found in red beet, cactus fruits, pokeberries and flowers like bougainvillia. The pigments are red and yellow in colour.

24.6.7 Quinones and Xanthones

They are found in cell sap of flowering plants, fungi, bacteria and algae. Their colour ranges from pale yellow to black.

24.6.8 Carotenoids

These are a group of lipid soluble hydrocarbons. They are the principal colouring matter of carrot roots. They are widely distributed in plant world and found in green leaves, yellow and red fruits and many roots. Carotenes obtained from natural extracts of annatto, saffron, paprika, tomatoes, etc are used as food colourants.

24.6.9 Synthetic colours

A number of synthetic colourants are used in food materials. They may functions as colour stabilizers, colour fixatives, colour retention agents, etc. Even though colours have no role in nutritive valus of foods, they are frequently added to restore the natural colour which is lost during processing.

The synthetic colours are generally manufactured from coal tar. They are generally more suitable in terms of colouring power, uniformity, stability and cost. They are used in carbonated breverages, gelatin dessert, candies, bakery products etc. Many coaltar compounds are carcinogenic and many countries have totally banned or restricted the use of these compounds.

Food colours also include inorganic materials like iron oxide to give redness and titanium dioxide to intensify whiteness.

Some synthetic colours used are

Red: Ponceau 4R, carmoisine, erythrosine

Yellow: Tartrazine, Sunset yellow FCF

Blue: Indigo carmine, Brilliant blue FCF

Green: Fast green FCF

Lesson 21 Food Preservators

25.1 Introduction

Preservative for food may be defined as any chemical compound and/or process, when applied to food, retard alterations caused by the growth of microorganisms or enable the physical properties, chemical composition and nutritive value to remain unaffected by microbial growth.

25.2 Requirements of a good preservative

The requirements of a good preservative are:

- Simple and economical compounds and easy availability
- Have good inhibitory action against a wide range of microorganisms
- Have low order of toxicity - safe and no carcinogenic
- Have high stability in the environment of food (in terms of pH, temperature, redox potential, moisture etc) in which it is added
- Do not alter the identity and quality of the product
- Should be practical and compatible with product processing
- Should not adversely affect the nutritive value of the product
- Should have sufficient solubility in the medium prevailing in the food

25.3 Classification of Preservatives

Preservatives are classified into two classes class I and class II.

25.3.1 Class I preservatives: They include most of the natural substances and their addition in the foods is generally not restricted. Examples include:

- Common salt
- Sugar
- Dextrose
- Glucose
- Spices
- Vinegar or acetic acid
- Honey
- Edible vegetable oil

25.3.2 Class II preservatives: They include some natural substances as well as synthetic compounds. Their use is restricted and are added only to specified products and at permitted concentrations. Examples include:

- Benzoic acid including salts theirof
- Sulphurous acid including salts theirof
- Nitrates and nitrites of sodium or potassium
- Sorbic acid including its sodium, potassium and calcium salts
- Nicin
- Propionic acid and its salts
- Methyl or propyl para-hydroxy benzoate
- Sodium diacetate
- Sodium, potassium and calcium salts of lactic acid

25.4 Mode of action of preservatives

The chemical preservatives interfere with cell membrane of microorganisms, their enzymes or their genetic mechanisms. The interference can be caused in many ways, some of which are : changing the properties of preoteins and nucleic acids (e.g., formaldehyde), inactivation of enzyme mechanisms (e.g. formaldehyde), release of active Oxygen which reacts with amino acids, aldehydes and ketones (e.g., H_2O_2), raising redox potential to such a level which is not suitable for microbial growth (e.g., H_2O_2, nitrates), changing pH of medium to such a level which is not suitable for microbial growth (e.g., acetic acid), neutralize the acid produced by microorganisms (e.g., carbonates and bicarbonates), changing water activity so that microorganisms cannot use water for their growth (e.g., salt, sugar), inhibiting synthesis of DNA & RNA (esters of p-hydroxy benzoic acid), etc.

25.5 Commonly used Preservatives

Following are the commonly used preservatives, their mode of action and products in which they are used.

25.5.1 Sodium Chloride: Salt is used to control microorganisms in foods such as butter, cheese, olives, meat, fish, etc. It causes dehydration by drawing out water from the tissue cells. It also interferes with action of proteolytic enzymes and stops action of microorganisms.

25.5.2 Sugar: Sugar is used as preservative in foods like syrups and confectionery products, jams, jellies, marmalades, etc. Sugar has high osmotic pressure which is unfavourable for growth and reproduction of most species of bacteria.

25.5.3 Sulphur dioxide: It is used in treatment of fruits and vegetables. It is used to extend shelf life of fresh grapes, to kill undesirable microorganisms during wine making, in manufacture of fruit juices and also to prevent browning reactions. Sulphur dioxide is used in the form of gas (SO_2), Sodium or potassium bisulphites ($NaHSO_3$, $KHSO_3$), sulphites (Na_2SO_3, K_2SO_3) and metabisulphite ($Na_2S_2O_5$, $K_2S_2O_5$).

25.5.4 Acetic acid: It is used in the form of vinegar to preserve pickled vegetables. Acetates of sodium, potassium and calcium are used in bread and other baked foods. The acid is also used in ketchups, mayonnaise, etc. The antimicrobial activity of acetic acid is due to the low pH it creates.

25.5.5 Propionic acid: It is used in the form of sodium and potassium salts in bakery products. The salts are active against molds and some bacteria.

25.5.6 Benzoic Acid: Benzoic acid and its Sodium salt are widely used as preservatives. The acid form exhibits antimicrobial activity. It is active against yeast and bacteria. It is used in acid foods like fruit juices, carbonated breverages, pickles etc.

25.5.7 Parabens: These are esters of p-hydroxy benzoic acid. They are effective against molds and yeasts.

25.5.8 Epoxides: Epoxides like ethylene oxides and propylene oxide are used in preserving dry items like nuts and spices. They are cyclic ethers and used in gaseous form. The epoxides destroy all microorganisms including spores and viruses.

25.5.9 Sorbic Acid: Sorbic acid is a naturally occurring, unsaturated fatty acid. It is sparingly soluble in water and hence Sodium or Potassium salts of Sorbic acid are used. Sorbic acid and its salts are effective against yeasts and molds as well as bacteria. Sorbates are widely used as preservatives in preserving dairy products, fruits and vegetables, bakery products, confectioneries, meat, fish, etc.

25.5.10 Nisin: Nisin is an antibiotic produced by bacterium *Lactococcus lactis*. It is active against only limited microorganisms, particularly spore producing gram positive bacteria. It is used in canned foods and other food products.

25.5.11 Lactic acid and its salts: It is formed during fermentation of lactose by lactic acid bacteria. Lactic acid is a mild antiseptic and is used along with other preservatives. It is not commonly used and used in some types of pickles (with acetic acid) and biscuits.

25.5.12 Sugar: It is a disaccharide and is made of glucose and fructose units. It is effective against bacteria and molds. It is used in fruit products like jams, jellies, squashes etc, dairy products like condensed milk, sweets, etc.

Lesson 22 Vitamins

26.1 Introduction

At the beginning of last century, it was found that small quantities of unknown substances are essential for life, in addition to carbohydrates, fats and proteins. These food substances were originally thought to be bases, and hence the name vitamine (vital amine) was given to them (amine means base). Later it was discovered that these substances are not basic and hence the letter e was dropped, and the name vitamin was given to them.

Vitamins are organic substances necessary in small amounts for normal growth, maintenance and reproduction. All higher vitamins require vitamins but every vitamin is not required by all of them. For example, humans require Vitamin C in their diet, but animals like dogs, cats and rats synthesize this vitamin in their body and do not need it in their food.

26.2 Classification

Vitamins differ widely in their chemical nature. They are classified based on their solubility. The vitamins A, D, E and K are soluble in fats and oils and are known as fat soluble vitamins. The vitamins of group B and vitamin C are water soluble and are known as water soluble vitamins.

26.3 Functions

Different vitamins have different functions. Most of the water soluble vitamins function as coenzymes of enzymes. The functions of various vitamins will be discussed in following sections.

26.4 Fat Soluble Vitamins

Fat soluble vitamins are generally present in foods containing high amounts of fat, such as butter, cream, oil seeds, fats of meat and fish, etc. They are not excreted in the urine, and can accumulate in human body leading to toxic results in high concentration.

26.4.1 Vitamin A

Vitamin A is an alcohol ($C_{20}H_{29}OH$). Its chemical name is retinol and is so named because of its association with retina of the eye. The active forms are aldehyde (retinal) and acid (retinoic acid). It is stable to heat to some extent. If heated for a long time in contact with air, it gets destroyed.

26.4.1.1 Functions of Vitamin A

Vitamin A is essential for vision in night. It is also helpful in maintaining health of epithelial cells, which secrete mucous, which protects the skin and membranes against microorganisms. It also affects protein synthesis and is necessary for growth and maintenance of skeletal muscles and soft tissues.

26.4.1.2 Deficiency disorders of Vitamin A

Prolonged deficiency may lead to night blindness, xerophthalmia (keratinization of cornea) and decreased defense against microorganisms because the mucous membranes cannot function properly.

26.4.1.3 Sources of Vitamin A

It is found in food items like meat, milk, fish, etc. In animals, its highest concentration is found in the liver. It is also present in plant sources like carrot, pumpkin and green leafy vegetables. The plant sources contain precursor of Vitamin A known as carotenoids, which are the orange and yellow pigments of fruits and vegetables.

26.4.2 Vitamin D

It is a steroid vitamin. Five forms of vitamin D are known as vitamin D_1 to D_5 . Out of these, the forms D_2 and D_3 are most important in humans. Vitamin D_2 is ergocalciferol and vitamin D_3 is cholecalciferol. Vitamin D is very stable and operations like storage, processing and cooking do not affect its activity.

26.4.2.1 Functions of Vitamin D

Vitamin D is a precursor of hormone 1,25-dihydroxycholecalciferol, which is formed by liver and kidney. This hormone is necessary for growth and mineralization of bones and teeth. Vitamin D is essential for absorption and maintaining proper levels of calcium and phosphate.

26.4.2.2 Deficiency disorders of Vitamin D

In children, deficiency of vitamin D, leads to Rickets, in which bones are weak and assume a bent form, joints are enlarged and chest is narrow due to distortion of ribs. In adults, deficiency leads to loss of calcium from bones which results in increased of fractures.

26.4.2.3 Sources of Vitamin D

It is found in small quantities in butter, cream, egg-yolk and liver. The best source is fish liver oil. In the body, ergosterol which is obtained from plant sources is converted into vitamin D when ultraviolet light falls on the skin.

26.4.3 Vitamin E

The activity of Vitamin E is due to mixture of four tocopherols (α, β, γ and δ), out of which α-Tocopherol is the biologically most active form.

26.4.3.1 Functions of Vitamin E

Vitamin E possesses antioxidant property. It prevents formation of peroxides from polyunsaturated fatty acids. It protects cell membrane from deterioration caused by peroxides.

26.4.3.2 Deficiency disorders of Vitamin E

The deficiency of Vitamin E results in increased fragility of red blood cells and muscle damage.

26.4.3.3 Sources of Vitamin E

It is present in cereals, green plants, egg-yolk, milk fat, butter, meat, nuts and vegetable oils.

26.4.4 Vitamin K

It occurs in two forms. Vitamin K_1 (phylloquinine) is present in green plants and Vitamin K_2 (menaquinone) is formed in intestine by action of bacteria.

26.4.4.1 Functions of Vitamin K

It is necessary for synthesis of proteins like prothrombin, which are involved in blood clotting.

26.4.4.2 Deficiency disorders of Vitamin K

The deficiency of vitamin K increases blood clotting time, which results in haemorrhage and uncontrolled bleeding.

26.4.4.3 Sources of Vitamin K

Green leafy vegetables like spinach, cabbage and lettuce are best sources of vitamin K. It is also present in fruits, cereals, dairy products and meat. It is also produced in intestine by bacteria.

26.5 Water Soluble Vitamins

Water soluble vitamins are not stored in human body and if excess quantities are ingested, they are excreted in the urine. Therefore they should be taken in diet every day. These vitamins are lost easily during cooking process.

26.5.1 Thiamine (Vitamin B-1)

It is stable when dry but solutions are unstable in presence of heat or alkali. In acidic pH, it is heat stable. It is also destroyed by oxidation and reduction process.

26.5.1.1 Functions of Thiamine

It reacts with phosphoric acid to form thiamine pyrophosphate, which as a coenzyme It is required during biological oxidation of glucose.

26.5.1.2 Deficiency disorders of Thiamine

Mild deficiency results in fatigue, depression, irritability, loss of appetite and lethargy. Severe deficiency causes beri-beri, whose symptoms are disorders of nervous system, cardiovascular system and digestive tract.

26.5.1.3 Sources of Thiamine

The sources of vitamin B-1 are unpolished cereals, pulses, nuts, liver, meat, egg yolk and fish.

26.5.2 Riboflavin (Vitamin B-2)

Chemically it belongs to a group of flavins, which are yellow coloured fluorescent pigments. It is orange yellow in colour. On exposure to light, it loses its activity.

26.5.2.1 Functions of Riboflavin

It forms part of two coenzymes flavin mononucleotide (FMN) and flavin dinucleotide (FAD), which is required in catalyzing oxidation-reduction reactions of the cell.

26.5.2.2 Deficiency disorders of Riboflavin

Its deficiency results in cracks in corner of mouth, reddened lips, swollen and reddened tongue. The deficiency also results in disorders of eyes.

26.5.2.3 Sources of Riboflavin

The main sources of this vitamin are milk and dairy products, liver, eggs and leafy vegetables. Dried yeast, pulses and meat also contain vitamin B-2.

26.5.3 Niacin

Nicotinic acid and nicotinamide are two naturally occurring chemicals with niacin activity. It is resistant to heat, light acids and alkali.

26.5.3.1 Functions of Niacin

It is a part of two coenzymes nicotinamide adenine dinucleotide (NAD) and nicotinamide adenine dinucleotide phosphate (NADP). These coenzymes help in releasing energy from carbohydrates, fats and proteins.

26.5.3.2 Deficiency disorders of Niacin

The symptoms of niacin deficiency are weakness, indigestion, ulcers of mouth and tongue. Pellagra is the disease associated with prolonged deficiency of niacin. The symptoms of pellagra are dermatitis, diarrhea and dementia. Skin lesions on exposure to sunlight, neurological symptoms and mental changes are also associated with niacin deficiency.

26.5.3.3 Sources of Niacin

Meat, yeast, fish, groundnuts, pulses and whole grain cereals are good sources of niacin. It can be synthesized by bacteria in the intestine.

26.5.4 Pyridoxine (Vitamin B-6)

Vitamin B-6 is a group of three substances having biological activity. They are pyridoxine, pyridoxal and pyridoxamine of which pyridoxine is the most stable form.

26.5.4.1 Functions of Pyridoxine

Pyridoxine in the form of pyridoxal phosphate is a coenzyme of many enzymes involved in carbohydrate, protein and lipid metabolism. It is required in transamination, deanimation, desulphuration and decarboxylation reactions.

26.5.4.2 Deficiency disorders of Pyridoxine

Deficiency of vitamin B-6 results in depression, confusion and convulsions. It also causes dermatitis around the eyes, eyebrows and mouth, soreness of mouth and reddening of tongue.

26.5.4.3 Sources of Pyridoxine

Meat, liver, vegetables and whole grain cereals are good sources of vitamin B-6.

26.5.5 Folic Acid

It belongs to a group of compounds called pterins. Many chemical forms of Pteroylmonoglutamic acid (PGA, Folic acid) have vitamin activity. Folic acid is unstable to heat in acid medium, and is inactivated also by oxidation.

26.5.5.1 Functions of Folic Acid

In the body folic acid is converted into many coenzyme forms which are required for transfer of one-carbon groups.

26.5.5.2 Deficiency disorders of Folic Acid

Deficiency of folic acid results in poor growth, blood disorders and disturbances of gastrointestinal tract and metabolism.

26.5.5.3 Sources of Folic Acid

Green leafy vegetables (spinach, asparagus and broccoli), dried beans, liver and kidney are rich sources of folic acid.

26.5.6 Biotin

It is a sulphur containing vitamin, stable to heat and light but unstable in strong acid and alkali. It is susceptible to oxidation.

26.5.6.1 Functions of Biotin

Biotin is a coenzyme taking part in reactions in which carbon dioxide is added or removed.

26.5.6.2 Deficiency disorders of Biotin

Anorexia, nausea, vomiting, mental depression and dermatitis are some of the symptoms associated with biotin deficiency.

26.5.6.3 Sources of Biotin

Liver, kidney, egg yolk and groundnuts are good sources of biotin. It can be synthesized by bacteria in the intestine.

26.5.7 Pantothenic acid

It is stable to heat in solution and is destroyed by dry heat and alkalies.

26.5.7.1 Functions of Pantothenic acid

It is a part of coenzyme A which is involved in acylation reactions.

26.5.7.2 Deficiency disorders of Pantothenic acid

Deficiency of this vitamin is rare. The symptoms of deficiency include pain in arms and legs, loss of appetite, nausea, indigestion and increased susceptibility to infections.

26.5.7.3 Sources of Pantothenic acid

It is abundant in animal tissues, whole grain cereals and pulses. It also occurs in milk, vegetables and fruits. It is also synthesized by bacteria in the intestine.

26.5.8 Cobalamine (Vitamin B-12)

This vitamin contains cobalt metal ion and hence the name is given as Cobalamine. It is the most complex vitamin. It is water soluble and stable in pH range 4-6.

26.5.8.1 Functions of Cobalamine

It is a part of coenzymes which are essential in transfer of methyl groups. They are necessary in normal metabolic functioning in all cells and also in nucleic acid metabolism.

26.5.8.2 Deficiency disorders of Cobalamine

Deficiency of this vitamin is uncommon. One of the diseases associated with deficiency of this vitamin is pernicious anaemia, which in severe cases leads to damage of spinal cord, leading to sensory disturbances, weakness and paralysis.

26.5.8.3 Sources of Cobalamine

Milk, cheese, eggs, sea food, meat, liver and kidney are good sources of this vitamin. Vitamin B-12 is not present in plant sources like grains, vegetables, fruits etc. It is synthesized by bacteria in the intestine.

26.5.9 Ascorbic acid (Vitamin-C)

It is a hexose derivative and can be converted to dehydro ascorbic acid by oxidation. Both the forms have vitamin activity.

26.5.9.1 Functions of Ascorbic acid

It helps in healing of wounds, fractures, bruises and reduces liability to infection. It is also involved in metabolism of some amino acids.

26.5.9.2 Deficiency disorders of Ascorbic acid

Deficiency of vitamin C leads to scurvy, in which the collageneus structure weakens which results in haemorrhage. Other symptoms include weakness, loss of appetite, anemia, tenderness to touch, swollen gums, loosening of teeth and diseases of bone joints.

26.5.9.3 Sources of Ascorbic acid

Citrus fruits, berries, guava, capsicum and green leafy vegetables are the excellent sources of vitamin C.

Module 10. Lubricants properties, mechanism, classification and tests

Lesson 23. Lubricants : Classification and properties

A substance which is capable of reducing friction between two surfaces which are sliding over each other is called Lubricant. Due to Lubricant the co-efficient of friction between two rubbing surfaces is reduced. The loss of energy due to friction is considerably reduced in this manner. Petroleum is the main source of Lubricants, but synthetic Lubricants have also been prepared for specific purpose. The lubricant acts in a number of manners. It acts as a coolant by removing the heat of friction generated as a result of rubbing of surfaces. In lubrication it does not allow a direct contact between the rubbing surfaces .A thin film of lubricant lies between these rubbing surfaces under proper condition of lubrication. In internal combustion engines, it acts as a seal by sealing the piston & cylinder wall at compression rings .Hence there is no leakage of gases at high pressure in the combustion chamber. Lubrication also avoids power loss in the IC engine.

The main features of lubrication are:

1. It reduces wear and tear and surface deformation, by avoiding direct contact between the rubbing surfaces.
2. It reduces the loss of energy in the form of heat by acting as a coolant.
3. It reduces the efficiency of the machine by reducing the waste of energy.
4. It reduces expansion of metal by local frictional heat.
5. It minimizes the liberation of frictional heat and hence avoids seizure of moving surfaces.
6. It prevents unsmooth motion relative motion of the moving or sliding parts.
7. It reduces the maintenances as well as running cost of the machine to a large extent.
8. As seen above it also acts as a seal in IC engines.

