



## Syllabus

### Module 1 : Polymers

- Introduction, Classification, Hydrocarbon Molecules, Thermoplastic, Thermosetting Polymers.
- Basic concepts Molecular Weight, Molecular Shape, Polymer Crystallinity, Crystallization, Melting and Glass Transition Phenomena.
- Viscoelasticity, Deformation Fracture, Defects in Polymers.
- Polymerization, Addition, Polymerization, Copolymerization and Condensation Polymerization, Polymer Additives Plastics, Elastomers, Vulcanization.
- Advanced Polymer Material, Conducting Polymers, Electrical Properties of Polymers, Liquid Crystal Properties, Molecular Electronics and Polymers and Supramolecular Chemistry.
- Fabrication of Polymers.

(i) Compression Moulding (ii) Injection Moulding (iii) Transfer Moulding (iv) Extrusion Moulding.

Synthesis Properties and Uses of PE, PMMA, Formaldehyde resin, Polymer Composite Materials.

(Refer chapter 1)

### Module 2 : Water

- Hardness of water, effect of hard water in the manufacture sector, types of hardness, determination of hardness by EDTA method and Problems.
- Softening of water by i) lime soda method with equations in general. Hot-cold lime soda method and problems ii) zeolite process and problems iii) Ion exchange method iv) reverse osmoses, ultrafiltration and its industrial applications.
- Methods to determine extent of water pollution i) BOD ii) COD.
- Methods to control water pollution.
- Industrialisation - materials cycle and pollution. Recycling issues.

(Refer chapter 2)

### Module 3 : Lubricants

- Definition, classification, characteristic properties, problems on acid value and saponification value, theories of lubrication.
- Additives for lubricants, selection of lubricant.

(Refer chapter 3)

### Module 4 : Energy

- Classification. Solar energy, hydropower, wind power, Biomass energy using bio technology, Hydrogen as a fuel.
- Solar energy, Production of electricity using solar energy. Rechargeable alkaline storage batteries, Nickel Hydrogen Batteries, Rechargeable Lithium ion batteries

(Refer chapter 4)

### Module 5 : Phase Rule and Steels

- Gibbs Phase Rule, One Component System Water. Two Component System Iron - Carbon Equilibrium Diagram with Microstructures.
- Limitations and Application of Phase Rule.
- Plain Carbon Steel: Limitations.
- Introduction to Alloy Steels, special steels.

Principles of shape memory effect and its applications.

### Module 6 : Nano-materials

- Introduction to nano – materials.
- Graphite, fullerenes, carbon nanotubes, nanowires, nanocones, Haeckelites. Their electronic and mechanical properties.
- Production methods for CNTS
- Applications of nano materials in
  - i) Medicine ii) Catalysis iii) Environmental Technologies iv) Electronics and related fields.
  - v) Mechanics..

### Theory Examination

- Question paper will be comprising of total 7 questions, each of 15 marks.
- Only 5 questions need to be solved.
- Q. 1 will be compulsory and based on entire syllabus.
- Remaining questions will be mixed in nature. (e.g. – suppose Q. 2 has part (a) from module 3 then part (b) will be from any module other than module 3.)
- In question paper weightage of each module will be proportional to number of respective lecture hours as mentioned in the syllabus.

### Term work

- Term work shall consist of minimum five experiments and a written test.
  - The distribution of marks for term work shall be as follows,
- |   |   |           |
|---|---|-----------|
| Laboratory work (Experiments and Journal) | : | 10 marks. |
| Test (at least one)                       | : | 10 marks. |
| Attendance (Practical and Theory)         | : | 05 marks. |
- The final certification and acceptance of term-work ensures the satisfactory performance of laboratory work and minimum passing in the term-work.



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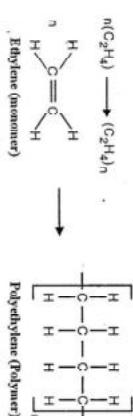
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High Polymers and Elastomers

1.1 Introduction

- The compounds formed by large number of small molecules (called monomers) linked together are known as *polymers* [poly = many].
  - The polymers are giant molecules with high molecular masses. For example, the monomer ethylene, gets linked with many other ethylene molecules to form polyethylene, or large number of vinyl chloride molecules combine to form polyvinyl chloride.
  - Thus the single repeating unit is called as *monomer*, and the resultant high molecular weight compound is called as polymer.
  - The total number of single monomer units combined together to form a polymer is known as *degree of polymerization*.
  - On the basis of this physical property, the polymers with high degree of Polymerisation are known as high polymers while those having comparatively low degree of polymerisation are known as *oligopolymers*.
  - The molecular weights of high polymers are generally in the range of  $10^4$  to  $10^6$ . Hence, these are also known as macromolecules.

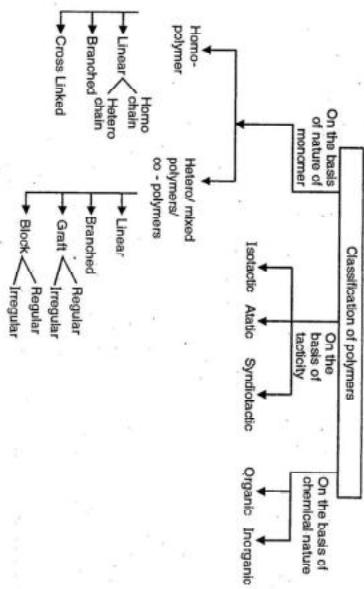


## 1.2 Classification of Polymers

The polymers are also classified on the basis of

- Sylabus**

  - Introduction
  - Classification
  - Hydrocarbon Molecules
  - Thermoplastic
  - Thermosetting Polymers
  - Basic Concepts Molecular Weight
  - Molecular Shape
  - Polymer Crystallinity
  - Crystallization
  - Melting and Glass Transition Phenomena
  - Viscoelasticity
  - Deformation Fracture
  - Defects in Polymers
  - Polymerization
  - Addition
  - Polymerization
  - Copolymerization and Condensation Polymerization
  - Polymer Additives Plastics
  - Elastomers, Vulcanization
  - Advanced Polymer Material
  - Conducting Polymers
  - Electrical Properties of Polymers
  - Liquid Crystal Properties
  - Molecular Electronics and Polymers and Supramolecular Chemistry.
  - Fabrication of Polymers
  - i) Compression Moulding
  - ii) Injection Moulding
  - iii) Transfer Moulding
  - iv) Extrusion Moulding. Synthesis Properties and Uses of PE, PMMA, Formaldehyde resin, Polymer Composite Materials.

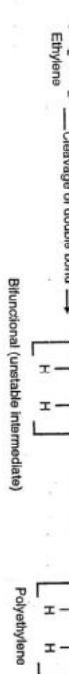


### 1.2.1 Homopolymers and Co-polymers

The macromolecules formed by identical monomers, are known as *homopolymers* and those with different monomers are known as *mixed polymers* or *co-polymers*.

The classification of polymers is shown in tree form. Each main class of polymers are been subdivided into other subclasses. The diversity in structural arrangement of components of monomer units make the *polymer*, *regular* or *irregular*, *homo* or *hetero*, *linear*, *branched*, or *cross linked*, *block* or *graft*.

*Polyethylene* is an example of *homopolymer*. Other examples of this class are, *polyvinyl chloride*, *polyvinyl acetate (PVA)*, *polyvinyl alcohol*, *polystyrene*, *polytetrafluoro ethylene (teflon)*, *polysypropylene* etc.



*C<sub>n</sub>-polymers* are the compounds formed by two *different small molecules*. For example in *polystyrene* *butadiene*, one molecule of *butadiene* combines with one molecule of *styrene*. The product obtained acts as a monomer to get the polymer.

- On the basis of arrangement of monomeric units in polymer, these are named as *linear*, *branched* or *cross linked* (three dimensional structures).

If the main chain of the polymer is of same atoms, it is known as *homochain polymers* while if is of different atoms it is known as *heteropolymer*.

e.g. — C — C — C — C —      Homochain polymer

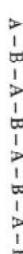
— C — O — C — O — C — O —      Heterochain polymer

• Co-polymer is named as *regular* or *irregular* on the basis of arrangement.

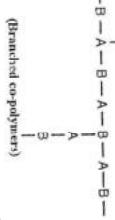
e.g. — A — B — A — B — A — B — A —      Regular

— A — B — B — A — B — A — A — B — B —      Irregular

If co-polymer chain possesses relatively long sequence of like monomers, it is called as *block co-polymer* where as if co-polymer possesses branched structures in which the monomer segments are not in same sequence on branch and backbone, it is known as *graft co-polymers*.



(Linear co-polymers)



- Some examples of linear high polymers are rubber, polyethylene, cellulose, polyvinyl acetate etc. Polyethylene may also have branched chains.

The vulcanised rubber is the best known example of cross-linked polymers in which  $\text{S-S}$ -cross links are joined irregularly.

The polymer structure becomes *three dimensional cross linked or network polymer* if cross linking is very extensive. Example of this category are *urea formaldehyde* and *phenol formaldehyde resins*.

- In such polymers in the final stage of Polymerisation three dimensional cross linking occurs. This makes the polymer *very hard and rigid*.
- In some resins this type of cross linking occurs in cold conditions, known as *cold setting* while in some others it occurs on heating in final stage, then the polymers are known as *thermohardening or thermosetting*.

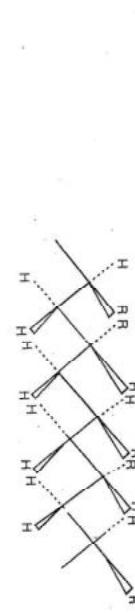
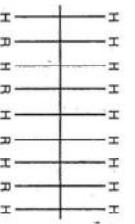
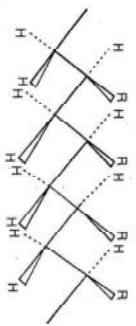
### 1.2.2 Tacticity

► [Dec. 2007 !]

Polymers are also classified on the basis of configuration of macromolecule known as *Tacticity of polymers*.

- Isotactic polymers
- Atactic polymers
- Syndiotactic polymers

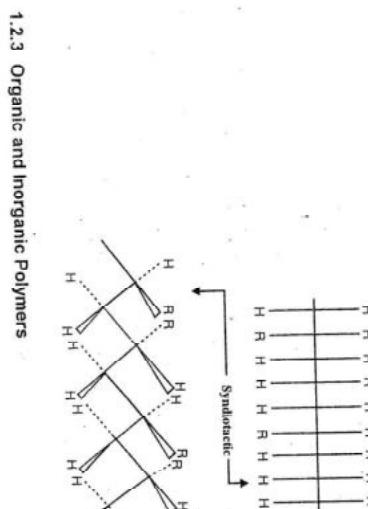
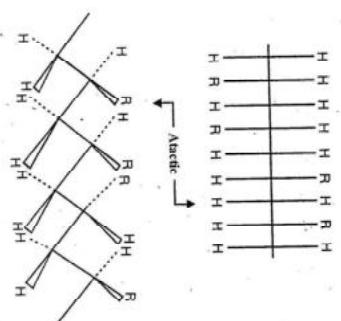
In *isotactic*, the head to tail configuration in macromolecule with respect to functional group is iso, i.e. all the functional groups lie on the *same side* of the chain.



In *syndiotactic polymers*, the functional groups occupy the alternating position.

The physical properties of polymers vary, on the basis of the position in which a functional group is attached in macromolecule.

- In *atactic*, the head to tail configuration in macromolecule with respect to functional group is iso, i.e. all the functional groups lie on the *same side* of the chain.



### 1.2.3 Organic and Inorganic Polymers

- On the basis of *chemical composition*, the polymers are also called either *organic or inorganic polymer*.
- Generally in organic polymers, *carbon with or without N, S, O forms the skeleton* while in inorganic, other elements form the skeleton.

- These are examples of homo-organic polymers. Other examples of organic polymers are polysaccharides, proteins, DNA, RNA, etc. Man made organic polymers include PVC, PP, PVA, PE, UF, polyesters, polyamides, polyurethanes, synthetic rubbers etc.

Polyethylene:



Epoxy polymers:



Polyvinyl chloride:



Polyethylene:



Polyvinyl acetate:



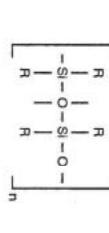
Polyethylene:



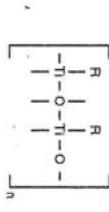
- Inorganic polymers* are those in which atoms other than carbon form the skeleton of polymer. *Polysiloxanes* or *polytitanoxanes* are the examples of polymers where side chain may be of organic nature. They are also known as elemento-organic or hetero-organic polymers. *Polysilanes* are purely inorganic in nature. Other examples of this class are *MgO polymer* or *hydrogen boron*.

**Examples :**

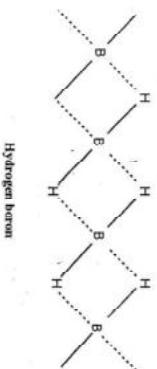
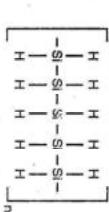
Polysiloxanes:



Polythioethanes:

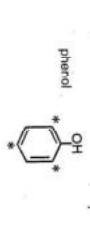


Polysilanes:



Magnesium oxide polymer

Epichlorohydrin:



➤ [Dec. 2007, May 2008 !]

**1.3 Polymerisation**

The reaction of monomers to form a polymer is known as polymerization. The polymers are formed mainly by :

- Addition Polymerisation (Chain polymerization)
- Condensation Polymerisation (Step polymerization).

- The monomers with three or higher functionality, are also known as "polyfunctional".
- In practice, bifunctional monomers are used to maximum extent.

### 1.3.1 Hydrocarbon Molecule

- These molecules are named so because they consist of only carbon and hydrogen in different numbers.

- Generally the molecule containing  $\pi$  bond conjugate/mn conjugate system are chosen as monomers for polymerisation process.

- Such hydrocarbon monomer molecules are highly useful because the  $\pi$  bond between  $C = C$  can be broken very easily simply by,

- absorption of light
- on heating

- on catalytic free radical reaction

This step is commonly known as "Initiation" which gives rise to two active sites around a  $\pi$  bond system.

### Examples



- Many other examples are in this category, few to name are, 1-butene, 2-butene, butadiene, isoprene, iso-butylene, vinyl chloride, acrylonitrile, etc.
- Such monomers, by and large, are used to form rubbers, because of their nature i.e. lower softening point.

### Types of polymerisation :

Broadly two types of Polymerisation are used as :

- |      |                                   |
|------|-----------------------------------|
| (i)  | Addition/Chain polymerization     |
| (ii) | Condensation/Step polymerization. |

### 1.3.2 Addition/Chain Polymerisation

► [ May 2004, Dec. 2006 ]

The word *chain*, indicates *elongation* of carbon skeleton to form a polymer.

- Generally such a Polymerisation involves the ( $C = C$ ) link in monomer.

- The double bond breaks and as a result two single bonds on either side of each carbon are formed and thereby elongation of carbon chain continues.

- The product of this type of Polymerisation is *exact multiple of monomer number, having no by-product or loss of any molecule*. Thus,

- Addition Polymerisation is undergone by monomers having  $C = C$  linkage. e.g. ethylene, vinyl chloride, propylene, butadiene, styrene etc.
- The rate of reaction is *very high*.
- The Polymerisation reaction involves *three steps* such as,

(a) *Initiation*

(b) *Propagation or branching and*

(c) *Termination*

Initiation requires normally an *initiator or catalyst*. The initiator may be,

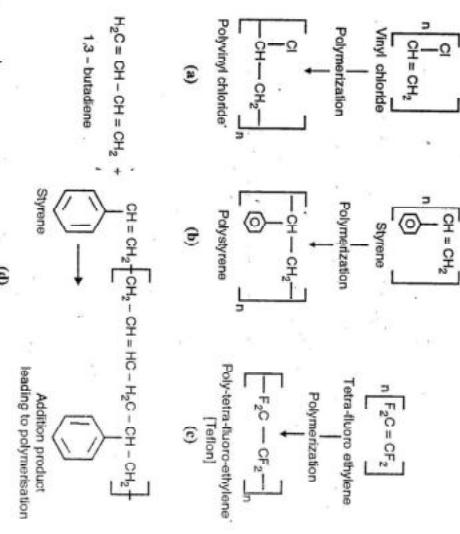
- Free radicals
- Ions or
- Co-ordination compounds

- Commonly used initiators are  $H_2O$ ,  $H^+$ ,  $H^-$ ,  $R'$  alkenes etc. The Polymerisation reactions stop (termination step) only if it is interrupted with chain transfer. Otherwise reaction continues till monomers are available.

- The addition Polymerisation may be between same monomers or between two different monomer species which react to form a third monomer which in turn form a polymer.

- If two same monomers join to form polymer, the method is known as *chain polymerisation* while if two monomers combine to form a product which in turn acts as a monomer the method is known as co-polymerization. Generally polymers of very high molecular weight are formed by this method.
- The various examples of addition/chain Polymerisation and of co-Polymerisation are as shown below.

- In these (a), (b) and (c) are the examples of chain polymerization, (b) is the polymer where only side chain of styrene takes active part in forming polymer while benzene ring remains intact. (d) is an example of co-polymerization, where butadiene and styrene combine to give an addition product, which acts as a monomer to form poly-butadiene co-styrene polymer popularly known as Buna-S.



### 1.3.3 Condensation/Step Polymerisation

► [ May 2004, Dec. 2004, May 2006, Dec. 2006, May 2007, Dec. 2007 ! ]

The monomers having certain functional groups such as  $-\text{OH}$ ,  $-\text{COOH}$ ,  $-\text{NH}_2$  etc. show the tendency to undergo polymerizations by the elimination of one molecule of a simple by-product such as  $\text{H}_2\text{O}$ ,  $\text{HCl}$ , salt or alcohol etc. Unlike addition/chain polymerizations, polymer loses simple molecules at every combination.

Thus,

- Condensation Polymerisation is undergone by the monomers which possess functional groups.
- Generally monomers are like acids, amines, alcohols, phenols, carbonyl compounds etc.
- This type of Polymerisation occurs stepwise, hence the rate of Polymerisation is comparatively low.

#### Example

##### 1. Phenolformaldehyde or Bakelite

- It is prepared by condensing phenol with formaldehyde in the presence of acidic/alkaline catalyst.

The initial reaction results in the mono, di and trimethylphenols depending on the ratio of phenol to formaldehyde, the kind of catalyst, the temperature and the time of reaction.

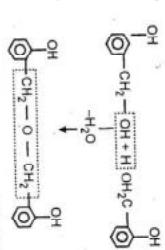
- Then the reaction between methanol's hydroxyl group and the hydrogen in the benzene ring of phenol, producing a methylene linkage or



- Between the methanol's hydroxyl group and the hydrogen in the benzene ring of phenol, producing a methylene linkage or

In both the cases, water molecule is eliminated.

Elimination of water molecule is shown in the reactions.



- In the next step, the two linkages formed, combine together to form the cross linked structure of methylene bridge and ether linkage to get the monomer of phenol formaldehyde. To get macro molecule, this monomer combines. The strength of Bakelite depends upon molecular weight.

The different parameters which govern the final form of polymer product are,

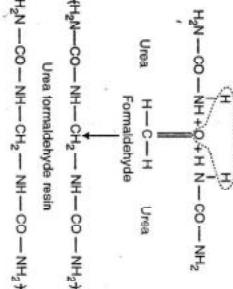
**Molecular structure of phenotannaldehyde**

The diagram shows the chemical structure of phenotannaldehyde. It consists of a repeating unit enclosed in brackets with a subscript 'n'. The unit contains two hydroxyl groups (OH) connected by a methylene bridge (-CH<sub>2</sub>-O-). Each hydroxyl group is attached to a para-phenylene ring (a benzene ring with a -CH<sub>2</sub>- group at the para position). The para-phenylene rings are further linked by a methylene bridge (-CH<sub>2</sub>-O-CH<sub>2</sub>-).

## 2. Ureaformaldehyde

- In the formation of ureaformaldehyde, hydrogen from  $\text{NH}_2$  group of urea condenses with oxygen to form ureaformaldehyde with free valency and eliminates water molecule as shown in reaction.

These terminated groups further condense with formaldehyde to form long chains, thus the urea formaldehyde can be represented as,



### 3. Nylon (6 : 6)

- This is also formed by condensation of hexamethylene diamine and adipic acid. The reaction is as,

1.5 Molecular Shape

- Temperature plays an important role for shape of polymer molecule.

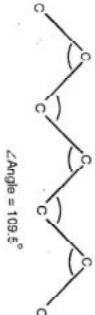
Polymer molecules can not remain linear, because of high number of monomer forming very long chains.

When the monomers combine, particularly hydrocarbon molecules, an angle of  $109.5^\circ$  is formed and maintained on the carbon atoms in polymer molecule.

**1.5 Molecular Shape**

  - (iii) Concentration : Higher the concentration of monomer, DP increases.
  - (iv) Catalyst : Presence of a catalyst in appropriate concentration helps in increasing DP.

$\angle$ Angle =  $109.5^\circ$



Thus, the two modes of reactions, give different types of polymers.

- With different degree of temperatures, the polymer molecule shows different shapes. Few shapes are represented as,



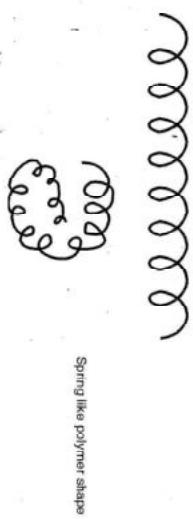
Normal



Extended



Random



Spring like polymer shape

- Thus polymers show different shapes, which normally depends upon,

- Molecular weight
- Degree of polymerisation
- Temperature.

The dimensions of polymer chains are never same.

### 1.6 Molecular Weights of Polymer

- The determination of molecular weight of a polymer is highly important because the properties of polymer are totally governed by its molecular weight.

- If polymer is of low molecular weight, then, it is generally softer and vice-versa.

#### Average molecular weight:

- In polymerisation reaction, when a monomer faces initiation, it gives rise to a reactive species, i.e. either anion or cation or free radical.
- The type of the reactive species depends upon the path of mechanism.
- In the second step, the propagation or chain elongation occurs.

- This step continues till the monomer molecules are available and also till terminator is applied.

- The final step termination, is random, and therefore the polymer molecule formed from same monomer units also differs in its size, shape and weight.

- Hence, concept of 'average molecular weight' is considered for polymer molecules.

- Thus there are different types of average molecular weights are in practice such as,

- Number average M.W. ( $\bar{M}_n$ )
- Weight average M.W. ( $\bar{M}_w$ )
- Viscosity average M.W. ( $\bar{M}_v$ )

#### Number Average M.W. ( $\bar{M}_n$ )

- To determine  $\bar{M}_n$ , the following method is used in practice.

Suppose, a sample contains  $n$  polymer molecules out of which say

$n_1$	molecules	have	M.W	$M_1$
$n_2$	molecules	have	M.W	$M_2$
$n_3$	molecules	have	M.W	$M_3$
.....	and so on			

Then,

Number Average M.W ( $\bar{M}_n$ ) of sample would be,

$$\bar{M}_n = \frac{n_1 M_1 + n_2 M_2 + n_3 M_3 + \dots}{n_1 + n_2 + n_3}$$

$$= \frac{\sum n_i M_i}{\sum n_i}$$

Similarly DP can also be calculated,

$$\bar{DP}_n = \frac{\sum n_i (\bar{DP}_i)}{\sum n_i}$$

Also,

$$\bar{M}_n = m \cdot (\bar{DP})_n$$

Where,  $m$  = molecular weight of monomer in the sample.

### Weight Average M.W ( $\bar{M}_w$ ) :

For a sample

Let  $W$  = weight with  $M_w$  as M.W.

$W_1$  = weight with  $M_{w1}$  as M.W.

$W_2$  = weight with  $M_{w2}$  as M.W. and so on.

$$\bar{M}_w = \frac{\sum W_i M_i}{\sum W_i} = \frac{W_1 M_1 + W_2 M_2 + W_3 M_3 + \dots}{W_1 + W_2 + W_3 + \dots}$$

Then,

$$= \frac{\sum n_i M_i^2}{\sum n_i M_i} \dots \text{(as } W_i = n_i M_i)$$

Note : generally  $\bar{M}_w > \bar{M}_n$

- In the similar way other viscosity average molecular weight concept also can be derived.

Determination of average molecular weights can be carried out as,

(1)  $\bar{M}_n$  by measurement of colligative properties such as elevation in b.p.

(2)  $\bar{M}_w$  by light scattering experiments which are used for molecular size determination.

Finally polymers are categorised in following four forms, on the basis of their end uses.

Form of polymer	Significant properties for end uses	Examples
A Plastic	Plasticity, mouldability	PVC, PE
B Rubbers	Elasticity, vulcanisability	Isoprene Neoprene
C Resins	Resinous / Viscous fluid form, Ability to form cross-linked polymer.	PF, UF.
D Fibres	Tensile strength	ropes strings nets.

## 1.7 Plastics

These **high polymers** are the substances with high molecular weights which may occur in nature or be synthesized.

- The natural high polymers such as *cellulose, starch and proteins* are present in our food.
- Rubber is another natural high polymer with many applications while plastics are the high polymers which are generally synthetic.

The name plastic refers to its meaning that these are the polymers which mould themselves into articles by heat and pressure.

- As mostly plastics are synthetic these are also known as *synthetic resins*.
- Over the years the plastics have taken the place of metal in various uses.

### 1.7.1 Classification of Plastics

On the basis of setting manner in final stage of manufacture the plastic materials or plastic articles are classified in two classes ;

- (i) Thermo plastic
- (ii) Thermo setting

The characteristics of these two types is given below.

- #### 1.7.1.1 Thermo Plastics or Thermosoftening Plastics
- These show reversible change on heating i.e. they soften on heating but regain their original properties on cooling.
  - They gain or lose hardness with rise or fall in temperature. Their chemical nature does not get affected even on repeated heating and cooling, i.e. the changes are more of physical nature.

- If these resins are softened, they retain their softness at that temperature.
- These resins can be reclaimed from waste, and they are soft, weak and less brittle as compared to former type of plastics resins.
- The method usually used to manufacture polymers is addition polymerisation.
- They are generally long chain linear polymer with occasional or no cross linking.
- They are soluble in specific organic solvents.

- Examples of this class of resins are cellulose nitrate, polyacrylates, ethyl cellulose, polyvinyl resins, styrene or polystyrene resins, polyamides (nylons) polyethers, polypropylene, polyethylene etc.

### 1.7.1.2 Thermo Setting Plastics

- These are the polymers, which on heating change irreversibly into hard and rigid materials.
- This melt of polymer when set into a mould to form an article, is almost a permanent set.
- On reheating the article does not soften again, thus inhibiting irreversibility.
- They are hence known as *thermo hardening plastics* or *permanent setting resins* and during moulding acquire three dimensional cross linked structure with strong covalent bonds.
- On reheating, these bonds retain their strength and hence such a plastic does not soften on reheating.
- Thermo setting plastics can not be reclaimed from waste due to their irreversibility.
- They are hard, strong and brittle than thermo plastics.
- The method by which these are formed is called as *condensation polymerisation*.
- They are insoluble in almost all organic solvents, due to their cross linked three dimensional structure.
- Phenol formaldehyde / bakelite, amino plastics and alkyl plastics, epoxy plastics, silicon plastics etc. are the best known examples of *thermosets*.

### 1.7.2 Comparison of Plastics

► [ Dec. 2003, May 2005, Dec. 2005, May 2006, May 2008 ]

Sr. No.	Thermoplastics or thermosoftening Plastics	Thermosetting Plastics or Thermohardening Plastics
1.	These are formed by addition Polymerisation	These are formed by condensation Polymerisation only
2.	They are long chain linear polymer with negligible cross links.	These have three-dimensional network structure with number of cross links
3.	Structural formula:	Structural formula:
	$\text{--R--R--R'--R''--R--R--}$	$\begin{array}{ccccccc}   &   &   &   &   &   &   \\ \text{--R--R--R--R--R--} & & & & & & \\   &   &   &   &   &   &   \\ \text{--R--R--R--R--R--} & & & & & & \\   &   &   &   &   &   &   \\ \text{--R--R--R--R--R--} & & & & & & \\   &   &   &   &   &   &   \end{array}$

### 1.8 Compounding of Plastics

► [ May 2004, May 2005, Dec. 2005, Dec. 2006, May 2007 ]

- Plastics are manufactured synthetically using raw materials mostly from natural gas and petroleum, or from coal mines, forests, farms, paper and textile mills. The petroleum contains mainly the open chain or aliphatic hydrocarbons and ring compounds normally comprising of
  - (i) N-paraffin series ( $C_n H_{2n+2}$ )
  - (ii) Isoparaffin series ( $C_n H_{2n+2}$ )
  - (iii) Olefin series
- and the ring compounds normally of:

- (a) Naphthalene series or  
 (b) Intermediate distillates of heavy oil and  
 (c) Residues (lubricating oil etc.)

- In addition to the raw materials chosen, the plastics are generally compounded with some other substances so as to impart certain specific properties to the product.
  - Usually such moulding compositions are prepared from two or more of the following material groups which are named according to their function
- |  |
|--|
| (i) Binders e.g. resins                    |
| (ii) Fillers or extenders                  |
| (iii) Pigments or dyes or colouring agents |
| (iv) Catalysts or accelerators             |
| (v) Plasticisers                           |
| (vi) Lubricants                            |
| (vii) Stabilizers.                         |

#### Binders

- Binders hold the other constituents together during manufacture.

Usually natural or synthetic resins or cellulosic derivatives are used as binders, which are high molecular weight substances.

- Binders influence the properties of plastics.

- The type of the treatment during moulding operation also depends upon binders.

- If binder used has comparatively low molecular weight, then plastic article gets moulded easily and vice versa.

#### Fillers or extenders

- Fillers or extenders impart better tensile strength, hardness, finish, workability, opacity etc to the plastic material.
- They also reduce cost of the plastic per unit weight.
- The fillers may be of organic or inorganic origin.

- Examples**

#### Organic fillers

Wood flour, Cotton pulp, Paper pulp, carbon black, Graphite, Powdered rubber etc.

#### Inorganic fillers

Ashbestos, powdered mica, silicate clays, talc, kieselguhr, Zn and Pb oxides, Cd and Ba sulphides, metals Fe, Pb, Cu, Al in powdered form, etc.

- The percentage of filler varies with types of plastic.

- The highest percentage can be up to 50 % of the total moulding mixture.

- The fillers which are added only to improve the mechanical strength of the plastic are known as *reinforcing fillers*.

- Cabourundum, quartz, mica improve hardness of plastic material whereas, barium salts help to make the plastic impervious to x-rays.

- The heat and corrosion resistance can be improved by adding asbestos.

#### Pigments / Dyes / Colouring matter

- These impart desired colour to plastic.

- Organic dyestuffs and inorganic pigments are used for this purpose in small proportion.

#### Catalysts or accelerators

- These are used to increase the rate of polymerisation of fusible resin binder to form cross linked infusible form during moulding operations.

- Generally thermosetting plastics involve use of catalyst normally an acidic or basic catalyst depending upon the type of thermosets.

- The catalyst are added in small quantities.

- Commonly used catalysts are hydrogen peroxide, benzyl peroxide, metallic oxides etc.

#### Plasticisers

- These help to increase the plasticity of the plastics.
- The adequate quantity of plasticiser also helps to soften the plastic at comparatively lower temperature.
- Plasticizer are essentially used in thermo softening plastics

- Functions of plasticizers are to
  - (a) Enhance flexibility or plasticity.
  - (b) Decrease brittleness.
  - (c) Reduce the viscosity of resins so that they can be moulded even at high temperature and pressure.
  - (d) Lower softening temperature.
  - (e) Lower moulding or remoulding temperature.
  - (f) Increase flame proofness of plastic.
  - (g) Increase workability during moulding.
- The plasticizers when mixed with plastic, in finished stage occupy the position with uniform distribution between the polymer molecules.
- This type of dispersal of plasticizers reduces the forces of intermolecular attraction and thereby increases tendency of sliding or moving.
- Thus the plastics which are plasticized possess high percentage of flexibility.
- The commonly used plasticizers are lubricants, camphor, alkyl phosphates, vegetable oils, fatty acids etc.
- They are added to the extend of 8 – 10 % of the total bulk of plastic.
- *Plasticizers are not used in thermosets, they are added in thermo softening resins only.*
- The plasticizers used are normally liquids and hence only disadvantage is, if they are not consistent, they ooze out in finished product.
- E.g. cresyl diphenyl phosphates, tricresyl phosphate, triphenyl phosphate, butylphthalate, diethyl phthalate, di-iso-decyphthalate etc. are the examples of cyclic organic plasticizers, while adipic acid esters, epoxidised esters or esters of oleic, stearic, phosphoric, azelaic acid are certain acrylic plasticizers added to synthetic resins.
- Non-drying vegetable oils are also used as plasticizers.
- Lubricants**
  - Lubricants help during moulding operations, especially during low or room temperature moulding.
  - The use of lubricants imparts flawlessness, and glossy finish to the plastic products.

This is because the lubricants tend to get dispersed towards outer surface of the finished product, hence during moulding, they form a layer between the article and mould. This layer prevents the plastic material from sticking to the surface of the mould, and thereby facilitating the moulding operations.

Commonly used lubricants are soaps, or esters of fatty acids such as oleic and stearic acids or waxes.

#### Stabilisers

- Stabilizers help to improve thermal stability of the plastic.
- These are required especially in the processing stage for plastics, which have tendency to decompose or change their colours at moulding temperatures.

### 1.9 Fabrication of Plastics or Moulding of Plastics

► [ Dec. 2003, Dec. 2007, May 2008 ! ]

- The fabrication is the process in which the prepared resins in the form of granules or powder are converted into desired shape by using various machines or moulds.
- There are many ways by which, the compound materials are transformed into finished articles.
- The basic principle involved in this is partially melting (softening) resinous mass by the application of heat.
- These softened resins are further compressed in dies/moulds with the help of high pressure to get the desired shape.
- In the case of thermosetting plastics moulded hot plastic is ultimately solidified through further polymerisation, called curing or setting stage while it is still in the mould.
- In the case of thermo softening plastic, the moulded plastic material is further cooled or chilled for solidification of article.
- For thermosoftening plastic material, injection moulding, extrusion, blow moulding, vacuum forming techniques are usually used.
- For thermosetting plastics compression moulding, transfer moulding and laminating techniques are generally employed. Some important methods of fabrication are described below.

- The following methods for fabrication are in practice.

- |  |
|--|
| (1) Compression moulding : suitable for thermosets   |
| (2) Injection moulding : suitable for thermoplastics |
| (3) Transfer moulding : suitable for thermosets      |
| (4) extension moulding : suitable for thermoplastics |

### 1.9.1 Compression Moulding

► [Dec. 2003, May 2005 !]

- It is one of the most common method for moulding thermosetting materials which can withstand high temperature and pressure.
- This process consists of compressing the molten resinous material into the desired shape by the use of moulds, heat and pressure.
- A predetermined quantity of resin powder or pellets is usually preheated to about 120°C before the cavity of the heated mould is filled with it.
- After charging the mould, the two parts of mould are carefully brought together under low pressure. (Refer Fig. 1.9.1.)
- It is then compressed by hydraulic pressure.
- Pressures from 2,000 to 10,000 p.s.i are used.
- This pressure and heat allow the resin to melt and flow, thereby filling the cavity between the two parts of the mould.
- The material in the mould is kept for the specified time under a correct temperature and pressure for a proper cure. The curing is done either by heating (in case of thermosetting) or cooling (in case of thermoplastics).
- After curing, the moulded articles are taken out by opening the mould apart.
- A variety of products ranging from ash trays and electric switch boxes to radio and television cabinets are manufactured this way.

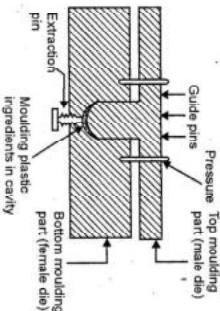


Fig. 1.9.1 : Compression moulding of plastics

### 1.9.2 Injection Moulding

- It is one of the most widely used processes for converting thermoplastic raw materials into finish product.
- It is fundamentally simple and easy to operate and capable of producing a very wide range of industrial and domestic articles.
- In this process a predetermined quantity of the granular or powdered resin is fed into a heated cylinder from where it is injected at a controlled rate through a nozzle into the tightly locked mould by means of a screw arrangement or by piston plunger as shown in the Fig. 1.9.2.

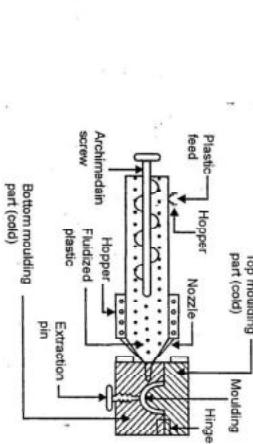


Fig. 1.9.2 : Injection moulding of plastic

### 1.9.3 Transfer Moulding

► [May 2004 !]

- It is method which uses the principle of injection moulding and is used for thermosetting materials.

#### 1.9.4 Extrusion Moulding

► [Dec. 2005!]

- When relatively intricate designs are required in the fabricated products, especially when metal insets are to be fabricated, transfer moulding is used.
- Though transfer moulding is a combination of injection and compression moulding, it differs from both these methods.
- In this moulding, powdered resins are placed in a heated chamber, maintained at a minimum temperature at which the powdered resins just begins to become plastic.
- This plastic material is then injected through an orifice into the mould by plunger, working at a high pressure.
- Due to a very high friction developed at the orifice, the temperature of the material at the time of ejection from the orifice rises to such an extent that the moulding powder becomes almost liquid, and consequently it flows quickly into the mould which is heated upto curing temperature required for setting.
- The moulded article is then ejected mechanically.

**Advantages**

- Intricate shapes not attainable by compression moulding can readily be produced.
- Article produced is free from flow mark.
- Even thick pieces cure almost completely and uniformly.
- Finishing cost of fabricated article is almost entirely eliminated.
- Blistering is almost eliminated, since air and excluded gases are expelled in the plasticizing chamber itself.
- Mould cost is less, since it involves very low abrasive action.
- Fine wires and glass fibers can be inserted into the mould.

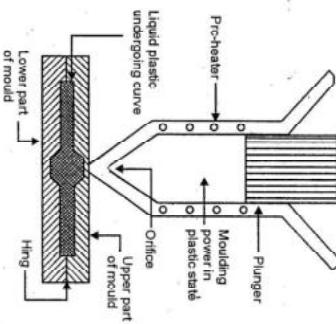


Fig. 1.9.3 : Transfer moulding of plastic

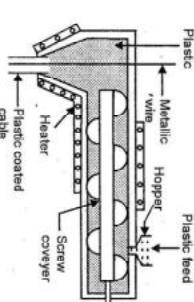


Fig. 1.9.4 : Moulding of insulated electric cable by extrusion moulding vertical

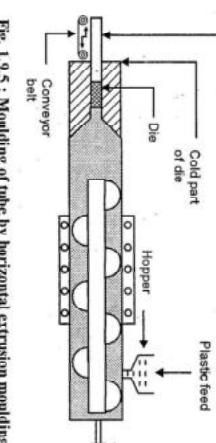


Fig. 1.9.5 : Moulding of tube by horizontal extrusion moulding

## 1.10 Synthesis, Properties and Uses of Various Plastics

IPE, PS, PMMA, Formaldehyde Resin

### 1.10.1 Poly Ethylene

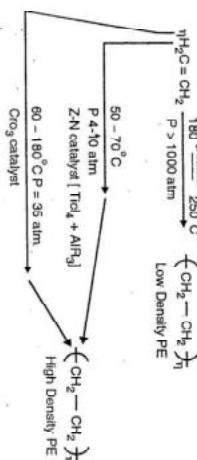
► [Dec. 2005, May 2007, Dec. 2007 !]

There are two types of poly Ethylenes,

- (i) LDPE
- (ii) HDPE

### Synthesis

They are synthesised at different temperature, pressure and using different catalyst.



### Specific properties

#### LDPE

1. Density is low (0.91 – 0.925 gm/cc).
2. Crystallinity is < 40%.
3. Softening temperature about 120°C.

#### HDPE

1. Density is high (0.94 – 0.965 gm/cc).
2. Crystallinity (> 90%).
3. Softening temperature about 145°C.
4. Excellent insulator of electricity.

### General properties of PE

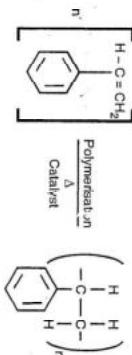
1. It is rigid, waxy, translucent and a non-polar material.
2. It exhibits considerable chemical resistance to strong acids, alkalis and salt solution at room temperature.
3. It is good insulator of electricity.
4. It is swollen and permeable to most oils and organic solvents, particularly kerosene.
5. Due to highly symmetrical chain structure polyethylene crystallizes very easily.

### Uses

For making

1. High frequency insulator parts.
2. Bottle caps
3. Flexible bottles
4. Kitchen and domestic appliance
5. Toys
6. Sheets for the packaging materials' chemicals plants, tubes, pipes, coated wires and cables.
7. Bags for packaging etc.

### 1.10.2 Poly Styrene



The π bond in side chain breaks on initiation thereby creating two active sites which takes part in propagation to form PS polymer.

### Properties

1. Polystyrene is a transparent, light (sp. gravity 1.05 to 1.07 g/cm<sup>3</sup>) and stable material.
2. It has excellent moisture resistance.
3. It can be nitrated by fuming nitric acid and sulphonated by conc. H<sub>2</sub>SO<sub>4</sub>, at about 100 °C to yield water soluble emulsion.
4. It is a highly electric insulating material.

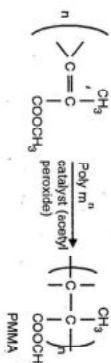
**1.10.4 Formaldehyde Resins**

The two resins of this types discussed here are

1. It is highly resistant to acids and has a good chemical resistance.
2. It has a relatively low softening range (90 to 100 °C) and is brittle.
3. Refrigerator parts, battery cases
4. High frequency insulators
5. Lenses
6. Indoor-lighting panels etc.

**1.10.3 PMMA (Polymethyl Methacrylate)****Synthesis**

PMMA is (also called as Lucite/plexiglass). Synthesised by Polymerisation reaction of methyl methacrylate using a catalyst. Most commonly used catalyst is acetyl peroxide.

**Properties**

1. It is transparent and colourless plastic.
2. Easy to mould in desired shapes.
3. Refractive index is 1.59
4. At lower temperature (R.T.) it is brittle and rigid
5. When heated slowly, acquires rubber like properties at about 65°C where as so items at about 130°C.

**Uses**

Use for making

1. Artificial eyes
2. Screens for TV
3. Air crafts, light fixtures
4. Also used in optical instruments, bone splints, adhesives, paints etc.
5. In skylights, decorative articles etc.

In moulding of articles like

1. Toys, combs, buttons
2. Buckets, radio and television parts
3. Refrigerator parts, battery cases
4. Indoor-lighting panels etc.