27.2 CLASSIFICATION OF LUBRICANTS

Lubricants can be broadly classified, on the basis of their physical state, as follows: (1) Liquid lubricants or lubricating oils; (2) Semi-solid lubricants or greases, and (3) Solid lubricants.

27.2.1 Lubricating oils

Lubricating oils reduce friction and wear between two moving/sliding metallic surfaces by

providing a continuous fluid film in-between them. They also act as: (a) cooling medium; (b) sealing agent, and (c) corrosion preventer. Good lubricating oil must possess: (a) low pressure (or high boiling point), (b) adequate viscosity for particular service conditions, (c) low freezing point, (d) high oxidation resistance. (e) Heat stability, (f) non-corrosive properties, (g) stability to decomposition at the operating temperatures. Lubricating oils are further classified as:

(1) Animal and vegetable oils: Before the advent of the petroleum industry, oils of the vegetable and animal origins were the most commonly used lubricants. They posses good oiliness (a property by virtue of which the oil sticks to the surface of machine parts, even under high temperatures and heavy loads). However, they: (i) are costly, (ii) undergo oxidation easily forming gummy and acidic products and get thickened on coming in contact with air, (iii) have some tendency to hydrolyze, when allowed to remain in contact with moist-air or aqueous medium. So at present, they are rarely used as such.

Actually, they are used as "blending agent" with other ' lubricating oils (like mineral oils) to produce desired effects in the latter.

(2) Mineral or petroleum oils are obtained by distillation of petroleum. The length of the hydrocarbon chain in petroleum oils varies between about 12to 50 carbon atoms. The shorter-chain oils have lower viscosity than the longer-chain hydrocarbons. These are the most widely used lubricants, because they are; (i) cheap, (ii) available in abundance, and (iii) quite stable under service conditions. However, they possess poor oiliness as compared to that of animal and vegetable oils. Tile oiliness of petroleum oils can be increased by the addition of high molecular weight compounds like oleic acid, stearic acid, etc.

Purification : Crude liquid petroleum oils contain lot of impurities (like wax, asphalt,etc.) and consequently, they have to be thoroughly purified before being put to use.(i) The wax, if not removed, raises the pour-point and renders the lubricating oil unfit for use at low temperatures. (ii) Certain constituents get easily oxidized under working conditions and cause sludge formation. (iii) Some constituents mainly asphalt, undergo decomposition at higher temperatures, causing carbon deposition and sludge formation. A number of processes are used for removing these unwanted impurities by using Dewaxing or acid refining or by solvent refining.

(3) Blended oils: No single oil saves as the most satisfactory lubricant for many of the modern machineries. Typical properties of petroleum oils are improved by incorporating specific additives. These so-called 'blended oils' give desired lubricating properties, required for particular machinery. The following additives are employed

(i) Oiliness-carriers: Oiliness of a lubricant can be increased by addition of an oiliness-carrier like vegetable oils (e.g., coconut oil, castor oil) and fatty acids (like palmitic acid, stearic acid, oleic acid. etc.).

(ii) Extreme-pressure additives: Under extreme-pressure, a thick film of oil is difficult to maintain, and the oil need to have a high oiliness. Besides improving oiliness directly, high-pressure additives are used. .these additives contain certain materials which are absorbed on the metal surface or react chemically with metal, producing a surface a layer of low shear-strength on the metal surface, thereby preventing the tearing up of the metal. Another property of high-pressure additives is that they react, at high temperature on metal surfaces, forming surface alloys so as to prevent the welding together of the rubbing parts under severe operating conditions.

The main substances added for high-pressure lubrication are :(a) fatty ester, acids, etc., which form oxide film with the metal surface ; (i) organic materials, which contain sulphur ; (c) organic chlorine compounds ; (d) organic phosphorus compounds. High-pressure lubricants also contain some lead in order to produce thin film of lead sulphide and other lead compounds on the surfaces of machines like gear teeth.

(iii) Pour-point depressing additives used are phenol and certain condensation products of chlorinated wax with naphthalene. These prevent the separation of wax from the oil.

(iv) Viscosity-index improvers are certain high molecular weight compounds like hexanol.

(v) Thickeners such as polystyrene are materials usually of molecular weight between 300 and 3,000. They are added in order to give the lubricating oil a higher viscosity.

(vi) Antioxidants or inhibitors, when added to oil, retard oxidation of oil by getting them- selves preferentially oxidized. They are particularly added in lubricants used in internal combustion engines, turbines, etc., where oxidation of oil is a serious problem. The antioxidants are aromatic, phenolic or amino compounds.

(vii) Corrosion preventers are organic compounds of phosphorus or antimony. They protect the metal from corrosion by preventing contact between the metal surfaces and the corrosive substances.

(viii) Abrasion inhibitors like tricresyl phosphate.

(ix) Antifoaming agents (like glycols and glycerol) help in decreasing foam formation.

(x) Emulsifiers such as sodium salts of sulphonic acid.

(xi) Deposit inhibitors are detergents such as the salts of phenol and carboxylic acids. Deposits are formed in internal combustion engine, due to imperfect combustion. Such additive disperses and cleans the deposits.

27.2.2 GREASES OR SEMI-SOLID LUBRICANTS

Lubricating grease is a semi - solid, consisting of a soap dispersed throughout liquid lubricating oil. The liquid lubricant may be petroleum oil or even synthetic oil and it may contain any of the additives for specific requirements. Greases are prepared by saponification of fat (such as tallow or fatty acid) with alkali (like lime, caustic soda, etc.), followed by adding hot lubricating oil while under agitation. The total amount of

mineral oil added determines the consistency of the finished grease. The structure of lubricating greases is that of a gel. Soaps are gelling agents, which give an interconnected structure (held together by intermolecular forces) containing the added oil. At high temperatures, the soap dissolves in the oil, whereupon the interconnected structures cease to exist and the grease liquefies. Consistency of greases may vary from a heavy viscous liquid to the of a stiff solid mass. To improve the heat-resistance of grease, inorganic solid thickening agents (like finely divided clay, bentonite, colloidal silica, carbon black, etc.) are added.

Greases have higher shear or frictional resistance than oils and, therefore, can support much heavier loads at lower speeds. They also do not require as much attention unlike the lubricating liquids. But greases have a tendency to separate into oils and soaps. Grease are used : (i) in situations where oil cannot remain in place, due to high load, low speed, intermittent operation, sudden jerks, etc. e.g. rail axle boxes, (ii) in bearing and gears that work at high temperatures ; (iii) in situations where bearing needs to be sealed against entry of dust, dirt, grit or moisture, because greases are less liable to contamination by these ; (iv) in situations where dripping or spurting of oil is undesirable, because unlike oils, greases if used do not splash or drip over articles being prepared by the machine. For example, in machines preparing paper, textiles, edible articles, etc.

The main function of soap is thickening agent so that grease sticks firmly to the metal surfaces. However, the nature of the soap decides: (a) the temperature up to which the grease can be used; (b) its consistency; (c) Its water and oxidation resistance. So, greases are classified after the soap used in their manufacture. Important greases are: (i) Calcium-based greases or cup-greases are emulsions of petroleum oils with calcium soaps. They are, generally, prepared by adding requisite amount of calcium hydroxide to hot oil (like tallow) while under agitation. These greases are the cheapest and most commonly used. They are insoluble in water, so water resistant. However, they are satisfactory for use at low temperatures, because above 80°C, oil and soap begins to separate out.

(ii) Soda-base greases are petroleum oils, thickened by mixing sodium soaps. They are not water resistant, because the sodium soap content is soluble in water. However, they can be used up to 175°C. They are suitable for use in ball bearings, where the lubricant gets heated due to friction.

(iii) Lithium-based greases are petroleum oils, thickened by mixing lithium soaps. They are water-resistant and suitable for use at low temperatures [up to 15°C] only.

(iv) Axle greases are very cheap resin greases, prepared by adding lime (or any heavy metal hydroxide) to resin and fatty oils. The mixture is thoroughly mixed and allowed to stand, when grease floats as stiff mass. Filters (like talc and mica) are also added to them. They are water-resistant and suitable for less delicate equipments working under high loads and at low speeds. Besides the above, there are greases prepared by dispersing solids (like graphite, soapstone) in mineral oil. These are mostly used in rail axle boxes, machine bearings, tractors rollers, wires ropes etc.

27.2.3 SOLID LUBRICANTS

Solid lubricants are used where: (i) operating conditions are such that a lubricating film cannot be secured by use of lubricating oils or greases; (ii) contamination (by the entry of dust or grit particles) of lubricating oil or grease is unacceptable, (iii) the operating temperatures or load is too high even for a semi-solid lubricant to remain in position; and (iv) combustible lubricants must be avoided.

The two most usual solid lubricants employed are graphite and molybdenum disulphide. Graphite consists of a multitude of flat plates, one atom thick, which are held together by only weak bonds, so that the force to shear the crystals parallel to the layers is low. Consequently, the parallel layers slide over one another easily. Usually, some organic substances are mixed solid lubricants so that they may stick firmly to the metal surface.

On the other hand, molybdenum disulphide has a sandwich like structure in which a layer of a Mo atoms lies between two layers of S atoms. Poor interlaminar attraction is responsible for low shear strength in a direction parallel to the layers. Solids lubricants are used either in the dry powder or mixed with water or oil. The solids fill up the low spots in the surfaces of moving parts and form solid films, which have low frictional resistance. The usual coefficient of friction between solid lubricants is between 0.005 and 0.01.

(a) Graphite is the most widely used of all solid lubricants. It is very soapy to touch, non-inflammable and not oxidized in air below 375°C. In the absence of air, it can be used upto very much higher temperatures. Graphite is used either in powdered form or as suspension. Suspension of graphite in oil or water is brought about with the help of an emulsifying agent like tannin. When graphite is dispersed in oil, it is called 'oildag' and when it is dispersed in water; it is called 'aquadag'. Oildag is found particularly useful in internal combustion engines, because it forms a film between the piston rings and the cylinder and gives a tight-fit contact, thereby increasing compression. On the other hand, oildag is useful where a lubricant free from oil is needed. e.g., foodstuffs industry. Graphite is also mixed with greases to form graphite-greases, which are used at still higher temperatures.

Uses: As lubricant in air-compressors, lathes, general machine-shop works, foodstuffs industry, railway track-joints, open gears, chains, cast iron bearings, internal combustion engine, etc. (b) Molybdenum disulphide possesses very low coefficient of friction and is stable in air up to 400°C. Its fine powder may be sprinkled on surfaces sliding at high velocities, when it fills low spots in metal surfaces, forming its film. It is also used along with solvents and in greases. Besides the more important graphite and molybdenum disulphide, other substances like soapstone, talc, mica, etc., are also used as solid lubricants.

27.3 SYNTHETIC LUBRICANTS

Petroleum-based lubricants can be used under abnormal conditions like extremely high

temperature, chemically reactive atmosphere, etc. By employing certain specific additives. However, synthetic lubricants have been developed which alone can meet the most drastic and severe conditions such as those existing in aircraft engines, in which the same lubricant may have to use in the temperature range of -50°C and 250°C. Such a lubricant should possess low freezing point, high viscosity-index and also should be non-inflammable.

Modern synthetic lubricants possess, in general, the following distinguishing characteristics: (1) non-inflammable, (ii) high flash points, (iii) high thermal stability at high operating temperatures, (iv) high viscosity-index, (v) chemical stability, etc. Important synthetic lubricants are given below.

(1) Polymerized hydrocarbons like polyethylene, polypropylene, polybutylene in the molecular weight range of 500 to 50,000 are residue-free, light in color, free from non-hydrocarbon impurities, chemically non-reactive and high temperature lubricants.

(2) Polyglycols and related compounds like polyethylene glycol, polypropylene glycol, polyglycidyl ethers, and higher polyalkylene oxides can be used as water-soluble as well as water-insoluble lubricants in rubber bearings and joints. Polyglycidyl ethers and higher polyalkylene oxides are water-insoluble, but they can absorb a considerable amount of water. Their viscosity-index is high and these are used in roller bearings of sheet glass manufacturing machines. It may be pointed that polyethylene oxides undergo thermal decomposition (at high temperature) to evolve volatile oxidisable products, so these are not useful as lubricants at high temperatures.

(3) Organic amines, imines and amides are good synthetic lubricants, since they possess low pour-points and high viscosity-index. They can be used under temperature conditions of -50°C to 250°C

(4) Silicones are very good synthetic lubricants, because are not oxidized below 200°C and possess high viscosity-index. These are frequently used for low temperature lubrication purposes. It may be pointed have that silicones are oxidized quickly above 200°C and undergo cracking process at about 230°C, so they are not employed for high temperature applications.

(5) Fluorocarbons are not decomposed by heat, not easily oxidizable and chemically inert and resistant to chemicals, except molten sodium.

27.4 LUBRICATING EMULSIONS

An emulsion is two-phase system, consisting of a fairly coarse dispersion of two immiscible liquids, the one being dispersed as fine droplets in the other. The disperse (or the internal) phase is the liquid that is broken into droplets. The surrounding liquid is known as the continuous or external or dispersing phase. Usually, the size of dispersed droplets varies from 1 to 6 micron. A dispersion system consisting of two immiscible liquids is inherently unstable, and to increase its stability, a third agent, called emulsifier or emulsifying agent, is added. Emulsifiers are compounds exhibiting both polar and non-polar character. The emulsifier molecule contains a hydrophobic-end and a hydrophilic end. Hydrophobic-end of the molecule is preferably wetted by oil; whereas the hydrophilic-end is wetted by water. Thus, emulsifier molecule is adsorbed at the interface of the two phases (oil and water), resulting in the formation of a protective film around the dispersed droplets. A Sodium Soap molecule illustrates well the functioning of an emulsifier. The sodium soap is the sodium salt of a long chain fatty acids like $C_{15}H_{31}COONa$, possessing a hydrophilic group -COONa and hydrophobic-end, $C_{15}H_{31}$.

Geometric calculations have shown that the maximum amount of dispersed phase in the other liquid can be 74.02% of the total volume. Thus, a water-oil emulsion mixture with less than 26% oil would tend to form an O/W emulsion; whereas a mixture with more than 74% oil would result in a W/O emulsion. Composition between 26 and 74% can result in both types of emulsion.

(a) Oil in-water emulsions are obtained by adding oil containing about 3-20% water-soluble emulsifying agent to a suitable quantity of wafer. The most usual emulsifying agents are sodium soaps and sodium and potassium salts of sulphonic acids. The main use of such an emulsion is as cooling and lubricating liquid for cutting tools. Another use is lubrication for certain rather heavy sliding components such as pistons in marine diesel engines and large internal combustion engines. Such emulsions also give rust protection.

(b) Water-in-oil emulsions are prepared by 'mixing together water containing about 1 to 10 % water-soluble emulsifier (Like alkaline-earth soap, e.g., calcium stearate) with oil. These emulsions possess much higher viscosity than that of the oil from which they are prepared. An emulsion which uses about 40% water by volume is widely used to lubricate compressors and pneumatic tools. They provide cooling effect (due to the evaporation of water), besides lubrication action.

Lesson 24. Properties and analysis of lubricants

The most important properties of lubricants which are of prime importance in lubrication are viscosity, viscosity temperature relation, viscosity index, volatility etc. In order to get efficient lubrication, there should be no change in these properties during lubrication .Moreover there should be no effect of any chemical change such as decomposition, oxidation, reduction at higher temperature and emulsification during lubrication. The behavior of a lubricating oil or lubricant is determined by its viscosity. Viscosity is defined as the force in dynes necessary for the movement of 1 sq. cm. layer of fluid with a velocity of 1 cm per sec, past another parallel layer 1 cm away. The unit usually employed is centipoises. The measurement of viscosity is usually done in C.G.S units and the unit is stoked. In case of thin oils, which have very low viscosity, it is measured in centi- stokes. The viscosity measured

28.1 PROPERTIES OF LUBRICATING OILS

28.1.1 Viscosity is the property of a liquid or fluid by virtue of which it offers resistance to its own flow. A liquid in a state of steady flow on a surface may be supposed to consist of a series of parallel layers moving one above the other. Any two layers will move with different velocities; top layer move faster than the next lower layer, due to viscous drag (i.e., internal friction). Consider two layers of a liquid separated by a distance, d and moving with a relative velocity difference, v. Then, force per unit area (F) required maintaining this velocity difference is given by:

$F = \eta v / d$

Where η (eta) is a constant of a liquid, called coefficient of viscosity.

Viscosity is the most important single property of any lubricating oil, because it is the main determinant of the operating characteristics of the lubricant: (i) if the viscosity of the oil is too low. a liquid oil film cannot be maintained between two mooing/sliding surfaces, and consequently, excessive wear will take place. On the other hand, (ii) If the viscosity is too high, excessive friction will result. The viscosity is temperature depending property.

Measurement of viscosity of lubricating oil is made with the help of an apparatus called

the viscometer. In a viscometer, a fixed volume of the liquid is allowed to flow, from a given height, through a standard capillary tube under its own weight and the time of flow in seconds is noted. The time in seconds is proportional to true viscosity. Oswald viscometer, Redwood viscometers, Saybolt viscometer are used, for measuring viscosities of lubricating oils. The results are expressed in terms of time taken by oil to flow through particular instrument. For example, if time of flow of oil through Redwood viscometer at 20°C is 100 seconds, then its viscosity is 100 Redwood seconds at 20°C. Now a day Brookfield viscometer is commonly used for determining the viscosity of lubricating oils.

28.1.2 Flash and fire-points: Flash point is the lowest temperature at which the oil lubricant gives off enough vapours that ignite for a moment, when a tiny flame is brought near it; while fire-point is ' the lowest temperature at which the vapours of the oil burn continuously for at least five seconds, when a tiny flame is brought near it. In most cases, the fire-points are 5 to 40° higher than the flash-points. The flash and fire-points do not have any bearing with the lubricating property of the oil, but these are important when oil is exposed to high temperature service. A good lubricant should have flash point at least above the temperature at which it is to be used. These safeguards against risks of fire, during the use of lubricant. The flash and fire-points are, usually, determined by using Pensky-Marten's apparatus.

28.1.3 Cloud and pour-points: When an oil is cooled slowly, the temperature at which it becomes cloudy or hazy in appearance, is called its cloud-point while the temperature at which the oil ceases to flow or pour, is called its pour-point. Cloud and pour-points indicate the suitability of lubricants in cold conditions. Lubricant used in a machine working at low temperatures should possess low pour-point; otherwise solidification of lubricant will cause jamming of the machine. It has been found that presence of waxes in the lubricating oil raise the pout-point. Determination of pour-point is carried out with help of pour-point apparatus.

28.1.4. Emulsification: It is the property of oils to get intimately mixed with water, forming a mixture, called emulsion. Certain oils form emulsions with water easily. Emulsions have a tendency to collect dirt, grit,. Foreign matter etc., thereby causing abrasion and wearing out of the lubricated parts of the machinery. So, good lubricating oil should form an emulsion with water, which breaks off quickly. The tendency of lubricant-water emulsion to break is determined by A.S.T.M. test. In this, 20 ml of oil is taken in a test-tube and steam at 100^{o}C is bubbled through it, till the temperature is raised to 90^{o}C. The tube is then placed in a bath maintained at 90^{o}C and the time in seconds is noted, when the oil and water separate out in distinct layers. The time in second in which oil and water emulsion separates out in distinct layers, is called steam emulsion number (S.E.N.). A goad lubricant should possess a low steam emulsion number.

28.1.5. Volatility: When lubricating oil is used in heavy machinery working at high temperature, a portion of oil may vaporize; leaving behind a residual oil, which have different lubricating properties (like increased viscosity). Good lubricant should have low, volatility. The volatility of oil is determined by an apparatus, called vaporimeter, which consists essentially of a furnace heated by some fuel gas. In the centre of the furnace passes a coiled-form of copper tube, through which air can be passed. A known weight of oil under examination is taken in a platinum crucible, which is then introduced into the copper tube. Dry air at a rate of 2 litres/min is passed through the copper tube. After 1 hour of heating, the crucible is taken out, cooled and weighed. The loss is weight is calculated as percentage of the original weight of oil taken.