**1.10.4.1 Phenol Formaldehyde Resins**

► [Dec. 2004, May 2005, Dec. 2006, May 2007]

**Synthesis**

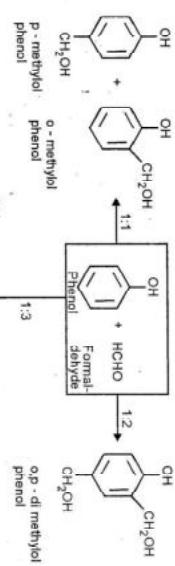
These are synthesised by condensation polymerisation.

Raw materials: Phenol or Resorcinol Formaldehyde or Furfural

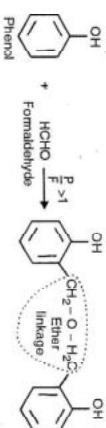
This Thermoset (PF) is prepared as per following steps.

**Step 1 : Preparation of O,O,P-tri methylol phenol resin****Step 2 : Polymerisation of O-methylol phenol to give Novolac (Low M. W.) with linear structure.****Step 3 : Heating Novolac to form highly cross-linked polymer Bakelite**

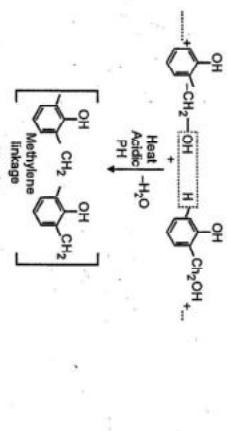
Step 1: Phenol and Formaldehyde react with each other to give different products depending upon the ratio of the reactants as shown below,

**Uses**

**Step 2 :** Mono-methylol phenol (i.e. ortho or para) can undergo Polymerisation to give low molecular weight polymer known as Novolac.

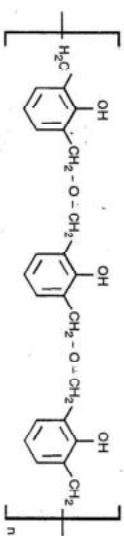


**Applied Chemistry - I (M.U.)**



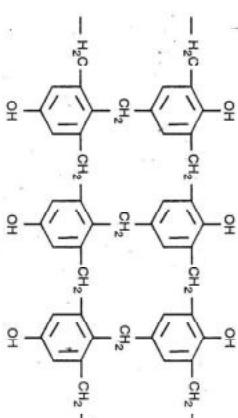
The linear polymer obtained as above is a thermoplastic, and dissolves in few aromatic solvents. Hence, is generally converted into a thermoset – bakelite

The product with ether linkage gives a polymer called as Resole as,



**Step 3:** The Novolac obtained in step 2 is simply heated at about 150°C using a catalyst whereby a highly cross linked product, bakelite is obtained.

Structure of bakelite is,

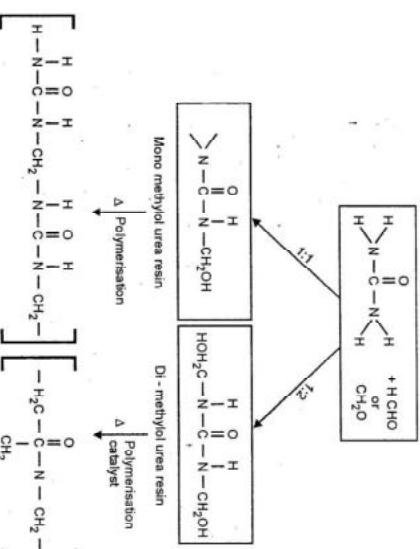


**Reaction**

- These are also called as amino resins or amino plants.
- In general amino organic compounds and Formaldehyde combine by condensation polymerisation to give these resins.
- In this particular types of resin, organic amine being urea, reacts with Formaldehyde and polymerises to give resin.

► [ Dec. 2003, Dec. 2004, May 2006, May 2007, May 2008 ! ]

**Synthesis**



- Phenolic resins or bakelite is a rigid, hard and infusible solid.
- They are scratch resistant, water resistant and insoluble solids.
- They are resistant to non-oxidising acids, salts and many organic solvents, but get attacked by alkalis, because of the presence of free hydroxyl group in their structures.
- They possess excellent electrical insulating character.

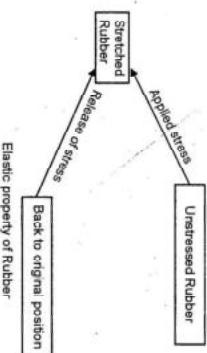
**Properties of Urea Formaldehyde**

1. Urea formaldehyde resins give clear, water-white products of good tensile strength.
2. They possess good electrical insulating character.
3. They possess good chemical resistance (exception : strong acids and alkalies) great hardness, great light stability and good abrasion-resistance.
4. Resistant to water.
5. Resistant to heat/flame.

**Uses of Urea Formaldehyde**

1. It is used for bonding grinding wheels.
2. Used as a binder of glass fibres, rock wool etc. which are used for filtration and insulation purpose.
3. Used as a binder for foundry cores.
4. Used as a cation exchange resin in water softening.
5. Used in bonding plywood.
6. Used as an electrical insulation.
7. For decorative articles like plates drinking glasses, dishes etc.

**1.11 Elastomers or Rubber**

- The organic polymers possessing elasticity to the extent of nearly 200 to 300 percent are known as Elastomers or Rubber.
  - The rubber gets elongated on stretching and gets back to its original dimensions on removal of stress i.e. it possesses the property of elasticity.
- 
- Elastic property of Rubber:

Important properties of rubber are its

- (i) Flexibility.
- (ii) Strength.
- (iii) Impermeability to water.
- (iv) High resistance to abrasion etc.

Due to these properties rubber is highly useful for industrial as well as domestic purposes.

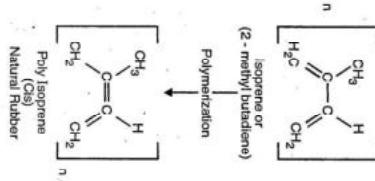
**1.12 Types of Rubber**

Rubber is of two types :

- |  |
|--|
| (1) Natural rubber : Obtained from natural sources.  |
| (2) Synthetic/Artificial rubber : Made synthetically |

**1.12.1 Natural Rubber**

- Natural rubber is obtained from latex, a milky emulsion, collected from rubber tree. The bark of rubber is cut at intermittent places.
- The latex starts dripping which is collected in a container.
- It is nothing but the milky white watery emulsion of isoprene.
- The percentage of isoprene is about 30-40% and remaining is water.
- The proportion of isoprene and water depends upon the age of rubber tree.
- On earth, there are about 500 species of rubber trees.
- In latex, the rubber hydrocarbon (isoprene) is dispersed in water which is stabilised due to natural proteinous substances and some fatty acids.
- The latex thus collected is further processed to get natural rubber.
- During this process, the isoprene molecules get polymerized to form long coiled chain of polyisoprene, by reaction,



Natural Rubber

### 1.12.1.1 Processing of Latex

- The latex collected from tree is mixed with water in excess and then strained (filtered).
- The latex free from dirt or dust is preserved using preservative such as ammonia.
- Later by coagulation method rubber is separated.

- To get rubber the dilute latex is treated with small quantity of formic and acetic acid.
- The acid treatment helps the rubber hydrocarbon to get coagulated to form a solid known as crude rubber.

The composition of crude rubber is nearly 90-95% rubber hydrocarbon ( $C_5H_{10}$ ), 2-4% proteins, and 1-2% resins.

- Formic acid makes the pH in the range of 4.75-5.
- The coagulum formed is then washed and treated further to get crepe rubber, smoke rubber, gutta percha, balata etc.

### 1.12.1.2 Crepe Rubber

- The washed coagulum is allowed to stand so that the water gets drained out.
- The rubber coagulum is then made into sheets by passing through creping machines.
- The two rollers of creping machine are 0.5 m wide and 3 mm apart.
- These rollers have grooves on their surface. Which gives rubber sheets an uneven surface.
- The sheet of rubber is then washed, if necessary, and dried at about 50°C in dry and hot air.

- This rubber does not have all the desirable properties.
- It softens and becomes sticky in summer while becomes hard and brittle in winter.
- Hence, it is not used as such, but compounded and vulcanized to meet the requirements of its use.

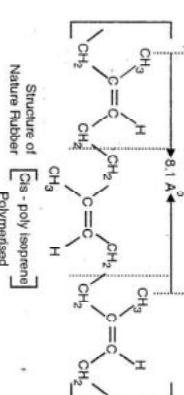
### Smoked rubber

- To the coagulum, acetic acid or formic acid are added and the mixture is stirred thoroughly.
- This mixture is kept in tanks undisturbed for about 16 hours.
- A tough mass of coagulum is then formed.
- It is then passed through a series of rollers to form sheets; which are then hung for about 4 days in smoke house, where the temperature is in the range of 40°-50°C.
- The dry smoked rubber is translucent, amber coloured sheet, which does not get affected by bacteria or fungi.

- The properties of this type of rubber are also improved further by compounding and vulcanization.

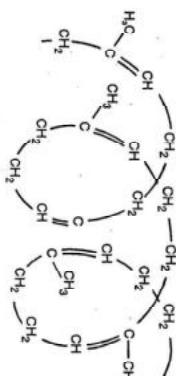
### 1.12.1.3 Structure

Natural rubber is cis-polyisoprene which can be represented as,



### Structure of Natural Rubber [cis-poly-isoprene] polymerised

- Being cis form, the polymer develops coiled structure, and hence possesses elasticity.
- Molecular weight ranges between 1 lak to 5 laks.
- When molecule is in linear / coiled form, the distance between methyl groups of the two monomeric units lying in same plane is  $8.1\text{ \AA}^2$  (as shown in structure) and all -  $\text{CH}_3$  groups are oriented outward.

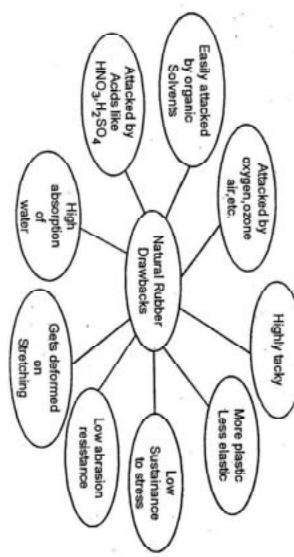


#### 1.12.14 Properties and Drawbacks of Natural Rubber

The natural rubber has following properties, (drawbacks) :

1. Its plasticity is greater than elasticity. It cannot sustain stress. Thus when stretched to a great extent, it undergoes deformation permanently.
  2. It has large water absorption tendency, which makes it weak.
  3. It has very low tensile strength ( $20 \text{ kg/cm}^2$ ).
  4. Due to large percentage of unsaturation in its structure, it is easily attacked by various reagents such as  $\text{HNO}_3$ , conc.  $\text{H}_2\text{SO}_4$ , organic solvents, air, oxygen, ozone etc. and as a result gets gradually disintegrated.
  5. It possesses high percentage of tackiness (property of developing stickiness on surface) which makes it difficult to store the rubber stocks.
  6. Durability and abrasion resistance of natural rubber is very low.
- Thus the natural rubber does not have the desirable properties.
- Hence to make its maximum use, it is essential to improve its properties by means of certain catalyst.
- Any catalyst used to improve the drawbacks of natural rubber is known as a vulcanizing agent, and the process by which the undesirable properties of natural rubber are improved upon is known as vulcanization.

► [Dec. 2003 !!]



#### 1.13 Vulcanization

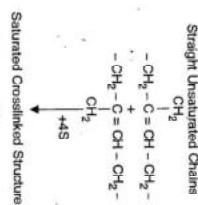
► [Dec. 2004, May 2005, Dec. 2005, May 2007, Dec. 2007, May 2008 !!]

- To improve the properties of raw rubber, it is compounded with some chemicals like sulphur,  $\text{H}_2\text{S}$ , benzyl chloride etc.
  - Most important of all the process of compounding (vulcanizing) is the addition of sulphur.
  - The process consists of heating the crude rubber with sulphur to a high temperature.
  - The sulphur combines chemically at the double bond in the rubber molecule. Vulcanization brings about stiffening of the rubber by a sort of cross-linking and consequently preventing intermolecular movement or sliding of rubber springs.
  - The extent of stiffness or loss of elasticity of vulcanized rubber depends upon the amount of sulphur added.
  - For example, a tyre rubber may contain 3 to 5% sulphur, but a battery case rubber may contain as much as 30% sulphur.
- The changes in properties that take place due to vulcanization is shown as below:

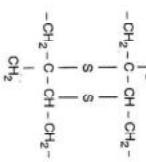
Undesirable properties	Improvement
Tacky	Non-tacky
Weak	Strong
Plastic	Elastic
Soluble	Insoluble

### 1.13.1 Vulcanizing Agents

- Generally, S, H<sub>2</sub>S, O<sub>2</sub>, Cl<sub>2</sub> and other organic compounds like quinone, di-azo-benzene or benzoyl peroxide etc. are used as vulcanizing agent.
- The temperature range is normally 100-140°C at which the sulphur cross linkages are developed making rubber tough and resistant to the attacks of various chemicals.
- The process makes rubber mechanically strong, and chemically resistant to attack of common chemicals.
- The vulcanization is also brought about by using certain oxides such as ZnO, MgO, HgO etc.



Saturated Crosslinked Structure



### 1.13.2 Advantages of Using Vulcanization

Vulcanized rubber possesses the following properties :

- 1. It has good tensile strength and extensibility when tensile force is applied.
- 2. It possesses low water absorption tendency.
- 3. It has higher resistance to oxidation and to abrasion.
- 4. It has much higher resistance to wear and tear.
- 5. It is a better electrical insulator.
- 6. It is resistant to organic solvent, fats and oils.
- 7. It is easy to manipulate the vulcanized rubber to produce the desired shapes.
- 8. Its useful temperature range is 40-150°C.
- 9. Its tackiness is only slight.

### 1.14 Synthetic Rubber: The need

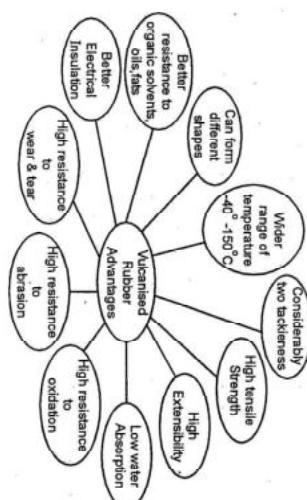
Natural rubber is obtained from Rubber Trees.

- But with growing demands, the production of natural rubber is not sufficient.
- Hence, rubber like materials are needed to be synthesised using chemicals.

#### Synthetic rubber :

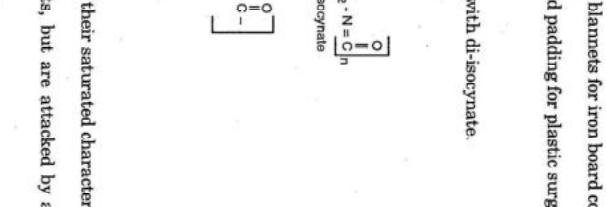
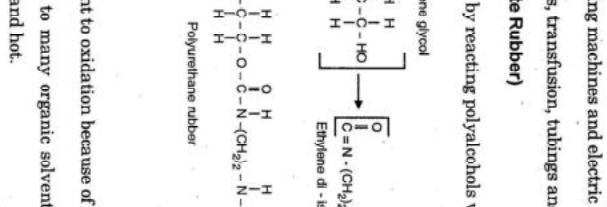
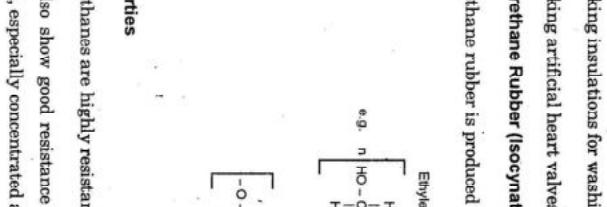
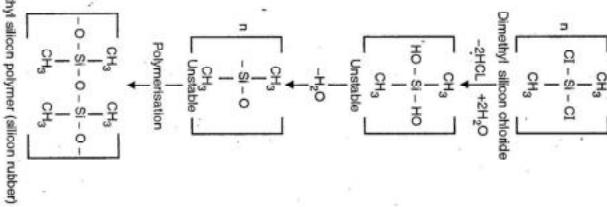
- Synthetic rubber is any vulcanizable artificially prepared rubber like product which can be stretched more of its original length, but it returns rapidly to its approximate original shape and dimensions when the stretching force is released.
- Synthetic rubber is produced artificially from other chemicals which differs in chemical composition and properties from those of the natural rubber.
- Therefore, synthetic rubbers are only rubber like products, which can also be vulcanized.
- Most commonly produced synthetic rubber are :

1. Silicon rubber
2. Poly urethane rubber
3. Buna-S and Buna-N
4. Styrene – Butadiene rubber



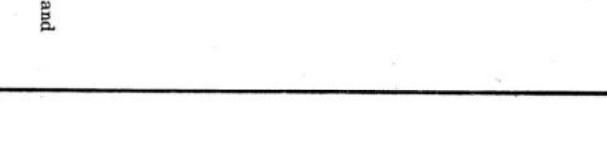
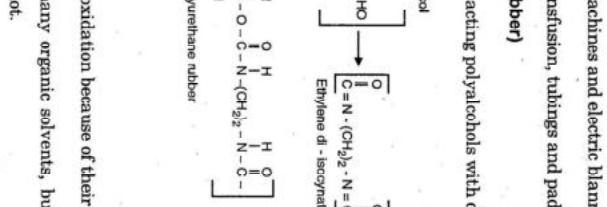
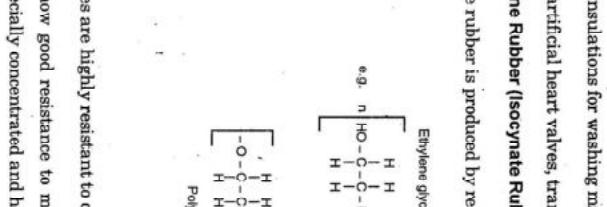
### 1.14.1 Silicon Rubber

- Silicon rubbers are produced by Polymerisation of dimethylsilicon hydroxide.
- Silicon rubbers have a quite different type of polymer structure from any of the other synthetic rubbers as in the case of silicon rubbers, the chain structure does not involve a long chain of carbon atoms, but a sequence of silicon and oxygen atoms as shown above.



### 1.14.2 Properties

- In this polymer, inter-chain forces are very weak and thus, there is no crystallization of chains on stretching.
- They possess exceptional resistance to prolonged exposure to sunlight, weathering, oils, boiling water, dilute acids and alkalis.
- They remain flexible in the temperature range of 90-250°C and hence are used in making tyres of aircrafts, as they prevent damage on landing.



### 1.14.3 Uses

- As a sealing material in search lights and in aircraft engines.
- For manufacture of tyres for fighter aircrafts.
- For insulating the electrical wiring in ships.
- As adhesive in electronic industry.
- For making insulations for washing machines and electric blankets for iron board covers.
- For making artificial heart valves, transfusion, tubings and padding for plastic surgery.

### 1.14.4 Polyurethane Rubber (Isocyanate Rubber)

Polyurethane rubber is produced by reacting polyalcohols with di-isocyanate.

#### 1.14.5 Properties

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

#### 1.14.6 Uses

For surface coatings and manufacture of foams and spandex fibre.

### 1.15 Compounding of Rubber

- Compounding is mixing of the raw rubber with other substances so as to impart the product's specific properties, suitable for a particular job.
- The following materials may be incorporated depending on the service conditions of the item to be made from it.

1. Softeners and plasticizers
2. Vulcanising agents
3. Accelerators
4. Antioxidants
5. Colouring matter/pigments
6. Reinforcing fillers.

### 1. Softeners and plasticizers

- These are added to give the rubber greater tenacity and adhesion.
- Important materials are vegetable oils, waxes, stearic acid etc.

### 2. Vulcanising agents

- The main substance added is sulphur.
- Depending upon the nature of product required, the percentage of "S" is added, it varies between 0.15 to 32%.
- Many other vulcanizing agents added to rubber are sulphur monochloride, hydrogen sulphide, benzoyl chloride etc.

### 3. Accelerators

- These materials drastically shorten the time required for vulcanization.
- The most usual accelerators used are 2-mercaptol, benzothiazol and zinc alkylxanthate.

### 4. Antioxidants

- Natural rubber undergoes oxidation. For this antioxidation materials such as complex amines, polyphosphites are added.
- But, these materials get darken in the presence of light and therefore, a substance like  $\beta$ -naphthol is used.

### 5. Colouring matter/pigment

- These are added to give the rubber product the desired colour.
- For white products, titanium dioxide pigments are used while for coloured products pigments like chromium oxide-Green, ferric oxide-Red, antimony sulphide-Crimson, lead chromate-Yellow are added.
- Most common of all reinforcing fillers especially for the manufacture of motor car tyres is carbon black.
- Other materials such as zinc oxide,  $\text{CaCO}_3$ ,  $\text{MgCO}_3$  are very widely used.

### 1.16 Applications of Rubber

Rubber is used in the manufacture of following types of goods :

#### 1. Tyres

The manufacture of tyres is the leading application of rubber.

#### 2. V-Belts and Conveyor Belts

V-belts for transmission of power and conveyor belts for conveying many types of goods such as grain, sand, coal, ice, ore etc. are manufactured out of rubber. Using textile cores or flexible steel wires, V-belts made out of rubber are quiet compact, non-slipping, shock absorbing, clean and have long life and low cost.

#### 3. Rubber Lined Tanks

Rubber lined tanks are used in chemical engineering plants to resist the corrosive action of chemical processed. The best metals for lining with rubber are steel and aluminium.

#### 4. Gaskets

Rubber is used for the manufacture of gaskets for sealing many types of materials such as refrigerator cabinet door seals, cooker autoclaves.

#### 5. Mountings

Mountings are sections of rubber sandwiched between two metal plates. Mountings reduce or isolate machine vibrations, prolong the life and improve the quietness of the equipment.

► [ May 2005 ! ]

## 6. Hoses

All types of hoses are manufactured from rubber.

## 7. Electrical industries

Due to remarkable resistance to electricity, hard rubber is largely used in electrical industry as insulating coating for wires and cables used for electrical power transmission. It is also used in switch board panels, plugs, sockets, telephone receivers, battery cases and electrical gloves.

## 8. Articles

Due to elasticity strength and toughness, it is used for making rubber bands, tubes for bicycles, automobiles and aeroplanes, golf balls, surgical goods and mechanical rubber goods.

## 9. Medicare

Rubber is also used for making heart valves, transfusion tubing and padding for plastic surgery.

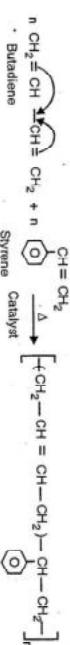
## 10. Fuel

Rubber like polysulphide rubber is used as a solid propellant fuel for rocket motors.

## 1.17 Co-polymerisation

► [ May 2005, Dec. 2007 ! ]

- Copolymerisation is nothing but specific type of addition polymerisation.
- In this the monomers of more than one type are involved.
- Copolymerisation has *unique importance* in the industry.
- This is because products formed by copolymerisation show the *specific properties* of the monomers.
- Sometimes such special properties are further enhanced or sometimes unique properties in the product as a result of the reaction between two different types of monomers.
- Thus copolymerisation gives rise to *variety* of the products.
- Thus several useful and commercially important polymers are formed by copolymerisation.



e.g. Styrene butadiene rubber (SBR - GR - S)

Acrylonitrile rubber NBR or GR-A

- Example 1 : Polyvinyl chloride has
  - (a) high glass transition temperature
  - (b) less solubility
  - (c) less flexibility
- But when vinyl chloride monomer is copolymerised with small amount of vinyl acetate the product obtained is highly flexible material.

- Example 2 : Ethylene copolymerised with propylene and also propylene copolymerised with butadiene gives rise to plastics resistant to oxygen, O<sub>2</sub> and heat.
- Properties of the copolymers depend on the relative amount of the two monomers constituting a polymer and also on the type of monomer.

## 1.18 Other Important Properties of Polymers

► [ Dec. 2007 ! ]

- Polymer molecules are of different types as given in classification.
- Based on nature, the macromolecules have certain properties specifically unique may be varying in extent.
- Following are few important properties :

1. Polymer crystallinity
2. Melting and glass transition phenomenon
3. Viscoelasticity of polymers
4. Electrical properties of polymers
5. Conductivity of polymers.

### 1.18.1 Polymer Crystallinity

► [ Dec. 2007 ! ]

It is a property a polymer exhibits in varying extent, which is based on the pattern of arrangement of molecules of polymer.

A polymer is said to be 'crystalline' if all molecules are arranged in orderly compact manner with symmetrical orientation, with higher force of attraction between two chains.

Crystalline polymers generally,

1. Posses high density
2. Strong, hard but brittle
3. Have sharp MP.

This property can be calculated by density measurement of sample and of other known highly crystalline to highly amorphous polymer. Then,

$$\% \text{ crystallinity} = \frac{\text{density of sample (d)} - \text{Density of highly crystalline (dc) polymer}}{\text{dc} - \text{da}}$$

### 1.18.2 Visco-elasticity of Polymers

► [Dec. 2007]

Physical state of a polymer is governed by chain length and molecular weight.

Based on molecular weight, polymers are either elastic solids or viscous liquids/flowy liquids.

These physical states are temperature sensitive.

If cooled slowly, polymer becomes hard and brittle, and vice-versa.

The time taken for cooling/heating also plays equally important role.

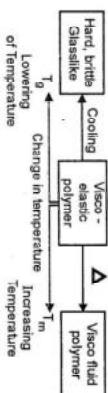
Thus with variation in temperature and time duration between the range of temperature, a polymeric material exhibits different range of viscosities. This behaviour of a polymer is known as "viscoelasticity".

### 1.18.3 Melting and Glass Transition

► [Dec. 2007, May 2008]

The behaviour of polymer with respect to its flow properties is temperature sensitive.

- When a polymer is cooled slowly, it becomes more and more viscous, finally becomes hard solid and brittle. At this stage polymer behaves like glass, and breaks if stressed.
- Glass Transition Temperature is defined as, "the lowest temperature beyond which the polymer becomes hard, glass-like and brittle and the high temperature above which it becomes flexible, soft and elastic like rubber."
- It is denoted as  $T_g$  and  $T_m$  respectively.
- Thus a polymer changes states as follows :



### 1.18.4 Electrical Properties of Polymers

- [Dec. 2007, May 2008]
- Polymers are generally used as insulators in electrical connections.
  - Conduction process requires free electrons in material; which are essentially absent in all polymers.
  - However, in recent years, the special polymers are synthesized to have conductivity.
  - This is developed by incorporating metal atom in the polymer molecules.
  - Due to presence of conducting metal element, the polymer also starts conducting electricity.
  - The elements like silicon or Germanium if incorporated, make polymer semiconductors, and conductivity ranges in  $10^{-9}$  to  $10^2 \text{ ohm}^{-1}/\text{cm}$  where as if polymer resin is filled with conducting elements like carbon black, metal oxides, metallic fibres etc., then conductivity can be increased even in the range of  $10^2$  –  $10^7 \text{ ohm}^{-1}/\text{cm}$ .
  - Such polymers which are made conducting are called as advanced polymeric materials or conducting polymers.

### 1.18.5 Advanced Polymeric Materials / Conducting Polymers

- [May 2008]
- Polymers, generally with high crystallinity, are more commonly develop conductivity more easily.
  - e.g. Cis-polyacetylene or poly para phenylene

These are following types of conducting polymers :

1. Intrinsically conducting polymers (ICP)
2. Doped Conducting Polymers (DCP)
3. Extrinsically Conducting Polymers (ECP)
4. Co-ordination conducting polymers (CCP) (Inorganic polymers)

Characteristics of each type are discussed in brief.

#### 1.18.5.1 ICP

- These possess conjugated  $\pi$  electrons backbone.
- When such polymer faces electric field, these electrons get excited, and hence move through polymeric material.
- The orbitals of conjugated  $\pi$  electrons get overlapped on the backbone and hence valence bands and conduction bands are developed which get distributed over entire surface of polymer.
- Appropriate proportion of conjugated  $\pi$  electrons makes polymer to conduct electricity very efficiently.

e.g. Polyacetylenes

Polyquinoline

Poly-p-phenylene

Poly-m-phenylene sulphides etc.

Aromatic : Polyaniline, polyanthrylene

Aromatic heterocyclic : polypyrrole, polythiophene, polybutadienylenne.

#### 1.18.5.2 DCP

- These are prepared by exposure of the polymer to a charged transfer agent either in gas phase or in liquid phase (i.e. solution).
- As compared to plain ICP, these have low I.P. but high E.A. Hence these can be easily oxidised or reduced.
- ICP can be made more conductive by creating + ve or - ve charge on its backbone by oxidation or reduction.

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This technique is called as "doping". There are two types of doping :

- |     |          |
|-----|----------|
| (1) | P-doping |
| (2) | N-doping |

- P-doping is a technique in which an ICP is oxidized with Lewis acid, creating the charge on backbone of polymer.

The Lewis acids used are known as p-dopant.

e.g.  $I_3$ ,  $Br_2$ ,  $ASF_6$ ,  $PF_6$ , Naphthylamine

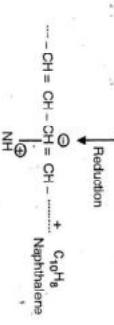
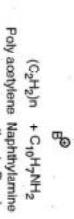


Poly Acetylene      Lewis Acid



- N-doping : This technique involves reduction of ICP with Lewis base to form negative charge on backbone of ICP.

e.g. Li, Na, Cu, teta butyl ammonium, Naphthyl amine



#### 1.18.5.3 ECP

- These are the conducting polymers which possess conductivity due to externally added ingredient in them.
- There are two types of ECPs,

1. **Conductive element filled polymer**
- In this type, resin or polymer is filled up with conducting element.

e.g. carbon black, metallic fibres, metal oxides etc.

- The polymer holds the metallic element, thus acting as a binder.
- Their conductivity is reasonable high.

#### Properties

- Cost is low.
- They are light in weight.
- Strong.
- Can be easily moulded.

#### 2. Blended conducting polymer

- These are nothing but blend of normal polymer with conducting polymer.
- The blending is either only physical change or in certain cases chemical change.
- They possess good mechanical properties.

#### 1.18.5.4 Co-ordination Conducting Polymers : (Inorganic polymers)

- These are inorganic in nature, in which a complex involved in transfer of charge is combined with polymer, and a metal atom is combined with polydentate ligands.
- They have very low degree of Polymerisation ( $\leq 18$ ).
- They are corrosion resistant.

#### 1.18.5.5 Applications of Conducting Polymers

- In rechargeable light height batteries.
- Optically display devices
- In wiring in aircrafts and aerospace components.
- In tele-communication systems.
- In electromagnetic screening material.
- Solar cells, photovoltaic devices, transistors, diodes, molecular wires and switches etc.

- This property governs other properties such as, solubility, flexibility, hardness etc. which are for normal and branched polymers in varying extent.
- But rarely the polymers are 100% crystalline, instead most of them are consists of crystallites embodied in amorphous matrix.
- This situation, being most common, the properties such as plasticity, toughness, flexibility and narrow range of melting point are justified.

#### 1.19 Effect of Structure of Polymer on its Properties

The properties of polymers are governed by molecular structure, mass, viscosity, etc. Some of the effect which are observed very prominently are as,

- |  |
|--|
| 1. Strength of polymer                         |
| 2. Dimensions of polymer (plastic deformation) |
| 3. Texture of polymer (fracture of plastic)    |

#### 1.19.1 Strength

This property is mainly influenced by bonding pattern forces in polymer molecule.

It is also governed by,

- Magnitude of bonding forces
- Distribution of bonding forces,
  - Primary (chemical in nature) forces
  - Secondary (Intermolecular in nature) forces.
- There are generally two types of forces of attraction.
- The strength of such molecules increases with chain length and molecular weight.

Example: PE, PVC, PS etc.

Simpler the chain, lower strength. Hence, as compared PVC or PS, Pr has lower strength as molecular is simple and uniform.

#### 1.19.2 Plastic Deformation and Fracture

- These are related to dimensional aspect of plastic and uniformity of texture, and are tested by applying stress or heat.
- Generally, thermoplasts get easily strained with stress or heat.
- Effect of heat also causes deformation and fracture in plastics.
- Due to heat, the bonds in polymer molecules get broken if the transition temperature exceeds.
- This causes breaking of chain, i.e. polymer undergoes fracture.

**1.19.2.1 Defects in Polymers**

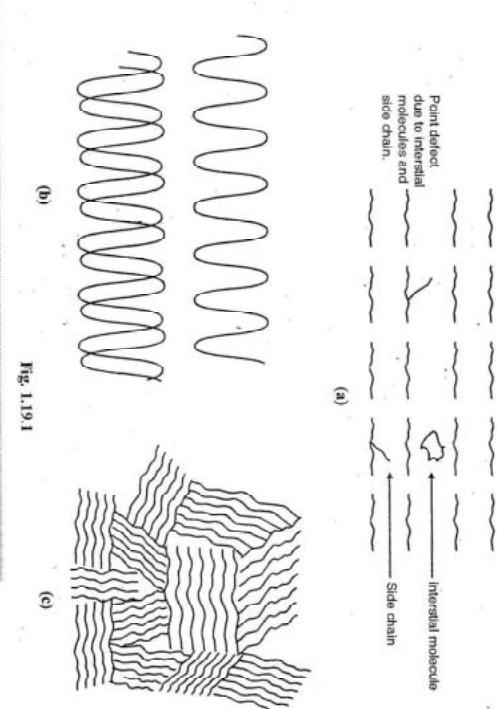
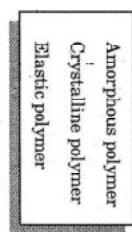
- Polymer is a material synthesized chemically by combining many monomer units.
- Many other chemicals, salts, metal alloys, organic compounds of varying size and mass are also synthesized by taking simple elements/compounds.
- During any such reactions many a times, the product formed is not up to mark with respect to the ideal nature of such a product expected.
- Any such short coming observed to be present in molecule is known as "defect" in structure/product.

In case of polymers also such defects occur giving rise to "Defective polymers".

Few such most commonly observed defects are listed below :

- Point defect
- Chain disorder defects
- Line defects
- Crystal lattice defect
- Dimensional defects.

The mechanical strength of plastic material classifies the plastics into following categories,



► [ May 2008 ! ]

**1.20 Supra molecular Chemistry and Molecular Electronics**

- Supramolecular chemistry** is a relatively new field of chemistry which focuses (quite literally) on going "beyond" molecular chemistry.
- Elastic polymer/Elastomers** : are highly flexible molecules. This is due to their structure, where long chain of monomeric units combined possess freely rotating groups in peculiar configuration.
- When stressed, chains are aligned in particular manner, while in unstretched condition, form configuration of irregularly coiled and entangled snarls as shown in Fig. 1.19.(c).

- Point Defects in polymers is due to certain vacant positions in crystal lattice, which is mainly caused due to presence of certain atoms in interstitial positions.
- Chain disorder defects are normally due to random end positions in polymer molecule.
- Line defects arise out of crystallization process, where edges get dislocated, causing defect.
- Crystall lattice defect is due to lattice positions. In this case regularity of chain is disturbed. Dimensional defects are caused due to irregular or random or overlapped folding of polymer chains especially on the surface of crystalline polymers.

Dimensional defects are caused due to irregular or random or overlapped folding of polymer chains especially on the surface of crystalline polymers.

- A cell (very complex) supramolecular system biopolymers such as nucleic acids, and proteins.
- A supramolecular assembly is a multi-component system of atoms, ions, and/or molecules, which are held together by non-covalent interactions such as hydrogen bonds, van der Waals forces, pi-pi interactions, and/or electrostatic effects.
- The latter mode of bonding is particularly important for assemblies involving metal ions. These various bonding interactions are far weaker than covalent bonding (which are the kind of bonds which hold molecules together) therefore supramolecular assemblies are usually far less stable than molecular compounds (for example, they can be more susceptible to breaking apart at high temperatures or if they are mixed with acid).

### 1.20.1 Formation of supramolecular Assemblies

► [ May 2008 ! ]

- The most common method is to use self-assembly techniques, in which the different components are mixed under given set of conditions (solvent, temperature, pH etc.) and then they are allowed to form assembly.
- Such self-assembly processes form a single product which is result of the countless possible combinations of the starting materials.
- Such supramolecule (product) is formed because it is the most thermodynamically stable arrangement of the constituent entities.
- If in case the combinations take some wrong path, which may be thermodynamically unfavoured, the molecule breaks immediately.

### 1.21 Polymer Composites

- These useful properties may lead to the application of these assemblies as and this is a list of random examples high-tech sensors for pollutants in air or water, compact information storage devices for next-generation computers, as high-performance catalysts in industrial processes, or as contrast agents for CAT scans.
- Supramolecular chemistry is intimately related to nanotechnology, and many promising nanotech devices are based on the principles of supramolecular chemistry.

#### Subdivisions in supramolecular chemistry

- Supernolecules
  - Host-guest chemistry
  - Helicates
  - Catenanes
  - Rotaxanes
  - Knotanes
- Supra molecular Assemblies
  - Micelles
  - Membranes
  - Vesicles
  - Liquid crystals

- This type of 'reversibility' is one of the unique features of supramolecular synthesis and this is the major difference between the supramolecular synthesis and the conventional molecular synthesis involving covalent bonds.
- In molecular synthesis, a reaction which goes down the 'wrong pathway' often ends up at a dead end and the material which is formed must in the end be separated from the desired product.
- One of the major goals of supramolecular chemists is the synthesis of supramolecular assemblies which have new functions that cannot appear from a single molecule or ion.
- These functions are based on novel magnetic properties, light responsiveness, catalytic activity, fluorescence, redox properties, etc., of supramolecular systems.

- About 30% of all polymers produced each year are used in the civil engineering and building industries.
- Load bearing and infill panels have been manufactured using composites.
- Complete structures have been fabricated where units manufactured from glass-reinforced polyester are connected together to form the complete system in which the shape provides the rigidity.
- Glass-reinforced plastics have been used in many other applications including pressure pipes, tank liners, and roofs.
- The material properties of the final component depend upon a design process that considers many factors which are characterised by
  - The anisotropic behaviour of the material
  - Micro-mechanical, elasticity, strength and stability properties.
- In the last decade, polymer composites have found application in the construction sector in areas such as bridge repair, bridge design, mooring cables, structural strengthening and stand-alone components **Polymer Composites**
- Polymers offer many advantages over conventional materials including lightness, resilience to corrosion and ease of processing.
- They can be combined with fibres to form composites which have enhanced properties, enabling them to be used as structural members and units.
- Polymer composites can be used in many different forms ranging from structural composites in the construction industry to the high technology composites of the aerospace and space satellite industries.
- Polymer composites were first developed during the 1940's, for military and aerospace applications.
- Considerable advances have been made since then in the use of this material and applications developed in various sectors including the construction sector.
- About 30% of all polymers produced each year are used in the civil engineering and building industries.
- Load bearing and infill panels have been manufactured using composites.

## 1.22 University Questions and Answers

**Dec. 2003**

**Q. 1** Give difference between thermoplastic and thermosetting plastics. (Section 1.7.2) (3 Marks)

**Q. 2** What are the drawbacks of raw rubber ? How are they improved ?  
(Section 1.12.1.4)

(6 Marks)

**Q. 3** Give preparation, properties and important uses of urea formaldehyde.  
(Section 1.10.4.2)

(6 Marks)

**Q. 4** What are the various methods used for fabrication of plastic ? Explain the compression moulding. (Sections 1.9 and 1.9.1)  
(4 Marks)

**May 2004**

**Q. 1** Differentiate between Addition polymerisation and Condensation polymerisation.  
(Section 1.3.2 and 1.3.3) (4 Marks)

**Q. 2** Describe transfer moulding in polymers. (Section 1.9.3) (6 Marks)

**Q. 3** What are the moulding constituents of plastic ? (Section 1.8) (6 Marks)

**Dec. 2004****May 2006**

- Q. 1** With the help of a suitable example explain condensation Polymerization. Name any two-thermosetting resins prepared by using condensation Polymerization.  
(Section 1.3.3) (4 Marks)
- Q. 2** Write the synthesis, properties and uses of anyone of the following:  
 (i) Phenol formaldehyde. (Section 1.10.4.1)  
 (ii) Urea formaldehyde. (Section 1.10.4.2)  
 (6 Marks)
- Q. 3** What is vulcanization? Explain, the mechanism of vulcanization with the help of suitable example. How is it helpful in removing the drawbacks of natural rubber?  
(Section 1.13) (4 Marks)
- May 2005**
- Q. 1** What are thermoplastic and thermosetting resins ? (Section 1.7.2) (2 Marks)
- Q. 2** Why plasticizers are added during moulding ? (Section 1.8) (2 Marks)
- Q. 3** What are applications of rubber ? (Give it with the specific property.)  
(Section 1.16) (4 Marks)
- Q. 4** Explain compression moulding. For which type of polymers it is applicable ?  
(Section 1.9.1) (4 Marks)
- Q. 5** Explain : Copolymerisation (Section 1.17) (3 Marks)
- Dec. 2005**
- Q. 1** What is the repeat unit of natural rubber ? (with structure) (Section 1.12.1.3) (2 Marks)
- Q. 2** Which type of moulding is used for coating the wires used for insulation ?  
(Section 1.9.4) (4 Marks)
- Q. 3** Differentiate :  
 (i) Thermoplastic and Thermosetting resins (any 3 points) (Section 1.7.2) (3 Marks)  
 (ii) LDPE and HDPE (any 2 points) (Section 1.10.1) (2 Marks)
- Q. 4** Explain any three moulding constituents of plastics (With 2 ex. of each)  
(Section 1.8) (6 Marks)

- Q. 1** Distinguish between thermoplastics and thermosetting resins. (Section 1.7.2) (5 Marks)
- Q. 2** Write short notes on : Condensation polymerization. (Section 1.3.3) (2 Marks)
- Q. 3** Write the synthesis, properties and uses of any one of the following :  
 (i) Phenol formaldehyde (Section 1.10.4.1)  
 (ii) Urea formaldehyde. (Section 1.10.4.2) (8 Marks)
- Q. 4** Write short notes on : Vulcanization (Section 1.13) (2 Marks)
- Dec. 2006**
- Q. 1** Write preparation, properties and uses of polyethylene. (Section 1.20) (3 Marks)
- Q. 2** What is polymerization ? Distinguish between addition and condensation polymerization.  
(Sections 1.3.2 and 1.3.3) (3 Marks)
- Q. 3** Write short notes on : Addition polymerization (Section 1.3.3) (3 Marks)
- Q. 4** Write synthesis, properties and uses of any one of the following :  
 Phenol formaldehyde. (Section 1.10.4.1) (3 Marks)
- Q. 5** Write short notes on :  
 (i) Vulcanization (Section 1.13)  
 (ii) Injection moulding (Section 1.8) (7 Marks)
- Q. 6** Distinguish clearly between : Natural rubber and vulcanized rubber. (Section 1.13)(3 Marks)
- May 2007**
- Q. 1** Explain condensation polymerisation with the help of suitable example.  
(Section 1.3.3) (3 Marks)
- Q. 2** Distinguish between LDPE and HDPE. (Section 1.10.1) (3 Marks)
- Q. 3** Write preparation properties and uses of :  
 (i) Ureaformaldehyde (Section 1.10.4.2)  
 (ii) Bakelite (Section 1.10.4.1) (6 Marks)
- Q. 4** What are plastics ? Write their main constituents. Write the functions and examples of each constituent. (Section 1.8) (6 Marks)

- Q. 5** Explain why and how vulcanization improves the properties of raw rubber.  
(Section 1.13)

**Dec. 2007**

- Q. 1** What is co-polymerization ? Explain with the help of suitable example.  
(Section 1.17)

**Q. 2** Explain the term "glass transition temperature". What is its significance ?  
(Section 1.18.3)

**Q. 3** Write the synthesis, properties and uses of Polythene. (Section 1.10.1)

**Q. 4** Explain any two of the following terms :

- (i) Crystallinity of polymer (Section 1.18.1)
- (ii) Tacticity (Section 1.2.2)
- (iii) Viscoelasticity (Section 1.18.2)

- Q. 5** What is polymerization ? Explain condensation polymerization with the help of an example.  
(Sections 1.3, 1.3.3)

**Q. 6** Explain vulcanization giving examples. Distinguish between vulcanized and non-vulcanized rubber. (Section 1.13)

- Q. 7** What is meant by fabrication of plastics ? Name different methods of fabrications. Explain transfer moulding with the help of a neat diagram. (Sections 1.9)

**May 2008**

- Q. 5** Explain the term 'vulcanization' with the help of a suitable example.  
(Section 1.13)

- Q. 6** Write the preparation, properties and uses of urea formaldehyde.  
(Section 1.10.4.2)

**Q. 7** Write short note on : Conducting polymers (Section 1.18.5)

□□□

**Q. 1** What is polymerization ? What are the conditions for polymerization ?  
(Section 1.3)

(2 Marks)

## 2.1 Introduction

# CHAPTER 2

## Water and its Treatment

Water is god's gift to all living creatures, from unicellular to multicellular and from plants to animals on earth.

The Earth's 71% surface area is occupied by water and the remaining 29% by land. The oceans contain nearly 97% of water as compared to that available on earth's surface. But ocean water, being saline, can not be used directly for drinking, agricultural and industrial purpose.

Hence, we are totally dependent on rain water and it is necessary to store water available from rains.

The quality of water is of vital concern for humans, since it is directly linked with human health.

Human body contains about 60% water.

Water plays an important role in various life processes in the human body. In our daily life water is used for drinking, bathing, cooking and washing purposes.

Water is also best solvent (also called as universal solvent) and it is used in many industries such as boiler industry for steam generation, textile, paper, pharmaceutical industry etc. for various solutions/surries; as a coolant in power plants, condensers etc.

Thus it is evident that, pure water is required by plants, animals to human being not only for self use but also for purposes of different manufacturing industries

Hence the purity of water is of utmost importance, because the rain water can not remain in the same state of purity when it falls on surface of earth. The water thus contaminated needs to be treated.

Water molecule has tendency to form intermolecular hydrogen bonding. It is polar in nature and its dielectric constant is 80, and dipole moment being 1.85 D.

The molecule is  $sp^3$  hybridised, angular shape as shown in Fig. 2.1.1.

- o Materials cycle and pollution
- o Recycling issues.

### Syllabus

#### ➤ Hardness of water :

- o Effect of hard water in the manufacture sector
- o types of hardness, determination of hardness by EDTA method and Problems.

#### ➤ Softening of water :

- 1) lime soda method with equations in general. Hot-cold lime soda method and problems
- i) zeolite process and problems
- ii) Ion exchange method
- v) reverse osmosis, ultrafiltration and its industrial applications.

#### ➤ Methods to determine extent of water pollution :

- i) BOD
- ii) COD,

#### ➤ Methods to control water pollution.

- Industrialisation
- o Materials cycle and pollution
- o Recycling issues.

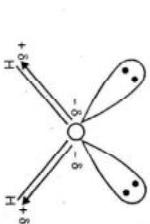


Fig. 2.1.1 :  $sp^3$  hybridised water molecule angular shape

## 2.2 Sources of Water

The sources of water are broadly classified as :

### Sources of Water



- 1. Rain water
- 2. Surface water
  - (i) River water
  - (ii) Sea water
  - (iii) Lake water
  - (iv) Under-ground water

### 2.2.1 Rain Water

- It is the purest form of naturally occurring water because it is obtained by evaporation of surface water (natural distillation process). But when it falls from sky to earth, it gets contaminated in the atmosphere due to the presence of several gases like  $\text{CO}_2$ ,  $\text{SO}_2$ ,  $\text{NO}_2$ ,  $\text{NH}_3$  etc. which get dissolved in it.
- Suspended solid particles, both of organic and inorganic nature also contribute to the contamination of water.
- After falling on earth, some amount of rain water percolates through the earth's crust and later on such accumulated stock of water is called as underground water.

### 2.2.2 Surface Water

Surface water is sub-classified as river water, sea water and lake water.

- (i) River water
  - Rain water falling on hills and mountains originate as springs which ultimately unite to form a river.
  - River water while flowing on surface of earth comes in contact with soil and minerals present in it.

### (ii) Sea water

- It is the most impure form of naturally occurring water.
- Rivers, when they join the sea, carry their organic and inorganic impurities with them to the sea.
- Continuous evaporation of sea water from its surface makes it more rich in its dissolved impurities.
- Sea water is very salty and contains about 3.5% salts out of which 2.5% is  $\text{NaCl}$ .
- It contains various other organic and inorganic impurities because after making use of water, the waste from domestic area as well as industries are thrown into sea, which makes sea water very impure and hence it cannot be used for domestic or industrial purposes.

### (iii) Lake water

- It is a result of accumulation of rain water in lower lying areas. Its chemical composition is almost constant and hardly needs any chemical treatment.
- It contains organic matter in quite a high quantity.
- Lake and pond waters are available to people of areas near to the lake only.

### (iv) Under-ground water

- About 1/3<sup>rd</sup> of rain water percolates into the soil during which many salts get dissolved in it.
- This water continues to move downwards till it touches the hard surface of the rock, then it moves upward in the form of spring.

### 2.3 Origin and Sources of Water Pollution

- Pure water shows a pH of 7, that means it is neither acidic nor basic. But when rain water falls on other surfaces, and gets accumulated in the form of water storages such as lakes, rivers etc. it comes in contact with several *minerals, oxides, sulphates, carbonates and bi-carbonates, dissolved gases etc.*

- As a result it gets contaminated; and all these impurities change the characteristics of water.

- Due to the dissolved salts, water becomes alkaline in nature. Alkalinity is due to carbonates, bi-carbonates or sulphates.

- The second change in the characteristics of water is hardness. Hardness is caused due to calcium and magnesium salts. Hardness is of two types:

- Carbonate hardness
- Non-carbonate hardness

Estimation and removal of hardness is very much essential, as the presence of hardness causing salts cause many problems during the use of hard water in industry and for domestic purposes.

### 2.4 Hard and Soft Water

- Soft water is defined as, "water which does not prevent lathering with soap".
- The contrary to this, hard water is defined as, "water which prevents lathering with soap".
- Thus this property or tendency of water is called as "hardness of water".

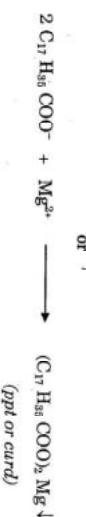
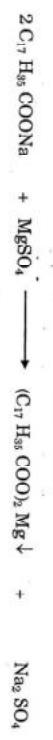
### 2.5 Hardness of Water

► [ Dec. 2003, May 2006, Dec. 2007 ]

- Hardness in water is that characteristic, which prevents the lathering of soap
- Hardness was originally defined as, "the soap consuming capacity of a water sample."
- Soaps generally consist of sodium salts of long chain fatty acids such as oleic acid, palmitic acid and stearic acid.

- The soap consuming capacity of water is reduced due to the presence of certain salts of calcium, magnesium and other heavy metals dissolved in it.

When the ions of these salts react with the sodium salts of long-chain fatty acids present in the soap, lather is not produced but it forms insoluble white scums or precipitates of calcium and magnesium soaps which do not possess any detergent value.



- Other metal ions like  $\text{Fe}^{2+}$ ,  $\text{Mn}^{2+}$  and  $\text{Al}^{3+}$  also react with soap in the same fashion, thus contributing to hardness.
- Further acids, such as carbonic acid can also cause free fatty acid to separate from soap solution and thus contribute to hardness.
- However, in practice, the hardness of a water sample is usually taken as a measure of its  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  content. Thus we can define hard and soft water as follows :

#### Hard water

Water which does not produce lather with soap solution readily but forms a white curd is called *hard water*.

#### Soft water

Water which lathers easily on mixing with soap solution is called *soft water*. Such type of water consequently does not contain dissolved calcium and magnesium salts in it.

## 2.6 Types of Hardness

There are two types of hardness, as :

### Types of hardness

1. Temporary or carbonate or alkaline hardness.
2. Permanent or non-carbonate or non-alkaline hardness.

### 2.6.1 Temporary or Carbonate or Alkaline Hardness

► [ Dec. 2007 ! ]

- It is defined as the hardness due to carbonates and hydroxides of the bicarbonates of calcium, magnesium and other hardness-producing metals.

- Temporary hardness is mostly removed by mere boiling of water, where bicarbonates are decomposed producing insoluble carbonates or hydroxides.



*Calcium bicarbonate*  
*(Insoluble)*



*Magnesium bicarbonate*



*Mg(HCO<sub>3</sub>)<sub>2</sub>*      *Sodium salt*

*Bi-carbonates*      *of stearic acid*

*Calcium and*  
*(Soluble soap)*  
*magnesium*  
*magnesium (Impurity)*

### 2.7 Factors Influencing Hardness of Water (Causes of Hardness)

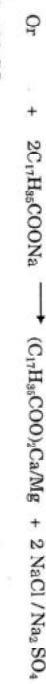
There are mainly three causes of hardness

### Causes of hardness

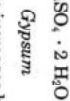
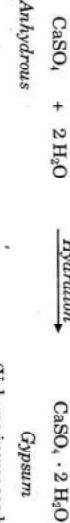
1. Dissolved minerals
2. Dissolved Oxygen
3. Dissolved Carbon-di-oxide

### 2.7.1 Dissolved Minerals

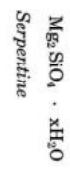
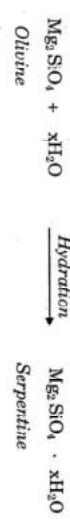
- Dissolved minerals are of iron, and other heavy metals. These metals are generated in atmosphere by vehicular and other pollution.



- They get assimilated in water when they form their soluble salts by combining with other halides / nitrates in atmosphere.
- Dissolution of minerals in water also takes place as water gets percolated through ground rocks or solid surface of earth.
- On contact with solid surfaces, water reacts with different constituents of rock.
- Due to these reactions, certain physical and chemical changes take place thereby making water contaminated.
- The products formed are salts of calcium and magnesium which are soluble in water. Thus contact with minerals influences hardness.
- Dissolution is followed by hydration process in which minerals like  $\text{CaSO}_4$  (Anhydrite) or  $\text{Mg}_2\text{SiO}_4$  (Olivine) react with water as,



(Volume increases by  $\approx 33\%$ )



### 2.7.2 Dissolved Oxygen

- Dissolved oxygen is also one of the major factor to influence the hardness in water.
- The process involves oxidation of oxides and other salts of metals which are present in water due to pollution caused by minerals.
- The oxidation and hydration is discussed as, D.O. influences oxidation and hydration of metal oxides / sulphides as,

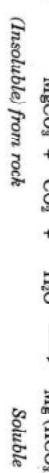
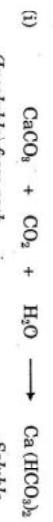
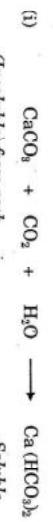


- $2\text{FeS}_2 + 7\text{O}_2 + 2\text{H}_2\text{O} \xrightarrow{(i) \text{Oxidation}} 2\text{FeSO}_4 + 2\text{H}_2\text{SO}_4$
- $\xrightarrow{(ii) \text{Hydration}}$
- Merlesite

These reactions indicate clearly how dissolved oxygen also influences hardness, of water.

### 2.7.3 Dissolved CO<sub>2</sub>

- The pH of water decreases due to dissolution of CO<sub>2</sub> from atmosphere. Due to this the dissolution of other minerals also increases.
- The following reactions are self explanatory that how dissolved CO<sub>2</sub> influences hardness of water,



- CO<sub>2</sub> also influences conversion of Ca / Na / K / Fe silicates and aluminium silicates (present in rocks) into soluble carbonates and bicarbonates. Some of them get converted into free silica, e.g.



- These products i.e. dissolved salts, fine clay, and free silica get collected in water, increasing its hardness.

- In addition to these factors, there are other pollutants also make water hard, e.g. heavy metals, industrial wastes, radioactive decay free acids etc.

### 2.8 Measurement of Hardness

► [Dec. 2004 I]

- The extent of hardness is measured in terms concentration of ions contributing to hardness.
- It is usually expressed in terms of equivalent amount of  $\text{CaCO}_3$ .

- The equivalents of  $\text{CaCO}_3$  is convenient precisely because the molecular weight of  $\text{CaCO}_3$  is 100 (equivalent weight is 50). The other reason this compound is being formed which gets precipitated during water treatment.
- 2.8.1 Calculation of Equivalents of  $\text{CaCO}_3$**
- The equivalents of  $\text{CaCO}_3$  for a hardness causing substance can be calculated by using following formula,
- Equivalent of  $\text{CaCO}_3$ ,
- $$= \frac{[\text{Mass of hardness producing substance}] \times [\text{Chemical equivalent of } \text{CaCO}_3]}{\text{Chemical equivalent of hardness producing substance}}$$
- $$= \frac{\text{Mass of hardness producing substance} \times 50}{\text{Chemical equivalent of hardness producing substance}}$$
- For example, 162 parts by mass of  $\text{Ca}(\text{HCO}_3)_2$  (or 2 equivalents) would react with the same amount of soap as 100 parts by mass of  $\text{CaCO}_3$  (or 2 equivalents).
  - Therefore, the mass of  $\text{Ca}(\text{HCO}_3)_2$  is multiplied by factor 50/81 or 100/162 to give mass in terms of  $\text{CaCO}_3$ .

Table 2.8.1 gives the multiplication factor for converting various substances into equivalents of calcium carbonates.

Table 2.8.1 : Calcium carbonate equivalents for salts

Dissolved salt	Molecular weights	Equivalent weight	Multiplication factor
<i>(1) Salts of calcium :</i>			
(a) $\text{Ca}(\text{HCO}_3)_2$	162	81	100 / 162
(b) $\text{CaSO}_4$	136	68	100 / 136
(c) $\text{CaCl}_2$	111	55.5	100 / 111
(d) $\text{CaCO}_3$	100	50	100 / 100
(e) $\text{Ca}(\text{NO}_3)_2$	164	82	100 / 164
<i>(2) Salts of magnesium :</i>			
(a) $\text{Mg}(\text{HCO}_3)_2$	146	73	100 / 146
(b) $\text{MgSO}_4$	120	60	100 / 120
(c) $\text{MgCl}_2$	95	47.5	100 / 95
(d) $\text{MgCO}_3$	84	42	100 / 84
(e) $\text{Mg}(\text{NO}_3)_2$	148	74	100 / 148

Dissolved salt	Molecular weights	Equivalent weight	Multiplication factor
<i>(3) Other salts/gases/acids :</i>			
(a) $\text{NaAlO}_2$	82	82	100 / 164
(b) $\text{Al}_2(\text{SO}_4)_3$	342	57	100 / 114
(c) $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$	278	139	100 / 278
(d) $\text{HCl}$	36.5	36.5	100 / 73
(e) $\text{CO}_2$	44	22	100 / 44
<i>(4) Ions :</i>			
(a) $\text{HCO}_3^-$	61	61	100 / 122
(b) $\text{CO}_3^{2-}$	60	30	100 / 60
(c) $\text{OH}^-$	17	17	100 / 34
(d) $\text{H}^+$	1	1	100 / 2

## 2.9 Units of Hardness

The following are the most common units of hardness :

- (i) Parts per million (ppm)
- (ii) Milligrams per litre (mg / litre)
- (iii) Grains per imperial gallon (gpg) or Clarke's degree ( $^{\circ}\text{Cl}$ )
- (iv) French degree ( $^{\circ}\text{Fr}$ )

- (i) Parts per million (ppm)
  - o One part per million (ppm) is a unit weight of solute per million unit weights of solution.
  - o In dilute solutions of density  $\approx 1$ , 1 ppm = 1 mg / litre. It is customary to express hardness in terms of equivalents of  $\text{CaCO}_3$ . Hence, all the hardness causing impurities are first converted in terms of their respective weights equivalent to  $\text{CaCO}_3$  and the sum total of the same is expressed in ppm.

Equivalent of  $\text{CaCO}_3$  for a hardness causing substance

$$= \frac{\text{Weight of the substance} \times 50}{\text{Chemical equivalent weight of the substance}}$$

- Thus, parts per million (ppm) is the parts of calcium carbonate equivalent hardness per  $10^6$  parts of water i.e. 1 ppm = 1 part of  $\text{CaCO}_3$  equivalent hardness in  $10^6$  parts of water.

### (ii) Milligrams per litre (mg / litre)

- It is the number of milligrams of  $\text{CaCO}_3$  equivalent hardness present per litre of water.

Thus, hardness of 1 mg / litre = 1 mg of  $\text{CaCO}_3$  equivalent hardness in 1 litre.

$$\begin{aligned} 1 \text{ litre of water} &= 1 \text{ kg} = 1000 \text{ g} = 1000000 \text{ mg} \\ &= 10^6 \text{ mg} \\ \therefore 1 \text{ mg/litre} &= 1 \text{ mg of } \text{CaCO}_3 \text{ equivalent per } 10^6 \text{ mg of water.} \\ \text{or } 1 \text{ mg/litre} &= 1 \text{ part of } \text{CaCO}_3 \text{ equivalent per } 10^6 \text{ parts of water.} \\ &= 1 \text{ ppm} \end{aligned}$$

- Hence, mg / litre has the same units as parts per million (ppm).

### (iii) Grains per imperial gallon (gpg) or Clarke's degree ( ${}^\circ\text{Cl}$ )

- It is the number of grains (1 / 7000 lb) of  $\text{CaCO}_3$  equivalent hardness per gallon (10 lb) of water or it is the parts of  $\text{CaCO}_3$  equivalent hardness per 70,000 parts of water.

Thus,

$$\begin{aligned} 1 {}^\circ\text{Clarke} &= 1 \text{ grain of } \text{CaCO}_3 \text{ equivalent hardness per gallon of water or} \\ 1 {}^\circ\text{Cl} &= 1 \text{ part of } \text{CaCO}_3 \text{ equivalent hardness per 70,000 parts of water} \end{aligned}$$

### (iv) French degree ( ${}^\circ\text{Fr}$ )

It is the parts of  $\text{CaCO}_3$  equivalent hardness per  $10^6$  parts of water. Thus,

$$1 {}^\circ\text{Fr} = 1 \text{ part of } \text{CaCO}_3 \text{ equivalent per } 10^6 \text{ parts of water.}$$

Inter-relationships between various units of hardness :

$$\begin{array}{llll} 1 \text{ ppm} & = 1 \text{ mg/litre} & = 0.1 {}^\circ\text{Fr} & = 0.07 {}^\circ\text{Cl} \\ 1 \text{ mg/litre} & = 1 \text{ ppm} & = 0.1 {}^\circ\text{Fr} & = 0.07 {}^\circ\text{Cl} \\ 1 {}^\circ\text{Cl} & = 1.43 {}^\circ\text{Fr} & = 14.3 \text{ ppm} & = 14.3 \text{ mg/l} \\ 1 {}^\circ\text{Fr} & = 10 \text{ ppm} & = 10 \text{ mg/l} & = 0.7 {}^\circ\text{Cl} \end{array}$$

## 2.10 Determination of Hardness of Water

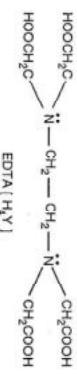
The hardness of water can be determined by following methods :

- EDTA method – Used most widely
- O' Heliner's method – Not used commonly
- Soap titration method – Not used commonly

► [ May 2000, Dec. 2006 ]

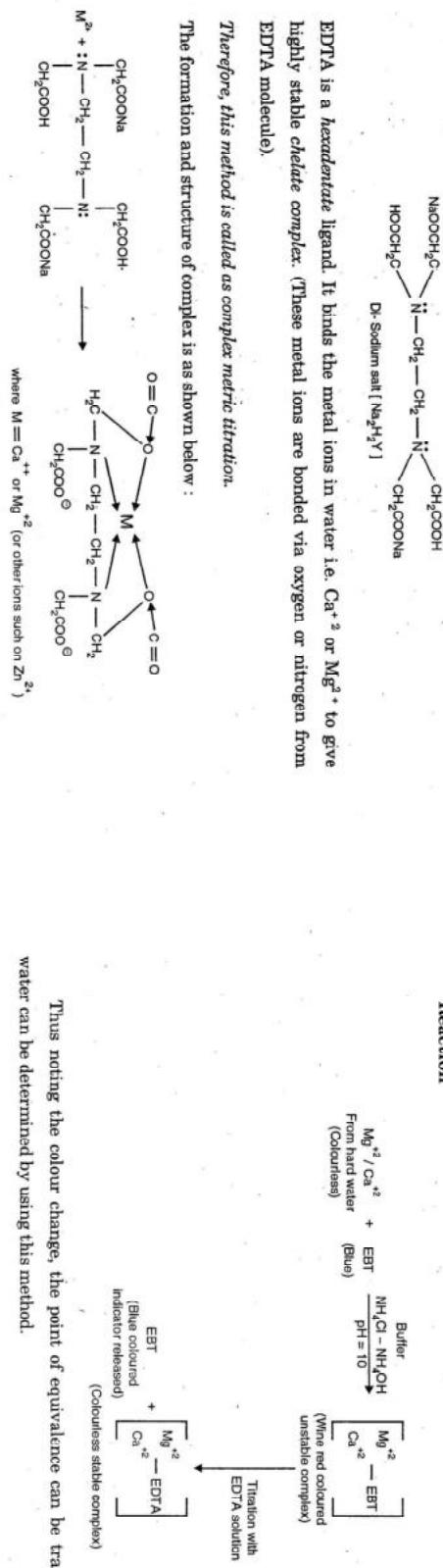
### 2.10.1 Determination of Hardness by EDTA Method

- EDTA is abbreviation of Ethylene diamine tetra acetic acid.

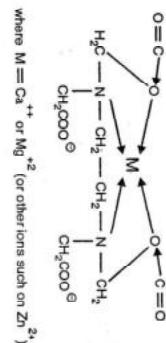


- This compound dissolves in water with great difficulty and in a very very small quantity.
- On the contrary its di-sodium salt dissolves in water quickly and completely. Hence for common experimental purpose, in place of EDTA, its di-sodium derivative is used.

### Reaction



### The formation and structure of complex is as shown below :



where M = Ca<sup>+2</sup> or Mg<sup>+2</sup> (or other ions such as Zn<sup>2+</sup>)

### 2.10.2 Principle of EDTA Method

► [May 2000, Dec. 2005, Dec. 2006]

- Ethylenediamine tetra acetic acid (EDTA) forms complexes with Ca<sup>2+</sup> and Mg<sup>2+</sup>, as well as with many other metal cations, in aqueous solution.

These complexes have the general formula as shown above.

- Thus, in a hard water sample, the total hardness can be determined by titrating Ca<sup>2+</sup> and Mg<sup>2+</sup> present in an aliquot of the sample with Na EDTA solution, using NH<sub>4</sub>C. NH<sub>4</sub>OH buffer solution of pH 10 and Eriochrome Black T as the metal indicator.

- At pH 10, EBT indicator form wine red coloured unstable complex with Ca<sup>2+</sup>/Mg<sup>2+</sup> ions in hard water.

- This complex is broken by EDTA solution during titration, giving stable complex with ions, and releasing EBT indicator solution which is blue in colour. Hence the colour change is from wine red to blue (EBT's own colour).

### 2.10.3 Procedure for EDTA Titration

► [ May 2000, Dec. 2005 ]

The steps involved in the determination of hardness of water are summarised here.

#### Step 1 : Preparation of reagents

#### Step 2 : Titration

The various solutions required can be made as follows :

##### (a) Standard hard water

One gram of pure, dry CaCO<sub>3</sub> is dissolved in the minimum quantity of dilute HCl. This solution is evaporated to dryness on a water bath. The residue left is dissolved in distilled water and the solution is diluted to 1 L. The hardness of this solution would be 1 mg of CaCO<sub>3</sub> equivalent per ml.

##### (b) EDTA solution

3.7 grams of pure EDTA crystals are mixed with 0.1 gram of MgCl<sub>2</sub>, and dissolved in distilled water and the solution is made to 1 litre.

##### (c) Indicator

0.5 gram of EBT is dissolved in 100 ml of alcohol.

## (d) Buffer solution of pH 10

67.5 grams of  $\text{NH}_4\text{Cl}$  are added to 570 ml of concentrated ammonia solution. The mixture is then diluted to 1 litre with distilled water.

**Step 2 : Titration**

The following steps are followed to estimate hardness of water sample :

## (a) Standardization of EDTA solution

50 ml of standard hard water is taken in a conical flask. 10 – 15 ml of buffer solution of pH 10, 4 – 5 drops of EBT indicator are added and the solution is titrated against EDTA solution till colour changes from wine red to deep blue. (Volume of EDTA solution =  $V_1$  ml).

## (b) Estimation of total, hardness

50 ml of hard water sample is titrated as above against EDTA solution (volume of EDTA =  $V_2$  ml).

## (c) Estimation of permanent hardness

50 ml of hard water sample is boiled for about 15 – 20 minutes, filtered, diluted with distilled water to make 50 ml and titrated as above against EDTA solution. (Volume of EDTA =  $V_3$  ml).

Using the data of  $V_1$ ,  $V_2$  and  $V_3$ , total and permanent hardness is calculated. The difference of these two values gives temporary hardness of water. (method is given on page 73)

**Advantages of EDTA method**

1. Highly accurate.
2. Highly convenient.
3. Highly rapid.

**2.11 Disadvantages of Hard Water****Effect of hard water**

## (1) Domestic purpose

- o Washing
- o Bathing

- o Cooking
- b Drinking

- (2) Industrial purpose

- o Textile industry

- o Sugar industry

- o Dyeing industry

- o Laundry industry

- o Paper industry

- o Concrete industry

- o Bakeries

- o Pharmaceutical industry

- (3) Steam generation purpose : In boilers

**(1) Domestic purpose**

Lot of water is used for domestic purpose as follows :

<i>Washing</i>	It causes wastage of soaps and forms sticky precipitates (Ca and Mg soaps) which stick to the fabric / cloth giving spots.
<i>Bathing</i>	It causes wastage of soaps, production of sticky scum on bucket / bath-tub and body. Thus, cleaning quality of soap is reduced and skin becomes dry and dark in colour
<i>Cooking</i>	Due to hardness of water, boiling point elevates which results into wastage of fuel and consumption of more time for cooking. Foods like pulses, beans, vegetables, etc. do not cook properly in hard water
<i>Drinking</i>	It causes harmful effects on digestive and urinary tract systems, apart from affecting the taste of water.

### (2) Industrial purpose

<b>Textile industry</b>	Hard water, if used in textile industries causes wastage of soap (used in washing yarn, fabrics, etc.) because of formation of Ca and Mg soap (pps). These precipitates of Ca and Mg soap adhere to the fabrics. These fabrics when dyed later, do not produce exact shade of the colour.
<b>Sugar industry</b>	Water containing sulphates, nitrates, alkali carbonates etc. if used in sugar refining, causes difficulties in crystallization of sugar and sugar so produced may undergo decomposition during storage.
<b>Dyeing industry</b>	If hard water is used in preparation of dyes, the organic dyes may react with impurities present in water. This causes imperfect shades and uneven spots on fabric when these same dyes are used in dyeing process.
<b>Laundry</b>	If hard water is used for laundry, wastage of soaps occurs. Moreover, salts of iron sometimes cause undesirable colouration or patches on the clothes.
<b>Paper industry</b>	Ca and Mg salts in hard water tend to react with chemicals and other materials employed to provide smooth and glossy finish to paper. Hard water containing iron salts may even affect the colour of the paper being produced.
<b>Concrete making</b>	Water containing chlorides and sulphates if used in concrete making, affects (slows down) the hydration of cement and hence final strength of concrete is reduced.
<b>Bakeries</b>	Water containing organic matters such as algae, fungi, bacteria etc. if used in bakeries affect the quality of material produced i.e. they are of poor quality.
<b>Pharmaceutical industry</b>	If hard water is used in making drugs, syrups, injections, etc. then it may produce certain undesirable products in them which may harm human beings.

### Specifications of water quality for various uses

Sr. No.	Purpose	Specification	Disadvantage if specification not met with
1.	Cooking	Soft and salt free	<ul style="list-style-type: none"> <li>• More fuel</li> <li>• Unpleasant taste</li> </ul>
2.	Drinking	Soft and salt free	<ul style="list-style-type: none"> <li>• Unpleasant taste</li> <li>• Digestive disorders</li> </ul>
3.	Textile industry	Soft, free from turbidity, organic matter, colour, Fe and Mn	<ul style="list-style-type: none"> <li>• Uneven dyeing</li> <li>• Foul smell</li> </ul>
4.	Laundry	Soft, free from colour, Fe and Mn	<ul style="list-style-type: none"> <li>• More soap and detergent consumption</li> <li>• Fe and Mn salts impart undesirable colour to fabric</li> </ul>
5.	Sugar industry	Soft water.	<ul style="list-style-type: none"> <li>• Deliquescent sugar</li> <li>• Problems in crystallisation</li> </ul>
6.	Dairies	Free from colour, odour and taste and also pathogens.	<ul style="list-style-type: none"> <li>• Contamination in dairy products.</li> <li>• May be toxic may lead to digestive disorders.</li> </ul>

Sr. No.	Purpose	Specification	Disadvantage if specification not met with
7.	Be average	Free from alkalinity	Undesirable taste as alkaline water neutralises the acids in fruits producing salts.
8.	Pharmaceutical industry	Soft water, free from acidity, alkalinity, turbidity, minerals.	<ul style="list-style-type: none"> <li>• difficulty in tablet making</li> <li>• syrups do not retain consistency.</li> </ul>

## 2.12 Boiler Troubles

If hard water obtained from natural sources is fed directly to the boilers, many problems may arise such as :

1. Sludge and scale formation
2. Caustic embitterment
3. Boiler corrosion
4. Priming and foaming

### 2.12.1 Sludge and Scale Formation

► [Dec. 2003, Dec. 2004] 1

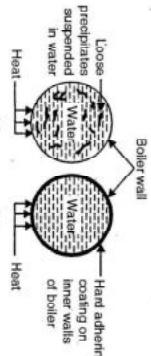


Fig. 2.12.1 : Sludge and scale formation

- Due to continuous evaporation of water in boilers, the concentration of dissolved salts in hard water increases progressively and finally when ionic product exceeds the solubility product, these salts are precipitated on the inner walls of the boiler.
- If the precipitates are loose, slimy, and floating, they are known as *sludges*.
- If the precipitated matter forms a hard adhering coating inside the boiler surface, they are called as *scales*.

#### (a) Sludge

##### Formation of sludge

- Sludge is a soft, loose and slimy precipitate formed in the boiler. Sludge can be easily removed with a wire brush.
- Sludges are formed in comparatively colder areas of boilers and are collected in areas where flow rate is slow or at bends in the pipes.

##### Causes of sludge formation

- Sludges 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.
- Sludges may lead to choking of pipes.

##### Disadvantages of sludge formation

- (i) Sludges are poor conductor of heat
- (ii) If sludges are formed along with scales, then former gets entrapped in latter and both get deposited as scales.
- (iii) Excessive sludges if formed in boilers, choke up pipe connection, plug opening, gauge-glass connection and disturb the working of boilers.

##### Prevention

Sludge formation can be prevented by,

- (i) Using soft water in boilers
- (ii) Frequent blow down operation i.e. drawing off a portion of the concentrated water (containing large amount of dissolved salts) and replacing it with fresh water

#### (b) Scales

##### Formation of scales

- Scales are hard deposits which stick very firmly to the inner surface of the boiler.

**Disadvantages of scale formation**(i) **Wastage of fuel**

- As the scales are hard and adherent, it is difficult to remove them even with the help of hammer and chisel.
- They are the main causes of boiler troubles.

**Causes of scale formation**

- Decomposition of  $\text{Ca}(\text{HCO}_3)_2$
- Deposition of  $\text{CaSO}_4$
- Hydrolysis of magnesium salts
- Presence of silica ( $\text{SiO}_2$ )

(1) **Decomposition of  $\text{Ca}(\text{HCO}_3)_2$** 

- The  $\text{CaCO}_3$  formed is soft.

- In low pressure boilers, it is the main cause of scale formation, however, in high pressure boilers,  $\text{CaCO}_3$  reacts to give  $\text{Ca}(\text{OH})_2$  as sludge and  $\text{CO}_2$ .

(2) **Deposition of  $\text{CaSO}_4$** 

- This is the main cause of scale formation in high pressure boilers. It is quite adherent and difficult to remove.
- When hard water containing  $\text{CaSO}_4$  is heated in boilers,  $\text{CaSO}_4$ , gets precipitated as hard scale on the heated portion of boilers and forms scale.

(3) **Hydrolysis of magnesium salts**

- Magnesium salts form a soft type of scale at high temperature in boilers.

(4) **Presence of silica ( $\text{SiO}_2$ )**

- Silica reacts with calcium and magnesium metals to form  $\text{CaSiO}_3$  and / or  $\text{MgSiO}_3$ , which gets deposited on the inner side of the boiler surface.
- These deposits are very difficult to remove.

### **Removal of scales**

The scales can be removed from time to time by following methods :

- If scales are *loosely adhering*, then they can be removed by *scraping* with a piece of wood or wire brush.
- If scales are *brittle*, then by giving *thermal shocks* (i.e. heating the boiler and then suddenly cooling with cold water) they can be removed.
- If scales are *hard and adherent*, then they can be removed by using some chemicals to dissolve them. e.g. CaCO<sub>3</sub> scales can be dissolved by using 5 to 10% HCl.
- If scales are *loosely adherent*, they can be removed by *frequent blow down operations*.

### **Prevention of scale formation**

For prevention of scale formation two types of treatments are given which are *Internal treatment* and *External treatment*.

#### **2.12.2 Internal Treatment**

► [ Dec. 2003, May 2004, Dec. 2004, May 2005, Dec. 2005, May 2006, Dec. 2006, May 2007 ]

"The treatment is accomplished by adding chemicals to boiler water."

- To precipitate the scale forming impurities in the form of *sludges* which can be removed by blow-down operation.
  - To convert them into *compounds* which will stay in *dissolved form* in water and hence do not cause any harm.
- Internal treatment is *corrective treatment* for removal of certain defects left in external treatment.

#### **Important internal treatment methods**

##### **(a) Colloidal conditioning**

- o In low pressure boilers, scale formation can be avoided by adding organic substances like *kerosene, tannin, agar-agar* etc.
- o Those substances get coated over the scale forming precipitates, thereby yielding non-sticky and loose deposits similar to sludge which can be removed by *blow down operation*.

##### **(b) Phosphate conditioning**

- o In high pressure boilers, scale formation can be avoided by adding *sodium phosphate*,
$$3\text{CaCl}_2 + 2\text{Na}_3\text{PO}_4 \longrightarrow \text{Ca}_3(\text{PO}_4)_2 \downarrow + 6\text{NaCl}$$
- c The soft sludge of Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub> and Mg<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub> (which is non-adherent and easily removable) can be removed by *blow down operation*.

*The main phosphates employed are :*

1. NaH<sub>2</sub>PO<sub>4</sub> [Sodium dihydrogen phosphate (acidic)]. When alkalinity of boiler water is too high and is required to be reduced to optimum value of pH 9.5 to 10.5, NaH<sub>2</sub>PO<sub>4</sub> salt is added because it is acidic in nature.
2. NaH<sub>4</sub>PO<sub>4</sub> [Disodium hydrogen phosphate (weakly alkaline)]. It is used when alkalinity of boiler water is adequate.
3. Na<sub>3</sub>PO<sub>4</sub> [Trisodium phosphate (alkaline)]. It is used when alkalinity of boiler water is low.

##### **(c) Carbonate conditioning**

- o In low pressure boilers, scale formation can be avoided by addition of Na<sub>2</sub>CO<sub>3</sub> (sodium carbonate) to boiler.



- o CaCO<sub>3</sub> formed can be removed by *blow down operation*.

##### **(d) Treatment with sodium aluminate (NaAlO<sub>2</sub>)**

- o When boiler water is treated with NaAlO<sub>2</sub> in solution, it gets hydrolysed to yield NaOH and Al(OH)<sub>3</sub>



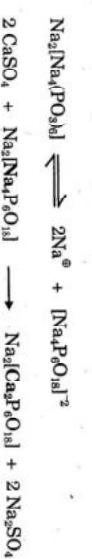
NaOH reacts with magnesium salts to form sludge.



- o Precipitates of Mg(OH)<sub>2</sub> and Al(OH)<sub>3</sub> produced inside the boiler entraps finely suspended and colloidal impurities, including oil drops and silica. The loose precipitates can be removed by *blow down operation*.

**(e) Calgon conditioning**

- Sodium hexametaphosphate  $\text{Na}_6[\text{Na}_4(\text{PO}_3)_6]$  is added to boiler water. It prevents the scale formation by forming soluble complex compound. e.g.

**(f) Electrical conditioning**

- This is achieved by using sealed glass bulbs containing mercury connected to a battery which are set floating in the boiler.
- When water boils, due to high temperature mercury bulbs emit electrical discharges which prevent the precipitates to stick to the sides of boiler and this prevents scale formation.

**(g) Radioactive conditioning**

- Small tablets which contain radioactive salts are placed inside the boiler water at few points.
- As water boils these tablets emit energy radiations and thus prevent scale formation.

**2.12.3 Caustic Embrittlement**

► [May 2004, May 2006, Dec. 2006 !]

**2.12.4 Boiler Corrosion**

► [Dec. 2001, May 2004, May 2007 !]

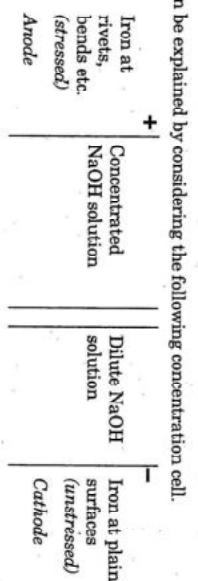
- Boiler corrosion can be defined as, "loss of boiler material or deterioration of its useful properties due to chemical or electrochemical interaction with its environment".
- Boiler corrosion occurs due to following reasons :

- (a) Dissolved oxygen
- (b) Dissolved carbon dioxide
- (c) Acids from dissolved salts present in water.

**(a) Dissolved oxygen**

- $\text{Na}_2\text{CO}_3$  in high pressure boilers decomposes to give sodium hydroxide and carbon dioxide.
- $$\text{Na}_2\text{CO}_3 + \text{H}_2\text{O} \longrightarrow 2\text{NaOH} + \text{CO}_2$$
 (This makes boiler water caustic).
- The water containing NaOH flows into the minute hair-cracks, in the inner wall of boiler, by capillary action. Here, water evaporates and the concentration of NaOH increases progressively.

- This caustic soda attacks the surrounding areas, thereby dissolving iron of boiler wall as sodium-ferroate. This causes embrittlement of boiler wall at a stressed parts like bends, joints, etc.





*This, the boiler gets corroded.*

### Removal of DO

- (i) Dissolved oxygen can be removed by adding calculated quantity of **scavengers** such as, sodium sulphite or hydrazine, sodium sulphide etc. The reactions are,



- With hydrazine, dissolved oxygen forms products such as nitrogen and water.

- Nitrogen is harmless. Therefore, **hydrazine is an ideal chemical for removal of dissolved oxygen.**

- On the other hand with Na<sub>2</sub>S and Na<sub>2</sub>SO<sub>3</sub>, sodium sulphate is formed which in **high pressure boilers, decomposes giving SO<sub>2</sub>.**

- SO<sub>2</sub> enters into steam pipes, and forms H<sub>2</sub>SO<sub>3</sub> (sulphurous acid) in steam condenser.

- Nowadays, Azamine 8001-RD has been employed for degassing water in minimum time.

- (ii) Dissolved oxygen can also be removed by mechanical de-aeration, i.e. by maintaining high temperature, low pressure and large exposed surface.

### (b) Dissolved carbon dioxide

- CO<sub>2</sub> gas dissolved in water, forms carbonic acid, which has slow corrosive effect on boiler material like any other acid.



- CO<sub>2</sub> is also released inside the boiler if water contains bicarbonates, which get decomposed as,



### Removal

It can be avoided by adding alkali from outside to neutralise the acid formed.

### 2.12.5 Priming and Foaming

- When boiler water contains large amount of dissolved salts and is steaming rapidly, some of the particles of the liquid water are carried along with the steam.

"The process of wet steam formation is known as priming".

### Priming is influenced by

- (a) Suspended and dissolved impurities
- (b) Sudden boiling
- (c) Faulty design of boiler
- (d) High velocity of steam

- "The formation of persistent foam or bubbles which do not break easily is known as foaming".

Foaming is influenced in the presence of substances like:

- Oil or grease* which greatly reduce surface tension,
- Alkalies* present is water.
- Clay* or organic matter
- Finely divided particles of sludge.*

Both these processes i.e. *priming* and *foaming* usually occur together. They are objectionable because,

- 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 efficiency of steam (or boiler indirectly).
- Dissolved salts may enter the parts of other machinery, where steam is being used, thereby decreasing the lift of machinery. Thus working of machinery is affected.
- Actual height of the water column cannot be judged properly, thereby making the maintenance, of the boiler pressure at a particular level difficult.

Priming can be avoided by :

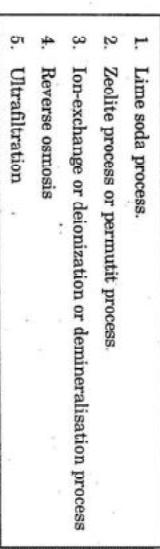
- Fitting mechanical steam purifiers.*
- Avoiding rapid changes* in steam production rate.
- Maintaining low *water levels* in boilers.
- Using *soft water* in boilers.