28.1.6. Carbon residue: Lubricating oils contain high percentage of carbon in combined form. On heating, they decompose depositing a certain amount of carbon. The deposition of such carbon in machine is intolerable, particularly in inert combustion engines and air-compressors. A good lubricant should deposit least amount of the carbon in use. The estimation of carbon residue is, generally, carried out by Conradson method. A weighed quantity of oil is taken in a silica crucible (about 65-85 ml capacity). The skidmore crucible is provided with a lid, having a small tube-type opening for the escape of volatile matter. The combination is then placed in a wrought Iron crucible (about 8 cm in dia and 6 mm high) covered with chimney-shaped iron hood (of about 10 cm diameter). The wrought iron crucible is heated slowly for 10 minutes, till flame appears. Slow heating is continued for 5 minutes more. Finally, strong heating is done for about 15 minutes, till vapours of all volatile matter are burnt completely. Apparatus is then allowed to cool and weight of residue left is determined. The result is expressed as percentage of the original weight of oil taken.

28.1.7 Corrosion stability of lubricating oil is estimated by carrying out corrosion test. A polished copper strip is placed in the lubricating oil for a specified time at a particular temperature. After the stipulated time, the strip is taken out and examined for corrosion effects. If the copper strip has tarnished, it shows that oil contains any chemically active substance. A good lubricant should not affect the copper strip. To retard corrosion effects of oil, certain inhibitors are added to them. Commonly used inhibitors are organic compounds containing phosphorus, arsenic, antimony, chromium, bismuth or lead.

28.1.8 Aniline point of oil is defined as the minimum equilibrium solution temperature. For equal volume of aniline and oil sample. Aniline point gives an indication of the possible deterioration of oil in contact with rubber sealing's, pickings, etc. Aromatic hydrocarbons have a tendency to dissolve natural rubber and certain types of synthetic rubbers. Consequently, low aromatic content in the lubricants is desirable. A higher aniline-point means a higher percentage of paraffinic hydrocarbons and hence, a lower percentage of aromatic hydrocarbons.

Aniline point is determined by mixing mechanically equal volumes of the oil sample and aniline in a test-tube. The mixture is heated, till homogeneous solution is obtained. Then, the tube is allowed to cool at a controlled rate. The temperature at which the two phases (oil and aniline) separate out is recorded at the aniline point.

28.1.9 Precipitation number is the percentage of asphalt present in oil. A known weight of the lubricant is dissolved in petroleum ether and centrifuged. The precipitated asphalt, if any, is filtered, washed, dried and weighed. It is the then expressed as percentage of weight of oil taken. Precipitation number is used to differentiate the differentiate classes of the lubricants

28.1.10 Specific gravity is very useful in identifying oil, as it gives an indication of the type of crude from which the lubricant has been prepared.

28.1.11 Ash content of oil is determined by heating strongly in air a known weight of oil in a crucible to a constant weight. The percentage of ash in lubricating oil, particularly in used-oil, is very useful in determining the materials that may cause abrasion and wear.

28.1.12 Neutralization number refers to the determination of acidic or basic constituents of an oil. Determination of acidic constituents is more common and it is referred to as Acid number or value, which is defined as the number of milligrams of KOH required to neutralize the free acids in 1 g of the oil. Generally, free acids are not present in the lubricants, unless refined in faulty manner. Lubricating oil should possess acid value less than 0.1. Value greater than 0.1 indicates that oil has been oxidized. This will, consequently, lead to corrosion, besides gum and sludge formation.

28.1.13 Saponification number is the number of milligrams of KOH required to saponify 1 g of oil. Mineral oils do not saponify at all, but vegetable and animal oils do. Consequently, this test helps us to ascertain whether the oil under reference is animal and vegetable oil or mineral or a compounded oil containing mineral and vegetable oils.

28.2 PROPERTIES OF GREASES

28.2.1 Consistency or yield value is expressed in terms of penetration, which is defined as the distance in tenth of millimetre that a standard cone penetrates vertically into the sample, under the standard conditions of load, temperature and time. The value of load, temperature and time are taken respectively as 150 g, 25^{o}C, and 5 seconds. Consistency of grease depends on the structure and Interaction of the gelling elements in it and to some extent on the viscosity of oil used. The consistency is determined by using Penetrometer.

28.2.2 Drop-point is the temperature at which it passes from the semi-solid to the liquid state. So this temperature determines the upper temperature limit of the applicability of the grease. The sample is taken in a metal cup, which has an opening of standard size in its bottom. It is then enclosed in a glass case, having a tight lid. A thermometer is also inserted in the cup, so that the bulb of the thermometer is just above the surface of grease sample. The combination is then placed in a glass beaker, containing water and provided with a stirrer. The beaker is heated slowly at a rate of 1^{o}C/minute. As the temperature is raised, the grease sample passes from a semi-solid to a fluid state. The temperature at which its first drop falls from the opening is recorded as drop-point.

28.3 CUTTING FLUIDS

Any liquid (such as oil, water or oil emulsion) or a gas used to cool as well as to lubricate is called a cutting fluid. Emulsions of oil-in-water are mostly used as cutting fluids. Cutting fluids are required for tools used in the machine shop for cutting, threading, sawing, planning, turning, drilling, etc. ; and the cutting fluid performs either of the fractions ; (i) to cool the tools, or (ii) to lubricate the tools, or (iii) to cool as well as to lubricate the tools.

In such machining operations, the friction is very high, due to close contact between the work-piece and the tool; and this generates large amounts of local heat, thereby the tool gets overheated and it may even lose its temper and hardness. Consequently, in such a case, the cutting fluid provides cooling, besides lubrication. In order to provide satisfactory service, the cutting fluid should possess :

1. good lubricating property
2. Low viscosity, so that the lubricant can easily fill in the cracks formed on the work-piece
3. Chemical Stability
4. Non-corrosive nature towards the metals of the work-piece as well as tool
5. High thermal conductivity.

28.3.1 Oil as cutting fluid: In fine work, a stream of oil (like lard or rape or sperm oil) is directed over the work-piece. Here the cutting fluid (the oil) acts more as lubricant and less as heat-carrying agent. When the speed is low and the pressure is high (e.g., in broaching), the oils are mostly used as cutting fluids. Compounded oils obtained by mixing petroleum oils with vegetable and animal oils are also used for such purposes.

28.3.2 Water as cutting fluid: in rough situation, like rough grinding and turning; only cooling action is sufficient. Water being good cooling agent and cheap, so it is mostly employed as cutting fluid. Water is primarily used, when only roaring is required, e.g., in high-speed operations

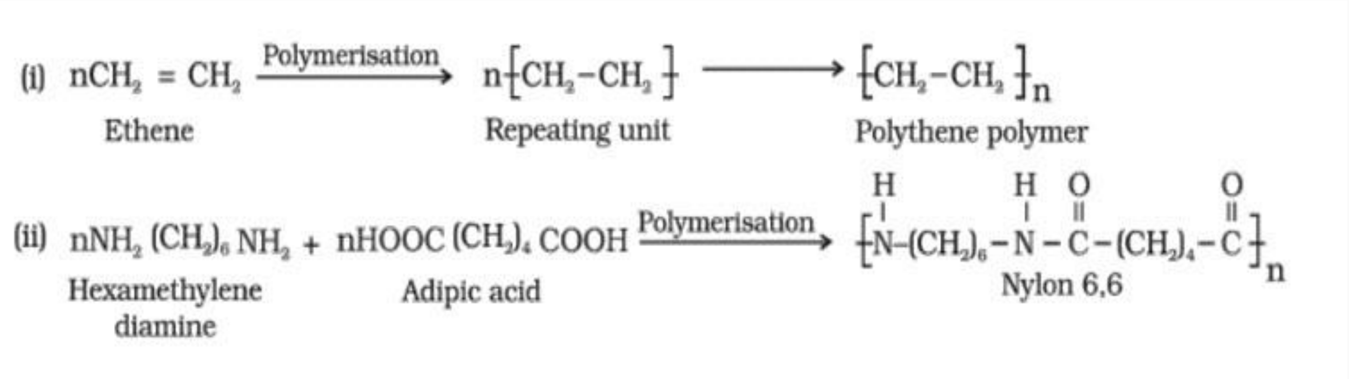
28.3.3 Emulsion as cutting fluid: in most cases, use of either water or oil alone is not satisfactory; and both a cooling agent and a lubricant are needed simultaneously. For such situations, oil-in-water emulsions are employed. These are employed by mixing small amount of petroleum oil in water, and then stabilizing by adding emulsifier (like soap, tallow oil, lard oil, sperm oil, sulphonated oils, e.g., H_2SO_4 -treated castor oil, chloro-sulphonated organic compounds, etc.). Moreover, to prevent gelling (or thickening) of the concentrate, glycols or alcohols are added. In addition to these, certain germicide (like sodium nitrite, triethanol amine) is added. Cutting emulsions serves as : Lubricant to reduce frictional heat and medium for the transfer of heat produced. In other words, use of cutting emulsions reduce power consumption as well as wear of tool. Before choosing a cutting fluid for a job it is, however, essential that it does not cause rusting of the metals involved.

Module 11. Polymers type of polymerization, properties, uses and methods for the determination of molecular weight of polymers

Lesson 25. Polymer : Classification and Its use

25.1 INTRODCTION

The word 'polymer' is made from two Greek words poly means many and mer means small unit or part. The polymer is defined as very large molecules having high molecular mass. These are also known as macromolecules, which are formed by joining of repeating small structural units on a large scale. The repeating structural units are derived from some simple and reactive molecules known as monomers and are linked to each other by covalent bonds. This process of formation of polymers from respective monomers is called polymerisation. The transformation of ethene to polythene and interaction of hexamethylene diamine and adipic acid leading to the formation of Nylon- 6, 6 are examples of two different types of polymerisation reactions.



$$\text{(i)}\quad nCH_2=CH_2 \xrightarrow{\text{Polymerisation}} n\left[CH_2-CH_2\right] \longrightarrow \left[CH_2-CH_2\right]_n$$

$$\text{(ii)}\quad nNH_2(CH_2)_6NH_2 + nHOOC(CH_2)_4COOH \xrightarrow{\text{Polymerisation}} \left[\overset{H}{\overset{|}{N}}-(CH_2)_6-\overset{H}{\overset{|}{N}}-\overset{O}{\overset{\|}{C}}-(CH_2)_4-\overset{O}{\overset{\|}{C}}\right]_n$$

29.2 Classification of Polymers :

Polymer can have different chemical structures, physical properties, mechanical behaviour, thermal characteristics etc. and can be classified in different ways.

Natural and synthetic polymer.
Organic and inorganic polymer.
Thermoplastic and thermosetting polymers.
Classification Based on the structure of the polymers.
Addition and condensation polymers.
Homopolymers and copolymers.
Fibres, plastics and elastomers.
Linear branched and cross-linked polymers.

(I) Natural and Synthetic Polymer:

Those polymers which are isolated from natural materials are called natural polymer. e.g. Cotton, silk, wool, and rubber etc.

Those polymers which are synthesized from low molecular weight compounds are called synthetic polymer. e.g. polyethylene, polystyrene, PC, PVA, P.V.C., etc.

(II) Organic and Inorganic Polymer:

A polymer whose backbone chain is made up of carbon atom is known as organic polymer. A polymer whose backbone chain is made up of only inorganic molecules and not of carbon atom is known as inorganic polymers. E.g. Glass, silicone, rubber etc.

(III) Thermoplastic and Thermosetting Polymer:

Thermoplastic: Those polymers which soften on heating and moulded or extruded in to required shapes are known as plastics for the manufacturing of a wide range of articles. E.g. Polyethylene, polypropelene, P.V.C, polystyrene, etc.

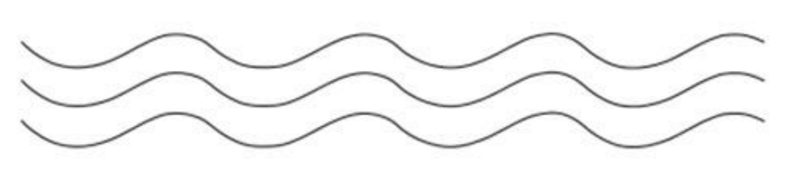
The process of heating, reshaping and retaining the same on cooling can be repeated several times.

Thermosetting Polymers: A sample of such material is gigantic molecule and heating does not soften it, since softening would require breaking of covalent bond. Indeed, heating may causes formation of additional cross-links and make the material harder, for this reason space network polymer are called thermosetting polymer. Such polymers, upon heating sets into an infusible mass and once sets cannot be reshaped. E.g. Phenol-formaldehyde (Bakelite), Urea-formaldehyde (polyurethane) etc.

(IV) Classification Based on the structure of the polymers

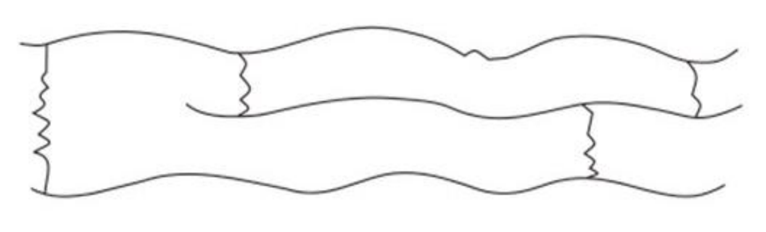
1. Linear polymers

These polymers consist of long and straight chains. The examples of Polymers are high density polythene, polyvinyl chloride, etc. These are represented as:



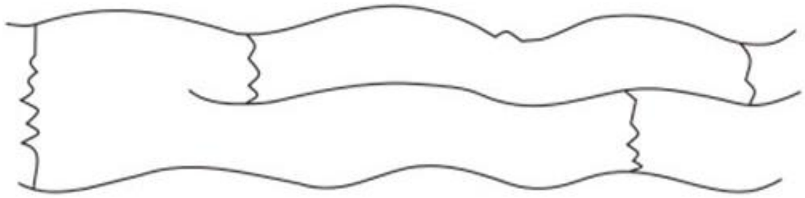
2. Branched chain polymers

These polymers contain linear chains having some branches, e.g., low density polythene. These are depicted as follows:



3. Cross linked or Network polymers

These are usually formed from bi-functional and tri-functional monomers and contain strong covalent bonds between various linear polymer chains, e.g. phenol-formaldehyde, melamine, etc. These polymers are depicted as follows:



(V) Addition and Condensation polymerization:

Addition polymerization: It is also known as chain reaction polymerization. There is series of reactions each of which consumes a reactive particle and produce another similar particle, each individual reaction thus depends upon the previous one. The reactive particles can be free radicals; cation or anion

$CH_2=CH_2 + Rad\cdot$ ——— $Rad\cdot -CH_2-CH_2\cdot$

$Rad -CH_2-CH_2\cdot + n(CH_2=CH_2)$ ——— $[-CH_2-CH_2-]-_n$

Polyethylene

Polymers are formed in two general ways.

(A) Addition polymerization (Chain reaction polymerization)

(B) Condensation polymerization (Step reaction polymerization)

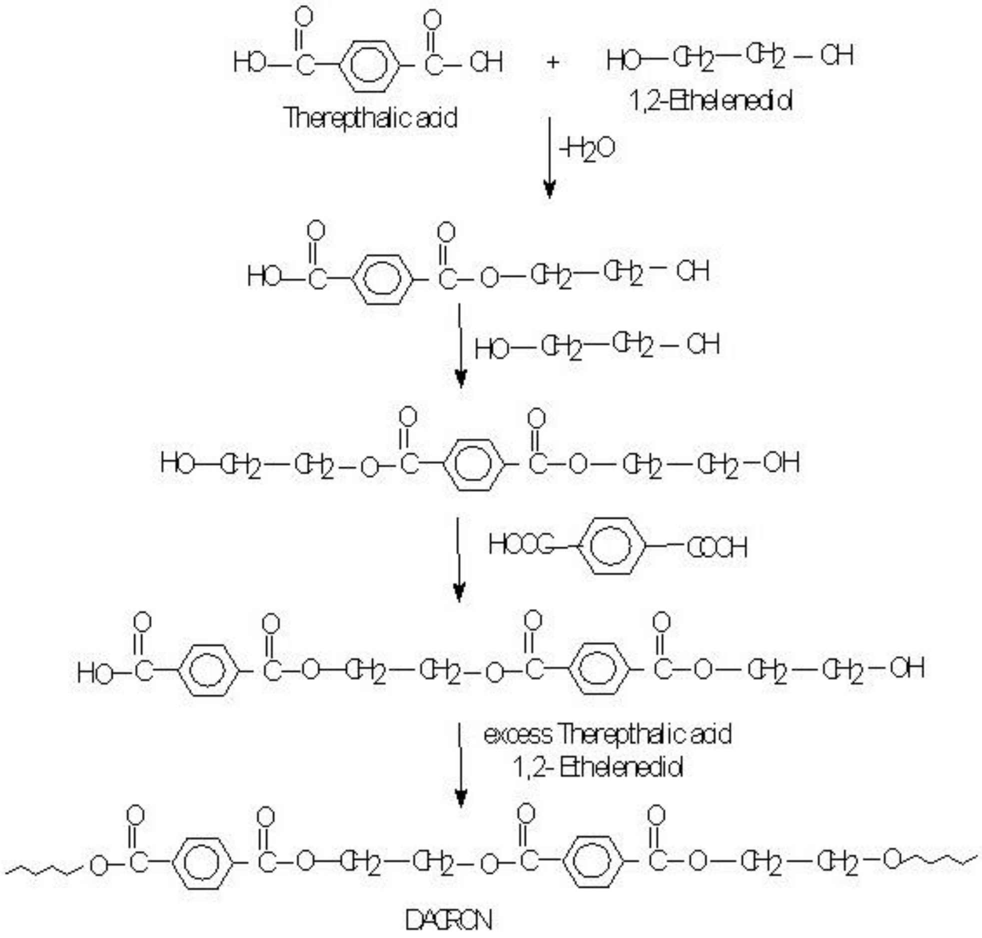
(A) Addition Polymerization: There is series of reactions each of which consumes a reactive particle and produce another similar particle, each individual reaction thus depends upon the previous one. The reactive particles can be free radicals; cation or anion

$CH_2=CH_2 + Rad\cdot$ ——— $Rad -CH_2-CH_2\cdot$

$Rad -CH_2-CH_2\cdot + n(CH_2=CH_2)$ ——— $[-CH_2-CH_2-]-_n$

Polyethylene

(B) Condensation Polymerization: There is a series of reactions each of which is essentially independent of the preceding one. Formation of polymer takes place because the monomer undergoes reaction at more than one functional group. E.g. A diol reacts with a dicarboxylic acid to form an ester but each moiety of the simple ester still contain a group that can react to generate another ester linkage and hence a large molecule and so on.



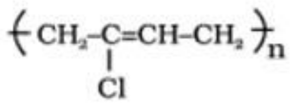
(VI) Homopolymers and copolymers

(VII) Classification Based on Molecular Forces

A large number of polymer applications in different fields depend on their unique mechanical properties like tensile strength, elasticity, toughness, etc. These mechanical properties are governed by intermolecular forces, e.g., van der Waals forces and hydrogen bonds, present in the polymer. These forces also bind the polymer chains. Under this category, the polymers are classified into the following four sub groups on the basis of magnitude of intermolecular forces present in them.

1. Elastomers

These are rubber – like solids with elastic properties. In these elastomeric polymers, the polymer chains are held together by the weakest intermolecular forces. These weak binding forces permit the polymer to be stretched. A few 'crosslinks' are introduced in between the chains, which help the polymer to retract to its original position after the force is released as in vulcanised rubber. The examples are buna-S, buna-N, neoprene, etc.



$$\left(CH_2-\underset{\underset{Cl}{|}}{C}=CH-CH_2 \right)_n$$

Neoprene

2. Fibres

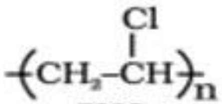
Fibres are the thread forming solids which possess high tensile strength and high modulus. These characteristics can be attributed to the strong intermolecular forces like hydrogen bonding. These strong forces also lead to close packing of chains and thus impart crystalline nature. The examples are polyamides (nylon 6, 6), polyesters (terylene), polyacrylonitrile etc.

$$\left(\overset{H}{\overset{|}{N}}-(CH_2)_6-\overset{H}{\overset{|}{N}}-\overset{O}{\overset{\|}{C}}(CH_2)_4-\overset{O}{\overset{\|}{C}}\right)_n$$

Nylon 6,6

3. Thermoplastic polymers

These are the linear or slightly branched long chain molecules capable of repeatedly softening on heating and hardening on cooling. These polymers possess intermolecular forces of attraction intermediate between elastomers and fibres. Some common thermoplastics are polythene, polystyrene, polyvinyls, etc.

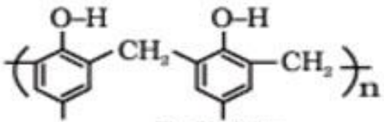


$$\left(CH_2-\overset{Cl}{\overset{|}{C}}H\right)_n$$

PVC

4 Thermosetting polymers

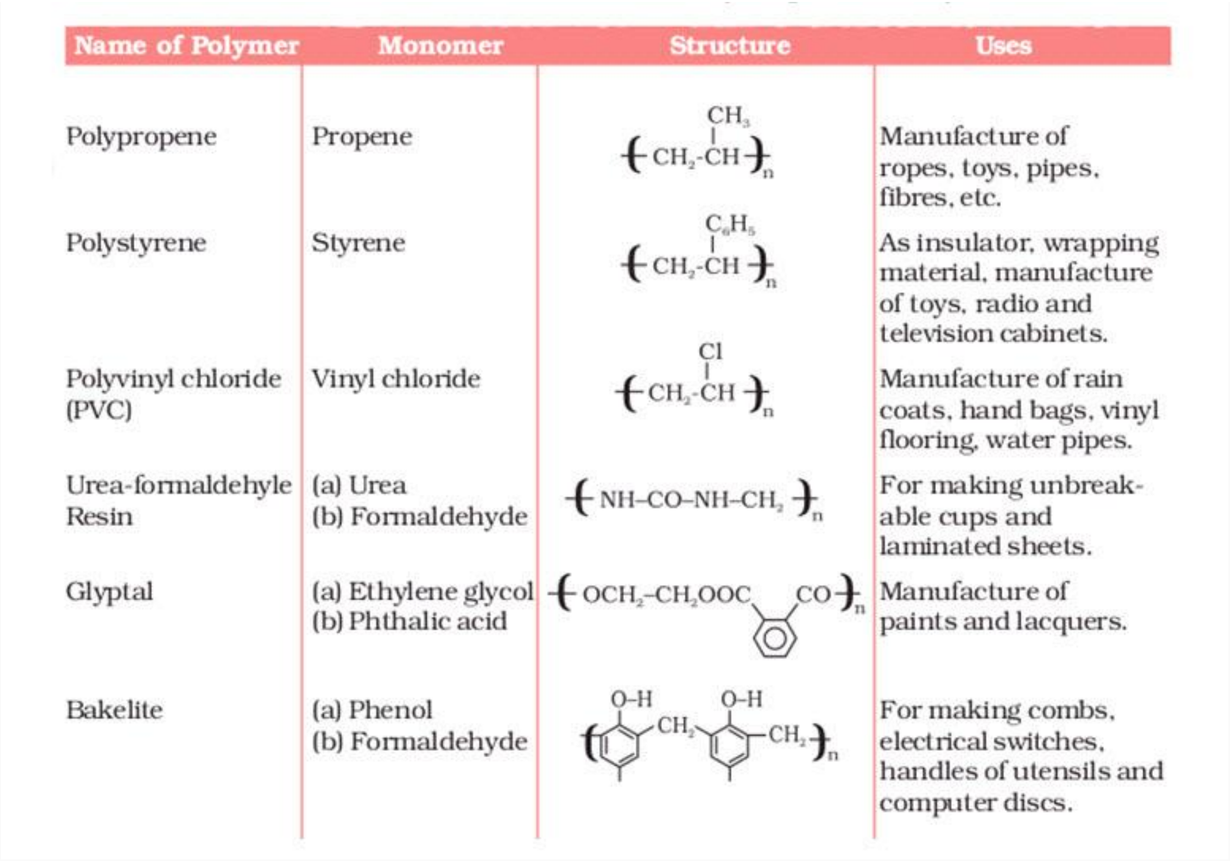
These polymers are cross linked or heavily branched molecules, which on heating undergo extensive cross linking in moulds and again become infusible. These cannot be reused. Some common examples are bakelite, urea-formaldelyde resins, etc.



Bakelite

Polymers of Commercial Importance

Besides, the polymers already discussed, some other commercially important polymers along with their structures and uses are given below in Table 15.1.



Name of Polymer	Monomer	Structure	Uses
Polypropene	Propene	$\left(CH_2\text{-}\underset{}{\overset{CH_3}{\overset{\vert}{CH}}} \right)_n$	Manufacture of ropes, toys, pipes, fibres, etc.
Polystyrene	Styrene	$\left(CH_2\text{-}\overset{C_6H_5}{\overset{\vert}{CH}} \right)_n$	As insulator, wrapping material, manufacture of toys, radio and television cabinets.
Polyvinyl chloride (PVC)	Vinyl chloride	$\left(CH_2\text{-}\overset{Cl}{\overset{\vert}{CH}} \right)_n$	Manufacture of rain coats, hand bags, vinyl flooring, water pipes.
Urea-formaldehyde Resin	(a) Urea (b) Formaldehyde	$\left(NH\text{–}CO\text{–}NH\text{–}CH_2 \right)_n$	For making unbreak-able cups and laminated sheets.
Glyptal	(a) Ethylene glycol (b) Phthalic acid	$\left(OCH_2\text{–}CH_2OOC \quad CO \right)_n$	Manufacture of paints and lacquers.
Bakelite	(a) Phenol (b) Formaldehyde	O-H CH₂ O-H CH₂ n	For making combs, electrical switches, handles of utensils and computer discs.

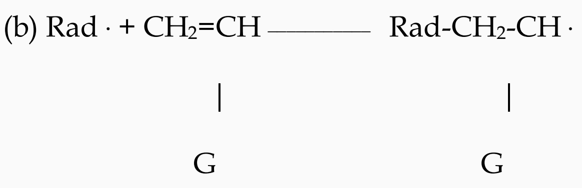
The common use of polymers in the manufacture of plastic buckets, cups and saucers, children's toys, packaging bags, synthetic clothing materials, automobile tyres, gears, electrical components, contact lenses, adhesives, medical supplies (i.e. bone cement and blood begs) and seals, electrical insulating materials and machine parts has completely revolutionised the daily life as well as the industrial scenario. Indeed, the polymers are the backbone of four major industries viz. plastics, elastomers, fibres and paints and varnishes.

(A) Chain Reaction Polymerization:

It is a series of reactions. In which an initiator such as peroxide is added to monomer to form a bigger free radical. This bigger radical adds to another monomer (alkene) to generate a still larger radical and so on. And finally at the chain termination large molecule known as polymer is produced. E.g. Polymerization of vinyl compound it proceeds via three steps.

(i) Chain initiating step: Free radical generated from initiator, adds to the double bond of monomer to form a new bigger free radical.

(a) Peroxide $\xrightarrow{\text{UV light}}$ Rad ·



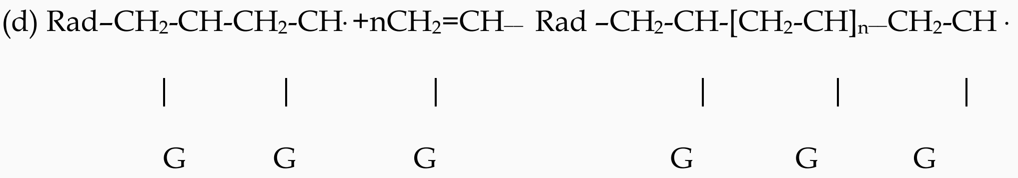
(b) $\mathrm{Rad}\cdot + \underset{\substack{\vert \\ G}}{CH_2{=}CH} \longrightarrow \mathrm{Rad}\text{-}\underset{\substack{\vert \\ G}}{CH_2\text{-}CH}\cdot$

(ii) Chain propagation:

(c)

$$\text{Rad-CH}_2\text{-}\underset{\underset{G}{|}}{\text{CH}}\cdot + \text{CH}_2\text{=}\underset{\underset{G}{|}}{\text{CH}} \longrightarrow \text{Rad –CH}_2\text{-}\underset{\underset{G}{|}}{\text{CH}}\text{-CH}_2\text{-}\underset{\underset{G}{|}}{\text{CH}}\cdot$$

(d)



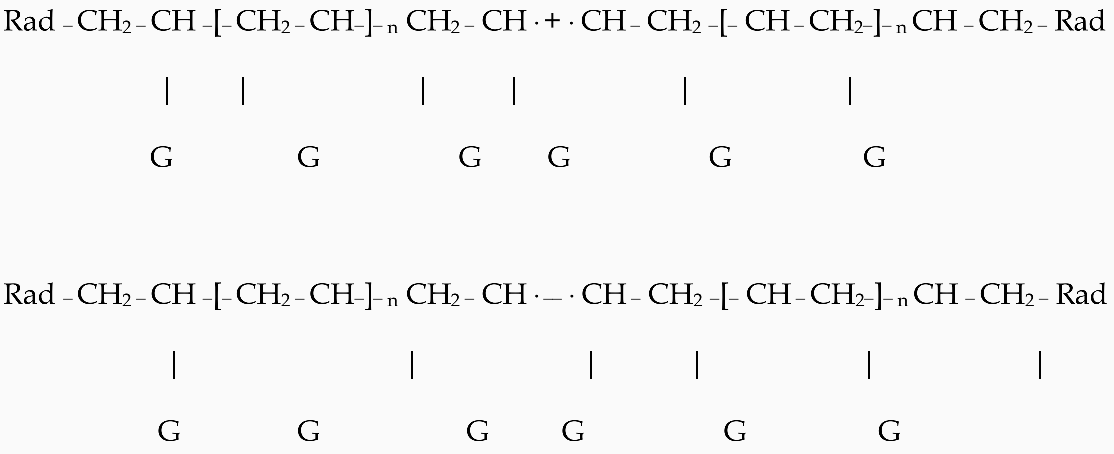
$$\text{Rad–CH}_2\text{-}\underset{\underset{G}{|}}{\text{CH}}\text{-CH}_2\text{-}\underset{\underset{G}{|}}{\text{CH}}\cdot + n\text{CH}_2\text{=}\underset{\underset{G}{|}}{\text{CH}} \longrightarrow \text{Rad –CH}_2\text{-}\underset{\underset{G}{|}}{\text{CH}}\text{-[CH}_2\text{-}\underset{\underset{G}{|}}{\text{CH}}]_n\text{–CH}_2\text{-}\underset{\underset{G}{|}}{\text{CH}}\cdot$$

In the propagation step, radical combines with second monomer molecule. This forms a new radical and then after many similar repetition produce large radical. Thus in each step consumption of free radical is accompanied by the formation of new; bigger free radical.

(iii) Chain Termination:

Reaction chain is terminated by combination or disproportionation of two free radicals.

(a) Combination the two radical may pair their odd electrons to produce a polymer.

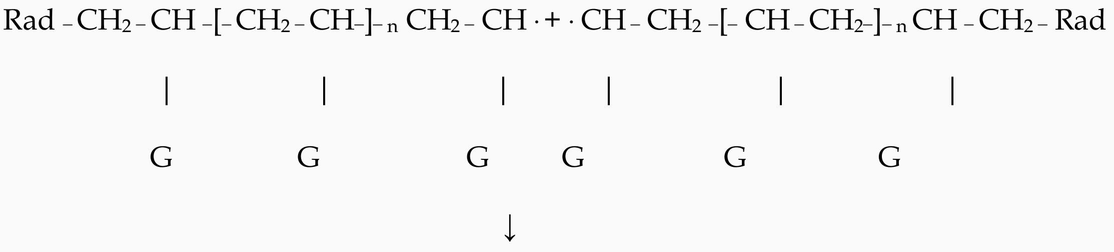


$$\text{Rad - CH}_2\text{ - }\underset{\underset{G}{|}}{\text{CH}}\text{ -[- CH}_2\text{ - }\underset{\underset{G}{|}}{\text{CH}}\text{-]-}_n\text{ CH}_2\text{ - }\underset{\underset{G}{|}}{\text{CH}}\cdot + \cdot\underset{\underset{G}{|}}{\text{CH}}\text{ - CH}_2\text{ -[- }\underset{\underset{G}{|}}{\text{CH}}\text{ - CH}_2\text{-]-}_n\underset{\underset{G}{|}}{\text{CH}}\text{ - CH}_2\text{ - Rad}$$

$$\text{Rad - CH}_2\text{ - }\underset{\underset{G}{|}}{\text{CH}}\text{ -[- CH}_2\text{ - }\underset{\underset{G}{|}}{\text{CH}}\text{-]-}_n\text{ CH}_2\text{ - }\underset{\underset{G}{|}}{\text{CH}}\cdot\text{—}\cdot\underset{\underset{G}{|}}{\text{CH}}\text{ - CH}_2\text{ -[- }\underset{\underset{G}{|}}{\text{CH}}\text{ - CH}_2\text{-]-}_n\underset{\underset{G}{|}}{\text{CH}}\text{ - CH}_2\text{ - Rad}$$

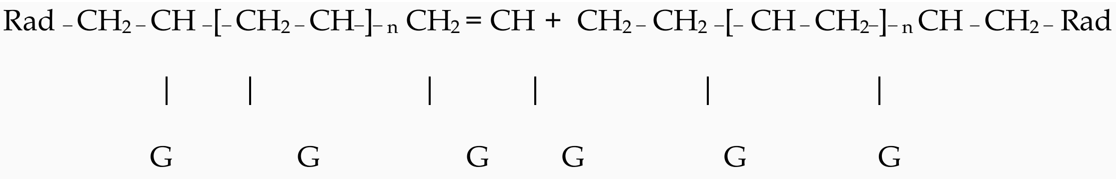
(b) The active site of one radical may strike on the second carbon in the chain of other radical. Here first one radical abstracts an H · from the other radical, which forms a

π-bond and produce a mixture of two polymers.



$$\text{Rad - CH}_2\text{ - }\underset{\underset{G}{|}}{\text{CH}}\text{ -[- CH}_2\text{ - }\underset{\underset{G}{|}}{\text{CH}}\text{-]-}_n\text{ CH}_2\text{ - }\underset{\underset{G}{|}}{\text{CH}}\cdot + \cdot\underset{\underset{G}{|}}{\text{CH}}\text{ - CH}_2\text{ -[- }\underset{\underset{G}{|}}{\text{CH}}\text{ - CH}_2\text{-]-}_n\underset{\underset{G}{|}}{\text{CH}}\text{ - CH}_2\text{ - Rad}$$

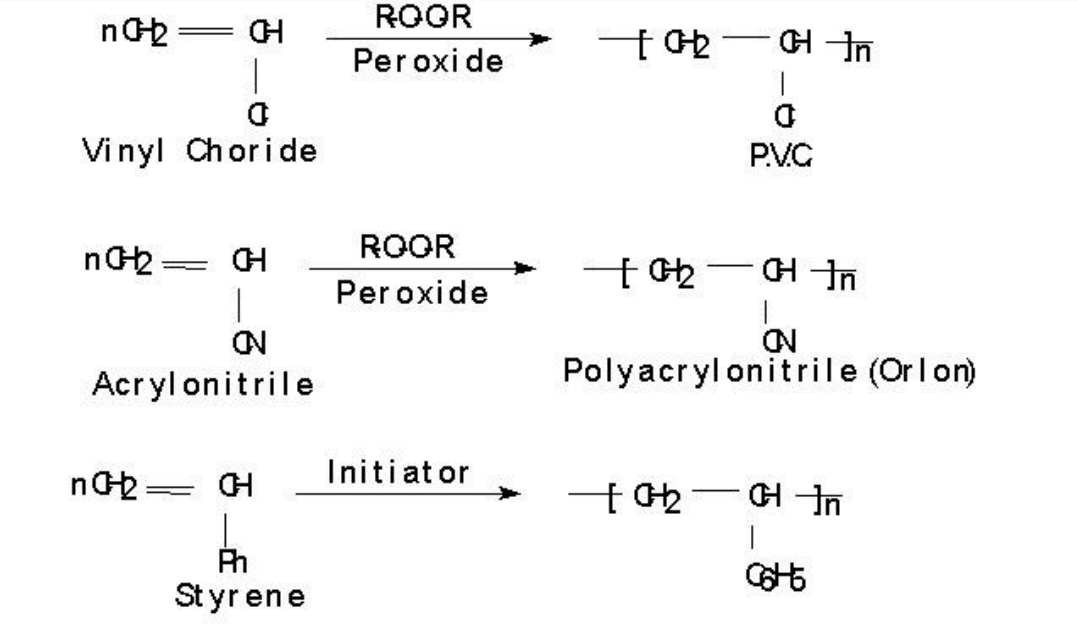
$$\downarrow$$



$$\text{Rad}-CH_2-\underset{G}{CH}-[-\underset{G}{CH_2}-CH-]_{n}\,\underset{G}{CH_2}=\underset{G}{CH}+CH_2-\underset{G}{CH_2}-[-CH-\underset{G}{CH_2}-]_{n}\,CH-CH_2-\text{Rad}$$

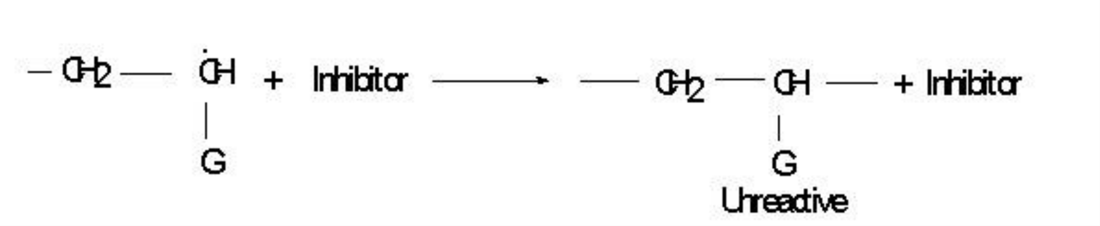
Mechanism of Free radical Vinyl Polymerization.

The polymerization of ethylene and substituted ethylene (i.e. styrene, acrylonitrite, vinyl chloride.)are carried out using free radicals; Which are generated in the presence of a small amount of an initiator such as peroxide. Here the reaction occurs at the doubly bonded carbons i.e. at the vinyl groups and hence is called vinyl polymerization. E.g.



Inhibitor:

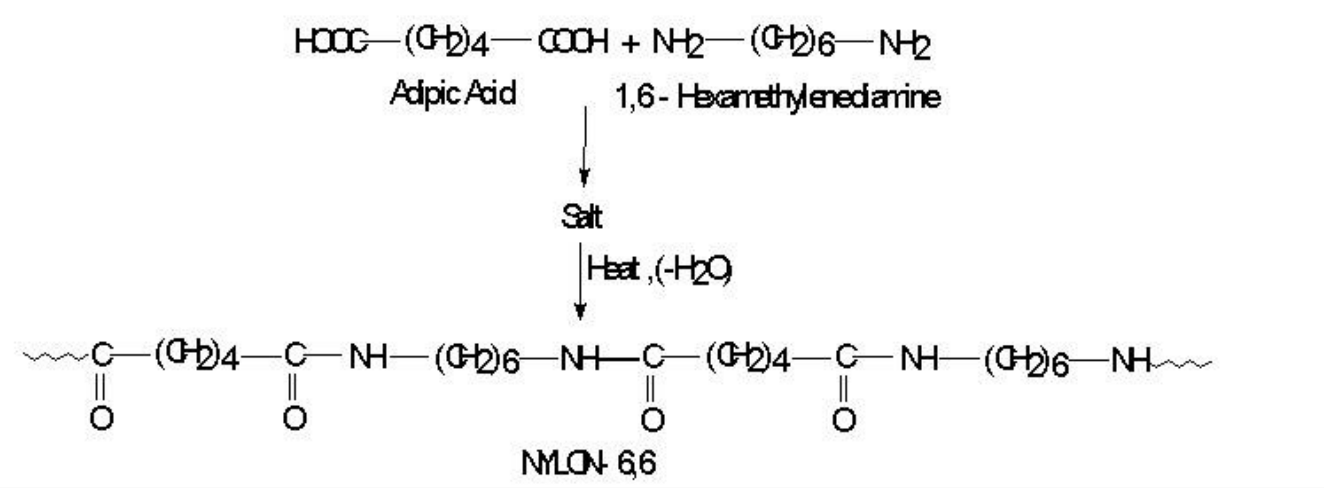
When compound such as phenols, quinones and some amines are added during polymerization process the growing free radical may react with such compound and therefore reaction chain is terminated, but no new one begun. Such compound is known as inhibitor.