Foaming can be avoided by :

- Adding castor oil* and antifoaming chemicals.
- Removing oil from boiler water by adding *sodium aluminate* ( $NaAlO_2$ )

### 2.13 Treatment of Hard Water

- Water used for industrial purposes should be sufficiently pure, free from all hardness producing salts especially Ca, Mg and Fe salts.
- The hardness of water is determined on the basis of the concentration of dissolved salts.
- "The process of removing or reducing concentrations of hardness causing salts from water is called as softening of water."
- Water used for steam generation should be perfectly soft to minimize boiler related troubles e.g. scale formation etc.



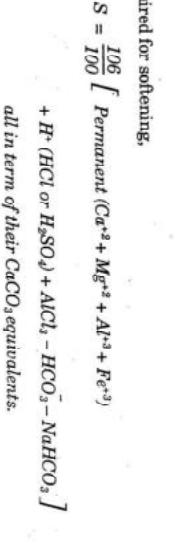
#### 2.13.1 Lime-Soda Process

► [ May 2000, Dec. 2002, May 2003, May 2004, Dec. 2004, May 2005, Dec. 2005, Dec. 2006, May 2007, Dec. 2007 ]

##### Principle

- In this method hard water is treated with calculated amounts of slaked lime,  $[Ca(OH)_2]$  and soda ash  $[Na_2CO_3]$  in reaction tanks, so as to convert hardness producing chemicals into insoluble compounds which are then removed by settling and filtration.
- Lime required for softening is calculated by using formula, as,

$$L = \frac{74}{100} [ \text{Temporary } Ca^{+2} + 2 \times \text{Temporary } Mg^{+2} \\ + \text{Permanent } (Ca^{+2} + Mg^{+2} + Al^{+3} + Fe^{+2}) \\ + CO_3^{2-} + H^+ (HCl \text{ or } H_2SO_4) + HCO_3^{-} - NaAlO_2 ]$$



- Soda required for softening,
- Normally, about 10 % excess of chemicals are added in the reaction tanks to complete the reactions quickly.

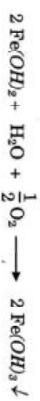
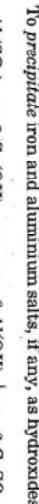
**(i) Reactions with lime**

Lime reacts in following ways, during softening of water.

1. To neutralise any free acid present. For example



2. To precipitate iron and aluminium salts, if any, as hydroxides.



3. To precipitate dissolved  $\text{CO}_2$  as  $\text{CaCO}_3$



4. To precipitate calcium bicarbonate as  $\text{CaCO}_3$



5. To precipitate magnesium salts as hydroxides.



6. To convert bicarbonate ions (like  $\text{NaHCO}_3$ ,  $\text{KHCO}_3$ , etc.) into carbonates



\*  $\text{CaCl}_2$  &  $\text{CaSO}_4$  produced are to be treated as permanent hardness.

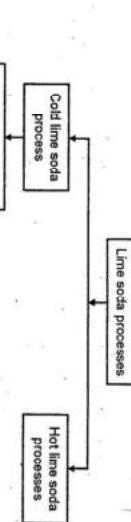
**(ii) Reactions with soda**

o Soda removes all the soluble permanent hardness due to calcium salts as



There are two types of lime soda processes as,

- |    |                         |
|----|-------------------------|
| 1. | Cold lime soda process. |
| 2. | Hot lime soda process.  |



### 1. Cold lime soda process

- When the chemicals are added to hard water at room temperature, the process is known as cold lime soda process.

- At room temperature, the precipitates are finely divided and do not settle easily, nor can they be easily filtered.

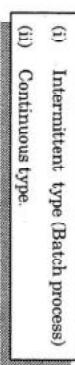
- It is therefore necessary to add coagulants like alum such as sodium aluminate etc.

- They help in the formation of coarse precipitates.



- Cold lime soda process provides water containing a residual hardness of 50 to 60 ppm.

The process can be of two types:



### (i) Intermittent type (batch process)

- In this Process, there is a set of two tanks which are used for softening water. Each tank has inlets for raw water and chemicals, and outlets for softened water and sludge.

- The tanks are equipped with mechanical stirrer.

- A calculated quantity of chemicals and raw water slowly enter the tank simultaneously and are allowed to mix thoroughly by mechanical stirring and contents of the tank are kept undisturbed for about two hours, during which precipitates settle down completely.

- The clear softened water is collected through a float pipe and sent to the filtering unit.

### (ii) Continuous type

In this there are three different types as follows:

#### (a) Conventional type

- In this process, raw-water and calculated amount of chemicals are continuously added from the top into an inner chamber of a vertical circular tank, provided with a paddle stirrer.
- Raw water and chemicals are thoroughly mixed due to continuous stirring and hence softening reactions take place. The sludge formed settles down at the bottom of the outer chamber from where it is removed from time to time through sludge outlet. The softened water, rising up passes through the filters (usually wood fibres), where traces of sludge are removed and filtered soft water passes through the outlet provided.

#### (b) Catalyst or spirator type

- In this type, the spirator consists of a conical tank and lower 2/3 rd of it is filled with catalyst.
- Raw water and chemicals enter the tank from bottom, below the catalyst bed.
- The catalyst is a finely granulated (0.3 to 0.6 mm diameter) insoluble material viz sand, graded calcite or green sand. The retention time is about 10 minutes.

- The sludge formed due to softening of water gets deposited on the catalyst. Hence, the catalyst granules increase in size which drains and dries rapidly.
- The softened water rises to the upper part of the tank from where it is drained off.

#### (c) The sludge blanket type

- In this type, the sludge blanket is made of previously formed precipitates through which treated water is filtered upwardly.

- Thus, all the three processes viz. mixing, softening and clarification take place in a single unit. Here, as the water is filtered upwardly, the added lime remains at the bottom, hence, there is no wastage of lime.
- The intimate contact of water with a large mass of solid phase prevents supersaturation or the formation of after deposits in the pipes, valves and tubes which carry effluent soft water.
- As a result, the effluent soft water is clear (turbidity  $< 10 \text{ mg/l}$ ) which does not require further filtration. The retention period is one hour (60 minutes).
- Thus, the sludge blanket type of water softening unit, due to its higher efficiency, smaller space requirements and shorter retention period is extensively used for coagulation and settling and also for water softening by cold lime-soda process.

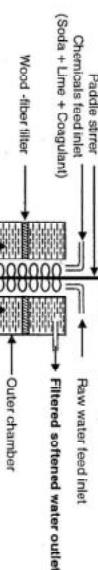


Fig. 2.13.1 : Continuous cold lime soda softener

## 2. Hot lime soda process

- When the chemicals are added at higher temperature ( $80^\circ\text{C}$  to  $150^\circ\text{C}$ ), the process is known as Hot lime soda process.
- At higher temperature (i) The reactions are fast (ii) Precipitation is more complete (iii) Settling rate and filtration rates are increased.
- As a result, the precipitate and sludge formed settle rapidly and coagulants, and also chemicals needed are in smaller quantities than that of cold process.
- Dissolved gases are eliminated from water to a certain extent. The softened water recovered has hardness of about 15 to 30 ppm.

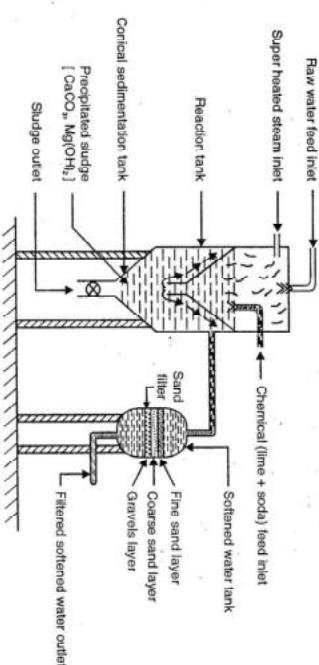


Fig. 2.13.2 : Continuous hot lime soda process

## Advantages of lime soda process

- It is a very economical process.
- This process increases pH value of the treated water, thereby corrosion of pipes is reduced.
- To a certain extent, iron and manganese are also reduced.
- Certain quantity of minerals are reduced from water.
- Alkaline nature of water reduces pathogenic bacteria present in water to considerable extent.
- Less amount of coagulants are required.

## Disadvantages of lime soda process

- The hardness of softened water is about 50-60 ppm by cold lime soda process which is not good for use in high pressure boilers, and about 15-30 ppm by hot lime soda process, which is also quite high for pressure boilers.
- Careful operation and skilled supervision are required for economical and efficient softening.
- Disposal of large quantity of sludge formed during process is a problem.

### 2.13.2 Zeolite or Permutit Process

- The name zeolite (Greek : Zein-boiling, lithos-stone) means *boiling stone*. The chemical formula of sodium zeolite may be represented as,
- $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot \text{xSiO}_2 \times \text{yH}_2\text{O}$  (where  $x = 2$  to 10 and  $y = 2$  to 6)
- (Zeolite = hydrated sodium aluminosilicate)

- "Zeolite is hydrated sodium alumino silicate capable of exchanging reversibly their sodium ions for hardness producing ions in water." Zeolites are also known as *permutsits*. Zeolites are of two types :
- Natural zeolites
  - Synthetic zeolites.

#### (i) Natural zeolites

- They are *amorphous and non-porous*. They are derived from green sands by washing, heating and treating with NaOH. The natural zeolites are *more durable* and are as follows :

e.g. *Natrolite*.

Formula for natrolite =  $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 4\text{SiO}_2 \cdot 2\text{H}_2\text{O}$

- Thomsonite* :  $(\text{Na}_2\text{O}, \text{CaO}) \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\frac{1}{2}\text{H}_2\text{O}$
- Natrolite* :  $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 4\text{SiO}_2 \cdot 2\text{H}_2\text{O}$
- Laumontite* :  $\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 4\text{SiO}_2 \cdot 4\text{H}_2\text{O}$
- Harmotome* :  $(\text{BaO}, \text{K}_2\text{O}) \cdot \text{Al}_2\text{O}_3 \cdot 5\text{SiO}_2 \cdot 5\text{H}_2\text{O}$
- Stibite* :  $(\text{Na}_2\text{O}, \text{CaO}) \cdot \text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2 \cdot 6\text{H}_2\text{O}$
- Brewsterite* :  $(\text{BaO}, \text{SrO}, \text{CaO}) \cdot \text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2 \cdot 5\text{H}_2\text{O}$
- Ptilolite* :  $(\text{CaO}, \text{K}_2\text{O}, \text{Na}_2\text{O}) \cdot \text{Al}_2\text{O}_3 \cdot 5\text{SiO}_2 \cdot 5\text{H}_2\text{O}$

#### (ii) Synthetic zeolites

- They are *porous and possess gel structure*. They are *prepared by heating together*:

- China clay, felspar and soda ash* and granulating the resultant mass after cooling.
- Solutions of *sodium silicate, aluminium sulphate* and *sodium aluminate*.

#### (c) Solutions of sodium silicate and aluminium sulphate.

#### (d) Solutions of sodium silicate and sodium aluminate.

► [ May 2000, Dec. 2001, Dec. 2002, May 2003, Dec. 2003, Dec. 2004, May 2005, May 2008 ]

#### Principle of zeolite-permutit process

When *hard water* is passed over a bed of sodium zeolite,  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  ions present in it are taken up by the zeolite simultaneously releasing equivalent  $\text{Na}^+$  ions in exchange for them. The water gets free from hardness causing cations, but gets more concentrated with sodium salts.

When zeolite gets exhausted it is *regenerated* and can be used again for softening water.

Reactions taking place during the softening process are :



Iron and manganese present in small quantities are also removed as follows :



#### Regeneration of zeolite - permuit bed

- When zeolite is completely converted into calcium and magnesium zeolites, it ceases to soften water, i.e. it gets exhausted. It is regenerated by treating with 10% brine solution.



- The washing containing  $\text{CaCl}_2$  and  $\text{MgCl}_2$  are led to drain and the regenerated zeolite bed thus obtained is reused for softening hard water again.

- "The process by which the exhausted zeolite is reclaimed / restored by treatment with 10 % brine solution is called as regeneration."

#### Process of softening water by zeolite-permutit method

- It operates alternatively as the softening run and the regeneration.

- During softening process the hard water from top enter at a specified rate and passes over a bed of sodium zeolite kept in a cylinder.

- Softened water containing sodium salts* is collected at the bottom of the cylinder and is taken out from time to time.

- The cations  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  are retained in zeolite bed and soft water rich in  $\text{Na}^{+}$  is collected.

After some time the zeolite bed gets exhausted.

- When zeolite bed gets exhausted, the softening run is discontinued and regeneration is started. During regeneration process, the following three operations are carried out.

- Back washing
- Salting (or brining) and
- Rinsing to get regenerated bed for reuse.

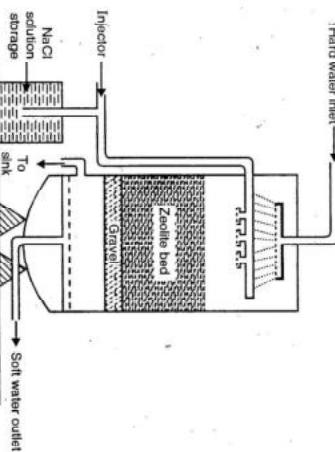


Fig. 2.13.3 : Zeolite Softener

- Water of about less than 15 (0 – 15) ppm hardness is produced.
- The process automatically adjusts itself for different hardness of incoming water
- Water obtained is quite clear,
- It requires less skill in maintenance as well as operation.
- The equipment is compact, occupying less space.
- No sludge formation because the impurities are not precipitated.

#### Disadvantages of zeolite process

- The treated water contains more sodium salts.
- The method only replaces  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  ions by  $\text{Na}^{+}$  ions, but leaves all acidic ions ( $\text{HCO}_3^-$  and  $\text{CO}_3^{2-}$ ) in soft water. Such soft water containing ( $\text{NaHCO}_3$ ,  $\text{Na}_2\text{CO}_3$ ) etc. when used in boilers,  $\text{NaHCO}_3$  decomposes to give  $\text{CO}_2$  which causes boiler corrosion and  $\text{Na}_2\text{CO}_3$  hydrolyses to  $\text{NaOH}$ , causing caustic embrittlement.

#### 2.13.3 Ion Exchange Process

► [ May 2003, May 2004, May 2005, May 2007 ]

- In this process, a reversible exchange of ions occur between the stationary ion-exchange phase and the external liquid mobile phase.
- "Ion-exchange resins are insoluble, cross-linked, long-chain high molecular weight organic polymers which are permeable due to their micro porous structure, and the functional groups attached to the chains are involved in the ion-exchanging properties."
- The purely synthetic organic exchangers are made by
  - Polycondensation and
  - Polymerisation.

- The functional groups are then introduced into the cross-linked resin network. It is these functional groups which decide the nature of the resin exchanger i.e. cationic or anionic.

The ion-exchange resins on the basis of their acidity or basicity are classified as follows:

### (1) Cation exchange resins ( $RH_2$ ) ( $RH^+$ )

- Resins containing acidic functional groups (-COOH,  $-SO_3H$ , etc.) exchange their  $H^+$  ions with other cations, which come in their contact are known as cation exchange resins. These are represent as  $RH^+$  or  $RH_2$ .

- These resins are capable of exchanging rapidly cations like  $Ca^{2+}$  and  $Mg^{2+}$  by hydrogen ions. For example : Divinyl benzene copolymer, formaldehyde resins, Amberlite IR - 120, Zeocarb, Dowex-50, Duolite, Sulphonated or carboxylated styrene etc. are some of the commercially available cation exchange resins.

Their exchange reactions with cations ( $Ca^{2+}$  and  $Mg^{2+}$ ) are as follows :



### (2) Anion exchange resins ( $R(OH)$ )

- The resin containing basic functional groups (e.g.  $-NH_2$ ,  $=NH$ , etc. as hydrochloride) exchange their anions with other anions, which come in their contact are called as anion exchange resins.

- These resins are capable of exchanging rapidly anions ( $Cl^-$ ,  $SO_4^{2-}$ ) by  $OH^-$  ions. They are represented as  $R^*$  and  $OH^-$  where  $R^*$  represents the insoluble matrix. For example amino-formaldehyde resins, copolymer of styrene and divinyl benzene, Amberlite 400, Zeolite -FF, etc. Their exchange reactions with anions ( $SO_4^{2-}$ ,  $CO_3^{2-}$  etc.) are as follows :



- Variation in polymer type and cross-linking causes variation in solubility and life of resin and the diffusibility of ions in an exchange process.

Types of ion-exchange	Functional groups
(1) Cation-exchangers	
(a) Strongly acidic	$SO_3H$
(b) Weakly acidic	$COOH$ or $-OH$
(2) Anion-exchangers	
(a) Strongly basic	$NR_3^+$ , $-CH_3, \equiv P^+$ etc.
(b) Weakly basic	$-NH_2$ , $(C_2H_4)_n$ , $(NH)_2$

### Principle of ion exchange process

When hard water is first passed through cation exchange bed which removes all cations like  $Ca^{2+}$ ,  $Mg^{2+}$ ,  $Na^+$  and releases hydrogen ions as,



Thus, sulphates, chlorides and bicarbonates are converted into corresponding acids  $HCl$ ,  $H_2SO_4$  and  $H_2CO_3$ . In other words, water collected from cation exchanger is free collected from all cations, but is acidic.

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



$H^+$  and  $OH^-$  ions are released from cation exchange and anion exchange bed respectively, which combine to produce water molecule, as,



- The soft water thus obtained is free from all the cations and anions.
- When column gets exhausted, it is set to regeneration ; and the process is continued. The water obtained is near to the *distilled water quality* ( $0 - 2 \text{ ppm}$ ).

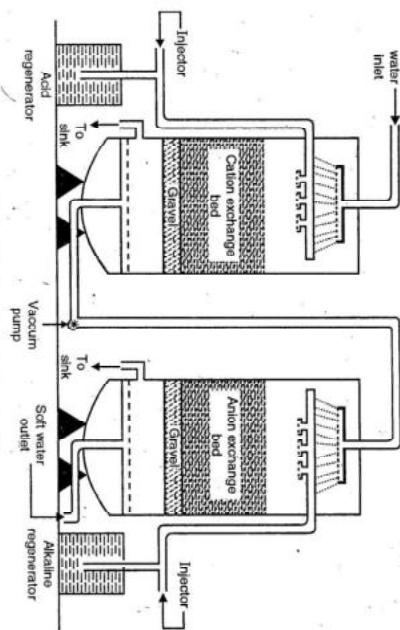


Fig. 2.13.4 : Demineralization of water

Thus, the water coming out from anion exchange bed becomes *free of cations as well as from anions*.

- The resulting ion-free water is *deionised water* or *demineralised water*.
- The water is finally freed from dissolved gases by passing it through a degasifier, which is a tower heated from both sides and is connected to a *vacuum pump*.
- High temperature and low pressure reduces the quantity of dissolved gases.
- Water obtained by this process is very near to distilled water, which is the requirement of boiler feed water. *This process is very good for high pressure boilers*.

#### Regeneration of exhausted resins

- The capability of these ion-exchange resins to exchange ions from hard water is based on their ion-exchange capacities.
- When their ion-exchange capacities are lost, they are said to be *exhausted*.
- When the resins are exhausted, the supply of water is stopped. The *exhausted* cation exchanger is *regenerated* by passing dilute HCl or  $\text{H}_2\text{SO}_4$  solution.
- When the resins are used again, if water contains sufficient temporary hardness, it is advisable to remove such hardness first by treating with lime.

#### Advantages of ion exchange process

- The process can be used to soften highly acidic or alkaline water
- It produces water of *low hardness (upto 2 ppm)*, therefore, it is good for high pressure boilers.

#### Disadvantages of ion exchange process

- The equipment is costly.
- If water contains *turbidity*, then the output of process is reduced. Turbidity should be below  $10 \text{ ppm}$ .

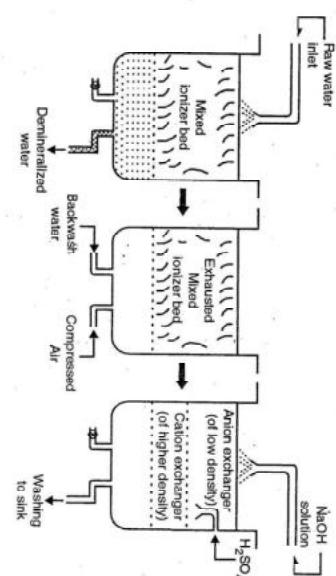


Fig. 2.13.5 : Regeneration of mixed ion exchange

- The hard water is first passed through cation exchange column and then through anion exchange column (Fig. 2.13.5).

### 2.13.4 Reverse Osmosis (RO)

► [May 2008 !]

#### Method :

- Membrane technique ( Reverse osmosis) :**
- Various membrane techniques are available, which selectively separate the solutes or contaminants on the basis of *pore size*.
- The types of membrane separation technologies include *reverse osmosis, hyperfiltration, ultrafiltration*, etc. But reverse osmosis is commonly used.

#### Principle of reverse osmosis ( RO) :

- The reversal of solvent flow, from higher concentration solution to lower concentration solution through a semipermeable membrane, by applying an external pressure slightly higher than the osmotic pressure of higher-concentration solution, is known as reverse osmosis.*
- Normal osmosis process* is shown in Fig. 2.13.6, where the solvent flows from *low concentration* solution to *higher concentration* solution, through the semipermeable membrane, until difference in water levels creates a sufficient pressure to counteract the original flow. The difference in levels represents *osmotic pressure* of the solution.
- In the reverse osmosis, we apply external pressure on the higher concentration solution slightly higher than its osmotic pressure.
- The flow of solvent takes place in *reverse direction* i.e. from higher concentration solution to lower concentration solution, through the SPM. Thus in RO, we separate water from its contaminants rather than contaminants from water.

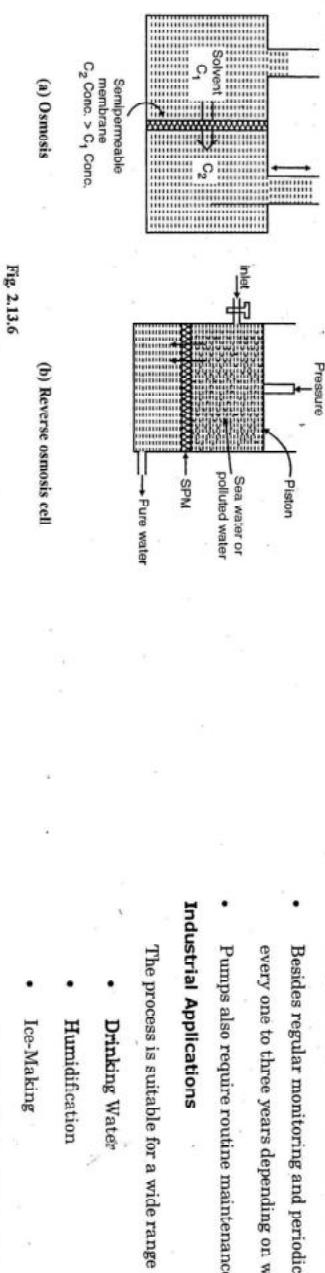


Fig. 2.13.6

(a) Osmosis

(b) Reverse osmosis cell

- Sea water or water polluted by ionic pollutants, is *filled in reverse osmosis cell*. A pressure of 200 – 800 psi is applied on it to force the solvent to pass through SPM. (SPM has such porosity that it allows only H<sub>2</sub>O molecules to pass through and higher sized ions / molecules are prohibited from passing).
- Membrane consists of a polymeric material film made of proper porosity, from materials like acrylics, polyamides, aramids etc.

#### Advantages of Reverse Osmosis Over Conventional Processes

- Compared with other conventional water treatment processes, reverse osmosis has proven to be the *most efficient means of removing salts, chemical contaminants and heavy metals, such as lead, from drinking water*.
- For waters with total dissolved solids of 200 or more, reverse osmosis is *less expensive than ion exchange*.
- Even at total dissolved solids of less than 200, it is preferred over ion exchange for removal of silica and organics.
- Compared with distillation, reverse osmosis use only a fraction of the total energy and does not have *high temperature problems or scaling and corrosion*.
- Today reverse osmosis systems have proven to be the *most economical and efficient means of improving the quality of water*.
- Simple to Operate and Maintain*
- Reverse osmosis systems come assembled, factory tested and in ready-to-operate condition. They are designed for efficiency and are simple to operate and maintain.
- Besides regular monitoring and periodic membrane cleaning, membranes need to be changed every one to three years depending on water quality, size of the system and pretreatment.
- Pumps also require routine maintenance.

#### Industrial Applications

The process is suitable for a wide range of applications, including:

- Drinking Water
- Humidification
- Ice-Making
- Car Wash Water Reclamation

- Ultrafiltration, is a separation process using membranes with pore sizes in the range of 0.1 to 0.001 micron.

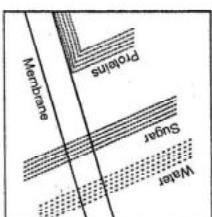


Fig. 2.13.7

- The other liquid stream is called *concentrate* which gets progressively concentrated in those species removed by the membrane.

In cross-flow separation, therefore, the membrane itself does not act as a collector of ions, molecules, or colloids but merely as a barrier to these species.

Typically, *ultrafiltration removes high molecular-weight substances, colloidal materials, and organic and inorganic polymeric molecules.*

Low molecular-weight organics and ions such as sodium, calcium, magnesium chloride, and sulfate are not removed.

Because only high-molecular weight species are removed, the osmotic pressure differential across the membrane surface is negligible.

Low applied pressures are therefore sufficient to achieve high flux rates from an ultrafiltration membrane.

*Flux of a membrane is defined as, "the amount of permeate produced per unit area of membrane surface per unit time."*

Generally flux is expressed as *gallons per square foot per day (GFD)* or as *cubic meters per square meters per day. (m<sup>3</sup>/m<sup>2</sup>/Day)*

Ultrafiltration membranes can have extremely high fluxes but in most practical applications the *flux varies between 50 and 200 GFD at an operating pressure of about 50 psig* in contrast, reverse osmosis membranes only produce between 10 to 30 GFD at 200 to 400 psig.

#### Industrial Applications

Ultrafiltration is used in industry to separate suspended solids from solution. The particles that are removed vary in size, and their removal is a function of the pore size.

(i) characteristics of the membrane

(ii) operating conditions

(iii) quality of feed.

- Paint recovery in the automotive industry

It is widely used in the fractionation of milk and whey, and in protein fractionation / Isolation

- Removal of colloids

Ultrafiltration is used in many industrial applications, including the power, food, pharmaceutical, biotechnology and semiconductor industries.

## 2.14 Methods to Determine Extent of Water Pollution

### 2.14.1 Biochemical Oxygen Demand (BOD)

► [Dec. 2007 !]

Waste water contains two types of organic matter :

- Biologically active or biologically degradable organic matter which can be oxidized by bacteria.
- Biologically active inorganic matter which can't be oxidized biologically.

Dissolved oxygen and organic matter present in water sample are closely related with each other. "The biochemical oxygen demand (BOD) of water is a measure of amount of oxygen required for the biological oxidation of organic matter under aerobic conditions, at 20°C and for a period of five days."

### Reaction



### (2) Procedure for determination of BOD

- BOD is directly related to the extent of pollution in waste water and industrial effluent.
- The higher the BOD of a sample the higher will be pollution caused by it. Drinking water should have BOD preferably less than 1 ppm.

### Principle of BOD

The principle involved in the determination of BOD is :

- The determination of dissolved oxygen (by Winkler's method) initially and
- Following a period of 5 days at 20°C.

The sample is maintained at this temperature for the period of testing.

$$\text{BOD} = (\text{DO})_1 - (\text{DO})_2$$

Where  $(\text{DO})_1$  = Dissolved oxygen of diluted water sample immediately after its preparation.

$(\text{DO})_2$  = Dissolved oxygen of diluted water sample after incubation for 5 days at 20°C, mg/L

$$x = \text{Fraction of sample} = \frac{\text{Volume of sample}}{\text{Total volume to which it was diluted}}$$

$$\text{BOD} = (\text{DO})_1 - (\text{DO})_2 \times \frac{\text{Volume of sample before dilution}}{\text{Volume of sample after dilution}} \quad \dots(1)$$

### Procedure for BOD

#### (1) Preparation of diluted water

The diluted water is prepared by adding 1ml of phosphate buffer pH = 7.2, 1 ml of magnesium sulphate (22.5 gm/L), 1 ml of  $\text{CaCl}_2$  (27.5 gm/L) and 1 ml of  $\text{FeCl}_3$  (0.25 gm/L) and making the volume of the solution to 1 litre.

The dilution depends upon the nature of the sample e.g.,

Sr. No.	Nature of sample	Dilution
(i)	Domestic waste water	2-5%
(ii)	Industrial waste	0.1-1%
(iii)	Polluted water	25-100%
(iv)	Raw and settled sewage	1-5%

- Two BOD bottles are filled upto the neck with diluted sample and numbered as 1 and 2.
- The dissolved oxygen in bottle number 1 is determined as per procedure described in (3) immediately i.e.  $(\text{DO})_1$ .
- The bottle number 2 is incubated for five days at 20°C in an incubator.
- The DO in bottle number 2 is determined as per procedure described in (3) i.e.  $(\text{DO})_2$ .
- The BOD of the sample is then calculated by using Equation (1).

**Significance of BOD :**

- The higher the BOD of a sample the higher the amount of decomposable organic matter in the sample and higher the pollution of the sample.
- Therefore, BOD

- (1) gives an idea about the extent of pollution at any time in the sewage sample
- (2) helps in pollution control.

**(3) Determination of dissolved oxygen :**

- Oxygen is slightly soluble in water. "The amount of oxygen dissolved in water at a particular temperature is known as dissolved oxygen."
- In fresh water the dissolved oxygen is 8 ppm.
- The solubility of dissolved oxygen decreases with increase in the salt concentration and with increase in temperature.
- It is generally expressed in ppm.

**Procedure for determination of dissolved oxygen:**

- 250 ml of the water sample is taken in a glass stoppered bottle.
- The contact with air is avoided as far as possible. 2 ml of manganese sulphate solution and 2 ml of alkaline KI solution are added using pipette, dipping the end well below the water surface.
- Bottle is stoppered, the contents are shaken vigorously. The precipitate formed is allowed to settle.
- When precipitate is settled, 2 ml of concentrate HCl is added, and contents are shaken till the precipitate gets dissolved completely.
- The colour of solution would turn dark yellow which is allowed to stand for about 5 mins pipette out 100 ml. of this solution and titrate it against N/100 hypo solution. When solution turns light yellow, add about 2 ml starch solution.
- The colour of solution would turn dark blue.
- Continue the titration with hypo solution till the deep blue colour of solution disappears.

Thus end point is disappearance of blue colour.

Let the volume of burette (hypo) solution be =  $V_2$  ml.

**Calculation:**

Volume of water sample =  $V_1$  = 100 ml taken for titration.

$$\text{Normality of hypo solution} = \frac{N}{100}$$

Now,  
 $N_1 V_1 = N_2 V_2$   
 i.e. Oxygen solution = Hypo solution

$$\therefore N_1 \times 100 = \frac{1}{100} \times V_2$$

Now,

$$\begin{aligned} \text{Strength of oxygen} &= N_1 \times 8 \text{ ppm/L} \\ &= \frac{V_2}{100 \times 100} \times 8 \times 100 \text{ mg/L} \end{aligned}$$

$$\therefore \text{Strength of oxygen} = 0.8 \times V_2 \text{ ppm.}$$

Using this procedure,  $(DO)_1$  and  $(DO)_2$  are calculated and using these values BOD is calculated for the sample.

**2.14.2 Chemical Oxygen Demand**

► [ Dec. 2007 ]

"The amount of oxygen required by organic matter in a sample water for its oxidation by strong oxidizing agent is known as Chemical Oxygen Demand or COD of the sample."

**Principle of determination of COD :**

- A known volume of sample is refluxed with a known excess of  $K_2Cr_2O_7$  solution in 50%  $H_2SO_4$ , in the presence of  $Ag_2SO_4$  (Catalyst), and  $HgSO_4$ .
- $K_2Cr_2O_7$  is strong oxidizing agent, in acidic medium. It oxidizes the organic matter into  $CO_2$  and  $H_2O$ .

**Note :** Organic matter of both types i.e. (i) Biologically oxidisable and (ii) Biologically inert

**Reaction :**

The unreacted dichromate solution is then titrated against std. FAS solution ( $\text{Fe}_2\text{SO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$ ) using ferroin as indicator. At end point blue colour changes to wine red.



#### Procedure for determination of COD

- Take 50 ml of sample in round bottom flask. Add 1 gm of  $\text{HgSO}_4$ .
- Attach condenser and add through condenser, 80 ml of  $\text{Ag}_2\text{SO}_4 - \text{H}_2\text{SO}_4$  solution, 25 ml  $\text{K}_2\text{Cr}_2\text{O}_7$  solution.
- Mix contents thoroughly. Reflux the mixture on water bath for about 1 hour. Wash condenser with distilled water, cool it, dilute it to 300 ml. Add 3-4 drops ferroin indicator.
- Titrate against standard FAS till blue colour changes to wine red.
- Let  $V_1$  ml. be the volume of FAS used.
- Repeat same procedure as blank. Let the reading be  $V_2$  ml.

#### Calculation :

Volume of sample taken = 50 ml

Volume of 1 N FAS used by sample =  $V_1$  ml

$\frac{1}{4}$  Volume of 1N FAS (Blank) =  $V_2$  ml.

Thus, Volume of 1N FAS solution equivalent to  $\text{K}_2\text{Cr}_2\text{O}_7$  solution used in oxidation =  $(V_2 - V_1)$  ml.

Now,

Sample = FAS

$N_1 V_1 = N_2 V_2$

$N_1 \times 50 = N_2(V_2 - V_1)$

$$\therefore N_1 = \frac{N_2(V_2 - V_1)}{50} = \frac{V_2 - V_1}{5} \quad (\because N_2 = 1\text{N})$$

$\therefore \text{COD} = N_1 \times \text{Equivalent weight}$

$$\begin{aligned} \therefore \text{COD} &= \frac{(V_2 - V_1)N}{50} \times 8 \text{ gm/L} \\ &= \frac{(V_2 - V_1) \times N}{50} \times 8 \times 1000 \text{ gm/L} \\ &= 160 \times N \times (V_2 - V_1) \text{ ppm} \end{aligned}$$

Thus the COD of sample can be calculated.

#### Significance of COD :

- It helps in designing the water treatment plant
- It helps in deciding the disposal of domestic effluents in various types of water streams.

#### 2.14.3 Difference between BOD and COD

► [Dec. 2006, May 2007]

Sr. No.	BOD	COD
1.	BOD of water is a measure of amount of oxygen required for the biological oxidation of organic matter under aerobic conditions at 20°C and for a period of 5 days.	The amount of oxygen required by organic matter in a sample of water for its oxidation by strong oxidizing agent is known as chemical oxygen demand
2.	BOD determination requires 5 days for completion of experiment.	The COD determination is quicker as it needs only three hours.
3.	Determination of BOD is based upon the determination of dissolved oxygen prior to and following a 5 days period at 20°C.	COD is determined by refluxing the sample with a known excess of $\text{K}_2\text{Cr}_2\text{O}_7$ and 50% $\text{H}_2\text{SO}_4$ and then titrating the unreacted $\text{K}_2\text{Cr}_2\text{O}_7$ solution against FAS solution.
4.	$BOD = \frac{(DO)_1 - (DO)_2}{x} \text{ ppm}$	$COD = \frac{(V_2 - V_1) \times N \times 8 \times 1000}{V} \text{ ppm}$
Where,		
Where		
$(DO)_1 = \text{DO in blank titration}$		
$(DO)_2 = \text{DO of the sample after}$		
$x = \frac{\text{Volume of sample}}{\text{Total volume to which it was diluted}}$		
5.	BOD is normally less than COD.	
COD is more than BOD as it is the measure of oxygen required for the oxidation of biologically oxidisable and biologically inert organic matter.		

## 2.15 Methods to Control Water Pollution

- Water gets polluted by organic and inorganic materials and gases derived from various industries such as mining, metal processing industries, tannery wastes, municipal wastes, food processing industries, etc.
- Water also gets polluted by particulate matter which is present around atmosphere.
- Control of water pollution has to be right at its origin, that is the various industries, which dispose the harmful by-product of their reactions in a careless manner which ultimately affects our water quality.
- The methods commonly employed to reduce or remove objectionable pollutants from water are sedimentation, filtration, biological oxidation, adsorption by activated carbon, chemical precipitation etc.
- All these methods are commonly adopted in sewage treatment.
- *Waste water treatment can be either.*
- (i) *Preventive treatment or*
- (ii) *Curative treatment.*
- The preventive treatment involves the steps to *reduce volume of waste water* or to reduce the *strength of pollutants*.
- By and large the volume reduction of waste water can be achieved, if the *industries recycle and reuse the water* used in the processes.
- In the second type i.e. *curative methods*, the waste water or polluted water has been treated by *physico-chemical and biological methods* or their combinations, depending upon the nature of pollutants.
- Physical methods remove *suspended solid or liquid pollutants* depending upon their densities.
- Other methods are reverse osmosis, electrodialysis, filtration, foam separation, porous bed filtration etc.
- These methods help in removal of fine particles, organic and inorganic dissolved materials.

### Activated sludge process for sewage treatment

#### Objectives of sewage treatment

The sewage that is collected from residences, public places, industries etc. is disposed off by letting it into a body of water such as river or sea or on land. But, before that, the sewage has to be treated for the following reasons :

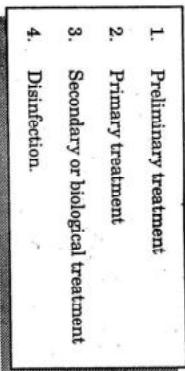
1. **To prevent pollution** of water into which the sewage is let off ; as the water may be used downstream for **drinking water supply**. This causes a health hazard as sewage contains pathogenic bacteria.
2. **To prevent offensive odour** in the water if the water is used for swimming, boating etc., and to the people living near the water or land where the sewage is disposed off, as it causes health hazard.
3. To prevent the destruction of fish and other aquatic life.
4. If the sewage has to be disposed of on land, the soil will become sewage sick after some time and cannot take any more sewage. This creates a very messy scene at the site and produces offensive odour polluting the entire atmosphere and affecting the neighbourhood.

#### 2.15.1 Broad Outline of Sewage Treatment by Activated Sludge Process

► [ May 2008 ]

- Sewage contains mineral and inorganic matter in suspension and in solution. It also contains living organisms, some of which may be dangerous.

- Hence, treatment of sewage has to be carried out. These treatment processes can be classified into the following categories :



#### 1. Preliminary treatment

- Waste water contains floating *suspended solids* such as rags, wood, metal, plastic, etc. These have to be removed as they interfere with the treatment process or mechanical equipments.

- In the preliminary treatment, these suspended impurities are removed.

#### 2. Primary treatment

- Primary treatment to sewage mainly consists of the sedimentation process to remove suspended organic solids.

- Chemicals are sometimes added* in primary clarifiers to assist in the removal of finely divided and colloidal solids or to precipitate phosphorous.

#### 3. Secondary or Biological treatment

- In this category, processes such as *filtration* or activated sludge process are included.
- Filtration is done in *contact beds* or *intermittent sand filters* or *trickling filters*.

- It removes finely divided suspended matter. In the activated sludge process, the sewage is biologically treated.

- A part of the digested sludge is added to the raw sewage together with oxygen which promotes coagulation of the suspended and colloidal matter.

- The matter which settles down at the bottom after treatment is called *sludge* and the liquid is called *effluent*.

- The *sludge* is disposed off in many ways such as drying beds, dumping into sea, etc.

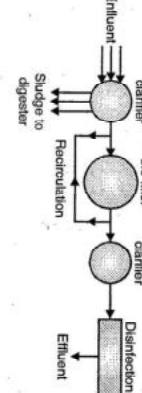


Fig. 2.15.1 : Stages in sewage treatment

- The *effluent* is also disposed off in many ways such as sewage farming, letting it into a natural drainage or sea. Stages in sewage treatments are shown in Fig. 2.15.1.

- Trickling filters* consists of circular beds, 2 - 5 m high, filled with porous lumpy materials, e.g. hard coke.

The waste water is poured on the *filter bed* with the help of a *rotatory sprinkler*.

- As the waste water percolates the filter bed, the *aerobic bacteria* grow using the organic matter in the sewage as their food.

It is necessary to maintain *highly aerobic condition*.

The organic matter undergoes biological oxidation due to these bacteria and the treated water is collected. Yield of this method is normally nearly 90% BOD.

The process is comparatively *very fast*, if the *aerobic condition is maintained*.

Second precaution to maintain the speed is the regular recirculation of the effluent so that filter does not get choked due to excess *biofilm growth* taking place.

#### 4. Disinfection

- After the secondary or biological treatment the effluent free from sludges is subjected to *disinfection*.

It is *chlorinated* to kill the bacteria which may remain in the effluent of sewage.

- Though activated sludge process broadly consists of all above stages, the number of stages or treatments given/required by water depend entirely upon the chemical analysis of water.

The severity of pollution is the sole criteria to choose one or more steps in combination to treat water, and the end use of water also plays role.

- If the water is only to be safely disposed off, then the treatment steps are chosen accordingly and vice versa.

## 2.16 Industrialisation and Its Effects

*Industrialisation is one of the major source for pollution both air and water pollution. The flue gases emitted from industries contribute to air pollution whereas effluent given out contributes to water pollution.*

The problem of water pollution being more serious simply because a large majority of industries are water based. Therefore a considerable volume of waste water is given out as effluent.

These effluents are varying in characteristics and are mainly based on the type of manufacturing/production the industry works for.

Hence, the problem of effluent treatment gets aggravated further, because no standard procedure for treatment can be recommended. Industrial effluents are generally discharged into water sources, either treated or many times even untreated which aggravates the problem of pollution of surface and subsoil water.

Thus rapid industrialisation has increased pressure on our water resources in two ways,

- (a) Increase in quantity of water required for industries.
- (b) Decrease in availability of clear water for use of pollution which is caused due to discharge of effluent (waste water).

### 2.16.1 Material Cycle and Pollution

- The characteristics of waste water from some of the important industries in India are given in Table 2.16.1.
- On the basis of these pollutional characteristics the industrial wastes can be categorised and the treatment methods can be considered.