Synthesis of NYLON-- 6,6

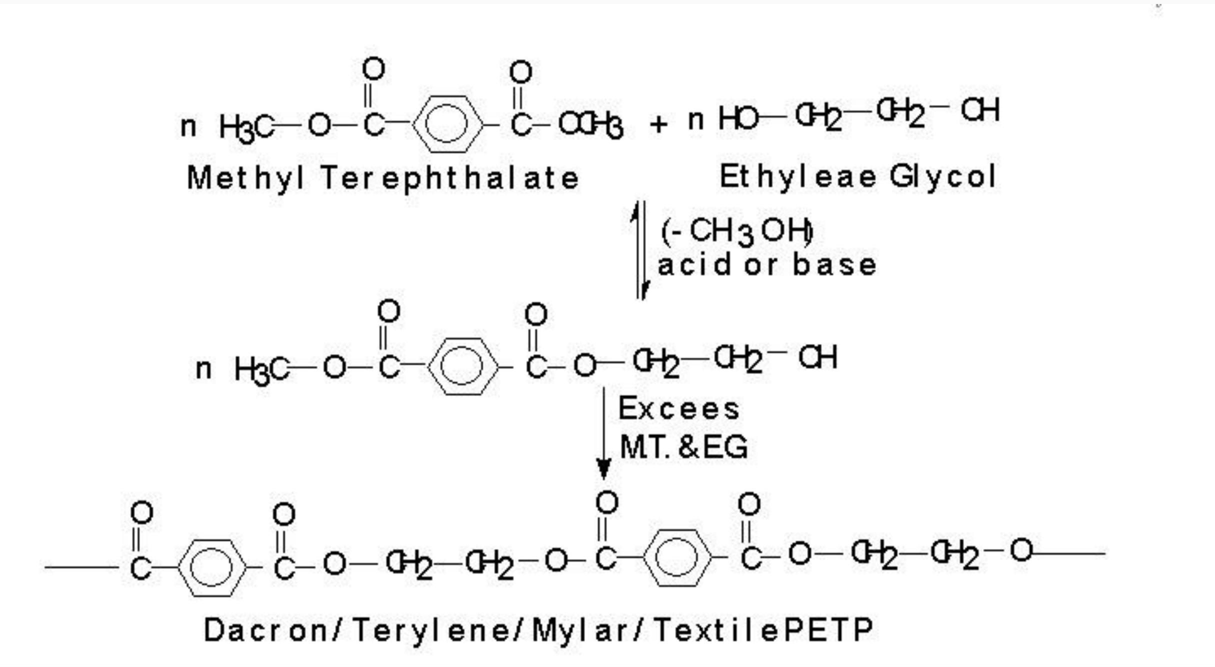
It is an example of step reaction Polymerization. In which Carboxylic acid that contains more than one –COOH group reacts with an amine that contains more than one –NH_2 group then the products are polyamides. Nylons are aliphatic polyamides. There are different types of nylons and are indicated by numbering systems. This numbers gives the number of carbon atom present in (first) the diamines and (second) in the dicarboxylic acid.

NYLON--6,6: It is prepared by the condensation between adipic acid and 1,6-hexanediamine.



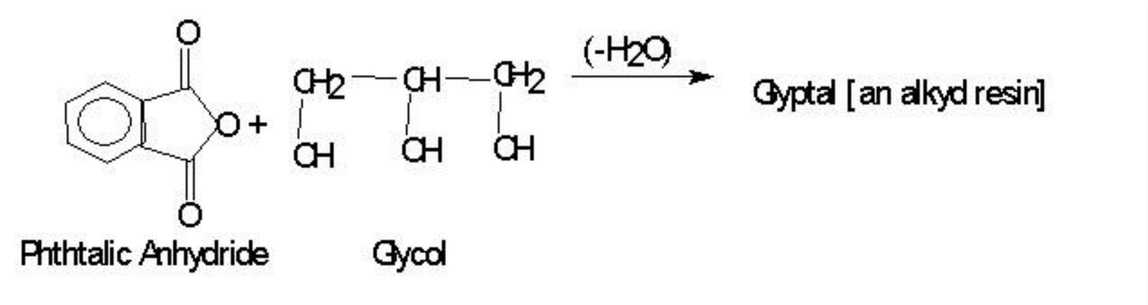
It is used as plastic as well as fibres. As a plastic it is used in gears and bearings. As a fiber it is used in tyres cord and rops.

POLYETHYLENE TEREPHTHALATE (PETP) (Terylene, Dacron): When Carboxylic acid or it's ester that contains more than one –COOH group or –COOR group reacts with diol then the products are,



They are use as fiber. It is commonly known as terylene. PETP is also used in to films of magnetic recording tapes. The material in sheet form also marketed as Malar.

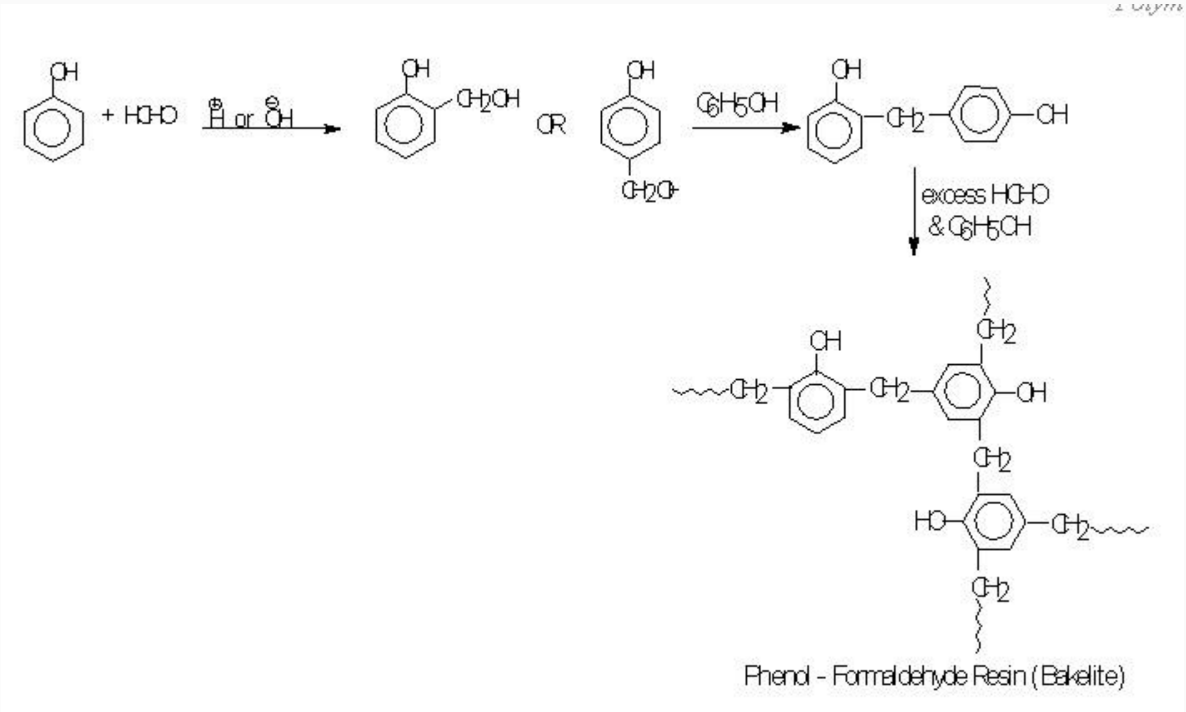
If each monomer molecules contains just two functional groups, growth can occur in only two direction and a linear polymer is obtained as in Dacron. But if reaction can occur at more than two positions in a monomer, there is a formation of a highly cross linked space network polymer as in glyptal, an alkyd resin.



Step Reaction Polymerization

Step reaction polymerization proceeds through a series of reaction in which two monomers each of which contains two functional groups are combined to produced high molecular weight substance and a small molecule like H_2O, HCl or CH_3OH.

Phenol - Formaldehyde (Bakelite) resins are formed by the poly condensation between phenol and formaldehyde. It can be catalysed by either acids or base.

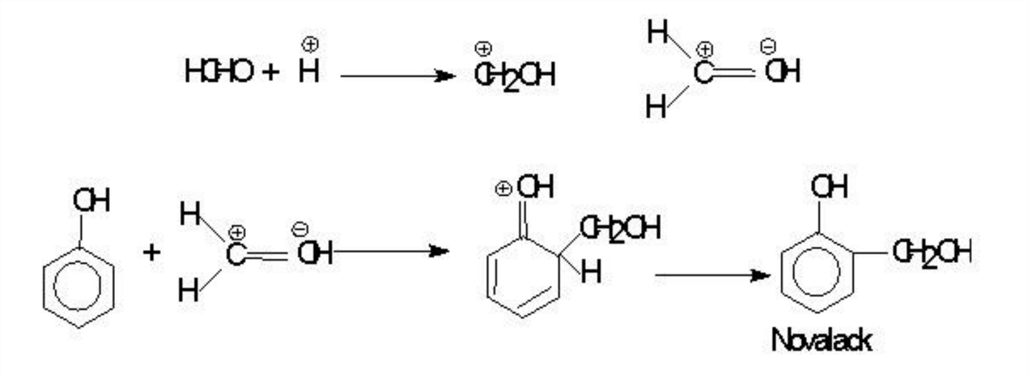


when phenol is treated with formaldehyde in presence of alkali or acid, there is obtained a high molecular weight Phenol – formaldehyde resin, in which many phenol resin are held together by -CH_2 groups. The stages involve in the formation of polymer seem to be the following. First phenol reacts with formaldehyde to form O- or P- hydroxylmethylphenol. Hydroxymethylphenol then reacts with another molecule of phenol, with the loss of H_2O, to form a compound in which two rings are joined by a -CH_2 link. This process is then continuous to yield a product of high molecular weight. Since three position in each phenol molecule are susceptible to attack, the final product contains many cross links and hence has a rigid three-dimensional structure. It is thus a space network polymer.

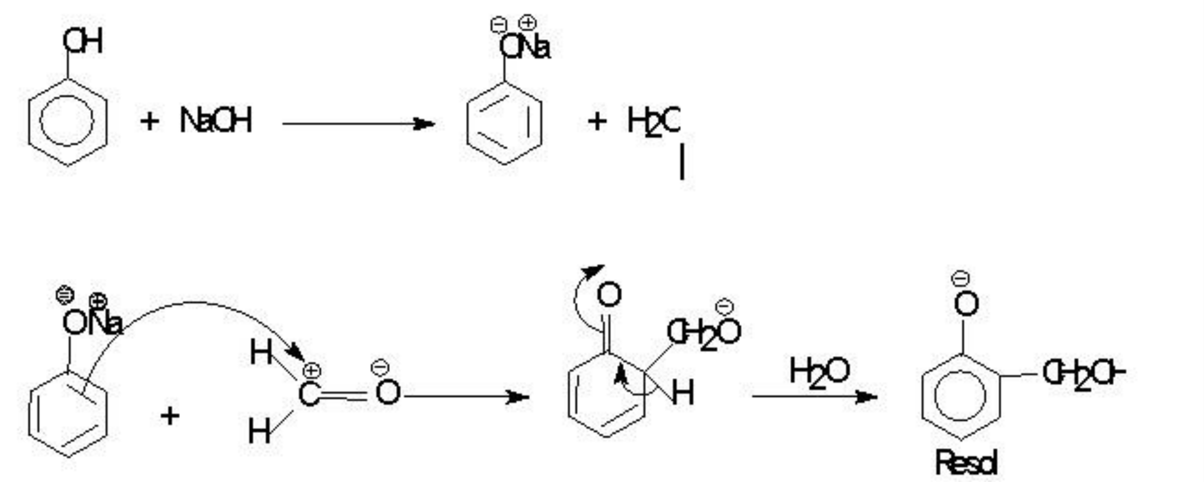
Mechanism of Phenol Formaldehyde

Phenol-Formaldehyde (PF) resins are formed by the polycondensation between phenol and formaldehyde. It is catalysed by either acid or base. It proceeds via electrophilic aromatic substitution. The first stage can be viewed as both electrophilic substitution on the ring by the electron deficient carbon of formaldehyde, and nucleophilic addition of the aromatic ring to the carbonyl group. Acid catalyzes reaction by protonating formaldehyde and increasing the electron deficiency of the carbonyl carbon. While base catalyzes reaction converting phenol in to more reactive phenoxide ion.

MECHANISM: (a) The acid catalysed reaction:

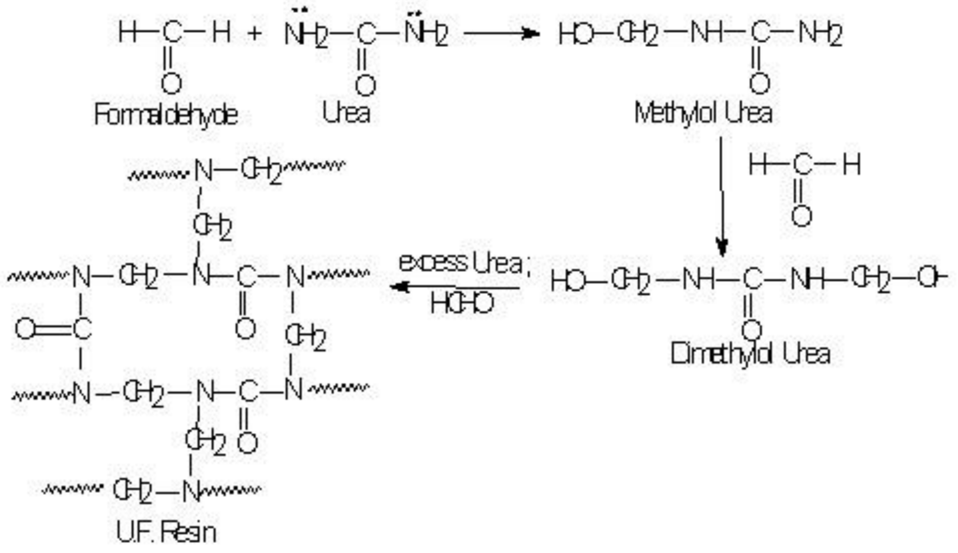


(b) Base catalysed reaction :



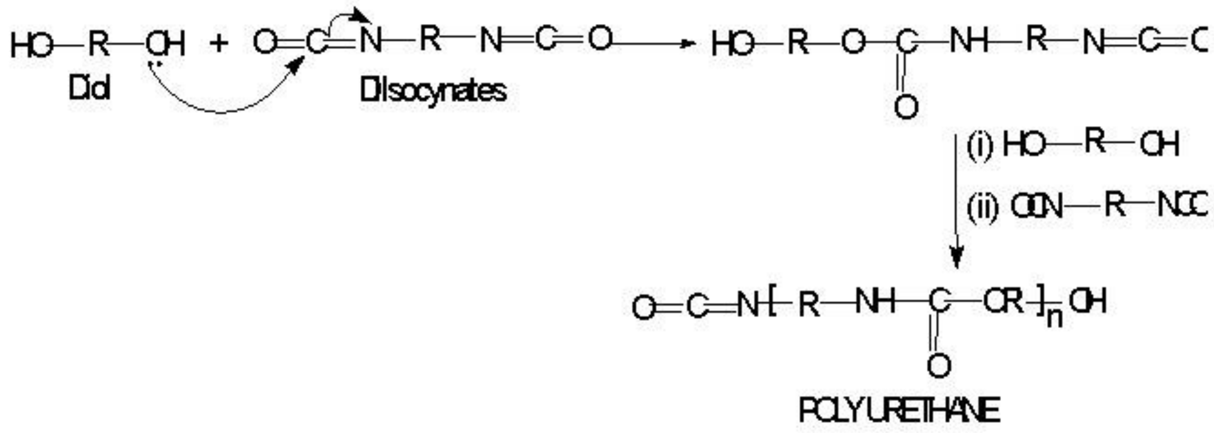
Urea – Formaldehyde Polymer:

When urea reacts with formaldehyde it produces methylol urea, dimethylol urea and so on. It is also step reaction polymerization. When excess urea and formaldehyde are their it will results in to three dimensional space - network Urea formaldehyde polymer. It is highly important molded plastic. Also used in textile finishing.

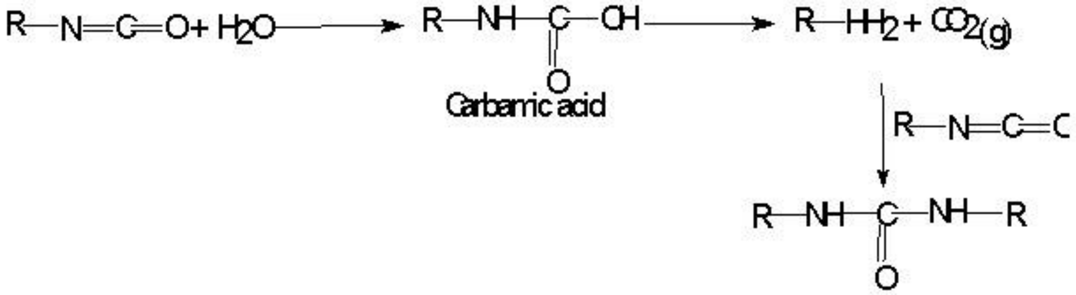


Polyurethane

When dihydroxy alcohols reacts with diisocyanaates will result in polyurethane are;

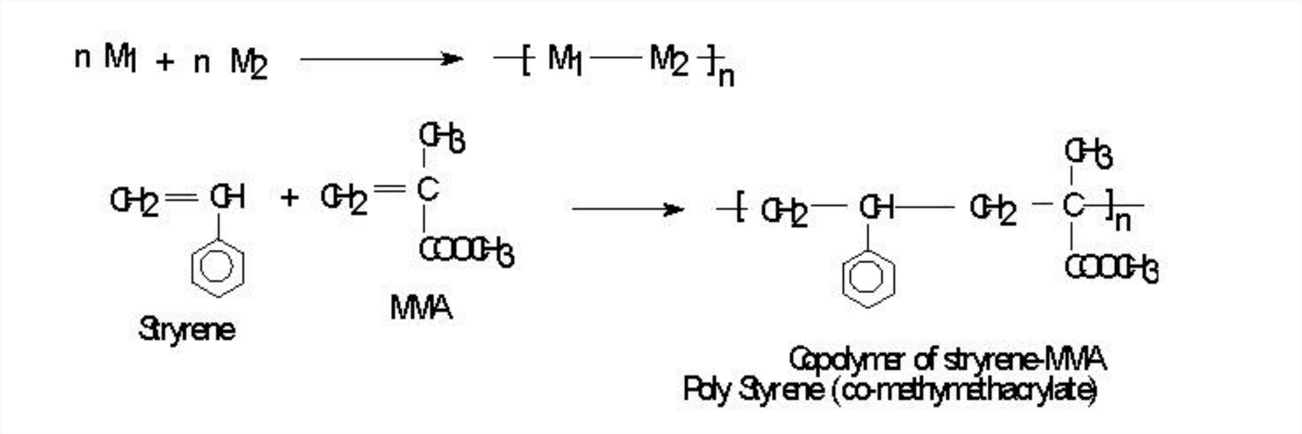


It is linear polymer and have a wide industrial application upon hydrolysis it gives polyurethane form.