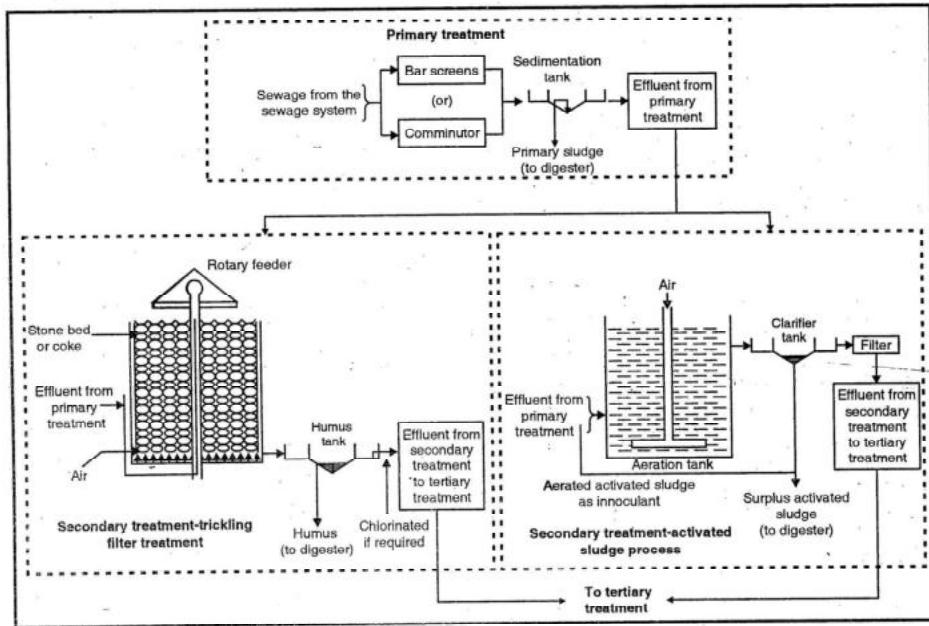


Fig. 2.15.2 : Schematic diagram of trickling/bio-filter

Table 2.16.1

Industry	Origin of major waste	Major characteristics	Major treatment and disposal method
Textiles	Processing fibres	High BOD, Colour, Highly alkaline, High suspended solids.	Biological treatment, aeration, trickling filtration, chemical precipitation, neutralisation.
Laundry	Washing of fabrics	High turbidity, alkalinity, organic solids.	Flootation, chemical precipitation, screening and absorption.
Pharmaceutical	Washings, Mycelium	High dissolved organic matter, suspended solids, vitamins etc.	Drying and evaporation.
Bakeries	Washings from utensils, floor etc.	Flour, sugar, oil etc. High BOD.	Biological oxidation.
Paper	Screening of paper pulp, Washing of fibres.	Acidity or alkalinity, colour, high suspended, colloidal dissolved solids etc.	Biological treatment, aeration, settling.

### 2.16.2 Recycling Issues

- The Table 2.15.1 give clear idea how essentially industrial waste require treatment before disposal.
- But problem of varying treatments points out at the fact that each industry must have the facility for disposal treatment of the waste produced during the process of manufacture.

### (b) Chemical characteristics

The chemical pollutional characteristics are mostly due to dissolved solids/matter. The effects are seen in terms of:

- Colour
- Odour
- Frothing
- Taste
- Hardness

The wastes produced by various industries are mainly show following three types of characteristics,

(a)	Physical characteristics.
(b)	Chemical characteristics.
(c)	Biological characteristics.

### (a) Physical characteristics

The quantities like total solids (i.e. total of floating matter, suspended impurities, colloidal matter etc. taken together), colour, odour, temperature are categorised as physical characteristics of waste water.

### Treatment for physical impurities

The following treatment can be given before disposal :

- Coarse, fine or bar screening to remove rags, paper, wood pieces etc.
- Breaking large size material into smaller size using devices like cutters, grinder or shredders.
- Sedimentation using plain sedimentation tanks to remove suspended organic solids. This may be followed by biological treatment.
- Grease traps are used to trap/remove unemulsified oils and other greasy materials from waste water/effluents.
- Grit chambers are used to arrest heavy inorganic settleable matter such as stones, dust, sand etc.

(vii) Increase in pH

**Treatment for chemical impurities**

Such as effluent can be treated by process like neutralisation, coagulation and flocculation, destruction of toxic substances by chemical reactions etc. The methods like coagulation and flocculation may be followed by filtration.

**(c) Biological characteristics**

Industrial effluent mainly contains bacteria and fungi. Other micro-organisms are by and large absent.

- The presence of these render biological characteristics to effluent. Other problem faced with these is their fast multiplication and their tendency to influence growth of micro-organisms in surrounding areas.
- Hence it is of utmost importance to treat them and make safe disposal of industrial effluent.

**Treatment for biological impurities**

The effluents contaminated with biological matter, requires to be treated, by various operations, either solely or in combination. Trickling filtration, activated sludge process, flocculation, chlorination, oxidation, aeration, ozonisation etc. are few to mention. The choice of method depends upon extent and type of pollution.

**2.16.3 Disposal of Industrial Effluents**

- The effluents treated for the dissolved matter of above mentioned different types, after treatment, can be recycled in plant in same industry.
- This is economical for the industry as well as useful for consuming water as natural resource. Moreover it can also be discharged into surface water course, or on the land. However, it has to be ensured that the treated effluent is safe for discharging or for reusing or for irrigation purpose.
- An additional point to mention, that some of treated effluents have a good manorial potential. This feature of effluent should be exploited, which will help in improved agricultural production, thereby enrichment of soil, which is in term useful in minimising/abatement of environmental pollution.

**2.17 Comparisons****2.17.1 Temporary Hardness and Permanent Hardness**

► [May 2008 !]

Table 2.17.1

Sr. No.	Temporary Hardness	Permanent Hardness
a.	The type of hardness, which can be removed by simple techniques such as boiling is known as temporary hardness.	The type of hardness, which cannot be removed by simple techniques is known as permanent hardness.
b.	It is due to bicarbonates carbonates hence also known as carbonate hardness.	It is due to other salts, hence known as non-carbonate hardness.
c.	It is due to dissolved bicarbonates of $\text{Ca}^{+2}$ , $\text{Mg}^{+2}$ , $\text{Fe}^{+2}$ etc.	It is due to other dissolved salts of $\text{Ca}^{+2}$ , $\text{Mg}^{+2}$ , $\text{Fe}^{+2}$ etc. such as chlorides, sulphates and nitrates.
d.	This is known as alkaline hardness.	This is known as non-alkaline hardness.
e.	Temporary hard water can be softened by <ol style="list-style-type: none"> <li>1. Only boiling.</li> <li>2. Treating only with lime.</li> </ol>	Permanent hard water can be softened by treating with soda.
f.	Temporary hard water if used in steam production, deposits precipitates of carbonates of $\text{Ca}^{+2}$ and hydroxides of $\text{Mg}^{+2}$ at the bottom of the container (boiler) known as sludges. These deposits harden to form scales. The reactions taking place are:	Permanent hard water if used in steam production, forms scales.
	$\text{Ca}(\text{HCO}_3)_2(\text{aq}) \xrightarrow{\Delta} \text{CaCO}_3 \downarrow + \text{H}_2\text{O} - \text{CO}_2 \uparrow$ $\text{Mg}(\text{HCO}_3)_2(\text{aq}) \xrightarrow{\Delta} \text{Mg}(\text{OH})_2 \downarrow + 2\text{CO}_2 \uparrow$	

### 2.17.2 Zeolite Process and Lime Soda Process

Table 2.17.2

Sr. No.	Zeolite Process	Lime Soda Process
a.	By this process, water with 0 – 15 ppm residual hardness is obtained.	By this process, water with 15 to 50 ppm residual hardness is obtained.
b.	The process is expensive, as cost of chemicals and that of plant is high, hence higher capital investment is needed.	The process is relatively cheap as cost of chemicals and that of plant is low.
c.	Operating cost is low, as exhausted zeolite bed can be regenerated by simple treatment i.e. passing brine solution through it.	Operating cost is higher because all the chemicals used i.e. lime, soda and coagulants are consumed in the process and cannot be regenerated.
d.	The size of the softening plant depends upon the hardness of the water. Hence, plant is compact and occupies less space.	The size of softening plant depends upon quantity of hard water to be softened. Hence, size is not compact, but increases with quantity of water and thus occupies more space.
e.	This process cannot be used for hot water, acidic water, turbid water and water with suspended impurities.	This process does not have any such restrictions.
f.	The process is simple and efficiency is high.	The process is not simple, as it involves settling coagulation and filtration, and hence efficiency is low.
g.	Process is disadvantageous because temporary hardness forms bicarbonates of sodium.	Process is advantageous, because temporary hardness gets completely removed as precipitates of $\text{CaCO}_3$ and $\text{Mg}(\text{OH})_2$ .
h.	The soft water obtained by this process creates problems in boilers because it contains bi-carbonates which lead to the formation of $\text{NaOH}$ and $\text{CO}_2$ at high temperature which cause caustic embrittlement.	The soft water obtained does not create problems of caustic embrittlement in boilers because the resultant products such as $\text{CaCO}_3$ and $\text{Mg}(\text{OH})_2$ are removed by filtration.

### 2.17.3 Ion-Exchange Process and Zeolite Process

Table 2.17.3

Sr. No.	Ion-Exchange Process	Zeolite Process
a.	This process can produce softened water with residual hardness ranging between 0 to 2 ppm.	This process can produce softened water with residual hardness ranging between 0 – 15 ppm.
b.	The resultant water is suitable for all types of boilers, especially high pressure boilers.	The resultant water is not suitable for use in high pressure boilers. Water can be used only in low or medium pressure boilers.
c.	The cation and anion exchange beds used are more expensive. Hence, capital cost is high.	Zeolite softener is comparatively cheap, hence capital cost is lower.
d.	The softening plant is not compact, hence occupies more space.	The softening plant is compact. Hence occupies less space.
e.	The process effectively removes all the hardness causing substances. It can also remove alkali metals such as Na or K, as chlorides or sulphates completely.	This process can remove only $\text{Ca}^{+2}$ , $\text{Mg}^{+2}$ , $\text{Fe}^{+2}$ and $\text{Mn}^{+2}$ ions. Hence, softened water contains salts like $\text{NaCl}_x$ , $\text{NaHCO}_3$ , $\text{Na}_2\text{SO}_4$ etc. in dissolved form.
f.	This process is useful for acidic as well as alkaline water.	This process is not useful for highly acidic water as acids affect zeolite bed, because zeolites get dissolved in.
g.	Soft water obtained does not cause caustic embrittlement in boilers and is suitable for boilers as it is free from $\text{Na}^+$ ions.	Soft water obtained is not suitable for boilers, due to the presence of $\text{NaHCO}_3$ which subsequently forms $\text{NaOH}$ , causing thereby caustic embrittlement in boilers.

## 2.17.4 Sludges and Scales

**Table 2.17.4**  
► [May 2000, Dec. 2001, May 2003, Dec. 2006 !]

Sr. No.	Sludges	Scales
a.	The loose and slimy precipitates which remain floating in water or get collected at the bottom of boiler are called as sludges.	The hard adhering deposits on the walls and bottom of the boiler are called as scales.
b.	Formation of sludges is mainly due to salts which have lower solubility in cold water as compared to that in hot water. For example, $MgCO_3$ .	Formation of scales is mainly due to salts which have higher solubility in cold water as compared to that in hot water. For example, $CaSO_4$ .
c.	Sludges remain suspended in boiler water unlike scales. Hence, though they are poor conductors of heat, problem of overheating boiler material does not arise.	Scales form a hard layer on walls of boiler and cause overheating of boiler material because they are poor conductor of heat.
d.	Due to sludges risk of explosion does not persist.	Due to scales explosion may take place.
e.	Blow down operation can remove sludges.	Blow down operation does not help to remove the scales.
f.	Wastage of fuel is comparatively less.	Wastage of fuel is very large.
g.	Methods for removal of sludges are :	Methods for removal of scales are :
(i)	Blow down operation.	Internal treatment by dilute acids.
(ii)	Scraping by wire brush.	Complexation. (iii) Thermal shocks.

## 2.18 Solved Problems

### 2.18.1 Problems based on Carbonates and Non Carbonates Hardness (Total, Permanent, Temporary Hardness)

**Problem 2.18.1:** What is the carbonate and non-carbonate hardness of a sample of water which has the following impurities per litre,

$$\begin{aligned} CaCO_3 &= 12.5 \text{ mg/lit.} & CaCl_2 &= 22.2 \text{ mg/lit.} \\ MgCO_3 &= 8.4 \text{ mg/lit.} & MgCl_2 &= 9.5 \text{ mg/lit.} \\ CO_2 &= 33 \text{ mg/lit.} & NaHCO_3 &= 6.8 \text{ mg/lit.} \end{aligned}$$

**Solution :**

#### ► Conversion in $CaCO_3$ equivalents

Salt	Qty. in ppm	Multiplication factor	$CaCO_3$ equivalent in ppm	Type of Hardness
$CaCO_3$	12.5	$12.5 \times \frac{100}{100}$	12.5	Carbonate
$MgCO_3$	8.4	$\frac{100}{84} \times 8.4$	10	Carbonate
$CaCl_2$	22.2	$22.2 \times \frac{100}{111}$	20	Non-carbonate
$MgCl_2$	9.5	$\frac{100}{95} \times 9.5$	10	Non-carbonate
$CO_2$	33	—	—	—
$NaHCO_3$	6.8	$\frac{100}{84} \times 6.8$	8.09 $\approx$ 8	Carbonate

Carbonate hardness is due to  $CaCO_3 + MgCO_3 + NaHCO_3$

$$= 12.5 + 10 + 8 = 30.5 \text{ ppm}$$

Nor-carbonate hardness is due to  $CaCl_2$  and  $MgCl_2$

$$= 20 + 10$$

$$= 30 \text{ ppm}$$

**Ans. :** Carbonate hardness = 30.5 ppm  
Non-carbonate hardness = 30 ppm

**Problem 2.18.2:** What is the carbonate and non-carbonate hardness of a sample of water which has the following impurities per litre,

$$\begin{aligned} \text{Ca(HCO}_3\text{)}_2 &= 40.5 \text{ mgs/lit;} \\ \text{CaCl}_2 &= 33.3 \text{ mgs/lit;} \\ \text{Ca(NO}_3\text{)}_2 &= 41.0 \text{ mgs/lit;} \\ \text{KNO}_3 &= 101 \text{ mgs/lit;} \\ \text{MgCO}_3 &= 33.6 \text{ mgs/lit.} \end{aligned}$$

**Solution :**

> Conversion in  $\text{CaCO}_3$  equivalents

Salt	Qty.	Multiplication factor	$\text{CaCO}_3$ equivalent in ppm	Type of Hardness
$\text{Ca(HCO}_3\text{)}_2$	40.5 mg	$40.5 \times \frac{100}{162}$	25	Carbonate
$\text{CaCl}_2$	33.3 mg	$33.3 \times \frac{100}{111}$	30	Non- carbonate
$\text{Ca(NO}_3\text{)}_2$	41 mg/l	$41 \times \frac{100}{164}$	25	Non - carbonate
$\text{KNO}_3$	101 mg/l	(Does not contribute to hardness)		
$\text{MgCO}_3$	33.6 mg	$33.6 \times \frac{100}{84}$	40	Carbonate

We know that carbonate hardness is due to bicarbonate (dissolved) of calcium, magnesium etc and permanent hardness or non-carbonate hardness is due to the presence of chlorides, sulphates and nitrates of calcium, magnesium and iron.

Carbonate hardness is due to  $\text{MgCO}_3$  and  $\text{Ca}(\text{HCO}_3)_2$

$$\begin{aligned} &= 40 + 25 \\ &= 65 \text{ ppm} \end{aligned}$$

Non-carbonate hardness is due to  $\text{CaCl}_2$  and  $\text{Ca}(\text{NO}_3)_2$

$$\begin{aligned} &= 30 + 25 \\ &= 55 \text{ ppm and} \end{aligned}$$

Ans. : Non-carbonate hardness = 55 ppm

Carbonate hardness = 65 ppm

**Problem 2.18.3:** What is the carbonate and non-carbonate hardness of water sample which has the following impurities :

$$\begin{aligned} \text{Ca(HCO}_3\text{)}_2 &= 40.5 \text{ ppm;} & \text{Mg(HCO}_3\text{)} &= 29.1 \text{ ppm;} \\ \text{CaCl}_2 &= 11.1 \text{ ppm;} & \text{MgCl}_2 &= 15.89 \text{ ppm;} \\ \text{NaCl} &= 28.5 \text{ ppm;} & \text{CO}_2 &= 22.0 \text{ ppm.} \end{aligned}$$

Express the results in ppm.

**Solution :**

> Conversion in  $\text{CaCO}_3$  equivalents

Salt	Qty. in ppm	Multiplication factor	$\text{CaCO}_3$ equivalent in ppm	Type of Hardness
$\text{Mg(HCO}_3\text{)}_2$	29.1	$29.1 \times \frac{100}{146}$	19.931	Carbonate
$\text{Ca}(\text{HCO}_3)_2$	40.5	$40.5 \times \frac{100}{162}$	25	Carbonate
$\text{CaCl}_2$	11.1	$11.1 \times \frac{100}{111}$	10	Non- carbonate
$\text{MgCl}_2$	15.82	$15.82 \times \frac{100}{95}$	16.652	Non- carbonate
$\text{NaCl}$	28.5			(Does not contribute no hardness)
$\text{CO}_2$	22.0			

Here,  $\text{NaCl}$  and  $\text{CO}_2$  don't cause by type of hardness.

Here, the carbonate hardness is due to the hardness of  $\text{Ca}(\text{HCO}_3)_2 + \text{Mg}(\text{HCO}_3)_2$

$$\begin{aligned} &\therefore \text{Carbonate hardness} = 19.931 + 25 \\ &= 44.931 \text{ ppm} \end{aligned}$$

while, non-carbonate hardness is due to the hardness of  $\text{MgCl}_2$  and  $\text{CaCl}_2$

$$\begin{aligned} &\therefore \text{Non Carbonate hardness} = 10 + 16.652 \\ &= 26.652 \text{ ppm} \end{aligned}$$

Ans. : Carbonate hardness = 44.931 ppm

Non-carbonate hardness = 26.652 ppm

**Problem 2.18.4:** Calculate the carbonate and non-carbonate hardness of a sample of water containing:

$$\begin{aligned} \text{MgCl}_2 &= 95 \text{ ppm}; & \text{MgSO}_4 &= 48 \text{ ppm}; \\ \text{Ca(HCO}_3)_2 &= 16.2 \text{ ppm}; & \text{KCl} &= 12 \text{ ppm}; \\ \text{Mg(HCO}_3)_2 &= 14.6 \text{ ppm} \end{aligned}$$

**Solution :**

Conversion in  $\text{CaCO}_3$  equivalents

Salt	Qty.	Multiplication factor	$\text{CaCO}_3$ equivalent in ppm	Type of Hardness
$\text{Ca}(\text{HCO}_3)_2$	16.2 ppm	$16.2 \times \frac{100}{162}$	10	Carbonate
$\text{Mg}(\text{HCO}_3)_2$	14.6 ppm	$14.6 \times \frac{100}{146}$	10	Carbonate
$\text{MgCl}_2$	95 ppm	$95 \times \frac{100}{95}$	10	Non-carbonate
$\text{MgSO}_4$	48 ppm	$48 \times \frac{100}{120}$	40	Non-carbonate
KCl	12 ppm	{ (Does not contribute to hardness)		

$$\text{Carbonate hardness} = [\text{Ca}(\text{HCO}_3)_2 + \text{Mg}(\text{HCO}_3)_2]$$

$$= 10 + 10 = 20 \text{ ppm}$$

$$\text{Non-carbonate hardness} = \text{MgCl}_2 + \text{MgSO}_4$$

$$= 10 + 40$$

$$= 50 \text{ ppm}$$

**Ans. :** Carbonate hardness = 20 ppm  
Non-carbonate hardness = 50 ppm

**Problem 2.18.5:** Find out temporary, permanent and total hardness in a sample of water with following impurities

- (i)  $\text{Ca}(\text{HCO}_3)_2 = 81 \text{ ppm}$
- (ii)  $\text{MgCO}_3 = 84 \text{ ppm}$
- (iii)  $\text{CaCl}_2 = 22.2 \text{ ppm}$
- (iv)  $\text{MgSO}_4 = 60 \text{ ppm}$
- (v)  $\text{KCl} = 30 \text{ ppm}$

**Solution :**  
Calculation of quantities in term of  $\text{CaCO}_3$  equivalents of impurities

Impurity/ies	Quantity	Multiplying factor	$\text{CaCO}_3$ equivalent in ppm
$\text{Ca}(\text{HCO}_3)_2$	81 ppm	$100/162$	50
$\text{MgCO}_3$	84 ppm	$100/84$	100
$\text{CaCl}_2$	22.2 ppm	$100/111$	20
$\text{MgSO}_4$	60 ppm	$100/120$	50
KCl	30 ppm	{ Does not contribute to hardness	

Temporary hardness is due to carbonates, and  
Permanent hardness is due to non-carbonates and

Total hardness is due to sum of both.

$$\text{Temporary hardness} = \text{Ca}(\text{HCO}_3)_2 + \text{MgCO}_3$$

$$= 50 + 100$$

$$\begin{aligned} \text{Permanent hardness} &= \text{CaCl}_2 + \text{MgSO}_4 \\ &= 20 + 50 \end{aligned}$$

$$\begin{aligned} &= 70 \text{ ppm} \\ \therefore \text{Total hardness} &= 150 + 70 \\ &= 220 \text{ ppm} \end{aligned}$$

**Ans. :** Temporary hardness = 150 ppm

Permanent hardness = 70 ppm

Total hardness = 220 ppm

**Problem 2.18.6:** Find out the temporary and permanent hardness in a sample of water with following impurities :

- $\text{MgCO}_3 = 29.2 \text{ ppm}$ ,
- $\text{CaCl}_2 = 22.2 \text{ ppm}$ ,
- $\text{MgSO}_4 = 36.0 \text{ ppm}$ ,
- $\text{MgCl}_2 = 142.5 \text{ ppm}$ .

(Dec. 2004)

**Solution :**

➤ Calculation of  $\text{CaCO}_3$  equivalents for impurities

Impurity/ies	Quantity	Multiplying factor	$\text{CaCO}_3$ equivalent in ppm
$\text{MgCO}_3$	29.2 ppm	100/84	34.76 ppm
$\text{MgSO}_4$	36 ppm	100/120	30 ppm
$\text{CaCl}_2$	22.2 ppm	100/111	20 ppm
$\text{MgCl}_2$	142.5 ppm	100/95	150 ppm

$$\text{Temporary hardness} = [\text{MgCO}_3]$$

$$= 34.76 \text{ ppm}$$

$$\text{Permanent hardness} = [\text{MgSO}_4 + \text{MgCl}_2 + \text{CaCl}_2]$$

$$= 30 + 150 + 20$$

$$= 200 \text{ ppm}$$

Ans. : Temporary hardness = 34.76 ppm

Permanent hardness = 200 ppm.

**Problem 2.18.7(A) :** A water sample contain:  
in terms of degree Clark, degree French and mg/lit.A. (Dec. 2006, 3 Marks)

**Solution :**

Given : Hardness of water = 304 ppm

Hardness in term of °Cl :

$$\therefore 0.07^\circ\text{Cl} = 1 \text{ ppm}$$

$$304 \text{ ppm} = 304 \times 0.07^\circ\text{Clarke}$$

$$= 21.28^\circ\text{Clarke}$$

Hardness in term of °Fr :

$$\therefore 0.1^\circ\text{Fr} = 1 \text{ ppm}$$

$$304 \text{ ppm} = 304 \times 0.1^\circ\text{Fr}$$

$$= 30.4^\circ\text{Fr}$$

Ans. :

Hardness in term of mg/lit

$$\therefore 1 \text{ ppm} = 1 \text{ mg/lit}$$

$$304 \text{ ppm} = 304 \text{ mg/lit}$$

Ans. : Hardness of water 304 ppm = 21.28 °Clarke

$$= 30.4^\circ\text{Fr}$$

$$= 304 \text{ mg/lit}$$

**Problem 2.18.7(A) :** A water sample contain:  
(i)  $\text{Ca}(\text{HCO}_3)_2 = 32.4 \text{ mg/l}$   
(ii)  $\text{Mg}(\text{HCO}_3)_2 = 29.2 \text{ mg/l}$   
(iii)  $\text{CaSO}_4 = 13.5 \text{ mg/l}$

Calculate temporary, permanent and total hardness  
(At. wt. C = 40, Mg = 24, H = 1, Ca = 12, O = 16, S = 32)

(May 2008, 2 Marks)

**Solution :**

Calculation of  $\text{CaCO}_3$  equivalents

Impurity/ies	Quantity	Multiplying factor	$\text{CaCO}_3$ equivalent in ppm
$\text{Ca}(\text{HCO}_3)_2$	32.4 mg/l	$32.4 \times \frac{100}{162}$	20
$\text{Mg}(\text{HCO}_3)_2$	29.2 mg/l	$29.2 \times \frac{100}{146}$	20
$\text{CaSO}_4$	13.5 mg/l	$13.5 \times \frac{100}{136}$	10

Thus, Temporary hardness =  $\text{Mg}(\text{HCO}_3)_2 + \text{Ca}(\text{HCO}_3)_2$

Given : Hardness of water = 304 ppm

Hardness in term of °Cl :

$$\therefore 0.07^\circ\text{Cl} = 1 \text{ ppm}$$

$$304 \text{ ppm} = 304 \times 0.07^\circ\text{Clarke}$$

$$= 21.28^\circ\text{Clarke}$$

Hardness in term of °Fr :

$$\therefore 0.1^\circ\text{Fr} = 1 \text{ ppm}$$

$$304 \text{ ppm} = 304 \times 0.1^\circ\text{Fr}$$

$$= 30.4^\circ\text{Fr}$$

Ans. :

Temporary Hardness = 40 ppm

Permanent Hardness = 10 ppm

Total Hardness = 50 ppm

**2.18.2 Problems based on Calculation of Hardness by EDTA Method****► [Dec. 2006 1]****Method of calculation**

- Titrations carried out in this method are:

1. 50 ml standard hard water (SHW) [containing 1 mg/ml  $\text{CaCO}_3$  equivalent hardness] against EDTA solution =  $V_1$  ml.
  2. 50 ml unknown hard water (HW) against EDTA solution =  $V_2$  ml.
  3. 50 ml unknown hard water after boiling and dilution against EDTA solution =  $V_3$  ml.
- Now,  $V_1$  ml. EDTA required by 50 ml. standard hard water = 50 mgs of  $\text{CaCO}_3$  equivalent.

(Since SHW contains 1 mg/ml  $\text{CaCO}_3$  equivalent hardness)

$$\therefore 1 \text{ ml EDTA solution} = \left[ \frac{50}{V_1} \right] \text{ mgs CaCO}_3 \text{ equivalent hardness.}$$

Now,  $V_2$  ml. EDTA solution is required by unknown hard water,

$$\text{Thus, total hardness in 50 ml} = \left[ \frac{V_2 \times 50}{V_1} \right] \text{ mgs CaCO}_3 \text{ equivalent hardness.}$$

$$\therefore \text{Total hardness of water (per litre)} = \left[ \frac{V_2}{V_1} \times 1000 \right] \text{ mgs/lit. (or ppm)}$$

Now,  $V_3$  ml. EDTA solution is required by 50 ml unknown hard water after boiling, i.e. on boiling, temporary hardness gets eliminated. Hence  $V_3$  ml. EDTA is towards permanent hardness of water sample.

$$\begin{aligned} \text{Thus, permanent hardness of waetr in 50 ml sample} &= \left[ V_3 \times \frac{50}{V_1} \right] \text{ mgs of CaCO}_3 \text{ equivalent hardness.} \\ \therefore \text{permanent hardness of water per litre} &= \left[ \frac{V_3}{V_1} \times 1000 \right] \text{ mgs/lit.} \end{aligned}$$

From above two equations we can calculate temporary hardness as

Temporary hardness = Total hardness - Permanent hardness

$$\begin{aligned} &= \left[ \frac{V_2}{V_1} \times 1000 \right] - \left[ \frac{V_3}{V_1} \times 1000 \right] \text{ mgs/lit. of CaCO}_3 \text{ or ppm} \\ &= \frac{1000}{V_1} (V_2 - V_3) \text{ mgs/lit. of CaCO}_3 \text{ or ppm.} \end{aligned}$$

**Problem 2.18.8: Convert the total hardness of water samples in ppm from  $\text{Cl}$  and  $\text{Fr}$ .****Solutions:**

- |      |  |
|------|--|
| (i)  | $\therefore 0.07^\circ\text{Clarke} = 1 \text{ ppm}$                                     |
|      | $\therefore 2.42^\circ\text{Clarke} = \frac{2.42}{0.07} \text{ ppm} = 34.57 \text{ ppm}$ |
| (ii) | $0.1^\circ\text{Fr} = 1 \text{ ppm.}$  |
|      | $3.6^\circ\text{Fr} = \frac{3.6}{0.1} \text{ ppm} = 36 \text{ ppm.}$                     |

**Ans. : Hardness of water**

$$\begin{aligned} 2.42^\circ\text{Clarke} &= 34.57 \text{ ppm} \\ 3.6^\circ\text{Fr} &= 36 \text{ ppm} \end{aligned}$$

**Problem 2.18.9: Convert the total hardness given in ppm as**

- 350 ppm  $\text{CaCO}_3$  equivalent [convert in Clarke]
- 500 ppm  $\text{CaCO}_3$  equivalent [convert in French]

**Solution:**

(i)

 $\therefore 1 \text{ ppm CaCO}_3 \text{ equivalent} = 0.07^\circ\text{Clarke}$  $\therefore 350 \text{ ppm CaCO}_3 \text{ equivalent} = (350 \times 0.07)$ 

$$= 24.5^\circ\text{Clarke}$$

(ii)

 $\therefore 1 \text{ ppm CaCO}_3 \text{ equivalent} = 0.1^\circ\text{French}$  $\therefore 500 \text{ ppm CaCO}_3 \text{ equivalent} = (500 \times 0.1)^\circ\text{French}$ 

$$= 50^\circ\text{French}$$

**Ans. :****Hardness of 350 ppm  $\text{CaCO}_3$  = 24.5  $^\circ\text{Clarke}$** **Hardness of 500 ppm  $\text{CaCO}_3$  = 50  $^\circ\text{French}$** **Problem 2.18.10: A water sample was found to contain following salts**

$$\begin{aligned} \text{Ca(HCO}_3)_2 &= 40.5 \text{ mgs/lit.} & \text{MgCl}_2 &= 23.75 \text{ mgs/lit.} \\ \text{CO}_2 &= 3 \text{ mgs/lit.} & \text{MgCO}_3 &= 21 \text{ mgs/lit.} \\ \text{CaCl}_2 &= 55.5 \text{ mg/lit.} & \text{SiO}_2 &= 6 \text{ mgs/lit.} \end{aligned}$$

**Calculate the carbonate and non-carbonate hardness of the water sample.**

**Solution :**

- Conversion of the quantities of all the chemicals in term of  $\text{CaCO}_3$ , equivalents in ppm.

Salv/Chemical	Qty in mgs/lit	Mol. wt.	Type of hardness it causes in water	$\text{CaCO}_3$ equivalent in ppm
1. $\text{Ca}(\text{HCO}_3)_2$	40.5	162	Carbonate	$40.5 \times \frac{100}{162} = 25$
2. $\text{MgCl}_2$	23.75	95	Non-carbonate	$23.75 \times \frac{100}{95} = 25$
3. $\text{MgCO}_3$	21	84	Carbonate	$21 \times \frac{100}{84} = 25$
4. $\text{SiO}_2$	6	60	Does not contribute to hardness	-
5. $\text{CO}_2$	3	44	-	-
6. $\text{CaCl}_2$	55.5	111	Non-carbonate	$55.5 \times \frac{100}{111} = 50$

**Step II :** Calculation of carbonate or temporary hardness in ppm of  $\text{CaCO}_3$ .

$$= [\text{CaCO}_3 \text{ equivalent in ppm of } \text{Ca}(\text{HCO}_3)_2 + \text{MgCO}_3]$$

$$= [25 + 25]$$

$$= 50 \text{ ppm.}$$

**Step III: Non-carbonate hardness (permanent)**

$$= [\text{CaCO}_3 \text{ equivalent in ppm of } \text{MgCl}_2 + \text{CaCl}_2]$$

$$= [25 + 50] = 75 \text{ ppm.}$$

**Ans. :** Carbonate hardness = 50 ppm

Non-carbonate hardness = 75 ppm

**Problem 2.18.11:** Calculate total, permanent and temporary hardness in ppm of  $\text{CaCO}_3$  equivalents for the sample of water containing following salts.

$$\text{Ca}(\text{HCO}_3)_2 = 17.5 \text{ mgs/lit.}; \quad \text{Mg}(\text{HCO}_3)_2 = 14.6 \text{ mgs/lit.};$$

$$\text{MgCl}_2 = 9.5 \text{ mgs/lit.}; \quad \text{MgSO}_4 = 12 \text{ mgs/lit.};$$

$$\text{MgCO}_3 = 8.4 \text{ mgs/lit.}; \quad \text{CaCl}_2 = 5.5 \text{ mgs/lit.};$$

$$\text{NaCl} = 35 \text{ mgs/lit.}$$

**Solution :**

- Conversion of all the quantities of various chemicals in terms of  $\text{CaCO}_3$  equivalents in ppm.

Impurity	Qty in mgs/lit	Mol. wt.	Type of hardness	$\text{CaCO}_3$ equivalent ppm
1. $\text{Ca}(\text{HCO}_3)_2$	17.5	162	Carbonate	$17.5 \times \frac{100}{162} = 10.8$
2. $\text{Mg}(\text{HCO}_3)_2$	14.6	146	Carbonate	$14.6 \times \frac{100}{146} = 10$
3. $\text{MgCl}_2$	9.5	95	Non-carbonate	$9.5 \times \frac{100}{95} = 10$
4. $\text{MgSO}_4$	12.0	120	Non-carbonate	$12 \times \frac{100}{120} = 10$
5. $\text{MgCO}_3$	8.4	84	Carbonate	$8.4 \times \frac{100}{84} = 10$
6. $\text{CaCl}_2$	5.5	111	Non-carbonate	$5.5 \times \frac{100}{111} = 5$
7. $\text{NaCl}$	35	58.5	Does not cause hardness	

➤ Calculation of carbonate (Temporary hardness)

$$= [\text{CaCO}_3 \text{ equivalent in ppm of } \text{Ca}(\text{HCO}_3)_2 + \text{Mg}(\text{HCO}_3)_2 + \text{MgCO}_3]$$

$$= [10.8 + 10 + 10]$$

$$= 30.8 \text{ ppm.}$$

➤ Calculation of non-carbonate (permanent) hardness

$$= [\text{CaCO}_3 \text{ equivalent in ppm of } \text{MgCl}_2 + \text{MgSO}_4 + \text{CaCl}_2]$$

$$= [10 + 10 + 5]$$

$$= 25 \text{ ppm.}$$

$\therefore$  Total hardness

$$= \text{Temporary hardness} + \text{Permanent hardness}$$

$$= (30.8 + 25) \text{ ppm} = 55.8 \text{ ppm.}$$

**Ans. :** Carbonate (Temporary hardness) = 30.8 ppm

Non-carbonate (Permanent) hardness = 25 ppm

Total hardness = 55.8 ppm

**Problem 2.18.12 :** 25 ml of  $\text{CaCl}_2$  solution (Strength 250 mgs  $\text{CaCO}_3$  per 200 ml) required 35 ml EDTA solution. Same EDTA solution was used to titrate 25 ml of unknown hard water which consumed 30 ml. of EDTA solution. Calculate the hardness of water sample.

**Solution :**

Strength of  $\text{CaCl}_2$  solution is given as 250 mgs of  $\text{CaCO}_3$  per 200 ml.

$$\begin{aligned} \text{That means } 25 \text{ ml. of } \text{CaCl}_2 &\text{ contains } = \left[ \frac{25 \times 250}{200} \right] \text{ mgs CaCO}_3 \\ &= 31.25 \text{ mgs CaCO}_3 \end{aligned}$$

Now, 25 ml  $\text{CaCl}_2$  solution requires 35 ml EDTA solution

$$\begin{aligned} \therefore 35 \text{ ml EDTA} &= 31.25 \text{ mgs CaCO}_3 \\ 1 \text{ ml EDTA solution} &= \frac{31.25}{35} \text{ mgs CaCO}_3 \end{aligned}$$

Now,

25 ml hard water requires 30 ml EDTA solution

$$\begin{aligned} &\equiv \left[ 30 \times \frac{31.25}{35} \right] \text{ mgs of CaCO}_3 \\ &\equiv 26.8 \text{ mgs of CaCO}_3 \end{aligned}$$

$$\begin{aligned} 1000 \text{ ml hard water} &= \left[ \frac{26.8 \times 1000}{25} \right] \text{ mgs of CaCO}_3 \text{ equivalent hardness} \\ \text{hardness of water} &= 1072 \text{ mgs of } \text{CaCO}_3 \end{aligned}$$

$$= 1072 \text{ mgslit. or ppm.}$$

**Ans. :** Hardness of water = 1072 ppm

**Problem 2.18.13 :** 50 ml of standard hard water (1 mg  $\text{CaCO}_3$ /ml) required 35 ml EDTA solution while sample hard water required 20 ml EDTA solution. After boiling the requirement of EDTA was 12 ml. Calculate the total permanent and temporary hardness of water.

**Solution :**

Strength of standard hard water is 1 mg. per ml  $\text{CaCO}_3$ .

$$\text{i.e. } 50 \text{ ml. standard hard water} = 50 \text{ mgs. } \text{CaCO}_3.$$

Now,

$$\begin{aligned} \therefore 50 \text{ ml standard hard water} &= 35 \text{ ml. EDTA solution.} \\ \text{That means } 35 \text{ ml. EDTA solution} &= 50 \text{ mgs of } \text{CaCO}_3. \end{aligned}$$

$\therefore 1 \text{ ml. EDTA solution} = \frac{50}{35} \text{ mgs of } \text{CaCO}_3.$   
50 ml. unknown hard water = 20 ml. EDTA

$$\begin{aligned} &= \left[ 20 \times \frac{50}{35} \right] \text{ mgs of } \text{CaCO}_3 \\ &\text{Thus total hardness per 50 ml} = \left[ \frac{20 \times 50}{35} \right] \text{ mgs of } \text{CaCO}_3. \end{aligned}$$

$$\begin{aligned} \text{Thus total hardness per litre} &= \left[ \frac{20}{35} \times 1000 \right] \\ &= 571.42 \text{ ppm.} \end{aligned}$$

Now,

After boiling, 50 ml water sample = 12 ml. EDTA

$$\begin{aligned} \text{Thus, permanent hardness per 50 ml} &= \left[ \frac{12 \times 50}{35} \right] \text{ mgs of } \text{CaCO}_3 \\ &= 17.14 \text{ mgs of } \text{CaCO}_3 \end{aligned}$$

$$\begin{aligned} \therefore \text{Permanent hardness per litre} &= \left[ \frac{17.14 \times 1000}{50} \right] \text{ mgs of } \text{CaCO}_3 \\ &= 342.86 \text{ ppm.} \end{aligned}$$

$$\begin{aligned} \text{Temporary hardness of water} &= \text{Total hardness} - \text{Permanent hardness} \\ &= (571.42 - 342.86) \text{ ppm.} \\ &= 228.56 \text{ ppm.} \end{aligned}$$

**Ans. :** Total hardness = 571.42 ppm

Permanent hardness = 342.86 ppm

Temporary hardness = 228.56 ppm

**Problem 2.18.14 :** 0.5 gm of  $\text{CaCO}_3$  is dissolved in dilute HCl and diluted to 500 ml. This solution requires 24.0 ml of EDTA using Eriochrome Black-T indicator. 50 ml of hard water sample requires 22.5 ml of the same EDTA. 50 ml of the water sample after boiling and filtering requires 20 ml of the same EDTA. Calculate the hardness in the sample (permanent and temporary).

**Solution :** Here it is given that 0.5 gm of  $\text{CaCO}_3$  is dissolved in dilute HCl and diluted to 500 ml. This solution requires 24.0 ml of EDTA using Eriochrome Black-T indicator. 50 ml of hard water sample requires 22.5 ml of the same EDTA. 50 ml of the water sample after boiling and filtering requires 20 ml of the same EDTA.

i.e. 500 mgs of  $\text{CaCO}_3$  is dissolved in dilute HCl and diluted to 500 ml.

$$\begin{aligned} \text{That means } 1 \text{ ml of this water contains } 1 \text{ mg of } \text{CaCO}_3. \\ \text{Now, } 500 \text{ mgs of } \text{CaCO}_3 &\text{ is dissolved in dil. HCl and diluted to 500 ml.} \\ \text{That means } 1 \text{ ml of standard hard water or } 25 \times 1 \text{ mg. of } \text{CaCO}_3 &= 24 \text{ ml of EDTA} \end{aligned}$$

$$\begin{aligned}\therefore 1 \text{ ml of EDTA} &= \frac{25}{24} \text{ mg of CaCO}_3 \\ &= 1.04 \text{ mg of CaCO}_3 \\ &\text{50 ml of a hard water sample consumes } 22.5 \text{ ml EDTA} \\ &\equiv 22.5 \times 1.04 \text{ mg CaCO}_3 \text{ equivalents} \\ &\equiv 23.4 \text{ mg CaCO}_3 \text{ equivalents} \\ &\therefore 1000 \text{ ml water sample contain } \frac{23.4 \times 1000}{50} \text{ mgs equivalents of CaCO}_3 \\ &= 468 \text{ mg/l of CaCO}_3 \\ &\therefore \text{total hardness} = 468 \text{ ppm}\end{aligned}$$

**Problems 2.18.15:** 0.2 gm of  $\text{CaCO}_3$  was dissolved in dil. HCl and diluted to 200 ml. 50 ml of this solution required 48 ml of EDTA solution for titration. 50 ml of hard water sample required 15 ml of EDTA solution. 50 ml of same water sample on boiling filtering required 10 ml of EDTA. Calculate hardness in ppm.

**Solution:** Here, 0.2 gm of  $\text{CaCO}_3$  was dissolved in dil. HCl and diluted to 200 ml.

i.e. 200 mgs. of  $\text{CaCO}_3$  was dissolved in dil. HCl and diluted to 200 ml.

So the concentration of  $\text{CaCO}_3$  is 1 mg/ml

Now,

50 ml of standard hard water  $\Rightarrow$  48 ml of EDTA

i.e.  $50 \times 1 \text{ mg of CaCO}_3 \Rightarrow 48 \text{ ml of EDTA}$

1 ml of EDTA  $\Rightarrow$  50/48 mg of  $\text{CaCO}_3$  i.e. 1.04 mg of  $\text{CaCO}_3$

Now, 50 ml hard water  $\Rightarrow$  15 ml of EDTA solution

i.e.  $1000 \text{ ml of hard water contains } \frac{1000}{50} \times 15.6 \text{ mg of CaCO}_3$

$\therefore 1000 \text{ ml of hard water contains } = \frac{1000}{50} \times 15.6 \text{ mg of CaCO}_3$   
 $= 312 \text{ mg/lit} = 312 \text{ ppm}$

Now, after boiling and filtering the solution, the temporary hardness is removed. So only the permanent hardness remains.

50 ml of standard hard water (after boiling)  $\Rightarrow$  10 ml of EDTA  
i.e.  $\Rightarrow 10 \times 1.04 \text{ mg of CaCO}_3$ , i.e. 10.4 mg  $\text{CaCO}_3$   
 $\therefore 1000 \text{ ml of hard water contains } = \frac{1000}{50} \times 10.4 = 208 \text{ mg/l of CaCO}_3$

Temporary hardness = Total hardness - Permanent hardness

$= 468 - 416 = 52 \text{ ppm}$

**Ans. :** Total hardness = 468 ppm

$$\begin{aligned}\text{Permanent hardness} &= 416 \text{ ppm} \\ \text{Temporary hardness} &= 52 \text{ ppm} \\ \text{Total hardness} &= 468 \text{ ppm} \\ \text{Permanent hardness} &= 416 \text{ ppm} \\ \text{Temporary hardness} &= 52 \text{ ppm}\end{aligned}$$

**Problem 2.18.16:** 50 ml of standard hard water containing 1 mg of pure  $\text{CaCO}_3$  per ml consumes 20 ml of EDTA, 50 ml of water sample consumes 25 ml of EDTA using Eriochrome Black-T indicator, 50 ml of water sample after boiling and filtering requires 18 ml of EDTA using same indicator. Calculate temporary and permanent hardness.

**Solution :** Here, concentration of standard hard water is 1 mg  $\text{CaCO}_3/\text{ml}$ .

Now, 50 ml of standard hard water  $\Rightarrow$  20 ml of EDTA

i.e.  $50 \times 1 \text{ mg of } \text{CaCO}_3 \Rightarrow 20 \text{ ml of EDTA}$

$\therefore 1 \text{ ml of EDTA} \Rightarrow 2.5 \text{ mg of } \text{CaCO}_3$

$\because 50 \text{ ml of sample water} \Rightarrow 25 \text{ ml of EDTA}$

$$= 25 \times 2.5 \text{ mg of } \text{CaCO}_3$$

$$= 62.5 \text{ mg of } \text{CaCO}_3$$

$\therefore 1000 \text{ ml of sample hard water contains}$

$$62.5 \times \frac{1000}{50} = 1250 \text{ mg of } \text{CaCO}_3$$

$$= 1250 \text{ mg/l} = 1250 \text{ ppm}$$

Now, after boiling and filtering, the temporary hardness is removed so only the permanent hardness remains.

50 ml of sample hard water  $\Rightarrow$  18 ml of EDTA

(after boiling)  $= 18 \times 2.5 \text{ mgs of } \text{CaCO}_3$  equivalents

$\therefore 1000 \text{ ml of sample hard water contains}$

$$= 45 \times 20 \text{ mgs of } \text{CaCO}_3$$

$$= 900 \text{ mg/litre of } \text{CaCO}_3 = 900 \text{ ppm}$$

$\therefore \text{Temporary hardness} = 1250 - 900$

$$= 350 \text{ ppm}$$

**Ans. :**

Total hardness = 1250 ppm

Permanent hardness = 900 ppm

Temporary hardness = 350 ppm

**Problem 2.18.17:** Calculate total hardness, in ppm, in given water sample :

- 50 ml standard hard water, containing 1 mg pure  $\text{CaCO}_3$  per ml, consumed 20 ml EDTA solution.
- 50 ml water sample consumed 30 ml EDTA solution using Eriochrome Black-T indicator.

(May 2005, 4 Marks)

**Solution :**

Given data

$$\begin{aligned} \text{Quantity of std. hard water} &= 50 \text{ ml} \\ &\quad (1 \text{ mg/ml } \text{CaCO}_3 \text{ equivalent}) \end{aligned}$$

$$\text{Quantity of EDTA solution consumed by SHW} = 20 \text{ ml}$$

$$\text{Quantity of water sample} = 50 \text{ ml}$$

$$\text{Quantity of EDTA solution consumed by sample} = 30 \text{ ml}$$

Standardisation of EDTA

$$\therefore 20 \text{ ml EDTA solution} = 50 \text{ ml SHW}$$

$$\therefore 1 \text{ ml EDTA solution} = \frac{50}{20} \text{ ml SHW.}$$

$$= \frac{50}{20} \times 1 \text{ mgs } \text{CaCO}_3 \text{ equivalent}$$

Calculation of total hardness

$$\begin{aligned} \therefore 50 \text{ ml HW} &\approx 30 \text{ ml EDTA solution} \\ \therefore 1 \text{ ml HW} &\approx \frac{30}{50} \text{ ml EDTA solution} \end{aligned}$$

$$\approx \frac{30}{50} \times \frac{50}{20} \text{ mgs. } \text{CaCO}_3 \text{ equivalent}$$

$$\therefore 1000 \text{ ml. HW} \approx \frac{30}{50} \times \frac{50}{20} \times 1000 \text{ mgs. } \text{CaCO}_3 \text{ equivalent}$$

$$\therefore \text{Total hardness} = 1500 \text{ ppm}$$

**Ans. :** Total hardness = 1500 ppm

**Problem 2.18.18:** 50 ml of a standard hard water containing 1 mg of pure  $\text{CaCO}_3$  per ml consumed 20 ml of EDTA. 50 ml of a water sample consumed 25 ml of same EDTA solution using Eriochrome Black-T indicators. Calculate the total hardness of water sample in ppm.

**Solution:** Here, concentration of standard hard water is 1 mg/ml  $\text{CaCO}_3$ .

Now, 50 ml of standard hard water  $\Rightarrow$  20 ml of EDTA

i.e.  $50 \times 1 \text{ mg of } \text{CaCO}_3 \Rightarrow 20 \text{ ml of EDTA}$

$\therefore 1 \text{ ml of EDTA} = 2.5 \text{ mg of } \text{CaCO}_3$

Now, 50 ml of sample hard water  $\Rightarrow$  25 ml of EDTA

i.e.  $25 \times 2.5 = 62.5 \text{ mg } \text{CaCO}_3$

Total hardness present per litre  $= 62.5 \times \frac{1000}{50} \text{ mg/litre}$

$$= 62.5 \times 20 \text{ mg/litre} = 1250 \text{ mg/litre}$$

$$\therefore \text{Total hardness present per litre} = 1250 \text{ ppm}$$

**Ans.:** Total hardness = 1250 ppm

**Problem 2.18.19:** 0.28 gm of  $\text{CaCO}_3$  was dissolved in HCl and the solution made up to 1 litre with distilled water. 100 ml of the above solution required 28 ml of EDTA solution. 100 ml of hard water sample required 33 ml of EDTA solution. After boiling 100 ml of this water, cooling and filtering and then titration required 10 ml of EDTA solution. Calculate each type of hardness of water. (Dec. 2002)

**Solution:** Here 0.28 g of  $\text{CaCO}_3$  is dissolved and made up to 1000 ml.

Concentration of standard hard water = 0.28 mg/ml

$\therefore 100 \text{ ml SHW} = 28 \text{ mgs of } \text{CaCO}_3$  equivalents

Now 100 ml of unknown hard water requires 33 ml of EDTA

i.e. 100 ml of unknown hard water contains =  $33 \times 1 \text{ mgs of } \text{CaCO}_3$  equivalents

**Problem 2.18.20:** 50 ml of standard hard water containing 1 mg of pure  $\text{CaCO}_3$  per ml consumed 20 ml of EDTA. 50 ml of water sample consumed 25 ml of EDTA solution using Eriochrome Black-T indicator. 50 ml of water sample after boiling, filtering etc. consumed 18 ml of EDTA using Eriochrome Black-T indicator. Calculate the various types of hardness of the sample. (Dec. 2003)

**Solution:** Concentration of SHW = 1 mg/ml  $\text{CaCO}_3$

Quantity of SHW (1 mg/ml  $\text{CaCO}_3$ ) = 50 ml

Quantity of EDTA consumed by 50 ml SHW = 20 ml

Quantity of HW sample = 50 ml

**Solution :****Given data**

Quantity of EDTA consumed after boiling = 25 ml  
 Hardness = ?  
 1 ml SHW = 1 mg  $\text{CaCO}_3$  equivalent

**Standardisation of EDTA**

$$\begin{aligned} \therefore 20 \text{ ml EDTA solution} &= 50 \text{ ml SHW} = 50 \text{ mgs } \text{CaCO}_3 \text{ equivalent} \\ \therefore 1 \text{ ml EDTA solution} &= \frac{50}{20} \text{ mgs } \text{CaCO}_3 \text{ equivalent} \\ &= 2.5 \text{ mgs of } \text{CaCO}_3 \text{ equivalent} \\ 1 \text{ ml EDTA solution} &= 2.5 \text{ mgs of } \text{CaCO}_3 \text{ equivalent} \end{aligned}$$

**Calculation of total hardness**

$$\begin{aligned} \therefore 25 \text{ ml EDTA} &= 50 \text{ ml. HW} = 25 \times 2.5 \text{ mgs of } \text{CaCO}_3 \\ &= 62.5 \text{ mgs of } \text{CaCO}_3 \text{ in 50 ml} \\ \therefore \text{Per litre} &= 62.5 \times \frac{1000}{50} = 62.5 \times 20 = 1250 \text{ mgs of } \text{CaCO}_3 \\ \text{Now, 50 ml of water after boiling} &= 18 \text{ ml of EDTA} \\ \therefore \text{permanent Hardness} &= 18 \times 2.5 \text{ mgs of } \text{CaCO}_3 \\ &= 45 \text{ mgs of } \text{CaCO}_3 \\ \therefore \text{Per litre} &= 45 \times 20 = 900 \text{ mgs of } \text{CaCO}_3 \\ \therefore \text{Total hardness} &= 1250 \text{ ppm} \\ \therefore \text{Permanent hardness} &= 900 \text{ ppm} \\ \therefore \text{Temporary hardness} &= 350 \text{ ppm} \end{aligned}$$

**Problem 2.18.20(A) :** 50 ml of standard hard water (1.2 g  $\text{CaCO}_3$  / lit) requires 32 ml of EDTA solution. 100 ml of water sample consumes 14 ml EDTA solution. 100 ml of boiled and filtered water sample consumes 8.5 ml EDTA solution. Calculate temporary hardness of this sample from above experimental data.

(May 2007, 5 Marks)

Standard hardwater has 1.2 g i.e.  $1.2 \times 1000 = 120$  mgs. of  $\text{CaCO}_3$  equivalent H per lit.

$$\begin{aligned} &= 120 \text{ mgs / lit.} \\ &= \frac{120}{1000} = 0.12 \text{ mg/ml } \text{CaCO}_3 \text{ equivalent H} \\ \therefore 50 \text{ ml SHW} &= 50 \times 1.2 \text{ mg } \text{CaCO}_3 = 60 \text{ mgs } \text{CaCO}_3 \\ \therefore 32 \text{ ml EDTA} &= 50 \text{ ml SHW} = 60 \text{ mgs } \text{CaCO}_3 \\ 1 \text{ ml EDTA} &= \frac{60}{32} = 1.5 \text{ mgs of } \text{CaCO}_3 \text{ equivalent H} \end{aligned}$$

**Calculation of total Hardness**

$$\begin{aligned} 100 \text{ ml H.W sample} &= 14 \text{ ml EDTA} \\ &= 14 \times 1.5 \text{ mgs of HW per 100 ml of HW} \\ &= 0.21 \text{ mgs of } \text{CaCO}_3 \\ \therefore \text{Total H per litre} &= 210 \text{ mgs of } \text{CaCO}_3 \end{aligned}$$

**Calculation of permanent hardness**

$$\begin{aligned} \therefore 100 \text{ ml of boiled water} &= 8.5 \text{ ml of EDTA} \\ &= 8.5 \times 1.5 \text{ mgs of } \text{CaCO}_3 \text{ in 100 ml} \\ &= 0.1275 \text{ mgs of } \text{CaCO}_3 \\ \text{Hence per litre} &= 127.5 \text{ mgs of } \text{CaCO}_3 \\ \text{H temporary} &= \text{H total} - \text{H permanent} \end{aligned}$$

$$\begin{aligned} &= 210 - 127.5 \\ &= 83.5 \text{ mgs of CaCO}_3 \end{aligned}$$

$\therefore$  Total hardness = 210 ppm

$\therefore$  Permanent hardness = 127.5 ppm

$\therefore$  Temporary hardness = 83.5 ppm

**Problem 2.18.20(B) :** A standard hardware contains 15 gm/l calcium carbonate. 20 ml of this water required 25 ml of EDTA solution. 100 ml of sample water required 18 ml of EDTA solution. Calculate temporary hardness of water.

(May 2008, 6 Marks)

**Solution :**

$$\begin{aligned} \text{Given :} \quad &\text{Concentration of SHW} = 15 \text{ g/lit} \\ &= 15000 \text{ mg / 1000 ml} \\ &= 15 \text{ mg/ml} \end{aligned}$$

$$\text{Volume of std water} = 20 \text{ ml}$$

$$\text{Volume of EDTA for SHW} = 25 \text{ ml} = V_1$$

$$\text{Volume of water sample} = 100 \text{ ml}$$

$$\text{Volume of EDTA for sample} = 18 \text{ ml} = V_2$$

$$\text{Volume of water sample (after boiling)} = 100 \text{ ml}$$

$$\text{Volume of EDTA for sample (after boiling)} = 12 \text{ ml} = V_3$$

$$\therefore 20 \text{ ml SHW} = 25 \text{ ml EDTA soln.}$$

$$\therefore 1 \text{ ml EDTA} = \left[ \frac{20}{25} \times 15 \right] \text{ mgs of CaCO}_3 \text{ Equation hardness}$$

$$= \frac{300}{25} \text{ mgs of CaCO}_3 \text{ Equation hardness}$$

$$= 12 \text{ mgs of CaCO}_3 \text{ Equation hardness}$$

Now,

$$100 \text{ ml water sample} = 18 \text{ ml EDTA solution}$$

$$= [18 \times 12] \text{ mgs of CaCO}_3 \text{ Equation hardness}$$

$$= 216 \text{ mgs of CaCO}_3 \text{ Equation hardness}$$

$$\begin{aligned} \text{New,} \quad &100 \text{ ml. water sample (after boiling)} = 12 \text{ ml. EDTA solution} \\ &\quad \equiv [12 \times 12] \text{ mgs of CaCO}_3 \text{ Equation hardness} \\ &\quad \therefore \text{per liter} = 1440 \text{ ppm.} \\ &\quad \therefore \text{permanent Hardness} = 1440 \text{ ppm.} \\ &\quad \therefore \text{Temporary Hardness} = 2160 - 1440 = 720 \text{ ppm.} \end{aligned}$$

Ans.

$$\text{Permanent Hardness} = 720 \text{ ppm.}$$

$$\text{Temporary Hardness} = 1440 \text{ ppm.}$$

### 2.18.3 Problems based on Lime Soda Process

Hints for solving numerical problems based on lime soda process.

- All the impurities consuming lime and/or soda, are to be converted in  $\text{CaCO}_3$  equivalents per litre.
- The impurities such as  $\text{NaCl}$ ,  $\text{KCl}$ ,  $\text{SiO}_2$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{Na}_2\text{SO}_4$  etc. should be ignored as they do not consume lime and soda.
- $\text{CaCO}_3$  or  $\text{MgCO}_3$  etc. should be considered as temporary hardness, due to bicarbonates of calcium and/or magnesium and to be taken for lime calculations only.
- The quantity of  $\text{Mg}(\text{HCO}_3)_2$  in terms of  $\text{CaCO}_3$  equivalents to be taken double, for calculations.
- If  $\text{NaHCO}_3$  or  $\text{KHCO}_3$  is present in water, then their  $\text{CaCO}_3$  equivalents per litre should be subtracted from soda calculations.
- Coagulants like sodium aluminate, aluminium chloride, aluminium sulphate etc. if used, their  $\text{CaCO}_3$  equivalents per litre should be calculated and taken into account as,

For  $\text{NaAlO}_2$  : Subtract from lime  
For  $\text{AlCl}_3, \text{Al}_2(\text{SO}_4)_3$  : Add in lime and soda both

Table 2.18.1

S.No	Constituent (s)	Reactions	Need
1.	$\text{Ca}(\text{HCO}_3)_2$ (Temp. Ca)	$\text{Ca}(\text{HCO}_3)_2 + \text{Ca}(\text{OH})_2 \rightarrow 2\text{CaCO}_3 \downarrow + \text{H}_2\text{O}$	L
2.	$\text{Mg}(\text{HCO}_3)_2$ (Temp. Mg)	$\text{Mg}(\text{HCO}_3)_2 + 2\text{Ca}(\text{OH})_2 \rightarrow 2\text{CaCO}_3 \downarrow + \text{Mg}(\text{OH})_2 + 2\text{H}_2\text{O}$	2L
3.	$\text{Mg}^{2+}$ (Perm. Mg from Mg Cl <sub>2</sub> or Mg SO <sub>4</sub> )	$\text{Mg}^{2+} + \text{Ca}(\text{OH})_2 \rightarrow \text{Mg}(\text{OH})_2 \downarrow + \text{Ca}^{2+}$ $\text{Ca}^{2+} + \text{Na}_2\text{CO}_3 \rightarrow \text{CaCO}_3 \downarrow + 2\text{Na}^+$ $\text{MgCl}_2 + \text{Ca}(\text{OH})_2 \rightarrow \text{Mg}(\text{OH})_2 \downarrow + \text{CaCl}_2$ $\text{CaCl}_2 + \text{Na}_2\text{CO}_3 \rightarrow \text{CaCO}_3 \downarrow + 2\text{NaCl}$ $\text{MgSO}_4 + \text{Ca}(\text{OH})_2 \rightarrow \text{Mg}(\text{OH})_2 \downarrow + \text{CaSO}_4$ $\text{CaSO}_4 + \text{Na}_2\text{CO}_3 \rightarrow \text{CaCO}_3 \downarrow + \text{H}_2\text{O} + \text{Na}_2\text{SO}_4$	L S (L + S) (L + S) (L + S)
4.	$\text{HCO}_3^-$ (e.g. NaHCO <sub>3</sub> )	$2\text{NaHCO}_3 + \text{Ca}(\text{OH})_2 \rightarrow \text{CaCO}_3 \downarrow + 2\text{Na}_2\text{O} + \text{Na}_2\text{CO}_3$	+ L - S
5.	$\text{Ca}^{2+}$ Ca <sub>3</sub> (Perm. Ca From CaCl <sub>2</sub> or CaSO <sub>4</sub> )	$\text{Ca}^{2+} + \text{Na}_2\text{CO}_3 \rightarrow \text{CaCO}_3 \downarrow + 2\text{Na}^+$ $\text{CaCl}_2 + \text{Na}_2\text{CO}_3 \rightarrow \text{CaCO}_3 \downarrow + 2\text{NaCl}$ $\text{CaSO}_4 + \text{Na}_2\text{CO}_3 \rightarrow \text{CaCO}_3 \downarrow + \text{Na}_2\text{SO}_4$	S S S
6.	$\text{CO}_2$	$\text{CO}_2 + \text{Ca}(\text{OH})_2 \rightarrow \text{Ca}^{2+} + 2\text{H}_2\text{O}$	L
7.	$\text{H}^+$ (free acids like HCl, H <sub>2</sub> SO <sub>4</sub> etc.)	$2\text{H}^+ + \text{Ca}(\text{OH})_2 \rightarrow \text{Ca}^{2+} + 2\text{H}_2\text{O}$ $\text{Ca}^{2+} + \text{Na}_2\text{CO}_3 \rightarrow \text{CaCO}_3 \downarrow + 2\text{Na}^+$ $2\text{HCl} + \text{Ca}(\text{OH})_2 \rightarrow \text{CaCl}_2 + 2\text{H}_2\text{O}$ $\text{H}_2\text{SO}_4 + \text{Ca}(\text{OH})_2 \rightarrow \text{CaSO}_4 + 2\text{H}_2\text{O}$ $\text{CaCl}_2 + \text{Na}_2\text{CO}_3 \rightarrow \text{CaCO}_3 \downarrow + \text{NaCl}$ $\text{CaSO}_4 + \text{Na}_2\text{CO}_3 \rightarrow \text{CaCO}_3 \downarrow + \text{NaSO}_4$	(L + S) L L S S

Note : Aluminium and iron salt may be present in water and they contribute to the permanent hardness or they may be added as coagulants.

Salt	Qty mg/lit	Mol. Wt.	Multiplication factor per lime	CaCO <sub>3</sub> equivalent of Lime (L) and Soda (S)	Requirement of Lime (L) and Soda (S)
CaCl <sub>2</sub>	55.5	111	$55.5 \times \frac{100}{111}$	50	S
SiO <sub>2</sub>	20	60	Does not react with lime/soda	-	-
NaHCO <sub>3</sub>	12.6	84	$12.6 \times \frac{100}{(84 \times 2)}$	7.5	Add in L Subtract in S.
KCl	250	74.5	Does not react	-	-
MgSO <sub>4</sub>	48	120	$48 \times \frac{100}{120}$	40	L + S
CO <sub>2</sub>	2.2	44	$2.2 \times \frac{100}{44}$	5	L
Mg(HCO <sub>3</sub> ) <sub>2</sub>	43.8	146	$43.8 \times \frac{100}{146}$	30	L
Fe <sup>++</sup>	2	55.8	$2 \times \frac{100}{55.8}$	3.58	L + S
AlCl <sub>3</sub>	10	133.5	$10 \times \frac{100}{133.5}$	7.5	L + S

**Problem 2.18.21:** Water sample was found to contain following salts.  
 $\text{CaCl}_2 = 55.5 \text{ mg/l}$   
 $\text{NaHCO}_3 = 12.6 \text{ mg/l}$   
 $\text{MgSO}_4 = 48 \text{ mg/l}$   
 $\text{Fe}^{++} = 2 \text{ ppm}$   
 $\text{AlCl}_3 = 10 \text{ ppm}$   
 $\text{Mg}(\text{HCO}_3)_2 = 43.8 \text{ mg/l}$   
Calculate the quantity of lime (85 % pure) and soda (95 % pure) for softening 50,000 litres of water.

**Solution :**  
**Calculation of CaCO<sub>3</sub> equivalents for impurities**

➤ Calculation of quantity of lime in grams, required for softening of water]

#### Lime requirements

$$L = \frac{74}{100} [Temporary Ca^{+2} + 2 \times Temporary Mg^{+2} + Permanent (Mg^{+2} + Fe^{+2} + Al^{+3} + H^+) (HCl \text{ or } H_2SO_4) + HCO_3^- - NaAlO_2] \times \frac{\text{Vol. of Water}}{10^6} \times \frac{100}{\% \text{ of purity}} \text{ kg}$$

all in term of their  $CaCO_3$  equivalents.

$$\begin{aligned} &= \frac{74}{100} [CaCO_3 \text{ equivalents of } (MgSO_4)^+ + 2 [Mg(HCO_3)_2] + NaHCO_3 + CO_2] \times \frac{\text{Litres of water} \times 100}{10^6 \times \% \text{ purity of lime}} \text{ kg} \\ &= \frac{74}{100} [40 + (30 \times 2) + 7.5 + 5 + 7.5 + 3.58] \times \frac{50000 \times 100}{10^6 \times 85} \text{ kg} \\ &= \frac{74}{100} [40 + 60 + 7.5 + 5 + 7.5 + 3.58] \times \frac{5}{85} \text{ kg} \\ &= 5.379 \text{ kgs of lime} \end{aligned}$$

➤ Calculation of quantity of soda required for softening and its cost

#### Soda requirements

$$S = \frac{106}{100} [Permanent (Ca^{+2} + Mg^{+2} + Al^{+3} + Fe^{+2} + H^+) (HCl \text{ or } H_2SO_4) - HCO_3^-] \times \frac{\text{Vol. of Water}}{10^6} \times \frac{100}{\% \text{ of purity}} \text{ kg}$$

all in term of their  $CaCO_3$  equivalents.

$$\begin{aligned} &= \frac{106}{100} [CaCO_3 \text{ equivalents of } CaCl_2 + MgSO_4] \times \frac{\text{Litres of water} \times 100}{10^6 \times \% \text{ purity of soda}} \text{ kg} \\ &= \frac{106}{100} [ + Fe^{+2} + AlCl_3 - NaHCO_3] \times \frac{50000 \times 100}{10^6 \times 95} \text{ kg} \\ &= \frac{106}{100} [50 + 40 + 3.58 + 7.5 - 7.5] \times \frac{50000 \times 100}{10^6 \times 95} \text{ kg} \\ &= \frac{106}{100} [93.58] \times \frac{5000}{95} \\ &= 5.2207 \text{ kgs} \end{aligned}$$

➤ Calculation of quantity of lime in grams, required for softening of water

#### Lime required

$$L = \frac{74}{100} [Temporary Ca^{+2} + 2 \times Temporary Mg^{+2} + Permanent (Mg^{+2} + Fe^{+2} + Al^{+3} + H^+) (HCl \text{ or } H_2SO_4) + HCO_3^- - NaAlO_2] \times \frac{\text{Vol. of Water}}{10^6} \times \frac{100}{\% \text{ of purity}} \text{ kg}$$

all in term of their  $CaCO_3$  equivalents.

$$\begin{aligned} &= \frac{74}{100} [MgCl_2 + HCl \text{ as their } CaCO_3 \text{ equivalents}] \times \frac{\text{Litres of water} \times 100}{10^6 \times \% \text{ purity of lime}} \text{ kg} \\ &= \frac{74}{100} [10 + 10] \times \frac{80000 \times 100}{10^6 \times 85} \text{ kg} = \frac{74}{100} [20] \frac{8}{85} \\ &= 1.392 \text{ kgs} \\ &\text{Cost} = 1.392 \text{ kgs} \times \text{Rs. 9} \\ &= \text{Rs. 12.53} \end{aligned}$$

➤ Calculation of quantity of soda required for softening and its cost

#### Soda requirements

$$S = \frac{106}{100} [Permanent (Ca^{+2} + Mg^{+2} + Al^{+3} + Fe^{+2} + H^+) (HCl \text{ or } H_2SO_4) - HCO_3^-] \times \frac{\text{Vol. of Water}}{10^6} \times \frac{100}{\% \text{ of purity}} \text{ kg}$$

all in term of their  $CaCO_3$  equivalents.

Ans. : Soda required = 5.379 kgs

Lime required = 5.2207 kgs

#### Solution :

#### ➤ Calculation of $CaCO_3$ equivalents for impurities

Salt/ chemical	Qty. in mg/lit	Mol. Wt.	Multiplication factor	$CaCO_3$ equivalents	Requirement of Lime (L) and / or Soda (S)
CaSO <sub>4</sub>	20.4	136	$20.4 \times \frac{100}{136}$	15	S
MgCl <sub>2</sub>	9.5	95	$9.5 \times \frac{100}{95}$	10	L + S
HCl	7.3	36.5	$7.3 \times \frac{100}{73}$	10	L + S

➤ Calculation of the amount of lime (85 % pure) and soda (80 % pure) required to soften 80,000 litres of water. What would be the total cost of chemicals if lime and soda are Rs. 9 and Rs. 35 per kg.

$CaSO_4 = 20.4; MgCl_2 = 9.5; HCl = 7.3$

Calculate the amount of lime (85 % pure) and soda (80 % pure) required to

$$\begin{aligned}
 &= \frac{106}{100} \left[ \text{MgCl}_2 + \text{CaSO}_4 + \text{HCl} \text{ as their CaCO}_3 \text{ equivalents} \right] \times \frac{\text{Litres of water} \times 100}{10^6 \times \% \text{ purity of soda kg}} \\
 &= \frac{106}{100} [10 + 15 + 10] \frac{80000 \times 100}{10^6 \times 80} \text{ kg} \\
 &= 3.71 \text{ kgs}
 \end{aligned}$$

$$\text{Cost} = 3.71 \text{ kgs} \times \text{Rs. } 35$$

$$= \text{Rs. } 129.35$$

**Ans. :** Lime required = 1.392 kgs;

**Cost of lime** = **Rs. 12.53;**

**Soda required** = 3.71 kgs

**Cost of soda** = **Rs. 129.35**

**Problem 2.18.23 :** Calculate the quantities of lime (85 % pure) and soda (90 % pure) required to

soften 1,00,000 litres of hard water containing following impurities.

$$\begin{aligned}
 \text{CaSO}_4 &= 27.2 \text{ mgs/lit.}; & \text{MgCl}_2 &= 47.5 \text{ mgs/lit.}; \\
 \text{MgSO}_4 &= 24 \text{ mgs/lit.}; & \text{CO}_2 &= 2.2 \text{ mgs/lit.}; \\
 \text{CaCl}_2 &= 11.1 \text{ mgs/lit.}; & \text{HCl} &= 1.825 \text{ mgs/lit.}; \\
 \text{AlCl}_3 &= 13.35 \text{ mgs/lit.}
 \end{aligned}$$

**Solution:**

> Calculation of CaCO<sub>3</sub> equivalents for impurities

Salt	Qty mg/lit	Mol. Wt.	Multiplication factor	CaCO <sub>3</sub> equivalent ppm	Requirement of Lime (L) and / or Soda (S)
CaSO <sub>4</sub>	27.2	136	$27.2 \times \frac{100}{136}$	20	S
MgSO <sub>4</sub>	24.0	120	$24 \times \frac{100}{120}$	20	L + S
CaCl <sub>2</sub>	11.1	111	$11.1 \times \frac{100}{111}$	10	S
MgCl <sub>2</sub>	47.5	95	$47.5 \times \frac{100}{95}$	50	L + S
CO <sub>2</sub>	2.2	44	$2.2 \times \frac{100}{44}$	05	L
HCl	1.825	36.5	$1.825 \times \frac{100}{73}$	2.5	L + S
AlCl <sub>3</sub>	13.35	133.5	$13.35 \times \frac{100}{133.5}$	10	L + S

#### > Calculation of quantity of lime in grams, required for softening of water

##### Lime requirements

$$L = \frac{74}{100} \int \text{Temporary Ca}^{+2} + 2 \times \text{Temporary Mg}^{+2} + \text{Permanent (Mg}^{+2} + \text{Fe}^{+2} + \text{Al}^{+3} + \text{H}^+ \text{ (HCl or H}_2\text{SO}_4\text{)}) + \text{HCO}_3^- - \text{NaAlO}_2 \text{)} \times \frac{\text{Vol. of Water}}{10^6} \times \frac{100}{10^6 \times \% \text{ of purity/kg}}$$

all in term of their CaCO<sub>3</sub> equivalents.

$$\begin{aligned}
 &= \frac{74}{100} \left[ \text{CaCO}_3 \text{ equivalents of MgSO}_4 + \text{CaCO}_3 \text{ equivalents of MgCl}_2 + \text{CaCO}_3 \text{ equivalents of AlCl}_3 \right] \times \frac{\text{Litres of water} \times 100}{10^6 \times \% \text{ purity of lime kg}} \\
 &= \frac{74}{100} [20 + 50 + 05 + 2.5 + 10] \frac{100000 \times 100}{10^6 \times 85} \text{ kg} \\
 &= \frac{74}{100} [87.5] \frac{10}{85} \text{ kg} \\
 &= 7.617 \text{ kgs}
 \end{aligned}$$

> Calculation of quantity of soda required for softening and its cost

##### Soda requirements

$$\begin{aligned}
 S &= \frac{106}{100} \int \text{Permanent (Ca}^{+2} + \text{Mg}^{+2} + \text{Al}^{+3} + \text{Fe}^{+2} + \text{H}^+ \text{ (HCl or H}_2\text{SO}_4\text{)}) - \text{HCO}_3^- \text{)} \times \frac{\text{Vol. of Water}}{10^6} \times \frac{100}{10^6 \times \% \text{ of purity/kg}}
 \end{aligned}$$

all in term of their CaCO<sub>3</sub> equivalents.

$$\begin{aligned}
 &= \frac{106}{100} \left[ \text{CaCO}_3 \text{ equivalents of CaSO}_4 + \text{CaCO}_3 \text{ equivalents of MgSO}_4 \right] \times \frac{\text{Litres of water} \times 100}{10^6 \times \% \text{ purity of soda kg}} \\
 &= \frac{106}{100} [20 + 20 + 10 + 50 + 2.5 + 10] \frac{100000 \times 100}{10^6 \times 90} \text{ kg} \\
 &= \frac{106}{100} [112.5] \frac{1}{9} \\
 &= 13.25 \text{ kgs of soda}
 \end{aligned}$$

**Ans. :** Lime required = 7.617 kgs

**Soda required** = 13.25 kgs

**Problem 2.18.24:** A sample of water was found to contain following salts :

$$\text{CaCO}_3 = 50 \text{ ppm.};$$

$$\text{Fe}_2\text{O}_3 = 20 \text{ ppm.};$$

$$\text{MgCO}_3 = 14.4 \text{ ppm.};$$

$$\text{Na}_2\text{SO}_4 = 20 \text{ ppm.};$$

$$\text{CaCl}_2 = 22.2 \text{ ppm.};$$

$$\text{SiO}_2 = 5 \text{ ppm.};$$

$$\text{MgCl}_2 = 9.5 \text{ ppm.};$$

$$\text{CO}_2 = 2.2 \text{ ppm.}$$

Calculate the amount of lime and soda required for softening 7500 litres of above water.

**Solution :**

➤ Calculation of  $\text{CaCO}_3$  equivalents for impurities

Salt	Qty in ppm	Mol. wt.	Multiplication factor	$\text{CaCO}_3$ equivalent ppm	Requirement of Lime (L) and / or Soda (S)
1. $\text{CaSO}_4$	50	100	$50 \times \frac{100}{100}$	50	S
2. $\text{MgCO}_3$	14.4	84	$14.4 \times \frac{100}{84}$	17.14	L
3. $\text{CaCl}_2$	22.2	111	$22.2 \times \frac{100}{111}$	20	S
4. $\text{MgCl}_2$	9.5	95	$9.5 \times \frac{100}{95}$	10	L + S
5. $\text{Fe}_2\text{O}_3$	20	Do not react with lime and soda both			
6. $\text{Na}_2\text{SO}_4$	20				
7. $\text{SiO}_2$	5				
8. $\text{CO}_2$	2.2	44	$2.2 \times \frac{100}{44}$	5	L

➤ Calculation of quantity of lime in grams, required for softening of water

#### Lime requirement

$$L = \frac{74}{100} \left[ \text{Temporary } \text{Ca}^{+2} + 2 \times \text{Temporary } \text{Mg}^{+2} + \text{Permanent } (\text{Mg}^{+2} + \text{Fe}^{+2} + \text{Al}^{+3} + \text{H}^+) \right. \\ \left. (\text{HCl or H}_2\text{SO}_4) + \text{HCO}_3^- - \text{NaAlO}_2 \right] \times \frac{\text{Vol. of Water}}{10^6} \times \frac{100}{\% \text{ of purity}} \text{ kg}$$

all in term of their  $\text{CaCO}_3$  equivalents.

$$= \frac{74}{100} \left[ \text{CaCO}_3 \text{ equivalents of } 2[\text{MgCO}_3] + \right] \times \frac{\text{Litres of water} \times 100}{10^6 \times \% \text{ Purity of lime}} \text{ kg}$$

$$= \frac{74}{100} [(2 \times 17.14) + 50 + 10 + 5] \times \frac{75000 \times 100}{10^6 \times 100} \text{ kg}$$

$$= \frac{74}{100} [99.28] \times \frac{75}{1000} \\ = 5.510 \text{ kgs of lime}$$

➤ Calculation of quantity of soda required for softening and its cost

#### Soda requirement

$$S = \frac{106}{100} \left[ \text{Permanent } (\text{Ca}^{+2} + \text{Mg}^{+2} + \text{Al}^{+3} + \text{Fe}^{+2} + \text{H}^+) (\text{HCl or H}_2\text{SO}_4) - \text{HCO}_3^- \right] \\ \times \frac{\text{Vol. of Water}}{10^6} \times \frac{100}{\% \text{ of purity}} \text{ kg}$$

all in term of their  $\text{CaCO}_3$  equivalents.

$$= \frac{106}{100} [\text{CaCO}_3 \text{ equivalents of } \text{CaCl}_2] \times \frac{75000}{10^6} \times \frac{100}{100} \text{ kg} \\ = \frac{106}{100} [20 + 10] \times \frac{75}{1000} \text{ kg}$$

$$= 2.385 \text{ kgs of soda}$$

Ans. : Soda required = 2.385 kgs

Lime required = 5.51004 kgs

**Problem 2.18.25:** 25000 litres of hard water containing following ions/chemicals are to be softened by lime soda process. Calculate the quantities of lime and soda (90 % pure each) required. Express the answers in kgs.

$$\text{Ca}^{++} = 30 \text{ ppm};$$

$$\text{Mg}^{++} = 21.6 \text{ ppm};$$

$$\text{CO}_2 = 4.4 \text{ ppm};$$

$$\text{H}_2\text{SO}_4 = 4.9 \text{ ppm}.$$

Calculate the cost of chemicals if lime is Rs. 7 per kg and soda is Rs. 35 per kg.

**Solution:**

➤ Calculation of  $\text{CaCO}_3$  equivalents for impurities

Impurity	Qty in ppm	Mol. wt./ionic wt.	Multiplication factor	$\text{CaCO}_3$ equivalent	Requirement of Lime (L) and / or Soda (S)
1. $\text{Ca}^{++}$	30	40	$30 \times \frac{100}{40}$	75	S
2. $\text{Mg}^{++}$	21.6	24	$21.6 \times \frac{100}{24}$	90	L + S
3. $\text{HCO}_3^-$	12.2	61	$12.2 \times \frac{100}{2 \times 61}$	10	Add in Lime (L), Subtract from Soda (S)
4. $\text{CO}_2$	4.4	44	$4.4 \times \frac{100}{44}$	10	L
5. $\text{H}_2\text{SO}_4$	4.9	98	$4.9 \times \frac{100}{98}$	05	L + S

➤ Calculation of quantity of lime in grams, required for softening of water

Quantity of lime

$$L = \frac{74}{100} \left[ \text{Temporary } \text{Ca}^{++} + 2 \times \text{Temporary } \text{Mg}^{++} + \text{Permanent } (\text{Mg}^{++} + \text{Fe}^{++} + \text{Al}^{++}) + \text{H}^+ \right] \times \frac{\text{Vol. of Water}}{10^6} \times \frac{100}{\% \text{ of purity}} \text{ kg}$$

$$(HCl \text{ or } H_2\text{SO}_4) + \text{HCO}_3^- - \text{NaAlO}_2$$

all in term of their  $\text{CaCO}_3$  equivalents.

$$= \frac{74}{100} \left[ \text{CaCO}_3 \text{ equivalents of Mg}^{++} \right] \times 10^6 \times \% \text{ purity of lime kg}$$

$$= \frac{74}{100} [90 + 10 + 10 + 05] \frac{25000 \times 100}{10^6 \times 90} \text{ kg}$$

$$= \frac{74}{100} [115] \frac{250}{900}$$

$$= 2.3638 \text{ kg of lime}$$

$$\therefore \text{cost of lime} = 2.3638 \times 7$$

$$= \text{Rs. 16.54}$$

➤ Calculation of quantity of soda required for softening and its cost

Quantity of soda

$$S = \frac{106}{100} \left[ \text{Permanent } (\text{Ca}^{++} + \text{Mg}^{++} + \text{Al}^{++} + \text{Fe}^{++} + \text{H}^+) (HCl \text{ or } H_2\text{SO}_4) - \text{HCO}_3^- \right]$$

$$\times \frac{\text{Vol. of Water}}{10^6} \times \frac{100}{\% \text{ of purity}} \text{ kg}$$

all in term of their  $\text{CaCO}_3$  equivalents.

$$= \frac{106}{100} [\text{CaCO}_3 \text{ equivalents of Ca}^{++} + \dots]$$

$$= \frac{106}{100} [\text{Mg}^{++} + \text{H}_2\text{SO}_4 - \text{HCO}_3^-]$$

$$= \frac{106}{100} [75 + 90 + 05 - 10] \frac{25000 \times 100}{10^6 \times 90}$$

$$= \frac{106}{100} [160] \frac{250}{900}$$

$$= 4.7111 \text{ kg of soda}$$

$\therefore \text{Cost of soda} = 4.7111 \text{ kg} \times 35 = \text{Rs. 164.88}$

Ans.: Quantity of lime required = 2.3638 kg

Quantity of soda required = 4.7111 kg

Cost of lime = Rs. 16.54

Cost of soda = Rs. 164.88

**Problem 2.18.26:** 40,000 litres of water is to be softened. On analysis the water is found to contain following impurities.

$$CaCO_3 = 0.03 \text{ gms};$$

$$MgCO_3 = 0.09 \text{ gms};$$

$$MgSO_4 = 0.035 \text{ gms};$$

$$NaCl = 0.12 \text{ gms};$$

$$CaSO_4 = 0.025 \text{ gms}.$$

Lime is 89 % pure and soda is 92 % pure.

**Solution :**

> Calculation of  $CaCO_3$  equivalents for impurities

Salt/Impurity	Qty in mgs/ltrs	Mol. wt.	Multiplication factor	$CaCO_3$ equivalent ppm	Requirement of Lime (L) and / or Soda (S)
1. $CaCO_3$	30	100	$30 \times \frac{100}{100}$	30	L
2. $MgCO_3$	90	84	$90 \times \frac{100}{84}$	107.14	L
3. $MgCl_2$	160	95	$160 \times \frac{100}{95}$	168.42	L + S
4. $MgSO_4$	35	120	$35 \times \frac{100}{120}$	29.17	L + S
5. $CaSO_4$	25	136	$25 \times \frac{100}{136}$	18.38	S
6. $NaCl$	120	58.5	$120 \times \frac{100}{58.5}$	205.13	-

$NaCl$  does not contribute to hardness. Hence, it is not to be taken in calculation for lime and soda.