CO-POLYMERIZATION

When a mixture of two or more different monomer is allowed to undergo polymerization, will results in to co-polymer. OR A polymer that contains two or more different kind of monomeric units in the same molecule are known as co-polymer. If the polymer is prepared from different type of monomers (M_1 & M_2) then the process is known as CO-POLYMERIZATION.



$$n\,M_1 + n\,M_2 \longrightarrow -[M_1-M_2]_n-$$

Copolymer of stryrene-MMA
Poly Styrene (co-methymethacrylate)

By the process of copolymerization the polymer can be made with different properties compare to homopolymerization. E.g. Polystyrene alone have a good electric insulation properties and can be molded in to parts for radios, television sets and automobiles etc. But when styrene is copolymerized with 30% butadiene adds toughness to the polymer. Styrene with acrylonitrite with (20-30%) increase resistance to impact and to hydrocarbons(solvent). Styrene with maleic anhydride produce polymer which on hydrolysis becomes water soluble and is used as a dispersant and sizing agent. Styrene with 75% butadiene produce an elastomer .

CLASSIFICATION OF COPOLYMER IN DETAIL.

If two monomers M_1 & M_2 are polymerized together four arrangements are possible in the polymer structure.

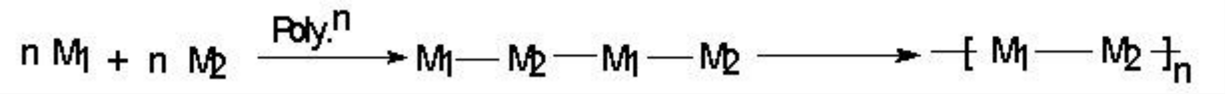
(i) Alternating copolymer.

(ii) Random copolymer

(iii) Block copolymer

(iv) Graft copolymer

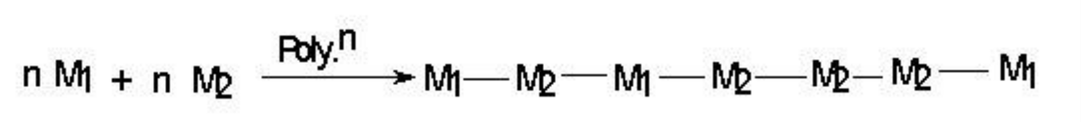
(i) Alternating copolymers : When the two monomer units alternatively in a linear fassion the product so obtained is called alternating copolymers.



$$n\,M_1 + n\,M_2 \xrightarrow{\text{Poly.}^n} M_1-M_2-M_1-M_2 \longrightarrow -[M_1-M_2]_n-$$

e.g. Styrene and methylmethacrylate.

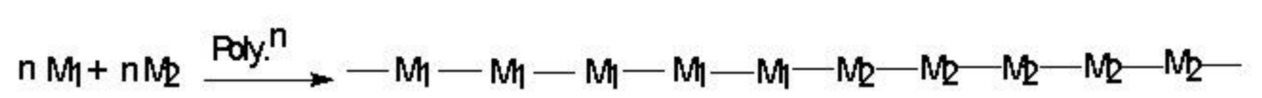
(ii) Random copolymer : When the two monomer are distributed randomly among the chain the product so obtain is called random copolymer.



$$n\,M_1 + n\,M_2 \xrightarrow{\text{Poly.}^n} M_1-M_2-M_1-M_2-M_2-M_2-M_1$$

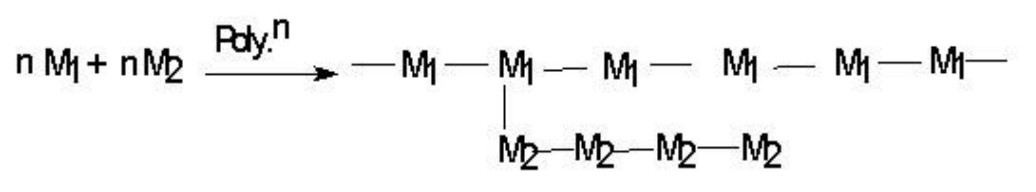
e.g. Styrene and butadiene.

(iii) Blocke copolymer : When the two monomer get inited in a block made up of one monomer alternate with block of another is called block copolymer. Here section made up of one monomer alternate with section of another.

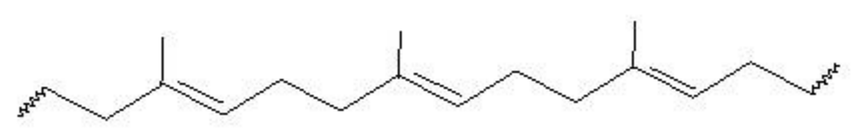


e.g. Ethylene oxide & Ethelene Terphthalate

(iv) Graft copolymer : A branch of one kind is grafted to a chain of another kind. The one monomer unit can be grafted (i.e. added in the form of branched chain) on the linear chain of a polymer molecules. Such branched polymer are known as graft copolymer



E.g. Natural rubber and acrylonitrite.



GUTTA PERCHA trans STEREOISOMER

Plastic: The molecular structure of plastics is of two general kinds. The linear and branched polymers may be more or less crystalline, and include some of the materials also used as fibers: nylon, e.g. They include the various polyalkenes we have mentioned: polyethylene, poly(vinyl chloride), polystyrene, etc. on heating, these polymers soften, and for this reason are called Theromoplastic. It is in this softened state that they can be molded or extruded.

Space-network polymers (or resins) are highly cross-linked to form a rigid but irregular three-dimensional structure, as in phenol-formaldehyde or urea-formaldehyde resins. A sample of such material is essentially one gigantic molecule; heating does not soften it, since softening would require breaking of covalent bonds. Indeed, heating may cause formation of additional cross-links and thus make the material harder; for this reason, these polymers are called Thermosetting polymers. This continuation of the polymerization process through heating is often coupled with the shaping of the product.

Some Important Definitions :

(a) Monomer : The individual small molecules from which the polymer is formed are known as monomers.

(b) Polymer : Polymers are macro molecules (giant) having high molecular weight and are made up of a great many simpler units – identical to each other or at least chemically similar – joined together in a regular way.

(c) Polymerization : The process by which the monomer molecules are linked together to form a bigger molecule (macro-) is called polymerization.

(d) Degree of polymerization : The number of repeating unit present in the polymer chain is called degree of polymerization (n).

(e) Plastics : When a polymer is shaped in to a hard and though utility articles by the applications of heat and pressure then it is used as plastics. E.g. P.V.C. polymethyl methacrylate (P.M.M.A.), poly styrene etc. which can be extruded as a sheets or pipes.

(f) Fibers : Fibers are long, thin, thread like bits of material that are having great tensile (pulling) strength in the direction of the fiber. E.g. nylon, terylene, polyester etc.

(g) Elastomers : Elastomer possesses the high degree of elasticity that is characteristic of rubber. It can be greatly deformed and stretched up to eight times of its original length and yet return to its original shape. E.g. natural rubber, synthetic rubber, silicon rubber.

(h) Co-polymer : Polymers which are made up of two or more different kind of monomers are known as copolymer e.g. styrene- butadiene copolymer.

(i) High polymers: Polymer which contains more than hundred monomers in their backbone is called high polymers.

(j) Initiator : Initiator is species which are responsible to initiate chain reaction by breaking down itself to form a free radical in presence of U.V. light or heating.

Lesson 26. Thermoplastic and Thermosetting polymers

30.1 Introduction

Thermoplastic:

A Thermoplastic, also known as a thermo softening plastic, is a polymer that becomes pliable or mouldable above a specific temperature, and returns to a solid state upon cooling. Most thermoplastics have a high molecular weight, whose chains associate through intermolecular forces; this property allows thermoplastics to be remoulded because the intermolecular interactions spontaneously reform upon cooling. In this way, thermoplastics differ from thermosetting polymers, which form irreversible chemical bonds during the curing process; thermoset bonds break down upon melting and do not reform upon cooling. These are formed by addition polymerization.

Thermoplastics pellets soften when heated and become more fluid as additional heat is applied. The curing process is completely reversible as no chemical bonding takes place. This characteristic allows thermoplastics to be remoulded and recycled without negatively affecting the material's physical properties.

There are multiple thermoplastic resins that offer various performance benefits, but most materials commonly offer high strength, shrink-resistance and easy bend ability. Depending on the resin, thermoplastics can serve low-stress applications such as plastic bags or high-stress mechanical parts.

Above its glass transition temperature, T_g, and below its melting point, Tm, the physical properties of a thermoplastic change drastically without an associated phase change. Within this temperature range, most thermoplastics are rubbery due to alternating rigid crystalline and elastic amorphous regions, approximating random coils.

Some thermoplastics do not fully crystallize above glass transition temperature Tg, retaining some, or all of their amorphous characteristics. Amorphous and semi-amorphous plastics are used when high optical clarity is necessary, as a light wave cannot pass through smaller crystallites than its wavelength. Amorphous and semi-amorphous plastics are less resistant to chemical attack and environmental stress cracking because they lack a crystalline structure.

Brittleness can be lowered with the addition of plasticizers, which interfere with crystallization to effectively lower T_g. Modification of the polymer through copolymerization or through the addition of non-reactive side chains to monomers before polymerization can also lower T_g. Before these techniques were employed, plastic automobile parts would often crack when exposed to cold temperatures. Recently, thermoplastic elastomers have become available

Thermoplastic Resins

Thermoplastic polymer resins are extremely common, and we come in contact with thermoplastic resins constantly. Thermoplastic resins are most commonly unreinforced, meaning, the resin is formed into shapes and have no reinforcement providing strength.

Examples of common thermoplastic resins used today, and products manufactured with them include:

1) PET (Polyethylene terphalate) - Water and soda bottles

2) Polyproplyene - Packaging containers

3) Polycarbonate - Safety glass lenses

4) PBT (Polybutylene terphalate) - Children's Toys

5) Vinyl - Window frames

6) Polyethlene - Grocery bags

7) PVC (Polyvinyl chloride) - Piping

8) PEI (Polyetherimide) - Airplane armrests

9) Nylon - Footwear

Many thermoplastic products use short discontinuous fibers as reinforcement. Most commonly fiberglass, but carbon fiber too. This increases the mechanical properties and is technically considered a fiber reinforced composite, however, the strength is not nearly as comparable to continuous fiber reinforced composites.

Advantages of thermoplastic Composites

There are two major advantages of thermoplastic composites. The first is that many thermoplastic resins have an increased impact resistance to comparable thermoset composites. In some instances, the difference is as high as 10 times the impact resistance.

The other major advantage of thermoplastic composites is the ability reform. See, raw thermoplastic composites, at room temperature, are in a solid state. When heat and pressure impregnate a reinforcing fiber, a physical change occurs; not a chemical reaction as with a thermoset.

This allows thermoplastic composites to be reformed and reshaped. For example, a pultruded thermpostic composite rod could be heated and remoulded to have a curvature. This is not possible with thermosetting resins. This also allows for the recycling of the thermoplastic composite at end of life. (In theory, not yet commercial)

Some common advantage of thermoplastic composites

1) Aesthetically-superior finishes

2) Chemical resistant

3) Hard crystalline or rubbery surface options

4) Eco-friendly manufacturing

Disadvantages of Thermoplastics:

Because thermoplastic resin is naturally in a solid state, it is much more difficult to impregnate reinforcing fiber. The resin must be heated to the melting point, and pressute is required to impregnate fibers, and the composite must then be cooled under this pressure. This is complex and far different from traditional thermoset composite manufacturing. Special tooling, technique, and equipment must be used, many of which is expensive. This is the major disadvantage of thermoplastic composites.

Advances in thermoset and thermoplastic technology are happening constantly. There is a place and a use for both, and the future of composites does not favour one over the other.

1) Generally more expensive than thermoset

2) Can melt if heated

Thermosetting

A thermosetting plastic, also known as a thermoset, is polymer material that irreversibly cures. The cure may be done through heat (generally above 200 °C (392 °F)), through a chemical reaction or irradiation such as electron beam processing. These are formed by condensation polymerization.

Thermoset materials are usually liquid or malleable prior to curing and designed to be moulded into their final form, or used as adhesives. Others are solids like that of the moulding compound used in semiconductors and integrated circuits (IC). Once hardened a thermoset resin cannot be reheated and melted back to a liquid form.

According to IUPAC recommendation: A thermosetting polymer is a prepolymer in a soft solid or viscous state that changes irreversibly into an infusible, insoluble polymer network by curing. Curing can be induced by the action of heat or suitable radiation, or both. A cured thermosetting polymer is called a thermoset.

The curing process transforms the resin into a plastic or rubber by a cross-linking process. Energy and/or catalysts are added that cause the molecular chains to react at chemically active sites (unsaturated or epoxy sites, for example), linking into a rigid, 3-D structure. The cross-linking process forms a molecule with a larger molecular weight, resulting in a material with a higher melting point. During the reaction, the molecular weight has increased to a point so that the melting point is higher than the surrounding ambient temperature, the material forms into a solid material.

Uncontrolled reheating of the material results in reaching the decomposition temperature before the melting point is obtained. Therefore, a thermoset material cannot be melted and re-shaped after it is cured. This implies that thermosets cannot be recycled, except as filler material

Thermosetting plastics are generally strong and resistant to heat, but they melt the first time they are heated to a high enough temperature and harden (set) permanently when cooled. They are used in situations where resistance to heat is important, e.g. on kitchen work surfaces, good-quality plastic cups, saucepan handles and plug casings.

Thermoset plastics contain polymers that cross-link together during the curing process to form an irreversible chemical bond. The cross-linking process eliminates the risk of the product remelting when heat is applied, making thermosets ideal for high-heat applications such as electronics and appliances.

Thermoset plastics significantly improve the material’s mechanical properties, providing enhances chemical resistance, heat resistance and structural integrity. Thermoset plastics are often used for sealed products due to their resistance to deformation.

Traditional Fiber Reinforced Polymer Composites, or FRP Composites for short, use a thermosetting resin as the matrix, which holds the structural fiber firmly in place. Common thermosetting resin include:

1) Polyester Resin

2) Vinyl Ester Resin

3) Epoxy

4) Phenolic

5) Urethane

The most common thermosetting resin used today is polyester resin, followed by vinyl ester and epoxy. Thermosetting resins are popular because uncured, at room temperature; they are in a liquid state. This allows for convenient impregnation of reinforcing fibers such as fiberglass, carbon fiber, or Kevlar.

Properties of Thermoset Resins

As mentioned, a room temperature liquid resin is easy to work with. Laminators can easily remove all air during manufacturing, and it also allows the ability to rapidly manufacture products using a vacuum or positive pressure pump. (Closed Molds Manufacturing) Beyond ease of manufacturing, thermosetting resins can exhibit excellent properties at a low raw material cost.

Properties of thermoset resins include:

1) Excellent resistance to solvents and corrosives

2) Resistance to heat and high temperature

3) Fatigue strength

4) Tailored elasticity

5) Excellent adhesion

6) Excellent finishing (polishing, painting, etc.)

7) Highly flexible design

8) Thick to thin wall capabilities

9) Excellent aesthetic appearance

10) High levels of dimensional stability

11) Cost-effective

Disadvantage:

1) Cannot be recycled

2) More difficult to surface finish

3) Cannot be remoulded or reshaped

In a thermoset resin, the raw uncured resin molecules are crossed linked through a catalytic chemical reaction. Through this chemical reaction, most often exothermic, the resin creates extremely strong bonds to one another, and the resin changes state from a liquid to a solid.

Examples

Some examples of thermosets are:

1) Polyester fibreglass systems: sheet molding compounds and bulk molding compounds).

2) Polyurethanes: insulating foams, mattresses, coatings, adhesives, car parts, print rollers, shoe soles, flooring, synthetic fibers, etc. Polyurethane polymers are formed by combining two bi- or higher functional monomers/oligomers.

3) Vulcanized rubber.

4) Bakelite, a phenol-formaldehyde resin used in electrical insulators and plasticware

5) Duroplast, light but strong material, similar to bakelite used for making car parts

6) Urea-formaldehyde foam used in plywood, particleboard and medium-density fibreboard.

7) Melamine resin used on worktop surfaces.

8) Epoxy resin used as the matrix component in many fiber reinforced plastics such as glass-reinforced plastic and graphite-reinforced plastic).

9) Polyimides used in printed circuit boards and in body parts of modern aircraft.

10) Cyanate esters or polycyanurates for electronics applications with need for dielectric properties and high glass temperature requirements in composites.

Some methods of molding thermosets:

1) Reactive injection molding (used for objects such as milk bottle crates)

2) Extrusion molding (used for making pipes, threads of fabric and insulation for electrical cables)

3) Compression molding (used to shape most thermosetting plastics)

4) Spin casting (used for producing fishing lures and jigs, gaming miniatures, figurines, emblems as well as production and replacement parts)

- **Processing Polymers**

Once a polymer with the right properties is produced, it must be manipulated into some useful shape or object. Various methods are used in industry to do this. Injection molding and extrusion are widely used to process plastics while spinning is the process used to produce fibers.

- **Injection Molding**

One of the most widely used forms of plastic processing is injection molding. Basically, a plastic is heated above its glass transition temperature (enough so that it will flow) and then is forced under high pressure to fill the contents of a mold. The molten plastic in usually "squeezed" into the mold by a ram or a reciprocating screw. The plastic is allowed to cool and is then removed from the mold in its final form. The advantage of injection molding is speed; this process can be performed many times each second.

- **Extrusion**

Extrusion is similar to injection molding except that the plastic is forced through a die rather than into a mold. However, the disadvantage of extrusion is that the objects made must have the same cross-sectional shape. Plastic tubing and hose is produced in this manner.

- FA **thermosetting plastic**, also known as a thermoset, is polymer material that irreversibly cures. The cure may be done through heat (generally above 200 °C (°F)), through a chemical reaction (two-part epoxy, for example), or irradiation such as electron beam processing.

Thermoset materials are usually liquid or malleable prior to curing and designed to be molded into their final form, or used as adhesives. Others are solids like that of the molding compound used in semiconductors and integrated circuits (IC). Once hardened a thermoset resin cannot be reheated and melted back to a liquid form. According to IUPAC recommendation: A thermosetting polymer is a pre-polymer in a soft solid or viscous state that changes irreversibly into an infusible, insoluble polymer network by curing. Curing can be induced by the action of heat or suitable radiation, or both. A cured thermosetting polymer is called a thermoset.

Process

The curing process transforms the resin into a plastic or rubber by a cross-linking process. Energy and/or catalysts are added that cause the molecular chains to react at chemically active sites (unsaturated or epoxy sites, for example), linking into a rigid, 3-D structure. The cross-linking process forms a molecule with a larger molecular weight, resulting in a material with a higher melting point. During the reaction, the molecular weight has increased to a point so that the melting point is higher than the surrounding ambient temperature, the material forms into a solid material. Uncontrolled reheating of the material results in reaching the decomposition temperature before the melting point is obtained. Therefore, a thermoset material cannot be melted and re-shaped after it is cured. This implies that thermosets cannot be recycled, except as filler material.

Properties

Thermoset materials are generally stronger than thermoplastic materials due to this three dimensional network of bonds (cross-linking), and are also better suited to high-temperature applications up to the decomposition temperature. However, they are more brittle. Since they are "set" (non-reformable), they tend not to be recyclable.

Examples

Some examples of thermosets are:

- Polyester fibreglass systems: sheet molding compounds and bulk molding compounds)

- Polyurethanes: insulating foams, mattresses, coatings, adhesives, car parts, print rollers, shoe soles, flooring, synthetic fibers, etc. Polyurethane polymers are formed by combining two bi- or higher functional

monomers/oligomers.

- Vulcanized rubber

- Bakelite, a phenol-formaldehyde resin used in electrical insulators and plasticware

- Duroplast, light but strong material, similar to bakelite used for making car parts

- Urea-formaldehyde foam used in plywood, particleboard and medium-density fiberboard

- Melamine resin used on worktop surfaces.

- Epoxy resin used as the matrix component in many fiber reinforced plastics such as glass-reinforced plastic and graphite-reinforced plastic)

- Polyimides used in printed circuit boards and in body parts of modern aircraft

- Cyanate esters or polycyanurates for electronics applications with need for dielectric properties and high glass temperature requirements in composites

- Mold or mold runners (the black plastic part in integrated circuits or semiconductors)

Thermosetting polymer 2?????????

Some methods of molding thermosets are:

- Reactive injection molding (used for objects such as milk bottle crates)

- Extrusion molding (used for making pipes, threads of fabric and insulation for electrical cables)

- Compression molding (used to shape most thermosetting plastics)

- Spin casting (used for producing fishing lures and jigs, gaming miniatures, figurines, emblems as well as production and replacement parts)

Lesson 27. Fibre and Rubber materials

31.1 Introduction of Spinning

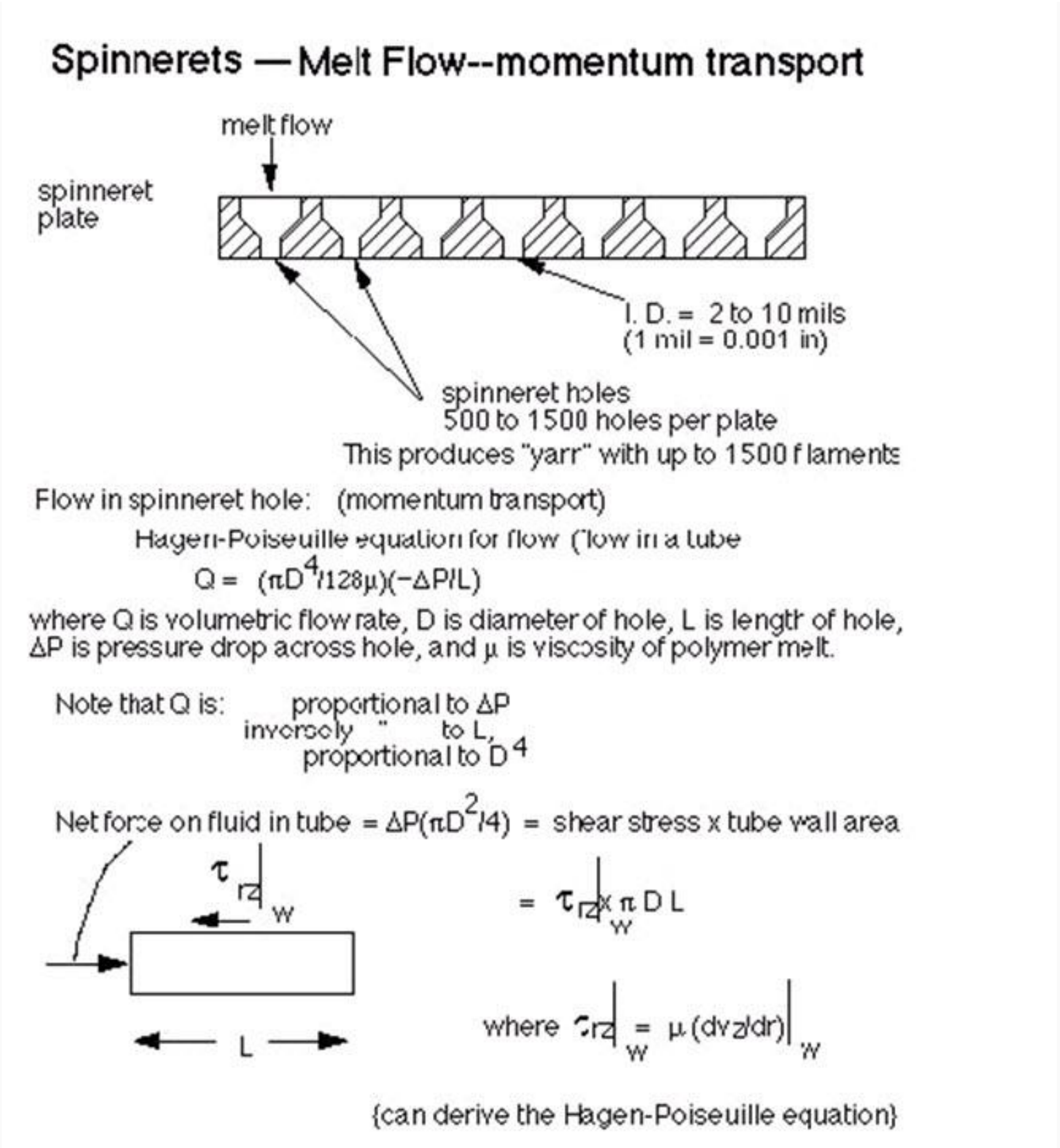
The process of producing fibers is called spinning. There are three main types of spinning: melt, dry, and wet. Melt spinning is used for polymers that can be melted easily. Dry spinning involves dissolving the polymer into a solution that can be evaporated. Wet spinning is used when the solvent cannot be evaporated and must be removed by chemical means. All types of spinning use the same principle, so it is convenient to just describe just one. In melt spinning, a mass of polymer is heated until it will flow. The molten polymer is pumped to the face of a metal disk containing many small holes, called the spinneret. Tiny streams of polymer that emerge from these holes (called filaments) are wound together as they solidify, forming a long fiber. Speeds of up to 2500 feet/minute can be employed in spinning.

As mentioned previously, fibers are formed by the extrusion of the polymer melt or spin dope through tiny holes in a spinneret plate. Such a plate may contain 1,000 holes or more. Textile fibers are relatively fine, so the diameter of the hole may be only a few mils, where one mil is 0.001 inches (25.4 µm). The thickness of the filament is generally not given in linear dimensions, but rather in terms of mass per length. For some reason the fiber industry has adopted the terms denier and denier per filament, dpf, to express the filament size. One dpf corresponds to a mass of 1 g in a length of 9000 meters ! If the density of the polymer is 1 g/cm^3, this would correspond to a diameter of 1.2 x 10^{-3} cm, or about half a mile. Typically, textile fibers are in the range of 3 to 15 dpf. Recall that one **gm** is roughly 1/30 of an ounce. In melt spinning, the filaments are normally drawn down, or stretched, just downstream of the spinneret holes. The stretch is of the order of 2 to 3x, so the spinneret hole may be 50 to 75% larger than the filament diameter when it is first cooled.

Additional post formation stretching may also be used, however, so that the final filament diameter may be one-half or less than the diameter of the spinneret hole. The spinneret hole is usually only slightly longer than its width, in part to minimize pressure drop at the plate. But the plate still has to be strong enough to withstand the upstream pressure. For this reason, the melt passes through a conical section before reaching the final spinneret hole, so that the plate can be relative thick (see slide). Pressure drop through this converging section is very difficult to calculate for these polymeric materials, because the extensional flow rheology is usually not well characterized. One can readily visualize the alignment of the polymer molecules in the converging section, where the polymer undergoes a severe stretching step. Ignoring this pressure loss, let us focus on the spinneret hole itself.

An important question here is whether one can use the Hagen-Poiseuille equation to compute the pressure drop in such a short tube. To help answer this question, we first compute the entrance length, which is approximately equal to the axial distance downstream from a tube entrance at which the momentum boundary layers merge at the center axis, where a fully parabolic profile is established. This distance, from Bird, Stewart, and Lightfoot, Transport Phenomena, p. 47, is Le/D = 0.035 Re (4-1).

where Le is the entrance length, D is the tube diameter and Re is the Reynolds number.



Spinnerets — Melt Flow--momentum transport

This produces "yarn" with up to 1500 filaments

Flow in spinneret hole: (momentum transport)

Hagen-Poiseuille equation for flow (flow in a tube

$$Q = (\pi D^4/128\mu)(-\Delta P/L)$$

where Q is volumetric flow rate, D is diameter of hole, L is length of hole, ΔP is pressure drop across hole, and μ is viscosity of polymer melt.

Note that Q is: proportional to ΔP
inversely " to L,
proportional to D^4

Net force on fluid in tube $= \Delta P(\pi D^2/4)$ = shear stress x tube wall area

$$= \tau_{rz}\big|_w \times \pi D L$$

where $\tau_{rz}\big|_w = \mu\,(dv_z/dr)\big|_w$

{can derive the Hagen-Poiseuille equation}

For a representative calculation, we consider nylon melt, with a viscosity of 200 Poises, being spun from a hole 10 mils in diameter at a final spinning speed of 2,000 ypm and a stretch of 5x between the spinneret and the final take-up. This means that the bulk velocity, ub, in the spinneret hole is 400 ypm. The Reynolds number, for a specific gravity of about one, is:

Re = ub D/n = 0.077

so the entrance length is less than 3 thousandths of the diameter of the hole. Therefore, we can safely use the Hagen-Poiseuille equation to calculate the pressure drop.

For the nylon example we just explored, the pressure drop is predicted, for a length of 3.0 mils, to be 2200 psi. This pressure drop might be a bit excessive in practice, but the method of calculation remains illustrative. One part of the calculation which was not taken into account is the power-law behaviour of most polymer melts and polymer solutions. Such behaviour usually is revealed by a shear-thinning response, in which the apparent viscosity decreases as shear rates increase. This would lead to significantly lower pressure drops for the spinneret plate.

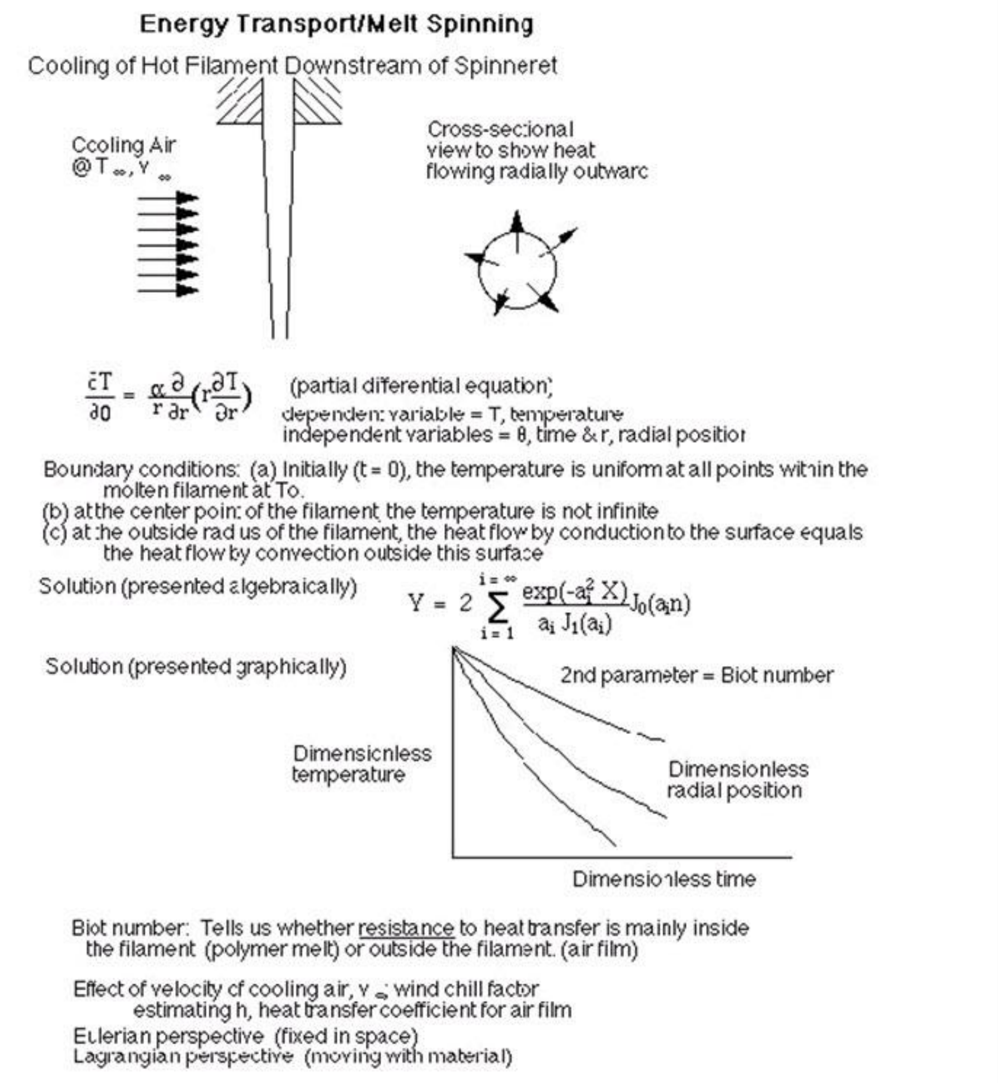
As the polymer exits the spinneret hole, it tends to swell and this swell is especially noticeable at low filament tensions. Apparently, the polymer molecules must coil under the shearing action within the hole and, as it exits, the polymer molecules are free to uncoil, as seen by an expansion of the polymer stream jetting out of the hole. This phenomenon is referred to as "die swell," and can even amount to a doubling or more of stream diameter. Even Newtonian fluids can be shown to exhibit a swelling at the exits of tubes, even at very low Re; the predicted extent of swell is about 14% for Newtonian fluids. Since, in fiber spinning, the filaments are under tension, the extent of die swell is considerably reduced. Furthermore, the extent of swell appears to have no influence of final filament properties. In order for the filaments to undergo stretching, some power must go into the stretching motion immediately downstream of the spinneret plate, but the amount of this power is negligible.

MELT SPINNING

In the spinning of molten polymers, such as nylon, polyester, and polypropylene, melt spinning begins with a cooling of the molten filament after it leaves the spinneret. At the same time, the filament is pulled downwards towards the take-up section and this resulting tension in the molten filament provides a stretching action in the molten filament itself. In most melt spinning operations the degree of stretch is of the order of 3x, which means that the velocity of the initially cooled, or solid, fiber is about three times the average velocity of the melt coming out of the spinneret. For some filaments, this initial stretch is very important in helping to establish properties in the polymer which depend on whether one deals with the properties in the fiber axis direction or in the fiber radius direction. This directional dependence of properties is called anisotropy and the usual example is that of a slab of wood, in which strength and fracture properties along the grain are quite different from properties across the grain. (With many fibers, however, these properties are controlled downstream, where the fibers are reheated, stretched further, and cooled again).

In any case, the polymer melt, once it comes out of the spinneret hole, starts to cool down and also starts to stretch out. Because the "apparent viscosity" of the melt increases rapidly as the melt cools, most of the stretching takes place in a region relatively close to the spinneret hole whereas "most" of the cooling takes place well away from this hole. But these terms and descriptions are not exact and are not easily quantified. The real advantage in using these descriptions is that it permits us to make a simplifying assumption as we analyze the melt spinning process. The assumption is: We can separate the stretching and cooling operations into two separate distinct regions, with the first occurring relative close to the spinneret (say, within 10% of the distance to the first take-up, or speed-control roll), and the second over the remaining distance to the first take-up roll. If need be, we could return later to this assumption to determine its degree of accuracy, but let us accept it for the moment.

The stretching region, within which the relatively long polymer molecules become aligned along the filament axis, might be characterized by very complex rheology. Within the field of polymer processing, rheology deals with the relationship between stress and the history of strain; for Newtonian fluids, you can recall that the fluid stress is proportional to the rate of strain (the shear rate). We are not really too concerned about the polymer melt rheology here, however, since it will not likely be important in determining the power required for the first drive or take-up roll. Frictional and interfacial stresses are likely to be far more important. Therefore, in terms of design considerations, we can probably ignore that part of the melt-spinning process in which the initial, post-spinneret stretching of the polymer melt occurs and focus instead on the cooling step of the melt spinning operation.



Energy Transport/Melt Spinning

Cooling of Hot Filament Downstream of Spinneret

$$\frac{\partial T}{\partial \theta} = \frac{\alpha}{r}\frac{\partial}{\partial r}\left(r\frac{\partial T}{\partial r}\right)$$

(partial differential equation)
dependent variable = T, temperature
independent variables = θ, time & r, radial position

Boundary conditions: (a) Initially (t = 0), the temperature is uniform at all points within the molten filament at To.
(b) at the center point of the filament, the temperature is not infinite
(c) at the outside radius of the filament, the heat flow by conduction to the surface equals the heat flow by convection outside this surface

Solution (presented algebraically)

$$Y = 2\sum_{i=1}^{i=\infty}\frac{\exp(-a_i^2 X)}{a_i J_1(a_i)} J_0(a_i n)$$

Solution (presented graphically)

Biot number: Tells us whether resistance to heat transfer is mainly inside the filament (polymer melt) or outside the filament. (air film)

Effect of velocity of cooling air, v_∞; wind chill factor
estimating h, heat transfer coefficient for air film
Eulerian perspective (fixed in space)
Lagrangian perspective (moving with material)

Perhaps the most important design consideration in the melt spinning process is the cooling of the filaments. In order to simplify our analysis, we restrict our focus to the point where the filaments have reached a uniform diameter (recall that we previously asserted that this is a relatively short distance) and that they are at some initial temperature which will be somewhat cooler (by about 20 C°) than the melt temperature at the spinneret exit. At this point, the temperature within the filament will depend on radial position, with the maximum occurring at the center, on the filament axis. We shall invoke an pproximation of a flat temperature profile, in which the temperature does not vary with r, in order to utilize existing mathematical solutions.

An important part of learning engineering is to learn how to take "appropriate shortcuts" which save time with little sacrifice in accuracy. This is one example. The melt spinning process is steady: viewing the spinning threadlines at a fixed position (the so called Eulerian perspective) shows that nothing appears to change with time. If one situates oneself on the moving threadline (figuratively, of course) there does certainly appear to be a time dependence to the temperature of the filament. This viewpoint of moving with the material is called the Lagrangian perspective. Whereas the Eulerian perspective requires you to measure the threadline temperature as a function of r, radial position within the filament, and z, axial position along the filament, in order to follow the cooling, the Lagrangian perspective allows you to follow the cooling as a function of r and t, where t is time. Zero time should be some convenient reference-here it would correspond to locating yourself on the filament at the end of the stretching region and at the "beginning" of the cooling region. This is equivalent to the cooling of an infinite rod which is fixed in space. The governing differential equation, which can be derived easily using shell balance techniques is:

where q is time and a is the thermal diffusivity of the polymer. The student will readily recognize this as a partial differential equation, since the temperature T depends on both r and q. In order to solve the equation quantitatively, one must specify initial and boundary conditions. The boundary is naturally R the outside radius of the filament. So the initial condition (q = 0)is simply:

T (r,q) = To for r< R ,where To is a constant.

We need two boundary conditions, corresponding to r = 0 and r = R. At r = 0,

T remains finite;

At r = R, the heat arriving at the surface by conduction from within must match the heat

leaving by convection:

at r = R and all q > 0. k is the thermal conductivity of the filament (we shall assume that this conductivity does not change as the polymer solidifies. h is the heat transfer coefficient governing the heat transfer from the surface to the surrounding air. An example of such a correlation for heat transfer from a cylinder in crossflow is given by Churchill and Bernstein

where NuD is the Nusselt number, hD/k, (k is the thermal conductivity of the fluid in crossflow and D is the cylinder diameter) and ReD is the Reynolds number based on the fluid in crossflow. Pr is the Prandtl number, n/a,and is also based on the crossflow fluid. The student will recall that an important advantage of presenting correlations in terms of dimensionless variables like Nu (dimensionless heat transfer coefficient) and Re (inertial stresses divided by viscous stresses) is that the resulting expression is often simpler, revealing more clearly the relationships among such variables.

We shall also assume that the heat of fusion is negligible, primarily because we want to simplify the calculation. This assumption, especially for crystalline polymers, could be very poor, however, and could lead an underestimate of the cooling time by a factor of two.

As engineers, or even as normal, sane people, we would not want to solve the differential equation for every single set of geometries, thermal diffusivities and initial and boundary conditions. We can avoid this needless energy expenditure if we express the differential equation in dimensionless form:

Y is called the unaccomplished temperature change, since it starts at unity at time zero and declines from there. n is the normalized radial position, and X is dimensionless time, sometimes called the Fourier number. One final dimensionless group, m, expresses the relative resistance outside the filament to that in the filament:

Finally, the initial and boundary conditions become:

Y = 1 at X = 0 and 0 < n < 1;

at n = 0 and X > 0.

at n = 1 and X > 0.