> Calculation of quantity of lime in grams, required for softening of water

Quantity of lime

$$L = \frac{74}{100} \left[ Temporary Ca^{+2} + 2 \times Temporary Mg^{+2} + Permanent (Mg^{+2} + Fe^{+2} + Al^{+3} + H^+) \right] \times \frac{Vol. of Water}{10^6} \times \frac{100}{\% \text{ of purity}} \text{ kg}$$

$$(HCl \text{ or } H_2SO_4) + HCO_3^- - NaAlO_2 \right] \times \frac{Vol. of Water}{10^6} \times \frac{100}{\% \text{ of purity}} \text{ kg}$$

all in term of their  $CaCO_3$  equivalents.

$$= \frac{74}{100} \left[ CaCO_3 \text{ equivalents of } CaCO_3 + MgSO_4 + MgCl_2 + 2 \times MgCO_3 \right] \times \frac{\text{Litres of water} \times 100}{10^6 \times \% \text{ purity of lime}} \text{ kg}$$

$$= \frac{74}{100} [30 + 29.17 + 168.42 + 2 \times 107.14] \frac{40000 \times 100}{10^6 \times 89} \text{ kg}$$

$$= \frac{74}{100} [441.87] \frac{4}{89}$$

$$= 14.695 \text{ kg of lime}$$

> Calculation of quantity of soda required for softening and its cost

Quantity of soda

$$S = \frac{106}{100} \left[ Permanent (Ca^{+2} + Mg^{+2} + Al^{+3} + Fe^{+2} + H^+ (HCl \text{ or } H_2SO_4)) - HCO_3^- \right] \times \frac{Vol. of Water}{10^6} \times \frac{100}{\% \text{ of purity}} \text{ kg}$$

all in term of their  $CaCO_3$  equivalents.

$$= \frac{106}{100} [CaCO_3 \text{ equivalents of } MgCl_2 + MgSO_4 + CaSO_4] \times \frac{\text{Litres of water} \times 100}{10^6 \times \% \text{ purity of soda}} \text{ kg}$$

$$= \frac{106}{100} [168.42 + 29.17 + 18.38] \frac{40000 \times 100}{10^6 \times 92} \text{ kg}$$

$$= \frac{106}{100} [215.99] \frac{4}{92}$$

$$= 9.954 \text{ kg of soda}$$

**Ans.:** Quantity of lime required = 14.695 kgs  
Quantity of soda required = 9.954 kgs

**Problem 2.18.27:** Calculate the quantities of lime and soda (90 % pure each) required to soften 85000 litres of water having following data.

$$CaCO_3 = 2.1 \text{ Clarke};$$

$$MgSO_4 = 0.21 \text{ Clarke};$$

$$CaSO_4 = 0.35 \text{ Clarke};$$

$$MgCl_2 = 0.63 \text{ Clarke};$$

$$KCl = 0.035 \text{ Clarke}$$

**Solution :****> Calculation of CaCO<sub>3</sub> equivalents for impurities**

Salt/Impurity	Qty in °Clarke	Conversion in ppm	Multiplication factor	CaCO <sub>3</sub> equivalent ppm	Requirement of Lime (L) and / or Soda (S)
CaCO <sub>3</sub>	2.1	0.07 °Clarke = 1 ppm	$\frac{2.1}{0.07} \times \frac{100}{100}$	30	L
MgCO <sub>3</sub>	0.63 = 1 ppm	0.07 °Clarke = 1 ppm	$\frac{0.63}{0.07} \times \frac{100}{84}$	10.71	L
CaSO <sub>4</sub>	0.35	0.07 °Clarke = 1 ppm	$\frac{0.35}{0.07} \times \frac{100}{136}$	3.676	S
MgSO <sub>4</sub>	0.21 = 1 ppm	0.07 °Clarke = 1 ppm	$\frac{0.21}{0.07} \times \frac{100}{120}$	2.50	L+S
MgCl <sub>2</sub>	0.063 = 1 ppm	0.07 °Clarke = 1 ppm	$\frac{0.063}{0.07} \times \frac{100}{95}$	0.947	L+S
KCl	0.035 = 1 ppm	0.07 °Clarke = 1 ppm	$\frac{0.035}{0.07} \times \frac{100}{74.6}$	0.670	-

Note : KCl should be ignored as it does not contribute to hardness.

**> Calculation of quantity of lime in grams required to soften 85000 litres of water.****Quantity of lime**

$$L = \frac{74}{100} \left[ \text{Temporary } Ca^{2+} + 2 \times \text{Temporary } Mg^{2+} + \text{Permanent } (Mg^{2+} + Fe^{2+} + Al^{3+} + H^+) \right]$$

$$(HCl \text{ or } H_2SO_4) + HCO_3^- - NaAlO_2 \right] \times \frac{\text{Vol. of Water}}{10^6} \times \frac{100}{\% \text{ of purity}} \text{ kg}$$

all in term of their CaCO<sub>3</sub> equivalents.

$$\begin{aligned} S &= \frac{106}{100} \left[ \text{Permanent } (Ca^{2+} + Mg^{2+} + Al^{3+} + Fe^{2+} + H^+ (HCl \text{ or } H_2SO_4)) - HCO_3^- \right] \\ &\quad \times \frac{\text{Vol. of Water}}{10^6} \times \frac{100}{\% \text{ of purity}} \text{ kg} \\ &= \frac{106}{100} [CaCO_3 \text{ equivalents of } CaSO_4] \times \frac{\text{Litres of water} \times 100}{10^6 \times \% \text{ purity of soda}} \text{ kg} \\ &= \frac{106}{100} [3.676 + 2.5 + 0.947] \times \frac{85000 \times 100}{10^6 \times 90} \text{ kg} \\ &= \frac{106}{100} [7.123] \times \frac{850}{900} \\ &= 0.713 \text{ kgs of soda} \end{aligned}$$

Ans. : Quantity of lime required = 0.713 kg

Quantity of soda required = 0.713 kg

**Problem 2.18.28 :** Calculate the quantities of lime (89 % pure) and soda (95 % pure) required for softening 20,000 litre water having following analysis.

$$\begin{aligned} HCl &= 14.5 \text{ mgs/litre} \\ MgCl_2 &= 9.5 \text{ mgs/litre} \\ Al_2(SO_4)_3 &= 34.2 \text{ mgs/litre} \\ KCl &= 30 \text{ mgs/litre} \end{aligned}$$

**Solution :****> Calculation of CaCO<sub>3</sub> equivalents for impurities**

Salt/Impurity	Qty in mgs/litre	Mol. wt.	Multiplication factor	CaCO <sub>3</sub> equivalent ppm	Requirement of Lime (L) and / or Soda (S)
HCl	14.6	36.5	$14.6 \times \frac{100}{36.5}$	20	L + S
Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	34.2	342	$34.2 \times 3 \times \frac{100}{342}$	30	L + S
MgCl <sub>2</sub>	9.5	95	$9.5 \times \frac{100}{95}$	10	L + S
KCl	30	74.6	-	-	-

Note : (i) 1 mole of Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> is equivalent to 3 moles of Ca(OH)<sub>2</sub>.

(ii) 2 moles of HCl are equivalent to 1 mole of Ca(OH)<sub>2</sub>.

➤ Calculation of quantity of lime in grams required to soften 20000 litres of water.

#### Quantity of lime in grams

$$L = \frac{74}{100} \int_{Temporary Ca^{+2} + 2 \times Temporary Mg^{+2} + Permanent (Mg^{+2} + Fe^{+2} + Al^{+3} + H^+)} [HCl \text{ or } H_2SO_4] + HCO_3^- - NaAlO_2] \times \frac{\text{Vol. of Water}}{10^6} \times \frac{100}{\% \text{ of purity kg}}$$

all in term of their  $CaCO_3$  equivalents.

$$= \frac{74}{100} [HCl + Al_2(SO_4)_3 + MgCl_2] \times \frac{\text{Litres of water} \times \frac{100}{10^6 \times \% \text{ purity of lime kg}}}{20000 \times \frac{100}{10^6 \times 89}}$$

$$= \frac{74}{100} [60] \frac{2}{89}$$

$$= 0.997 \text{ kgs of lime}$$

➤ Calculation of quantity of soda in grams required to soften 20000 litres of water.

#### Quantity of soda in grams

$$S = \frac{106}{100} \int_{Permanent (Ca^{+2} + Mg^{+2} + Al^{+3} + Fe^{+2} + H^+ (HCl \text{ or } H_2SO_4) - HCO_3^-)} [Vol. of Water \times \frac{100}{10^6} \times \frac{100}{\% \text{ of purity kg}}]$$

all in term of their  $CaCO_3$  equivalents.

$$= \frac{106}{100} [CaCO_3 \text{ equivalents of } HCl + Al_2(SO_4)_3 + MgCl_2] \times \frac{\text{Litres of water} \times \frac{100}{10^6 \times \% \text{ purity of soda kg}}}{20000 \times \frac{100}{10^6 \times 95}}$$

$$= \frac{106}{100} [60] \frac{2}{95}$$

$$= 1.338 \text{ kgs of soda}$$

Quantity of lime required = 0.997 kgs

Quantity of soda required = 1.338 kgs

Note :  $NaCl$  and  $SiO_2$  do not contribute to the hardness.

Ans. :

Solution:  
➤ Calculation of  $CaCO_3$  equivalents for impurities

Salt/Impurity	Qty in mg/lit	Mol.	Multiplication factor	$CaCO_3$ equivalent ppm	Requirement of Lime (L) and/or Soda (S)
$CaCO_3$	3.5	100	$3.5 \times \frac{100}{100}$	3.5	L
$CaSO_4$	6.8	136	$6.8 \times \frac{100}{136}$	5	S
$MgCO_3$	8.4	84	$8.4 \times \frac{100}{84}$	10	L
$MgCl_2$	5.7	95	$5.7 \times \frac{100}{95}$	6	L + S
$MgSO_4$	6.0	120	$6.0 \times \frac{100}{120}$	5	L + S
$SiO_2$	3.0	60	—	—	—
$NaCl$	11.7	58.5	—	—	—

- Calculation of quantity of lime in grams required to soften 35000 litres of water per day.

**Quantity of lime in grams**

$$L = \frac{74}{100} \left[ \text{Temporary } Ca^{2+} + 2 \times \text{Temporary } Mg^{2+} + \text{Permanent } (Mg^{2+} + Fe^{2+} + Al^{3+} + H^+) \right] + HCO_3^- - NaAlO_2 \times \frac{\text{Vol. of Water}}{10^6} \times \frac{100}{\% \text{ of purity kg}}$$

all in term of their  $CaCO_3$  equivalents.

$$= \frac{74}{100} \left[ \frac{[CaCO_3 \text{ equivalents of } CaCO_3 + 2 \times MgCO_3 + MgCl_2 + MgSO_4]}{10^6 \times \% \text{ purity of lime}} \right] \times \frac{\text{Qty of water in litre} \times 100}{10^6 \times \% \text{ purity of lime}}$$

$$= \frac{74}{100} [3.5 + 2 \times 10 + 5 + 5] \frac{35000 \times 100}{10^6 \times 85}$$

$$= \frac{74}{100} [34.5] \frac{35}{85}$$

$$= 1.051 \text{ kgs of lime required per day.}$$

$$\therefore \text{for February 2000 month, lime required}$$

$$= 1.051 \text{ kg} \times 29 \text{ days}$$

- Calculation of quantity of soda in grams required to soften 35000 litres of water for month of February 2000.

**Quantity of soda in grams**

$$S = \frac{106}{100} \left[ \text{Permanent } (Ca^{2+} + Mg^{2+} + Al^{3+} + Fe^{2+} + H^+) (HCl \text{ or } H_2SO_4) - HCO_3^- \right] \times \frac{\text{Vol. of Water}}{10^6} \times \frac{100}{\% \text{ of purity kg}}$$

all in term of their  $CaCO_3$  equivalents.

$$= \frac{106}{100} \left[ \frac{[CaCO_3 \text{ equivalents of } CaCO_3 + MgCO_3 + MgCl_2 + MgSO_4]}{10^6 \times \% \text{ purity of soda}} \right] \times \frac{\text{Litres of water} \times 100}{10^6 \times \% \text{ purity of soda}}$$

$$= \frac{106}{100} [5 + 5 + 6] \frac{35000 \times 100 \times 29}{10^6 \times 95}$$

$$= \frac{106}{100} [16] \frac{35}{95}$$

$$= 0.6248 \text{ kgs of soda}$$

For the month of February 2000, soda required

$$= 0.6248 \times 29$$

$$= 18.1192 \text{ kg}$$

- Ans. :      Quantity of lime required = 30.48 kg  
Quantity of soda required = 18.1192 kg

- Calculation of quantity of lime in grams required to soften 35000 litres of water per day.

**Quantity of lime in grams**

$$L = \frac{74}{100} \left[ \text{Temporary } Ca^{2+} + 2 \times \text{Temporary } Mg^{2+} + \text{Permanent } (Mg^{2+} + Fe^{2+} + Al^{3+} + H^+) \right] + HCO_3^- - NaAlO_2 \times \frac{\text{Vol. of Water}}{10^6} \times \frac{100}{\% \text{ of purity kg}}$$

all in term of their  $CaCO_3$  equivalents.

$CaCO_3$  and  $MgCO_3$  should be required as being present in the form of their bicarbonates and only their weights have been expressed in terms of  $CaCO_3$  and  $MgCO_3$ . KCl will not react with lime or soda and it does not contribute to hardness.

$$1 \text{ ppm} = 1 \text{ mg/ml}$$

- Calculation of  $CaCO_3$  equivalents for impurities

Salt/Impurity	Qty in mgs/lit	Mol. wt.	Multiplication factor	$CaCO_3$ equivalent ppm	Requirement of Lime (L) and / or Soda (S)
$MgCl_2$	9.5	95	$9.5 \times \frac{100}{95}$	10	L + S
$CaSO_4$	272	136	$272 \times \frac{100}{136}$	200	
$MgSO_4$	120	120	$120 \times \frac{100}{120}$	100	L + S
$H_2SO_4$	49	98	$49 \times \frac{100}{98}$	100	L + S
$SiO_2$	8				Does not cause hardness

- Calculation of quantity of lime in grams required for softening of water

**Quantity of lime**

$$L = \frac{74}{100} \left[ \text{Temporary } Ca^{2+} + 2 \times \text{Temporary } Mg^{2+} + \text{Permanent } (Mg^{2+} + Fe^{2+} + Al^{3+} + H^+) \right] + HCO_3^- - NaAlO_2 \times \frac{\text{Vol. of Water}}{10^6} \times \frac{100}{\% \text{ of purity kg}}$$

all in term of their  $CaCO_3$  equivalents.

**Applied Chemistry - I (MU)****Calculation of  $\text{CaCO}_3$  equivalents for impurities**

Salt/Impurity	Qty in ng/lit	Mol. wt.	Multiplication factor	$\text{CaCO}_3$ equivalent ppm	Requirement of Lime (L) and / or Soda (S)
$\text{MgCO}_3$	84	84	$84 \times \frac{100}{84}$	100	L
$\text{SiO}_2$	-	-	-	-	-
$\text{CaSO}_4$	68	136	$68 \times \frac{100}{136}$	50	S
$\text{MgSO}_4$	30	120	$30 \times \frac{100}{120}$	25	L + S
$\text{MgCl}_2$	19	95	$19 \times \frac{100}{95}$	20	L + S
$\text{CaCO}_3$	120	100	$120 \times \frac{100}{100}$	120	L

**Quantity of soda**

$$S = \frac{106}{100} \left[ \text{Permanent} (\text{Ca}^{+2} + \text{Mg}^{+2} + \text{Al}^{+3} + \text{Fe}^{+2} + \text{H}^{\circ} (\text{HCl or } \text{H}_2\text{SO}_4)) - \text{HCO}_3^- \right]$$

$$\times \frac{\text{Vol. of Water}}{10^6} \times \frac{100}{\% \text{ of purity kg}}$$

**Calculation of quantity of soda in grams required for softening water****Quantity of soda**

$$S = \frac{74}{100} \left[ \text{[MgSO}_4] + \frac{10}{[\text{MgCl}_2]} + \frac{50}{[\text{H}_2\text{SO}_4]} \right] \times \frac{10^6}{10^6} \times \frac{100}{95 \text{ kg}}$$

$$\begin{aligned} &= \frac{74}{100} \times 160 \times \frac{10^6}{10^6} \times \frac{100}{95 \text{ kg}} \\ &= \frac{74 \times 160}{95} \text{ kg} \\ &= 124.63 \text{ kg} \end{aligned}$$

**Calculation of quantity of soda in grams required for softening water****Quantity of soda**

$$S = \frac{106}{100} \left[ \text{Permanent} (\text{Ca}^{+2} + \text{Mg}^{+2} + \text{Al}^{+3} + \text{Fe}^{+2} + \text{H}^{\circ} (\text{HCl or } \text{H}_2\text{SO}_4)) - \text{HCO}_3^- \right]$$

$$\times \frac{\text{Vol. of Water}}{10^6} \times \frac{100}{\% \text{ of purity kg}}$$

all in term of their  $\text{CaCO}_3$  equivalents.

$$\begin{aligned} &= \frac{106}{100} [200 [\text{CaSO}_4] + 50 [\text{MgSO}_4] + 10 [\text{H}_2\text{SO}_4] + 10 [\text{MgCl}_2]] \times \frac{10^6}{10^6} \times \frac{100}{90 \text{ kg}} \\ &= \frac{106}{100} \times 360 \times \frac{100}{90} \text{ kg} = \frac{106 \times 360}{90} \\ &= 424 \text{ kg} \end{aligned}$$

**Ans. :      Quantity of lime required = 424 kg****Quantity of soda required = 124.63 kg****Problem 2.18.31:** A continuous lime soda softener was used to produce soft water, impurities present in the sample were.

$$\text{CaCO}_3 = 120 \text{ mg/l},$$

$$\text{SiO}_2 = 25 \text{ mg/l},$$

$$\text{MgSO}_4 = 30 \text{ mg/l},$$

$$\begin{aligned} &\text{MgCO}_3 = 84 \text{ mg/l}, \\ &\text{CaSO}_4 = 66 \text{ mg/l}, \\ &\text{MgCl}_2 = 19 \text{ mg/l}. \end{aligned}$$

Calculate the quantity of lime (80 % pure) and soda (88 % pure) required for softening 1 million litres of water.

**Solution :**

$\text{CaCO}_3$  and  $\text{MgCO}_3$  should be regarded as being present in form of their bicarbonates and only their weights have been expressed in terms of  $\text{CaCO}_3$  and  $\text{MgCO}_3$ .  $\text{SiO}_2$  will not react with lime or soda and so it doesn't contribute to hardness.

all in term of their  $\text{CaCO}_3$  equivalents.

$$S = \frac{106}{100} \left[ \text{Permanent} (\text{Ca}^{+2} + \text{Mg}^{+2} + \text{Al}^{+3} + \text{Fe}^{+2} + \text{H}^{\circ} (\text{HCl or } \text{H}_2\text{SO}_4)) - \text{HCO}_3^- \right]$$

$$\times \frac{\text{Vol. of Water}}{10^6} \times \frac{100}{\% \text{ of purity kg}}$$

all in term of their  $\text{CaCO}_3$  equivalents.

$$\begin{aligned} &= \frac{74}{100} [120 + 2(100) + 20 + 25] \times \frac{10^6}{10^6} \times \frac{100}{80 \text{ kg}} \\ &= \frac{74}{100} [365] \times \frac{100}{80} \text{ kg} \\ &= 337.62 \text{ kg of lime} \end{aligned}$$

**Calculation of quantity of soda in grams required for softening water.****Quantity of soda**

$$S = \frac{106}{100} \left[ \text{Permanent} (\text{Ca}^{+2} + \text{Mg}^{+2} + \text{Al}^{+3} + \text{Fe}^{+2} + \text{H}^{\circ} (\text{HCl or } \text{H}_2\text{SO}_4)) - \text{HCO}_3^- \right]$$

$$\times \frac{\text{Vol. of Water}}{10^6} \times \frac{100}{\% \text{ of purity kg}}$$

all in term of their  $\text{CaCO}_3$  equivalents.

$$= \frac{106}{100} [50 + 45] \times \frac{10^6}{10^6} \times \frac{100}{88} \text{ kg}$$

$$= \frac{106}{100} \times 95 \times \frac{100}{88}$$

**= 114.43 kg of soda**

**Ans. :**

**Lime required = 337.62 kgs**

**Soda required = 114.43 kgs**

**Problem 2.18.32 :**

A water sample on analysis gives the following data

$$\begin{aligned} Ca^{+2} &= 20 \text{ ppm}, & Mg^{+2} &= 24 \text{ ppm}, \\ CO_2 &= 30 \text{ ppm}, & HCO_3^- &= 150 \text{ ppm}, \\ K^+ &= 40 \text{ ppm}. & & \end{aligned}$$

Calculate the lime (97 % pure) and soda (91 % pure) required to soften 1 million litres of the water sample.

**Solution :**

➤ Calculation of  $CaCO_3$  equivalents of ions.

Salt/purity	Qty in mg/lit	Mol. wt.	Multiplication factor	$CaCO_3$ equivalent ppm	Requirement of Lime (L) and / or Soda (S)
$Mg^{+2}$	24	24	$\frac{100}{24} \times 24$	100	L + S
$Ca^{+2}$	20	40	$20 \times \frac{100}{40}$	50	S
$CO_2$	30	44	$30 \times \frac{100}{44}$	68.18	L
$HCO_3^-$	150	61	$150 \times \frac{100}{61 \times 2}$	122.95	Add in Lime (L), Subtract in Soda (S)
K <sup>+</sup>	40				(Does not contribute to hardness)

**Quantity of soda**

$$S = \frac{106}{100} \left[ Permanent (Ca^{+2} + Mg^{+2} + Al^{+3} + Fe^{+2} + H^+ (HCl \text{ or } H_2SO_4)) - HCO_3^- \right]$$

$$\times \frac{\text{Vol. of Water}}{10^6} \times \frac{100}{\% \text{ of purity}} \text{ kg}$$

all in term of their  $CaCO_3$  equivalents.

$$= \frac{106}{100} [Permanent Ca^{+2} + Permanent Mg^{+2} - HCO_3^-] \times \frac{10^6}{10^6} \times \frac{100}{91} \text{ kg}$$

$$= \frac{106}{100} [50 + 100 - 122.95] \times 1.099$$

$$= \frac{106}{100} [27.05] \times 1.099$$

$$= 31.5 \text{ kg of soda}$$

**Ans. : Soda required = 31.5 kgs**

**Problem 2.18.33 :** Calculate the amount of lime (80 % pure) and soda (85 % pure) required for softening 10 litres of hard water containing the following constituents.

$$\begin{aligned} Ca(HCO_3)_2 &= 162 \text{ ppm}; & MgCl_2 &= 9.5 \text{ ppm}; \\ NaCl &= 58.5 \text{ ppm}; & Mg(HCO_3)_2 &= 7.3 \text{ ppm}; \\ HCl &= 36.5 \text{ ppm}; & CO_2 &= 44.0 \text{ mg/l}; \\ CaCl_2 &= 111 \text{ ppm}; & MgSO_4 &= 60 \text{ ppm} \end{aligned}$$

➤ Calculation of quantity of lime in grams, required for softening of water

$$L = \frac{74}{100} \int [Temporary Ca^{+2} + 2 \times Temporary Mg^{+2} + Permanent (Mg^{+2} + Fe^{+2} + Al^{+3} + H^+ (HCl \text{ or } H_2SO_4)) + HCO_3^- - NaAlO_2] \times \frac{\text{Vol. of Water}}{10^6} \times \frac{100}{\% \text{ of purity}} \text{ kg}$$

all in term of their  $CaCO_3$  equivalents.

$$= \frac{74}{100} [Mg^{+2} + CO_2 + HCO_3^-] \times \frac{10^6}{10^6} \times \frac{100}{97} \text{ kg}$$

$$= \frac{74}{100} [100 + 68.18 + 122.95] \times 1.03$$

$$= 222.059 \text{ kg of lime}$$

➤ Calculation of quantity of soda in grams required for softening water.

**Solution :**

➤ To calculate the quantities of lime and soda, first all salts must be converted into their  $\text{CaCO}_3$  equivalents.

Salt/Impurity	Qty in mg/lit	Mol. wt.	Multiplication factor	$\text{CaCO}_3$ equivalent ppm	Requirement of Lime (L) and / or Soda (S)
$\text{Ca}(\text{HCO}_3)_2$	162	162	$\frac{100}{162} \times 162$	100	L
$\text{MgCl}_2$	9.5	95	$9.5 \times \frac{100}{95}$	10	L + S
NaCl	58.5	58.5	$58.5 \times \frac{100}{58.5}$	100	-
$\text{Mg}(\text{HCO}_3)_2$	7.3	146	$7.3 \times \frac{100}{146}$	5	L
HCl	36.5	36.5	$36 \times \frac{100}{(2 \times 36.5)}$	50	L + S
$\text{CO}_2$	44	44	$44 \times \frac{100}{44}$	100	L
$\text{CaCl}_2$	111	111	$111 \times \frac{100}{111}$	100	S
$\text{MgSO}_4$	60	120	$60 \times \frac{100}{120}$	50	L + S

➤ Calculation of quantity of lime in grams, required for softening of water

**Quantity of lime**

$$L = \frac{74}{100} \left[ \text{Temporary } \text{Ca}^{2+} + 2 \times \text{Temporary } \text{Mg}^{2+} + \text{Permanent } (\text{Mg}^{2+} + \text{Fe}^{2+} + \text{Al}^{3+} + \text{H}^+) \right]$$

$$(H\text{Cl} \text{ or } H_2\text{SO}_4) + \text{HCO}_3^- - \text{NaAlO}_2 \right] \times \frac{\text{Vol. of Water}}{10^6} \times \frac{100}{\% \text{ of Purity}} \text{ kg}$$

all in term of their  $\text{CaCO}_3$  equivalents.

$$\begin{aligned} &= \frac{74}{100} [\text{Permanent: Ca hardness} + \text{HCl} + \dots] \times \frac{10^6}{10^6} \times \frac{100}{85} \text{ kg} \\ &= \frac{106}{100} [100 + 60 + 50] \times \frac{100}{85} \text{ kg} \\ &= 261.882 \text{ kg of soda} \end{aligned}$$

Ans. :

Lime required = 266.0 kgs

Soda required = 261.882 kgs

**Problem 2.18.34:** Calculate the quantities of lime and soda (90 % pure each) required for softening 2500 litres of hard water containing following ions/chemicals.



$\text{H}_2\text{SO}_4 = 4.9 \text{ ppm}$  (May 2003)

**Solution :**

➤ Calculation of  $\text{CaCO}_3$  equivalents for impurities

Salt/Impurity	Qty in mg/lit	Mol. wt.	Multiplication factor	$\text{CaCO}_3$ equivalent ppm	Requirement of Lime (L) and / or Soda (S)
$\text{Ca}^{2+}$	30 ppm	40	$30 \times \frac{100}{40}$	75	S
$\text{Mg}^{2+}$	21.6 ppm	24	$21.6 \times \frac{100}{24}$	90	L + S
$\text{H}_2\text{SO}_4$	4.9 ppm	98	$4.9 \times \frac{100}{98}$	5	L + S
$\text{CO}_2$	4.4 ppm	44	$4.4 \times \frac{100}{44}$	10	L
$\text{HCO}_3^-$	12.2 ppm	122	$12.2 \times \frac{100}{122}$	10	Add in L and subtract in S
$\text{Fe}_2\text{O}_3$	15.4 ppm	Does not contribute			

➤ Calculation of quantity of lime in grams, required for softening of water

➤ Calculation of  $\text{CaCO}_3$  equivalents for impurities

Solution :

Quantity of lime

$$L = \frac{74}{100} \left[ \text{Temporary } \text{Ca}^{+2} + 2 \times \text{Temporary } \text{Mg}^{+2} + \text{Permanent } (\text{Mg}^{+2} + \text{Fe}^{+2} + \text{Al}^{+3} + \text{H}^+) \right. \\ \left. (\text{HCl or H}_2\text{SO}_4) + \text{HCO}_3^- - \text{NaAlO}_2 \right] \times \frac{\text{Vol. of Water}}{10^6} \times \frac{100}{\% \text{ of purity kg}}$$

all in term of their  $\text{CaCO}_3$  equivalents.

$$= \frac{74}{100} [90 + 5 + 10 + 10] \times \frac{25000}{10^6} \times \frac{100}{90} \text{ kg} \\ = 2.3638 \text{ kg}$$

➤ Calculation of quantity of soda in grams required for softening water.

Quantity of soda

$$S = \frac{106}{100} \left[ \text{Permanent } (\text{Ca}^{+2} + \text{Mg}^{+2} + \text{Al}^{+3} + \text{Fe}^{+2} + \text{H}^+ (\text{HCl or H}_2\text{SO}_4)) - \text{HCO}_3^- \right] \\ \times \frac{\text{Vol. of Water}}{10^6} \times \frac{100}{\% \text{ of purity kg}}$$

all in term of their  $\text{CaCO}_3$  equivalents.

$$= \frac{106}{90} [\text{Perm of Ca}^{+2} + \text{Perm of Mg}^{+2} + \text{H}_2\text{SO}_4 - \text{HCO}_3^-] \times \frac{25000}{10^6} \times \frac{100}{90} \text{ kg} \\ = \frac{106}{90} [75 + 90 + 5 - 10] \times \frac{25}{900} \\ = 4.7111 \text{ kg}$$

Ans. : Quantity of lime required = 2.3638 kg

Quantity of soda required = 4.7111 kg

**Problem 2.18.35:** Calculate the amount of lime (95 % pure) and soda (80 % pure) for softening

$$50,000 \text{ l. of water containing:} \\ \text{Mg}(\text{HCO}_3)_2 = 14.6 \text{ ppm;} \\ \text{Ca}(\text{HCO}_3)_2 = 8.1 \text{ ppm;} \\ \text{MgSO}_4 = 12 \text{ ppm;} \\ \text{Na}_2\text{SO}_4 = 15 \text{ ppm;} \\ \text{SiO}_2 = 12 \text{ ppm;} \\ \text{(May 2002)}$$

Salt/Impurity	Qty in mgs/lit	Mol. wt.	Multiplication factor	$\text{CaCO}_3$ equivalent	Requirement of Line (L) and / or Soda (S)
10	14.6 ppm	14.6	$14.6 \times \frac{100}{14.6}$	10	L + S
5	6.8 ppm	136	$6.8 \times \frac{100}{136}$	5	S
5	8.1 ppm	162	$8.1 \times \frac{100}{162}$	5	L
10	12 ppm	120	$12 \times \frac{100}{120}$	10	L + S
$\text{Na}_2\text{SO}_4$	15 ppm				
$\text{SiO}_2$	2 ppm				

Does not contribute lime and soda

➤ Calculation of quantity of lime in grams, required for softening of water

$$L = \frac{74}{100} \left[ \text{Temporary } \text{Ca}^{+2} + 2 \times \text{Temporary } \text{Mg}^{+2} + \text{Permanent } (\text{Mg}^{+2} + \text{Fe}^{+2} + \text{Al}^{+3} + \text{H}^+) \right. \\ \left. (\text{HCl or H}_2\text{SO}_4) + \text{HCO}_3^- - \text{NaAlO}_2 \right] \times \frac{\text{Vol. of Water}}{10^6} \times \frac{100}{\% \text{ of purity kg}}$$

all in term of their  $\text{CaCO}_3$  equivalents.

$$\text{Lime required} = \frac{74}{100} [\text{Temp. Ca} + 2 \times \text{Temp. Mg} + \text{Perm. Mg}]$$

$$\times \frac{50000}{10^6} \times \frac{100}{95} \text{ kg (95 % pure)} \\ = \frac{74}{100} [5 + (2 \times 10) + 10] \times \frac{50000}{10^6} \times \frac{100}{95} \text{ kg} \\ = \frac{74}{100} [35] \times \frac{5}{95} \text{ kg} \\ = 1.3631 \text{ kgs}$$

**Calculation of quantity of soda in grams required for softening water.**

$$S = \frac{106}{100} \left[ \text{Permanent} (Ca^{+2} + Mg^{+2} + Al^{+3} + Fe^{+2} + H^+ (HCl \text{ or } H_2SO_4)) - HCO_3^- \right] \\ \times \frac{\text{Vol. of Water}}{10^6} \times \frac{100}{\% \text{ of purity}} \text{ kg}$$

all in term of their  $CaCO_3$  equivalents.

$$\text{Soda required} = \frac{106}{100} [\text{Perm. of Ca} + \text{Mg}] \times \frac{50000}{10^6} \times \frac{100}{80} \text{ kg (80 % pure)}$$

$$= \frac{106}{80} [5 + 10] \times \frac{5}{80} \text{ kg}$$

$$= 0.9 \text{ kg}$$

all in term of their  $CaCO_3$  equivalents.

Ans. : Quantity of lime required = 1.3631 kg

Quantity of soda required = 0.9 kg

**Problem 2.18.36 :** Calculate the quantities of lime (86 % pure) and soda (90 % pure) required for softening 25,000 litres water having following analysis :-

$$HCl = 12.5 \text{ mgs/lit.}; \quad CaCO_3 = 35.2 \text{ mgs/lit.};$$

$$NaSO_4 = 8.8 \text{ mgs/lit.}; \quad Al_2(SO_4)_3 = 33.3 \text{ mgs/lit.};$$

$$MgCl_2 = 7.8 \text{ mgs/lit.}; \quad Fe_2O_3 = 18.6 \text{ mgs/lit.}$$

(Dec. 2002)

**Solution :**

**> Calculation of  $CaCO_3$  equivalents for impurities**

Salt/Impurity	Qty in mg/lit.	Mol. wt.	Multiplication factor	$CaCO_3$ equivalent ppm	Requirement of Lime (L) and / or Soda (S)
CaCO <sub>3</sub>	35.2 ppm	100	$35.2 \times \frac{100}{100}$	35.2	L
MgCl <sub>2</sub>	7.8 ppm	95	$7.8 \times \frac{100}{95}$	8.210	L + S
HCl	12.5 ppm	73	$12.5 \times \frac{100}{73}$	17.123	L + S
Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	33.3 ppm	114	$33.3 \times \frac{100}{114}$	29.210	L + S
Na <sub>2</sub> SO <sub>4</sub>	8.8 ppm	Does not contribute lime or soda			
Fe <sub>2</sub> O <sub>3</sub>	18.6 ppm	Does not contribute lime or soda			

**> Calculation of quantity of lime in grams, required for softening of water**

$$L = \frac{74}{100} \left[ Temporary Ca^{+2} + 2 \times Temporary Mg^{+2} + Permanent (Mg^{+2} + Fe^{+2} + Al^{+3} + H^+ (HCl \text{ or } H_2SO_4)) + HCO_3^- \right] \\ \times \frac{\text{Vol. of Water}}{10^6} \times \frac{100}{\% \text{ of purity}} \text{ kg}$$

all in term of their  $CaCO_3$  equivalents.

$$\text{Lime required} = \frac{74}{100} [Temp. Ca + Perm. Mg] \times \frac{25000}{10^6} \times \frac{100}{86} \text{ kg}$$

$$= \frac{74}{860} [35.2 + 8.210 + 17.123 - 29.210] \times 25 \text{ kg}$$

$$= 1.932454 \text{ kg}$$

all in term of their  $CaCO_3$  equivalents.

**> Calculation of quantity of soda in grams required for softening water.**

$$S = \frac{106}{100} \left[ \text{Permanent} (Ca^{+2} + Mg^{+2} + Al^{+3} + Fe^{+2} + H^+ (HCl \text{ or } H_2SO_4)) - HCO_3^- \right] \\ \times \frac{\text{Vol. of Water}}{10^6} \times \frac{100}{\% \text{ of purity}} \text{ kg}$$

all in term of their  $CaCO_3$  equivalents.

$$\text{Soda required} = \frac{106}{100} [Perm. Mg + Perm. Al] \times \frac{100}{90} \times \frac{25000}{10^6}$$

$$= \frac{106}{900} [8.210 + 17.123 + 29.21] \times 25 \text{ kg}$$

$$= 1.6084 \text{ kg}$$

all in term of their  $CaCO_3$  equivalents.

Ans. : Quantity of lime required = 1.932454 kg

Quantity of soda required = 1.6084 kg

**Problem 2.18.37 :** Calculate lime (80 % purity) and soda (90 % purity) required to soften 1 lakh litres of water containing the following impurities.

$$Mg(HCO_3)_2 = 7.1 \text{ mg/lit.}; \quad MgCO_3 = 4.2 \text{ mg/lit.};$$

$$Ca(HCO_3)_2 = 8.1 \text{ mg/lit.}; \quad CaCO_3 = 10 \text{ mg/lit.}$$

(Dec. 2001)

**Solution :**

➤ Calculation of  $\text{CaCO}_3$  equivalents for impurities

Salt/Impurity	Qty in mg/lit	Mol. wt.	Multiplication factor	$\text{CaCO}_3$ equivalent ppm	Requirement of Lime (L) and / or Soda (S)
$\text{Mg}(\text{HCO}_3)_2$	7.1	146	$7.1 \times \frac{100}{146}$	5	L
$\text{Ca}(\text{HCO}_3)_2$	8.1	162	$8.1 \times \frac{100}{162}$	5	L
$\text{MgCO}_3$	4.2	84	$4.2 \times \frac{100}{84}$	5	L
$\text{CaCO}_3$	10	100	$10 \times \frac{100}{100}$	10	L

➤ Calculation of quantity of lime in grams, required for softening of water

Quantity of lime

$$L = \frac{74}{100} \left[ \text{Temporary } \text{Ca}^{+2} + 2 \times \text{Temporary } \text{Mg}^{+2} + \text{Permanent } (\text{Mg}^{+2} + \text{Fe}^{+2} + \text{Al}^{+3} + \text{H}^+) \right. \\ \left. (\text{HCl or } \text{H}_2\text{SO}_4) + \text{HCO}_3^- - \text{NaAlO}_2 \right] \times \frac{\text{Vol. of Water}}{10^6} \times \frac{100}{\% \text{ of purity kg}}$$

all in term of their  $\text{CaCO}_3$  equivalents.

$$\text{Lime required} = \frac{74}{100} [\text{Temp. Ca} + 2 \times \text{Temp. Mg}] \times \frac{100}{\% \text{ purity}} \times \frac{10^5}{10^6} \\ = \frac{74}{800} [5 + 10 + 2 \times [5 + 5]] \text{ kg} \\ = \frac{74}{800} [35] \text{ kg} \\ = 3.2375 \text{ kg}$$

➤ Calculation of quantity of soda in grams required for softening water.

Quantity of soda

$$S = \frac{106}{100} \left[ \text{Permanent } (\text{Ca}^{+2} + \text{Mg}^{+2} + \text{Al}^{+3} + \text{Fe}^{+2} + \text{H}^+) (\text{HCl or } \text{H}_2\text{SO}_4) - \text{HCO}_3^- \right] \\ \times \frac{\text{Vol. of Water}}{10^6} \times \frac{100}{\% \text{ of purity kg}}$$

all in term of their  $\text{CaCO}_3$  equivalents.

**Solution :**

➤ Calculation of  $\text{CaCO}_3$  equivalents of impurities

Impurities	Quantity	Multiplying factor in ppm	$\text{CaCO}_3$ equivalent in ppm	Requirement of Lime (L) and / or Soda (S)
$\text{MgCl}_2$	95 ppm	100/95	100 ppm	L + S
$\text{CaSO}_4$	272 ppm	100/136	200 ppm	S
$\text{MgSO}_4$	120 ppm	100/120	100 ppm	L + S
$\text{H}_2\text{SO}_4$	49 ppm	100/98	50 ppm	L + S
$\text{SiO}_2$	4 ppm			Does not require lime and soda

(May 2006)

Calculate the lime and soda requirement in kg. For the softening of 10,000 litres of water if it is given that lime is 85 % pure and soda is 90 % pure.

**Solution :**

➤ Calculation of  $\text{CaCO}_3$  equivalents of impurities

$$\text{Soda required} = \frac{106}{100} \left[ \text{Perm. } (\text{Mg} + \text{Al} + \text{Fe}) + \text{HCl} + \text{H}_2\text{SO}_4 - \text{HCO}_3^- \right] \\ = \frac{106}{100} \times [0] = 0$$

$$\text{Ans : } \begin{aligned} \text{Quantity of lime required} &= 32375 \text{ kg} \\ \text{Quantity of soda required} &= 0 \end{aligned}$$

**Problem 2.18.38:** A water sample on analysis gave the following data :

(i)  $\text{MgCl}_2 = 95 \text{ ppm}$

(ii)  $\text{CaSO}_4 = 272 \text{ ppm}$

(iii)  $\text{MgSO}_4 = 120 \text{ ppm}$

(iv)  $\text{H}_2\text{SO}_4 = 49 \text{ ppm}$

(v)  $\text{SiO}_2 = 4 \text{ ppm}$

Calculate the lime and soda requirement in kg. For the softening of 10,000 litres of water if it is given that lime is 85 % pure and soda is 90 % pure.

➤ Calculation of quantity of lime in grams, required for softening of water

#### Quantity of lime

$$\begin{aligned}
 L &= \frac{74}{100} \left[ \text{Temporary } Ca^{+2} + 2 \times \text{Temporary } Mg^{+2} + \text{Permanent } (Mg^{+2} + Fe^{+2} + Al^{+3} + H^+) \right. \\
 &\quad \left. (HCl \text{ or } H_2SO_4) + HCO_3^- - NaAlO_2 \right] \times \frac{\text{Vol. of Water}}{10^6} \times \frac{100}{\% \text{ of purity kg}} \\
 &\text{all in term of their } CaCO_3 \text{ equivalents.} \\
 &= \frac{74}{100} [100 + 100 + 50] \frac{10000}{10^6} \times \frac{100}{85} \text{ kg} \\
 &= \frac{74}{100} [250] \frac{1}{85} \\
 &= \frac{74 \times 250}{8500} \text{ kg} \\
 &= 2.1765 \text{ kgs of lime}
 \end{aligned}$$

- Calculation of quantity of soda in grams required for softening water.

#### Quantity of soda

$$S = \frac{106}{100} \left[ \text{Permanent } (Ca^{+2} + Mg^{+2} + Al^{+3} + Fe^{+2} + H^+) (HCl \text{ or } H_2SO_4) - HCO_3^- \right]$$

$$\begin{aligned}
 &\times \frac{\text{Vol. of Water}}{10^6} \times \frac{100}{\% \text{ of purity kg}} \\
 &\text{all in term of their } CaCO_3 \text{ equivalents.}
 \end{aligned}$$

$$\begin{aligned}
 &= \frac{106}{100} [200 + 100 + 100] \times \frac{10000}{10^6} \times \frac{100}{90} \text{ kg} \\
 &= \frac{106}{100} [400] \frac{10000}{10^6} \times \frac{100}{90} \text{ kg} \\
 &= 106 \times \frac{4}{90} \text{ kg} \\
 &= 4.711 \text{ kgs.}
 \end{aligned}$$

Ans. : Lime required = 2.1765 kgs  
Soda required = 4.711 kgs.