The solution, Y(n, X) is then valid for any case of unsteady-state heat conduction within a cylindrical geometry with a uniform initial temperature and convective heat transfer from the surface to a surrounding fluid at a uniform temperature T . The solution is shown in graphical form on the slide and is available in almost all transport textbooks. The resulting charts are known variously as "Gurney-Lurie Charts" or "Heissler Charts," depending on which reference or form of charts you use. An analytical solution for a slightly less general case is given below. Note that, by use of dimensionless variables, we have successfully created a result which is applicable to a broad range of geometries and material properties. For the special case in which heat transfer resistance from the surface of the fluid to the surrounding fluid is negligible, one can set h, the heat transfer coefficient, to (this, of course, is equivalent to setting the temperature of that surface to that of the surrounding fluid for all q > 0) and the analytical solution is:

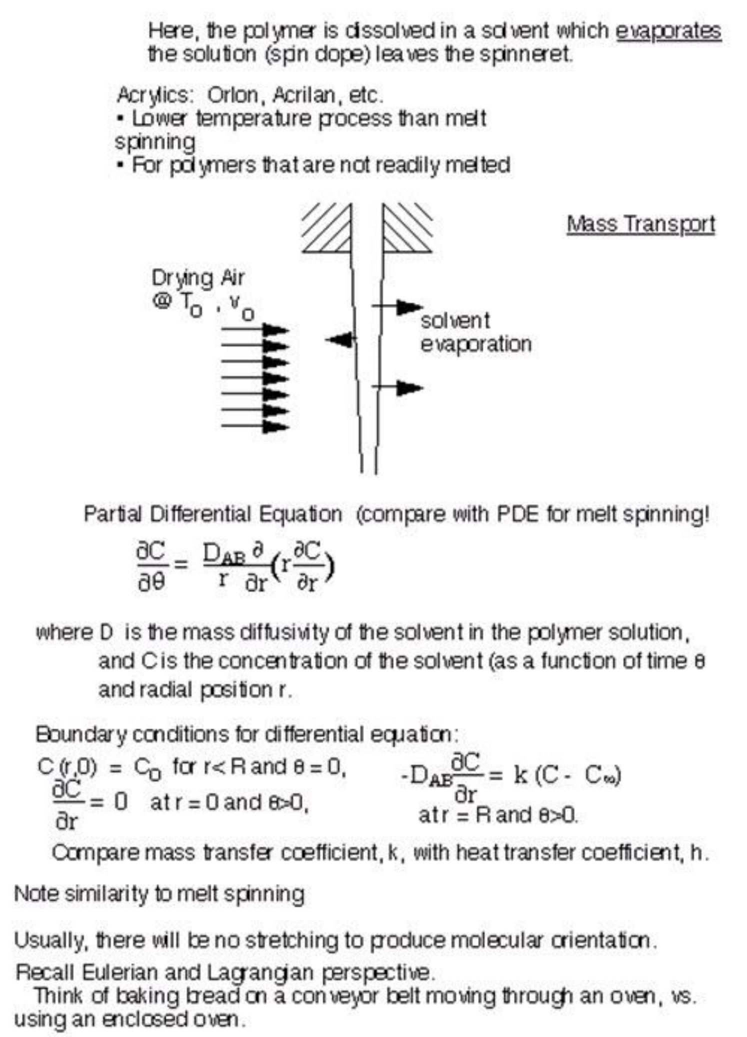
where J0 and J1 are Bessel functions of the first kind (zero and first order, respectively), and ai is the ith root of J0(ai) = 0. This solution is presented in the transport text Momentum, Heat, and Mass Transfer, by Bennett and Myers, 3rd ed., p. 286.

Key elements that you have learned in this section include:

Difference and relationship between Lagrangian and Eulerian perspective, Existence of unsteady-state heat conduction charts, Heat transfer resistance within objects relative to resistance outside these objects, Value of dedimensionalization as a means to obtain more general solutions to complex equations, A typical heat transfer correlation for heat transfer coefficient, h.

Spinning of synthetic fibers with a melt spinning process is conceptually simple, involving little more that the extrusion of molten polymer through fine holes and solidification of the resulting filaments by cooling.

DRY SPINNING



Here, the polymer is dissolved in a solvent which evaporates the solution (spin dope) leaves the spinneret.

Acrylics: Orlon, Acrilan, etc.
- Lower temperature process than melt spinning
- For polymers that are not readily melted

Partial Differential Equation (compare with PDE for melt spinning!

$$\frac{\partial C}{\partial \theta} = \frac{D_{AB}}{r}\frac{\partial}{\partial r}\left(r\frac{\partial C}{\partial r}\right)$$

where D is the mass diffusivity of the solvent in the polymer solution, and C is the concentration of the solvent (as a function of time θ and radial position r.

Boundary conditions for differential equation:

$C(r,0) = C_0$ for $r < R$ and $\theta = 0$, $\quad -D_{AB}\frac{\partial C}{\partial r} = k\,(C - C_\infty)$

$\frac{\partial C}{\partial r} = 0$ at $r = 0$ and $\theta > 0$, $\quad$ at $r = R$ and $\theta > 0$.

Compare mass transfer coefficient, k, with heat transfer coefficient, h.

Note similarity to melt spinning

Usually, there will be no stretching to produce molecular orientation.

Recall Eulerian and Lagrangian perspective.
Think of baking bread on a conveyor belt moving through an oven, vs. using an enclosed oven.

Unlike melt spinning, both dry and wet spinning use solvents in which the polymer dissolves. The resulting solution or suspension is a viscous "spin dope." This process necessarily introduces another species, which is subsequently removed, and therefore is more expensive than conventional melt spinning processes. It is used in cases where the polymer may degrade thermally if attempts to melt it are used or in cases where certain surface characteristics of the filaments are desired-melt spinning produces filaments with smooth surfaces and dry spinning produces filaments with rough surfaces. The rougher surface may be desirable for improved dyeing steps or for special yarn characteristics.

The term "dry spinning" is a bit misleading, since the polymer is certainly wet by a solvent. Presumably, the intent here was to distinguish the two methods of solvent removal for the two cases of dry and wet spinning. The solvent in dry spinning is a volatile organic species and this solvent starts to evaporate after the filament is formed, which is immediately downstream of the spinneret. Whereas melt spinning involved solidification by cooling, dry spinning produces solidification of the polymer by solvent removal.

Several commercial fibers, including acrylic fibers such as Orlon™, are made by a dry spinning process. You may recall that these acrylic fibers are popular as substitutes for wool fibers. In any case, the spinning step which defines, in large part, the spinning process is that of solvent removal from the filaments. In the case of Orlon, the polymer, polyacrylonitrile, is dissolved to a polymer concentration of 20 to 30 wt% in a dimethylformamide solvent. Warm gases (air - probably not, on account of the need for solvent recovery) are passed through the fiber bundle in the region just downstream of the spinneret.

This begins to look very much like the cooling crossflow in melt spinning. The solvent encounters both a diffusional resistance within the fiber and a convective resistance in moving from the surface of the filament to the crossflow gases.

Within the filament, the material property of greatest importance is DAB, the diffusivity of the solvent A through the filament here; we can characterize the diffusive flux of the solvent by:

$$N_A = -D_{AB}\frac{dC_A}{dr}$$

which is your familiar Fickian Diffusion equation. We use the ordinary derivative here because the process is steady and we have not yet begun to use the Lagrangian perspective we have.

$$\frac{\partial C}{\partial \theta} = \frac{D_{AB}}{r}\frac{\partial}{\partial r}\left(r\frac{\partial C}{\partial r}\right)$$

One point to emphasize here is the similarity of this equation to the Fourier heat conduction equation. If we then adopt the Lagrangian perspective, we have Comparison with the unsteady heat conduction equation reveals the equation to be identical with the exception that “a” is replaced by DAB and T by C. Both “a” and DAB have dimensions of length squared over time or units of cm²/s. The initial and boundary conditions are also practically identical to the heat transfer case, with the assumption of uniform concentration profile at time zero, and zero concentration gradient on the filament centerline and matching diffusive and convective flux at the filament surface:

C (r,0) = Co for r< R and q = 0,

$\frac{\partial C}{\partial r} = C$ at r = 0 and q>0 and

$$-D_{AB}\frac{\partial C}{\partial r} = k\,(C - C_{\infty})$$

at r = R and q>0

Instead of heat transfer coefficient, h, we have mass transfer coefficient, k. Correlations for k, expressed in terms of a dimensionless mass transfer coefficient, Sh (for Sherwood number) as a function of ReD and Sc, are also available. Sc is the ratio of momentum diffusivity to mass diffusivity, n/DAB, (for the cross flow fluid) and is comparable to the Prandtl number, n/a. Note that n and DAB are the momentum diffusivity and mass diffusivity of the gas in crossflow, and not of the polymer solution. One correlation for “k” is:

Sh = 0.281 (ReD)-0.4 where Sh = (kD/DAB). This correlation is a bit unusual, in that normally the mass transfer coefficient is found to be proportional to the diffusivity raised to a power less than unity. The reader may want to check other correlations to check whether this form may or may not be reasonable.

Just as we dedimensionalized the heat transfer equations, we can do the same for solvent diffusion. The resulting equations then are exactly identical to those for unsteady heat conduction.

$$\frac{\partial Y}{\partial X} = \frac{\partial^2 Y}{\partial n^2}$$

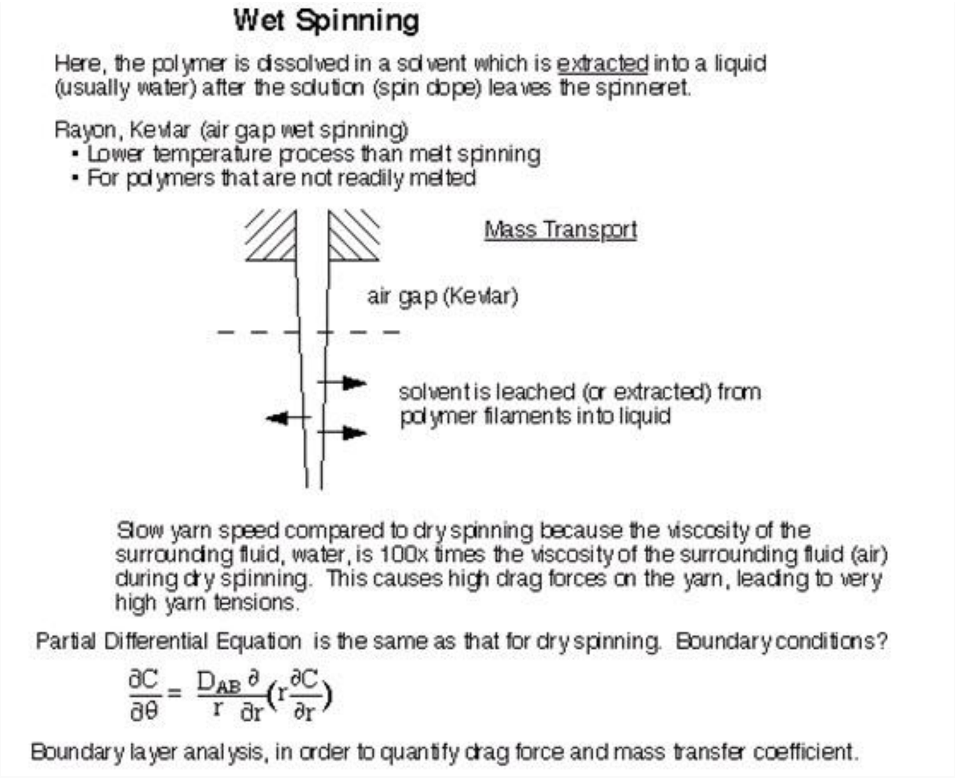
$$Y = \frac{C_{\infty} - C}{C_{\infty} - C_0},\; n = \frac{r}{R},\text{ and } X = \frac{D_{AB}\,\theta}{R^2}$$

$$m = \frac{D_{AB}}{k\,R}$$

Of course, T is replaced by C, a by DAB, h by k. Therefore, the same solution (graphical or analytical) is obtained and the same charts can be used to obtain quantitative predictions of the fiber spinning process. One can readily calculate, therefore, the Fourier number, X, required for the solvent concentration at the filament centerline to become less that 1% of the original value (Y < 0.01). From this value for X, the actual time (in a Lagrangian sense, remember) can be calculated. Finally, by multiplying this time by the yarn speed, the length of the solvent recovery section is obtained directly. The analogy here might be that of using a conveyor belt in a tunnel oven to bake bread. We can calculate the length of the tunnel oven, once we know the time to bake the bread and the speed of the conveyor belt.

Wet Spinning

Fibers produced by wet spinning include rayon and Kevlar. Rayon was originally developed as a synthetic substitute for silk and Kevlar was produced as a high-strength fiber for use in various aerospace and specialty-use applications. Furthermore, many commercial acrylic fibers are also produced by wet spinning.



Wet Spinning

Here, the polymer is dissolved in a solvent which is extracted into a liquid (usually water) after the solution (spin dope) leaves the spinneret.

Rayon, Kevlar (air gap wet spinning)
- Lower temperature process than melt spinning
- For polymers that are not readily melted

Mass Transport

air gap (Kevlar)

solvent is leached (or extracted) from polymer filaments into liquid

Slow yarn speed compared to dry spinning because the viscosity of the surrounding fluid, water, is 100x times the viscosity of the surrounding fluid (air) during dry spinning. This causes high drag forces on the yarn, leading to very high yarn tensions.

Partial Differential Equation is the same as that for dry spinning. Boundary conditions?

$$\frac{\partial C}{\partial \theta} = \frac{D_{AB}}{r}\frac{\partial}{\partial r}\left(r\frac{\partial C}{\partial r}\right)$$

Boundary layer analysis, in order to quantify drag force and mass transfer coefficient.

As with dry spinning, the polymer is dissolved or suspended in a solvent, to form a viscous "spin dope" and filaments are formed by extrusion through tiny holes in a spinneret plate. Kevlar, for example, will degrade thermally if attempts are made to melt it, and thus a solvent must be used. With wet spinning, the term more accurately depicts the process than with dry spinning, because the solvent is extracted or, perhaps more appropriately, leached, from the filaments by another liquid. In most cases, the second liquid is aqueous.

A major difference between wet spinning and either melt or dry spinning is that one is spinning into a fluid (liquid) with a much higher viscosity. Because this higher viscosity can translate into high shearing stresses on the surfaces of the filaments, the tension in the filaments can become quite high. For example, towing a buoy by a long line behind a boat can produce very high tensions in the line when compared with towing the same buoy by a short line. For long baths, the tension can become sufficiently high that the filaments might break, as their tensile strength is exceeded. To avoid this danger, much lower spinning speeds must be used. Whereas melt spinning may utilize spinning speeds of 2,000 yards per minute (80 mph), spinning speeds in wet spinning are usually less than 300 ypm.

Another difference with dry spinning is the capability of using many more spinneret holes in the case of wet spinning. The total number can approach 60,000 in a single spinneret plate, if the spinning is done directly into a coagulating or extracting liquid. Because the liquid is present, the filament forms a type of skin almost immediately and the potential for the filaments to touch and fuse is practically eliminated, compared with dry or melt spinning.

In the case of Kevlar the spin dope is relatively warm, about 100°C, and forms a viscous, liquid crystal. The solvent is sulfuric acid, at a concentration of about 80 wt% (20 wt% polymer). These liquid crystals are easily oriented by a stretching motion. Therefore, during the spinning process, the filaments are first extruded through an air gap, where the filaments undergo strains of 2 to 3x, which produces a high degree of molecular orientation in the filaments. This air gap is of the order of one inch. It also allows the spinneret plate to be warm (100°C) while the extraction bath can be cool (ca 15°C). The hot filaments then strike the cooling bath where the filaments are "quenched" and much of the orientation is locked in by the rapid cooling action. Subsequent to the quench step, the solvent is extracted, which requires a relatively long bath contact time. But the initial quenching step is crucial, since it allows for the oriented molecules to be "frozen" into position. This orientation is particularly important to the high-strength properties of Kevlar-the filaments, on a weight basis, are stronger that steel, almost by a factor of two. If one attempts to use the same process to produce Kevlar filaments of large diameter, the core of the filaments can lose its orientation, because the quench time to reach the core will increase with the square of the filament radius. The filament skin, or the outer part of the filaments, however, will have the orientation locked in and a high degree of orientation will exist there. This produces a so-called "skin-core" effect, in which the average properties of the filaments, expressed as tensile strength per unit cross-sectional area, will decline on account of a decreased average orientation. Kevlar, with its focus on strength development via "air-gap" wet spinning, is somewhat unique within the process of wet spinning. As with melt- and dry- spinning, the controlling part of the process is associated with development of the filament structure, either by cooling of the filament or by removal of the solvent. The equations for diffusion in wet spinning are identical to those for dry spinning, with the exception that the fluid passing outside the filaments is a liquid and not a gas.

Also, the flow may not be across the filaments, but even, partially, along the filaments. Therefore, the correlations and nature of the flow surrounding the filaments will result in different values for the surface mass transfer coefficient. Whether this will change the relative resistance dramatically will depend on the particular fiber to be produced and its dimensions and properties. The same graphical solutions described earlier can be used, however, to design a wet-spinning process, it may be necessary to predict the transport of momentum, heat, and mass in the region adjacent to the filament just downstream of the spinneret. One can use a so-called "boundary-layer" analysis to do this.

Treatment of such an analysis is beyond the scope of the present discussion of fiber spinning, but a brief description of the analysis is appropriate. One form of boundary-layer analysis involves von Karman integral boundary-layer techniques. The boundary layer starts at zero thickness at the first point where the fiber contacts the extracting liquid, and growing gradually radially outwards from each filament as one proceeds downstream. The velocity profile inside the boundary layer is assumed and all of the velocity change between the filament and the surrounding fluid is contained within this "momentum" boundary layer. Similarly, thermal and diffusional boundary layers contain all the changes in temperature and concentration, respectively. Based upon approximations of these velocity profiles, frequently assumed to be turbulent, the variation in filament drag with position can be predicted, along with local heat and mass transfer coefficients. The student is referred to Transport Phenomena, by Bird, Stewart, and Lightfoot, for additional details of such integral boundary-layer techniques.

Lesson 28. Testing methods for polymers

32.1 Introduction

- **Molecular Mass of Polymers**

Polymer properties are closely related to their molecular mass, size and structure. The growth of the polymer chain during their synthesis is dependent upon the availability of the monomers in the reaction mixture. Thus, the polymer sample contains chains of varying lengths and hence its molecular mass is always expressed as an average. The molecular mass of polymers can be determined by chemical and physical methods.

1. Number Average Molecular Weight

Consider a property which is only sensitive to the number of molecules present, a property that is not influenced by the size of any particle in the mixture. The best example of such properties is the colligative properties of the solutions such as boiling point elevation, freezing point depression and osmotic pressure. For such properties, the most relevant average molecular weight is the total weight of polymer divided by the number of polymer molecules. This average molecular weight follows the conventional definition for the mean value of any statistical quantity. In polymer science, it is called the number average molecular weight -$\overline{M}_N$.

Then the total weight of all polymers is

$$\boxed{\text{Total Weight} = \sum_{i=1}^{\infty} N_i M_i}$$

and the total number of polymer molecules is

$$\boxed{\text{Total Number} = \sum_{i=1}^{\infty} N_i}$$

As discussed above, the number average molecular weight is

$$\boxed{\overline{M_N} = \frac{\sum_{i=1}^{\infty} N_i M_i}{\sum_{i=1}^{\infty} N_i}}$$

2. Weight Average Molecular Weight

Consider of polymer property which depends not just on the number of polymer molecules but on the size or weight of each polymer molecule. A classic example is light scattering. For such a property we need a weight average molecular weight. To derive the weight average molecular weight, replace the appearance of the number of polymers of molecular weight i or Ni in the number average molecular weight formula with the weight of polymer having molecular weight i or NiMi. The result is

$$\boxed{\overline{M_W} = \frac{\sum_{i=1}^{\infty} N_i M_i^2}{\sum_{i=1}^{\infty} N_i M_i}}$$

3. Degree of polymerization

The degree of polymerization, or DP, is usually defined as the number of monomeric units in a macromolecule or polymer or oligomer molecule. For a homopolymer, there is only one type of monomeric unit and the number-average degree of polymerization is given by,

$$DP_n \equiv X_n = \frac{M_n}{M_0}$$

Where, Mn is the number-average molecular weight and M0 is the molecular weight of the monomer unit.

Food Chemistry is a major aspect of food science. Food chemistry deals with composition and properties of food and chemical changes it undergoes during handling, processing and storage.

Chemically food consists of carbohydrates, proteins, lipids, vitamins, minerals, preservators, colouring and flavouring reagents of food. In this module we will learn more about them in details.