**Problem 2.18.39 :** Calculate amount of Lime (90 % pure) and Soda (100 % pure) for 1 million lit. of water containing the following impurities :

$CaSO_4 = 136 \text{ ppm}$ ,  $H_2SO_4 = 49 \text{ ppm}$ ,  $MgCl_2 = 95 \text{ ppm}$ ,  $MgSO_4 = 60 \text{ ppm}$ ,  $SiO_2 = 50 \text{ ppm}$ .  
(Dec. 2005, 6 Marks)

➤ Calculation of  $CaCO_3$  equivalents of impurities

Impurity/ies	Quantity	Multiplying factor	$CaCO_3$ equivalent in ppm	Requirement of Lime (L) and / or Soda (S)
$CaSO_4$	136 ppm	100/136	100	S
$H_2SO_4$	49 ppm	100/98	50	L + S
$MgCl_2$	95 ppm	100/95	100	L + S
$MgSO_4$	60 ppm	100/120	50	L + S
$SiO_2$	50 ppm		Does not require lime/soda	

- Calculation of quantity of lime in grams, required for softening of water

#### Quantity of lime

$$\begin{aligned}
 L &= \frac{74}{100} \left[ \text{Temporary } Ca^{+2} + 2 \times \text{Temporary } Mg^{+2} + \text{Permanent } (Mg^{+2} + Fe^{+2} + Al^{+3} + H^+) \right. \\
 &\quad \left. (HCl \text{ or } H_2SO_4) + HCO_3^- - NaAlO_2 \right] \times \frac{\text{Vol. of Water}}{10^6} \times \frac{100}{\% \text{ of purity kg}}
 \end{aligned}$$

all in term of their  $CaCO_3$  equivalents.

$$\begin{aligned}
 \text{Lime required} &= \frac{74}{100} (H_2SO_4) \times \frac{100}{90} \times \frac{10^6}{10^6} \text{ kgs} \\
 &= \frac{74}{100} [50] \times \frac{100}{90} \times \frac{10^6}{10^6} \text{ kgs} \\
 &= 41.11 \text{ kgs}
 \end{aligned}$$

- Calculation of quantity of soda in grams required for softening water

#### Quantity of soda

$$S = \frac{106}{100} \left[ \text{Permanent } (Ca^{+2} + Mg^{+2} + Al^{+3} + Fe^{+2} + H^+) (HCl \text{ or } H_2SO_4) - HCO_3^- \right]$$

$$\begin{aligned}
 &\times \frac{\text{Vol. of Water}}{10^6} \times \frac{100}{\% \text{ of purity kg}} \\
 &\text{all in term of their } CaCO_3 \text{ equivalents.}
 \end{aligned}$$

$$\text{Soda required} = \frac{106}{100} [100 + 100 + 50] \times \frac{100}{100} \times \frac{10^6}{10^6} \text{ kgs}$$

$$= \frac{106}{100} [250] \text{ kgs}$$

$$= 265 \text{ kgs}$$

**Ans. :** Lime required = 41.11 kgs

Soda required = 265 kgs.

**Problem 2.18.40:** Calculate Lime (74 % pure) and soda (90 % pure) required for 5000 lit. of water containing following impurities:

$$\text{Mg(HCO}_3\text{)}_2 = 73 \text{ mg/lit.}$$

$$\text{CaCl}_2 = 222 \text{ mg/lit.}$$

$$\text{SiO}_2 = 15 \text{ mg/lit.}$$

**Solution:**  $\text{Ca(OH)}_2 = 120 \text{ mg/lit.}$

$\text{Ca(NO}_3\text{)}_2 = 164 \text{ mg/lit.}$

$\text{Ca(NO}_3\text{)}_2 = \text{traces}$  (May 2005)

➤ Calculation of  $\text{CaCO}_3$  equivalents for impurities

Impurity/ies	Quantity	Multiplying factor	CaCO <sub>3</sub> equivalent in ppm	Requirement of Lime (L) and / or Soda (S)
Mg(HCO <sub>3</sub> ) <sub>2</sub>	73 mg/lit	100/146	50	L
MgSO <sub>4</sub>	120 mg/lit	100/120	100	L + S
CaCl <sub>2</sub>	222 mg/lit	100/111	20	S
Ca(NO <sub>3</sub> ) <sub>2</sub>	164 mg/lit	100/164	100	S
SiO <sub>2</sub>	15 mg/lit	Does not require lime/soda		

➤ Calculation of quantity of lime required for softening of water

**Quantity of lime**

$$L = \frac{74}{100} \left[ \text{Temporary Ca}^{+2} + 2 \times \text{Temporary Mg}^{+2} + \text{Permanent } (\text{Mg}^{+2} + \text{Fe}^{+2} + \text{Al}^{+3} + \text{H}^{+}) \right. \\ \left. + \text{HCl or HSO}_4^- \right] \times \frac{\text{Vol. of Water}}{10^6} \times \frac{100}{\% \text{ of purity}} \text{ kgs}$$

all in term of their  $\text{CaCO}_3$  equivalents.

$$\text{Lime required} = \frac{74}{100} [2 \times 50 + 100] \times \frac{100}{74} \times \frac{5000}{10^6} \text{ kgs}$$

$$= \frac{74}{100} [200] \times \frac{100}{74} \times \frac{5000}{10^6} \text{ kgs}$$

$$= 1 \text{ kgs}$$

➤ Calculation of quantity of soda in grams required for softening water

$$S = \frac{106}{100} \left[ \text{Permanent } (\text{Ca}^{+2} + \text{Mg}^{+2} + \text{Al}^{+3} + \text{Fe}^{+2} + \text{H}^{+}(\text{HCl or H}_2\text{SO}_4)) - \text{HCO}_3^- \right] \\ \times \frac{\text{Vol. of Water}}{10^6} \times \frac{100}{\% \text{ of purity}} \text{ kg}$$

all in term of their  $\text{CaCO}_3$  equivalents.

$$\text{Soda required} = \frac{106}{100} [100 + 20 + 100] \times \frac{100}{90} \times \frac{5000}{10^6} \text{ kgs}$$

$$= \frac{106}{100} [220] \times \frac{100}{90} \times \frac{5000}{10^6} \text{ kgs}$$

$$= 1.209 \approx 1.3 \text{ kgs}$$

**Ans. :** Lime required = 1 kg  
Soda required = 1.3 kgs.

**Problem 2.18.41:** A water sample on analysis gave the following data :

1.  $\text{MgCl}_2$  95 ppm
2.  $\text{CaSO}_4$  272 ppm
3.  $\text{MgSO}_4$  120 ppm
4.  $\text{H}_2\text{SO}_4$  49 ppm
5.  $\text{SiO}_2$  4 ppm

Calculate lime and soda requirement in kg for the softening of 10,000 litres of water if it is given that lime is 85 % pure and soda is 90 % pure. (Dec. 2004)

➤ Calculation of  $\text{CaCO}_3$  equivalents for impurities

Impurity/ies	Quantity	Multiplying factor	CaCO <sub>3</sub> equivalent in ppm	Requirement of Lime (L) and / or Soda (S)
MgCl <sub>2</sub>	95 ppm	100/95	100	L + S
CaSO <sub>4</sub>	272 ppm	100/136	200	S
MgSO <sub>4</sub>	120 ppm	100/120	100	L + S
H <sub>2</sub> SO <sub>4</sub>	49 ppm	100/98	50	L + S
SiO <sub>2</sub>	4 ppm	Does not consume lime and soda		

➤ Calculation of quantity of lime in grams, required for softening of water

Quantity of lime

$$L = \frac{74}{100} \left[ \text{Temporary } Ca^{2+} + 2 \times \text{Temporary } Mg^{2+} + \text{Permanent } (Mg^{2+} + Fe^{2+} + Al^{3+} + H^+) \right. \\ \left. (HCl \text{ or } H_2SO_4) + HCO_3^- - NaAlO_2 \right] \times \frac{\text{Vol. of Water}}{10^6} \times \frac{100}{\% \text{ of purity}} \text{ kg}$$

all in term of their  $CaCO_3$  equivalents.

$$\text{Lime required} = \frac{74}{100} [100 + 100 + 50] \times \frac{100}{85} \times \frac{10000}{10^6} \text{ kgs}$$

$$= \frac{74}{100} [250] \times \frac{100}{85} \times \frac{10000}{10^6} \text{ kgs}$$

$$= 2.18 \text{ kgs}$$

➤ Calculation of quantity of soda in grams required for softening water

Quantity of soda

$$S = \frac{106}{100} \left[ \text{Permanent } (Ca^{2+} + Mg^{2+} + Al^{3+} + Fe^{2+} + H^+ (HCl \text{ or } H_2SO_4)) - HCO_3^- \right] \\ \times \frac{\text{Vol. of Water}}{10^6} \times \frac{100}{\% \text{ of purity}} \text{ kg}$$

all in term of their  $CaCO_3$  equivalents.

$$\text{Soda required} = \frac{106}{100} [100 + 200 + 100 + 50] \times \frac{100}{90} \times \frac{10000}{10^6} \text{ kgs}$$

$$= \frac{106}{100} [450] \times \frac{100}{90} \times \frac{10000}{10^6} \text{ kgs}$$

$$= 5.3 \text{ kgs}$$

$$\text{Lime required} = 2.18 \text{ kgs}$$

$$\text{Soda required} = 5.3 \text{ kgs.}$$

**Problem 2.18.42:** Calculate the amount of lime and soda required for 50,000 lit. of water sample containing :

$$CaCO_3 = 10 \text{ ppm},$$

$$Mg(HCO_3)_2 = 14.6 \text{ ppm},$$

$$CO_2 = 4.4 \text{ ppm},$$

$$CaCl_2 = 22.2 \text{ ppm},$$

$$MgCl_2 = 9.5 \text{ ppm},$$

$$SiO_2 = 2.8 \text{ ppm.}$$

➤ Calculation of  $CaCO_3$  equivalents of impurities

Impurities	Quantity	Multiplying factor	$CaCO_3$ equivalent in ppm	Requirement of Lime (L) and / or Soda (S)
$CaCO_3$	10 ppm	100/100	10	L
$Mg(HCO_3)_2$	14.6 ppm	100/146	10	L
$CO_2$	4.4 ppm	100/44	10	L
$CaCl_2$	22.2 ppm	100/11	20	S
$MgCl_2$	9.5 ppm	100/95	10	L + S
$SiO_2$	2.8 ppm		Does not contribute to Lime and Soda	

➤ Calculation of quantity of lime in grams, required for softening of water

Quantity of lime

$$L = \frac{74}{100} \left[ \text{Temporary } Ca^{2+} + 2 \times \text{Temporary } Mg^{2+} + \text{Permanent } (Mg^{2+} + Fe^{2+} + Al^{3+} + H^+) \right. \\ \left. (HCl \text{ or } H_2SO_4) + HCO_3^- - NaAlO_2 \right] \times \frac{\text{Vol. of Water}}{10^6} \times \frac{100}{\% \text{ of purity}} \text{ kg}$$

all in term of their  $CaCO_3$  equivalents.

$$\text{Lime required} = \frac{74}{100} [10 + 10 + 10 + 10] \times \frac{100}{100} \times \frac{50000}{10^6} \text{ kg}$$

$$= \frac{74}{100} [40] \times \frac{100}{100} \times \frac{50000}{10^6} \text{ kg}$$

$$= 1.48 \text{ kg}$$

➤ Calculation of quantity of soda in grams required for softening water

Quantity of soda

$$S = \frac{106}{100} \left[ \text{Permanent } (Ca^{2+} + Mg^{2+} + Al^{3+} + Fe^{2+} + H^+ (HCl \text{ or } H_2SO_4)) - HCO_3^- \right] \\ \times \frac{\text{Vol. of Water}}{10^6} \times \frac{100}{\% \text{ of purity}} \text{ kg}$$

all in term of their  $CaCO_3$  equivalents.

(May 2004, 4 Marks)

$$\text{Soda required} = \frac{106}{100} [20 + 10] \times \frac{100}{100} \times \frac{50000}{10^6} \text{ kg}$$

$$= 1.59 \text{ kg}$$

$$\text{Lime required} = 1.48 \text{ kg}$$

$$\text{Soda required} = 1.59 \text{ kg}$$

**Problem 2.18.43:** Calculate the amount of lime (92 % pure) and soda (95 % pure) required for softening 15,000 litres of hard water containing the following salts.

$$\text{CaCO}_3 = 68.2 \text{ mg/litre,}$$

$$\text{Mg(CHO}_3)_2 = 29.6 \text{ mg/litre,}$$

$$\text{MgSO}_4 = 36.0 \text{ mg/litre,}$$

$$\text{CaSO}_4 = 27.2 \text{ mg/litre,}$$

$$\text{Fe}_2\text{O}_3 = 19.3 \text{ mg/litre.}$$

(Dec. 2003, 6 Marks)

- Calculation of  $\text{CaCO}_3$  equivalents for impurities

Impurity/ies	Quantity mg/litre	Multiplying factor	CaCO <sub>3</sub> equivalent in ppm	Requirement of Lime (L) and / or Soda (S)
CaCO <sub>3</sub>	68.2	100/100	68.2	L
Mg(NO <sub>3</sub> ) <sub>2</sub>	29.6	100/148	20	S
Mg(HCO <sub>3</sub> ) <sub>2</sub>	58.4	100/146	40	L
MgSO <sub>4</sub>	36.0	100/120	30	L + S
MgCl <sub>2</sub>	95.0	100/95	100	L
CaSO <sub>4</sub>	27.2	100/136	20	S
Fe <sub>2</sub> O <sub>3</sub>	19.3		Does not consume lime or soda	

- Calculation of quantity of lime in grams, required for softening of water

#### Quantity of lime

$$L = \frac{74}{100} \left[ \text{Temporary } \text{Ca}^{+2} + 2 \times \text{Temporary } \text{Mg}^{+2} + \text{Permanent } (\text{Mg}^{+2} + \text{Fe}^{+2} + \text{Al}^{+3} + \text{H}^{+}) \right] \times \frac{\text{Vol. of Water}}{10^6} \times \frac{100}{\% \text{ of purity}} \text{ kg}$$

all in term of their  $\text{CaCO}_3$  equivalents.

$$\begin{aligned} \text{Lime required} &= \frac{74}{100} [\text{CaCO}_3 + \text{Mg(CHO}_3)_2 + \text{MgSO}_4 + \text{MgCl}_2] \times \frac{100}{92} \times \frac{15000}{10^6} \text{ kg} \\ &= \frac{74}{100} [68.2 + 40 + 30 + 100] \times \frac{100}{92} \times \frac{15000}{10^6} \text{ kg} \\ &= \frac{74}{100} [238.2] \times \frac{100}{92} \times \frac{15000}{10^6} \text{ kg} \\ &= 2.874 \text{ kg} \end{aligned}$$

- Calculation of quantity of soda in grams required for softening water

$$S = \frac{106}{100} \left[ \text{Permanent } (\text{Ca}^{+2} + \text{Mg}^{+2} + \text{Al}^{+3} + \text{Fe}^{+2} + \text{H}^{+} \text{ (HCl or H}_2\text{SO}_4) - \text{HCO}_3^-) \right]$$

all in term of their  $\text{CaCO}_3$  equivalents.

$$\begin{aligned} \text{Soda required} &= \frac{106}{100} [\text{MgCl}_2 + \text{MgSO}_4 + \text{Mg(NO}_3)_2 + \text{CaSO}_4] \times \frac{100}{95} \times \frac{15000}{10^6} \text{ kg} \\ &= \frac{106}{100} [100 + 20 + 30 + 20] \times \frac{100}{95} \times \frac{15000}{10^6} \text{ kg} \\ &= \frac{106}{100} [170] \times \frac{100}{95} \times \frac{15000}{10^6} \text{ kg} \\ &= 2.845 \text{ kg} \end{aligned}$$

Ans. :

$$\text{Lime required} = 2.874 \text{ kg}$$

$$\text{Soda required} = 2.845 \text{ kg}$$

- Problem 2.18.44** Calculate the quantities of lime (85% pure) and soda (95% pure) for softening one million litres of water if it has analysis as follows :

- (1)  $\text{CaCl}_2 - 49.95 \text{ ppm}$
- (2)  $\text{MgSO}_4 - 42 \text{ ppm}$
- (3)  $\text{NaHCO}_3 - 12.5 \text{ ppm}$
- (4)  $\text{SiO}_2 - 10 \text{ ppm}$
- (5)  $\text{NaCl} - 500 \text{ ppm}$
- (6)  $\text{Mg(HCO}_3)_2 - 51.1 \text{ ppm}$
- (7)  $\text{CO}_2 - 3 \text{ ppm}$
- (8)  $\text{Fe}^{+2} - 3 \text{ ppm}$

(Dec. 2006, 7 Marks)

**Solution :**

- Calculation of  $\text{CaCO}_3$  equivalents for impurities

Salt	Quantity in ppm	Molecular weight	Multiplication factor	$\text{CaCO}_3$ equivalent ppm	Requirement of Lime (L) and / or Soda (S)
$\text{CaCl}_2$	49.95	111	$49.95 \times \frac{100}{111}$	45	S
$\text{MgSO}_4$	42	120	$42 \times \frac{100}{120}$	35	L + S
$\text{NaHCO}_3$	12.6				
$\text{SiO}_2$	10				Does not contribute to hardness
$\text{NaCl}$	500				
$\text{Mg}(\text{HCO}_3)_2$	51.1	146	$51.1 \times \frac{100}{146}$	35	L
$\text{CO}_2$	3	44	$3 \times \frac{100}{44}$	6.8	L
$\text{Fe}^{2+}$	3	55	$3 \times \frac{100}{55}$	5.5	L + S
$\text{AlCl}_3$	15	133.5	$15 \times \frac{100}{133.5}$	11.2	L + S

➤ Calculation of quantity of lime in grams, required for softening of water

Quantity of lime

$$L = \frac{74}{100} [Temporary \text{ } \text{Ca}^{2+} + 2 \times Temporary \text{ } \text{Mg}^{2+} + Permanent \text{ } (\text{Mg}^{2+} + \text{Fe}^{2+} + \text{Al}^{3+} + \text{H}^+) \\ (H\text{Cl} \text{ or } H_2\text{SO}_4) + \text{HCO}_3^- - \text{NaAlO}_2] \times \frac{\text{Vol. of Water}}{10^6} \times \frac{100}{\% \text{ of purity}} \text{ kg}$$

all in term of their  $\text{CaCO}_3$  equivalents.

$$= \frac{74}{100} [2 \times 35 + 35 + 6.8 + 5.5 + 11.2] \times \frac{\text{Vol. of Water}}{10^6} \times \frac{100}{85} \text{ kg} \\ = \frac{74}{100} [70 + 35 + 6.8 + 5.5 + 11.2] \times \frac{10^6}{10^6} \times \frac{100}{85} \text{ kg}$$

$$= 111.8 \text{ kgs.}$$

➤ Calculation of quantity of soda in grams required for softening water

Quantity of soda

$$S = \frac{106}{100} \int Permanent \text{ } (Ca^{2+} + Mg^{2+} + Al^{3+} + Fe^{2+} + H^+ (HCl \text{ or } H_2SO_4)) - HCO_3^- \\ \times \frac{\text{Vol. of Water}}{10^6} \times \frac{100}{\% \text{ of purity}} \text{ kg}$$

all in term of their  $\text{CaCO}_3$  equivalents.

$$S = \frac{106}{100} [\text{CaCO}_3 \text{ equivalent of } \text{MgSO}_4 + \text{CaCl}_2 + \text{Fe}^{2+} + \text{AlCl}_3] \times \frac{10^6}{10^6} \times \frac{100}{95} \text{ kg}$$

$$= \frac{106}{100} [96.71 \times \frac{100}{95} \text{ kg}] \\ = 107.9 \text{ kgs}$$

Ans. : Lime required = 111.8 kg  
Soda required = 107.9 kg

**Problem 2.18.4(A)** Calculate lime (90% pure) and soda ash (90% pure) to soften 1,00,000 litres of water containing :

$$\text{Mg}(\text{HCO}_3)_2 = 146 \text{ mg/lit}$$

$$\text{MgCl}_2 = 95 \text{ mg/lit}$$

$$\text{Ca}(\text{HCO}_3)_2 = 81 \text{ mg/lit}$$

$$\text{CaCl}_2 = 111 \text{ mg/lit}$$

$$\text{Na}_2\text{SO}_4 = 15 \text{ mg/lit}$$

(May 2007, 6 Marks)

**Solution :****> Calculation of  $\text{CaCO}_3$  equivalents for impurities**

Salt	Qty (mg/lit)	Mol/wt	Multiplication factors	$\text{CaCO}_3$ equivalent per lime	Requirement of Lime (L) and / or Soda (S)
$\text{Mg}(\text{HCO}_3)_2$	146	146	$146 \times \frac{100}{146}$	100	L
$\text{Ca}(\text{HCO}_3)_2$	81	162	$81 \times \frac{100}{162}$	50	L
$\text{Na}_2\text{SO}_4$					Does not contribute
$\text{MgCl}_2$	95	95	$95 \times \frac{100}{95}$	100	S
$\text{CaCl}_2$	111	111	$111 \times \frac{100}{111}$	100	S
$\text{SiO}_2$					Does not contribute

**> Calculation of quantity of lime required for softening of water****Quantity of lime**

$$L = \frac{74}{100} \left[ \text{Temporary } \text{Ca}^{2+} + 2 \times \text{Temporary } \text{Mg}^{2+} + \text{Permanent } (\text{Mg}^{2+} + \text{Fe}^{2+} + \text{Al}^{3+} + \text{H}^+) \right. \\ \left. (\text{HCl or } \text{H}_2\text{SO}_4) + \text{HCO}_3^- - \text{Na}_2\text{CO}_3 \right] \times \frac{\text{Vol. of Water}}{10^6} \times \frac{100}{\% \text{ of purity}} \text{ kg}$$

all in term of their  $\text{CaCO}_3$  equivalents.

$$\begin{aligned} L &= \frac{74}{100} [100 + 2 \times 50 + 100 + 100] \frac{10^6}{10^6} \times \frac{100}{90} \text{ kg} \\ &= \frac{74}{100} \times (400) \times \frac{1}{9} \text{ kg} \\ &= 32.8 \text{ kg of lime} \end{aligned}$$

**> Calculation of quantity of soda required for softening water****Quantity of soda**

$$S = \frac{106}{100} \int P \text{ermanent } (\text{Ca}^{2+} + \text{Mg}^{2+} + \text{Al}^{3+} + \text{Fe}^{2+} + \text{H}^+) (\text{HCl or } \text{H}_2\text{SO}_4) - \text{HCO}_3^- / \\ \times \frac{\text{Vol. of Water}}{10^6} \times \frac{100}{\% \text{ of purity}} \text{ kg}$$

all in term of their  $\text{CaCO}_3$  equivalents.

$$S = \frac{106}{100} [100 + 100] \frac{10^6}{10^6} \times \frac{100}{90} \text{ kg}$$

**Solution :****Lime required = 32.8 kg****Soda required = 23.55 kg****Problem 2.18.44(B)**

Calculate the amount of lime (85% pure) and soda (90% pure) required for softening of 10,000 litres of boiler-feed water containing following impurities:



(At. wt. Ca = 40, Mg = 24, S = 32, O = 16, Cl = 35.5, H = 1, Si = 28)

**Solution :****Quantity of lime**

Salt	Qty (mg/lit)	Multiplication factors	$\text{CaCO}_3$ equivalent per lime	Requirement of Lime (L) and / or Soda (S)
$\text{Ca}(\text{HCO}_3)_2$	16.2	$16.2 \times \frac{100}{162}$	10 ppm	L
$\text{CaSO}_4$	6.8	$6.8 \times \frac{100}{136}$	5 ppm	L + S
$\text{CaCl}_2$	11.1	$11.1 \times \frac{100}{111}$	10 ppm	L + S
$\text{MgSO}_4$	6.0	$6.0 \times \frac{100}{146}$	5 ppm	L + S
$\text{Mg}(\text{HCO}_3)_2$	8.4	$8.4 \times \frac{100}{146}$	5.75 ppm	L
$\text{SiO}_2$	8.0		Does not contribute to hardness	

(May 2008, 6 Marks)

**Given :**

Purity of lime = 85 %

Purity of soda = 90 %

Quantity of water = 10000 liters

Quantity of lime =  $\frac{74}{100} [\text{Temporary Ca}^{+2} + 2 \times \text{Temporary Mg}^{+2} + \text{Permanent } (\text{Mg}^{+2} + \text{Fe}^{+2} + \text{Al}^{+3} + \text{H}^+(\text{HCl or H}_2\text{SO}_4)) + \text{HCO}_3^- - \text{NaAlO}_2] \times \frac{\text{Vol. of Water}}{10^3} \times \frac{100}{\% \text{ of purity}} \text{ kg}$

$$\begin{aligned}
 &= \frac{74}{100} [10 + 2(5.75) + 5] \times 10000 \times \frac{100}{85} \times \frac{1}{10^3} \\
 &= \frac{74}{100} [26.5] \times 10000 \times \frac{100}{85} \times \frac{1}{10^3} \\
 &= 8.268 \text{ kg}
 \end{aligned}$$

**Quantity of soda :**

$$\begin{aligned}
 &= \frac{106}{100} \text{ Permanent } (\text{Ca}^{+2} + \text{Mg}^{+2} + \text{Al}^{+3} + \text{Fe}^{+2} + \text{H}^+(\text{HCl or H}_2\text{SO}_4)) - \text{HCO}_3^- \\
 &= \frac{106}{100} [5 + 10 + 5] \times 1000 \times \frac{100}{90} \times \frac{1}{10^3} \text{ kg of soda} \\
 &= \frac{106}{100} [20] \times 10000 \times \frac{100}{90} \times \frac{1}{10^3} \text{ kg of soda} \\
 &= 23.55 \text{ kg}
 \end{aligned}$$

Ans. :

Lime Required = 8.268 kg

Soda Required = 23.55 kg

**Problem 2.18.44(C) :** Calculate lime (90%) pure and soda (95%) pure required for softening of 20000 liters of water containing following impurities :

- (i)  $\text{Ca}(\text{HCO}_3)_2 = 81 \text{ mg per liter}$
  - (ii)  $\text{MgCO}_3 = 42 \text{ mg per liter}$
  - (iii)  $\text{NaAlO}_2 = 4.1 \text{ mg per liter}$
  - (iv)  $\text{HCl} = 3.65 \text{ mg per liter}$
  - (v)  $\text{Ca}(\text{NO}_3)_2 = 82 \text{ mg per liter}$
  - (vi)  $\text{NaCl} = 4.5 \text{ mg per liter}$
- (At Wt. Ca = 40, H = 1, C = 12, O = 16, Mg = 24, Na = 23, Al = 27,  
Cl = 35.5, N = 14)
- (Det. 2007, 5 Marks)

**Solution :**  
**Calculation of  $\text{CaCO}_3$  equivalent :**

Salt	Qty (mg/lit)	Multiplication factors	$\text{CaCO}_3$ equivalent per lime	Requirement of lime (L) and / or Soda (S)
$\text{Ca}(\text{HCO}_3)_2$	81	$81 \times \frac{100}{162}$	50	L
$\text{MgCO}_3$	42	$42 \times \frac{100}{84}$	50	L
$\text{NaAlO}_2$	4.1	$4.1 \times \frac{100}{82}$	5	L - S
HCl	3.65	$3.65 \times \frac{100}{36.5}$	10	L + S
$\text{Ca}(\text{NO}_3)_2$	82			
NaCl	4.5			

Given :

Purity of lime = 90 %

Purity of soda = 95 %

Volume of rawwater = 20000 liter

Calculation of lime,

$$\text{Lime} = \frac{74}{100} [\text{Temporary Ca}^{+2} + 2 \times \text{Temporary Mg}^{+2} + \text{Permanent }$$

$$\begin{aligned}
 &(\text{Mg}^{+2} + \text{Fe}^{+2} + \text{Al}^{+3} + \text{H}^+(\text{HCl or H}_2\text{SO}_4)) + \text{HCO}_3^- - \text{NaAlO}_2] \times \frac{\text{Vol. of water}}{10^3} \times \frac{100}{\% \text{ of purity}} \text{ kg} \\
 &= \frac{74}{100} [50 + (2 \times 50) + 10 - 5] \times 20000 \times \frac{100}{90} \times \frac{1}{10^3} \\
 &= \frac{74}{100} [155] \times 20000 \times \frac{100}{90} \times \frac{1}{10^3} \text{ kg lime} \\
 &= 2.549 \text{ kg}
 \end{aligned}$$

Calculation of soda,

$$\begin{aligned} \text{Soda} &= \frac{106}{100} [\text{Permanent } (\text{Ca}^{+2} + \text{Mg}^{+2} + \text{Al}^{+3} + \text{Fe}^{+2} + \text{H}^+ \text{ (HCl or H}_2\text{SO}_4)) - \text{HCO}_3^-] \\ &\times \frac{\text{Vol. of water}}{10^6} \times \frac{100}{\% \text{ of purity}} \text{ kg} \\ &= \frac{106}{100} [10 - 5] \times 20000 \times \frac{100}{95} \times \frac{1}{10^6} \\ &= \frac{106}{100} [5] \times 20000 \times \frac{100}{95} \times \frac{1}{10^6} \\ &= 0.1 \text{ kg} \end{aligned}$$

Ans.

$$\text{Line Required} = 2.549 \text{ kg}$$

$$\text{Soda Required} = 0.1 \text{ kg}$$

#### 2.18.4 Problems based on Zeolite Process

**Problem 2.18.44(D) :** A zeolite bed, on softening 7000 litres of hard water, required 60 litres of 10 % NaCl solution for regeneration. Calculate the hardness of water in ppm.

**Solution :**

Quantity of NaCl consumed by zeolite bed = 10 % NaCl solution

i.e. 10 gms NaCl per 100 ml solution i.e. 100 gms/litre.

Thus, 1 litre solution  $\Rightarrow$  00 gms NaCl

∴ 60 litres solution  $\Rightarrow$  6000 gms NaCl

$\Rightarrow$   $\frac{6000 \times 50}{58.5}$  gms equivalent of CaCO<sub>3</sub>

$\Rightarrow$  5128.20 gms CaCO<sub>3</sub> equivalent



∴ 10 % NaCl solution  $\Rightarrow$  10 gms NaCl per 100 ml solution

∴ quantity of NaCl  $\Rightarrow$  100 gms NaCl/litre solution

∴ quantity of NaCl  $\Rightarrow$   $\frac{100 \times 50}{58.5} \times 1000$

Thus hardness of water sample  $\Rightarrow$  732.6 mgms equivalent of CaCO<sub>3</sub> per litre

Thus hardness of water sample = 732.6 ppm

**Ans. :** Hardness of water = 732.6 ppm.

**Problem 2.18.45 :** A water sample having hardness 250 ppm was softened by zeolite process. The exhausted zeolite bed required 50 litres of 15 % NaCl solution for regeneration. Calculate the quantity of water softened using the zeolite bed.

**Solution :**

$$\begin{aligned} 100 \text{ ml solution} &\Rightarrow 15 \text{ gms NaCl} \\ \therefore 1 \text{ litre solution} &\Rightarrow 150 \text{ gms NaCl} \\ \therefore 50 \text{ litres solution} &\Rightarrow 7500 \text{ gms NaCl} \\ &\Rightarrow \frac{7500 \times 50}{58.5} \text{ gms equivalents of CaCO}_3 \\ &\Rightarrow 6410.256 \text{ gms CaCO}_3 \text{ equivalent} \\ &\Rightarrow 6410256 \text{ mgms CaCO}_3 \text{ equivalent} \end{aligned}$$

Thus zeolite bed removed 6410256 mgms equivalent of CaCO<sub>3</sub> hardness.

∴ 250 ppm hardness  $\Rightarrow$  1 litre of water

$\therefore 6410256 \text{ ppm hardness} \Rightarrow \frac{6410256 \times 1}{250} \text{ litres of water}$

$\Rightarrow 25641.025 \text{ litres of water}$

$\approx 25641 \text{ litres of water}$

**Problem 2.18.46 :** A zeolite bed got exhausted after softening 5000 litres of water. Hardness of water was 250 mgms CaCO<sub>3</sub> equivalent per litre. How many litres of 10 % NaCl solution would be required to regenerate zeolite bed.

**Solution :**



∴ 10 % NaCl solution  $\Rightarrow$  10 gms NaCl per 100 ml solution

∴ quantity of NaCl  $\Rightarrow$  100 gms NaCl/litre solution

∴ quantity of NaCl  $\Rightarrow$   $\frac{100 \times 50}{58.5} \times 1000$

(equivalents to mgs of  $\text{CaCO}_3$ )  $\Rightarrow 85470 \text{ mgs CaCO}_3 \text{ equivalent/litre}$

Hardness of water softened was 250 ppm.

i.e. 1 litre of water  $\Rightarrow 250 \text{ mgs CaCO}_3 \text{ equivalent}$

$\therefore 5000 \text{ litres of water} \Rightarrow (5000 \times 250) \text{ mgs CaCO}_3 \text{ equivalent}$

$\Rightarrow 1250000 \text{ mgs CaCO}_3 \text{ equivalent}$

$\Rightarrow 1.25 \times 10^6 \text{ mgs CaCO}_3 \text{ equivalent}$

$\therefore 85470 \text{ mgs CaCO}_3 \text{ equivalent} \Rightarrow 1 \text{ litre NaCl solution}$

$\therefore 1.25 \times 10^6 \text{ mgs CaCO}_3 \text{ equivalent} \Rightarrow \frac{1.25 \times 10^6}{85470} \text{ liter NaCl solution}$

$\Rightarrow 14.625 \text{ litres NaCl solution}$

$\approx 14.7 \text{ litres of NaCl solution}$

**Ans.:** Volume of  $\text{NaCl}$  solution required = 14.7 litres

**Problem 2.18.47:** How many litres of 20 %  $\text{NaCl}$  solution would be required to regenerate an exhausted zeolite bed after it softened 20 litres of hard water of 375 ppm hardness. What should be the quantity of  $\text{NaCl}$  used in regeneration?

**Solution :**

Quantity of water softened = 20 litre

Hardness of water = 375 ppm

i.e. 20 litres water  $\Rightarrow 7500 \text{ mgs CaCO}_3 \text{ equivalent}$

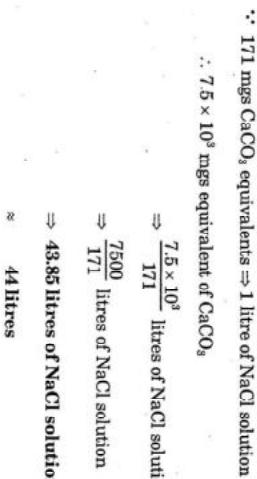
Now  $\text{NaCl}$  used is 20 % solution.

i.e. 20 gms per 100 ml solution

Or 200 gms per 1000 ml solution.

Equivalents of  $\text{CaCO}_3$  of this solution would be

$$\begin{aligned} &= \frac{200 \times 50}{58.5} \times 1000 \\ &= \frac{10000}{58.5} \\ &= 171 \text{ mgs} \end{aligned}$$



**Ans.:** Volume of  $\text{NaCl}$  solution required = 44 litres

**Problem 2.18.48:** The hardness of 25000 litres of water was completely removed using zeolite softener. For regeneration of exhausted zeolite bed, 200 litres of  $\text{NaCl}$  solution containing 20 gms per litre  $\text{NaCl}$  was required. Calculate the hardness of water sample.

**Solution :**

Using regeneration reaction,



Now, quantity of  $\text{NaCl}$  in regeneration

$$\begin{aligned} &= 200 \times 20 \\ &= 4000 \text{ gms NaCl} \end{aligned}$$

Thus  $(2 \times 58.5) \text{ gms NaCl} \Rightarrow 100 \text{ gms CaCO}_3$

$$\begin{aligned} \therefore 4000 \text{ gm NaCl} &\Rightarrow \frac{4000 \times 100}{2 \times 58.5} \\ &\Rightarrow \frac{4000 \times 100}{117} \\ &\Rightarrow 3418.8 \text{ gms of CaCO}_3 \\ &\Rightarrow 34180 \text{ mgs of CaCO}_3 \\ &\therefore 25000 \text{ litres of hard water} \Rightarrow 34180 \text{ mgs CaCO}_3 \\ &\therefore 1 \text{ litre of hard water} \Rightarrow \frac{34180}{25000} \text{ mgs of CaCO}_3 \\ &\Rightarrow 13.68 \text{ mgs of CaCO}_3 \\ &\Rightarrow 13.68 \text{ ppm} \\ &\therefore \text{Hardness of water sample} = 13.68 \text{ ppm} \end{aligned}$$

**Problem 2.18.49:** The hardness of  $10^4$  litres of a water sample was completely removed by a zeolite softener. The zeolite required 80 litres of NaCl solution, containing 1000 mg/l of NaCl, for regeneration. Calculate the hardness of water sample.

**Solution:**

Let the hardness of the water sample be  $x$  mg/l. Now it is given that 1 litre of NaCl solution contains 1000 mg of NaCl.

So 80 litres of solution contains  $80 \times 1000$  mg

$$= 80000 \text{ mgs of NaCl}$$

$$= 80000 \times \frac{50}{58.5} \text{ mg of CaCO}_3$$

$$= 68376.0 \text{ mg of CaCO}_3$$

But the total quantity of water is  $10^4$  litres.

So the hardness present in the water sample

$$= \frac{6876.0}{10^4}$$

$$= 6.8376 \text{ mg/lit}$$

$$= 6.84 \text{ mg/lit}$$

**Ans.:** Hardness of water = 6.84 mg/lit

**Problem 2.18.50:** The hardness of 75,000 litres of a water sample was completely removed by a permittit. The exhausted permittit then required 1500 litres of NaCl containing 117 mg of NaCl per litre for regeneration. Calculate the hardness of water sample.

**Solution:**

Let the hardness of the water sample be  $x$  mg/l

Now, 1 litre of NaCl contains 117 mg of NaCl

$\therefore$  1500 litres of NaCl contains  $1500 \times 117 = 175500$  mg of NaCl

58.5 mg of NaCl  $\equiv$  50 mgs of CaCO<sub>3</sub> equivalent hardness

$$= 175500 \times \frac{50}{58.5}$$

$$= 1,50,000 \text{ mgs of CaCO}_3 \text{ equivalents hardness}$$

But the total quantity of the water sample = 75,000 litre

$$\therefore 75000 \text{ lt. of water} = 1,50,000 \text{ mgs of CaCO}_3$$

$\therefore$  1 lt. of water  $= \frac{150000}{75000}$  mgs of CaCO<sub>3</sub>

$$= 2 \text{ mg/l of CaCO}_3$$

$$= 2 \text{ ppm CaCO}_3$$

**Ans.:** Hardness of water sample = 2 ppm

**Problem 2.18.51:** An exhausted zeolite softener was regenerated by passing 300 litres of NaCl solution, having a strength of 75 gm/litre of NaCl. How many litres of hard water sample, having hardness of 600 ppm can be softened using this softener.

**Solution:**

Here, let the quantity of the water sample be  $x$  litre

Now, the hardness of the water sample is 600 ppm

Hardness = concentration of NaCl  $\times$  litres of NaCl

$$= 75000 \times 300$$

$$= 225 \times 10^5 \text{ mg of NaCl}$$

$$= 225 \times 10^5 \times \frac{50}{58.5} \text{ mg of CaCO}_3$$

$$= 19230769.23 \text{ mg}$$

If 1 litre of water  $\equiv$  600 mgs of CaCO<sub>3</sub> equivalent hardness

$x$  litres of water  $\equiv 19230769.23$

$$\therefore x = \frac{19230769.23}{600}$$

$$= 32051.28 \text{ litres of water}$$

**Ans.:** 32051.28 litres of water sample can be softened

**Problem 2.18.52:** A zeolite softener was completely exhausted of NaZe by passing 100 litres of NaCl. How many litres of water of hardness 50 ppm can be softened by this softener? The concentration of NaCl is 200 mg/lit solution.

**Solution:**

Here, 1 litre of NaCl contains 1200 mg of NaCl

100 litre of NaCl contain  $100 \times 1200 = 12 \times 10^4$  mg of NaCl

$$= 12 \times 10^4 \times \frac{50}{58}$$

$$= 10254641.02 \text{ mg of CaCO}_3$$

Now this much mg of CaCO<sub>3</sub> is present  $\frac{10254641.02}{x}$  mg/l in  $x$  litres of water. So the hardness

but hardness = 50 ppm i.e. 50 mg/l

$$\begin{aligned} 50 &= \frac{1025641.02}{x} \\ x &= \frac{1025641.02}{50} \\ x &= 20512 \text{ litres of water} \end{aligned}$$

**Ans. :** 20512 litres of water can be softened

**Problem 2.18.53:** The hardness of 75,000 litres of a water sample was completely removed by a permitt. The exhausted permitt then required 1500 litres of NaCl containing 117 mg of NaCl per litre for regeneration. Calculate the hardness of water sample.

**Solution :**

$$1 \text{ lit. of NaCl solution} = 117 \text{ mg of NaCl}$$

$$\therefore 1500 \text{ lit. of NaCl} = 175.5 \text{ mg of NaCl}$$



$$50 \text{ mg of CaCO}_3 \text{ equivalent hardness} = 58.5 \text{ mg of NaCl}$$

$$175.5 \text{ g of NaCl present} = 1500 \text{ mg of CaCO}_3 \text{ equivalent}$$

This is present in 75000 of water i.e. 75,000 lit. of water contains 150,000 mg of CaCO<sub>3</sub> equivalent hardness.

$$\begin{aligned} 1 \text{ lit. of water contains} &= \frac{150,000}{75,000} \text{ mgs of CaCO}_3 \text{ equivalent hardness} \\ &= 2 \text{ mgs/lit.} \end{aligned}$$

**Ans. :** Hardness of water sample = 2 ppm or 2 mg/lit.

**Problem 2.18.54:** A zeolite softener was completely exhausted and was regenerated by passing 1000 litres of sodium chloride solution containing 100 gm-lit. of sodium chloride. How many lit. of water sample of hardness 500 ppm can be softened by this softener.

**Solution :** Let litres of water be x.  
(Dec. 2001)

Regeneration reaction is



Now 50 gm/litre of NaCl solution is used for regeneration.

$$\therefore \text{Quantity of NaCl used} = 150 \times 50$$

$$= 7500 \text{ gm}$$

$$\begin{aligned} \text{From equation } 2 \text{ NaCl} &= \text{CaCl}_2 = \text{CaCO}_3 \\ \therefore \text{NaCl} &= \frac{1}{2} \text{ CaCl}_2 = \frac{1}{2} \text{ CaCO}_3 \end{aligned}$$

i.e. 58.5 mgs NaCl = 50 mgs of CaCO<sub>3</sub> equivalent

$$\begin{aligned} \therefore 7500 \times 10^3 \text{ mgs NaCl} &= \frac{7500 \times 10^3 \times 50}{58.5} \\ &= \frac{75 \times 5 \times 10^6}{58.5} \end{aligned}$$

100 gm/lit. of NaCl solution is used for regeneration i.e. 1 lit. of solution contains 100 gm of NaCl salt 100 lit. of solution is used i.e.  $100 \times 1000$  gm of NaCl

$$= 10^6 \text{ gm of NaCl}$$

According to data, the water sample has 450 ppm hardness.

From the equation

$$\begin{aligned} 58.5 \text{ mg of NaCl} &= 50 \text{ mg of CaCO}_3 \text{ equivalent} \\ \therefore 10^6 \times 10^6 \text{ mg of NaCl} &= \frac{10^6 \times 10^6 \times 50}{58.5} \text{ mg of CaCO}_3 \text{ equivalent} \\ &= 8.547 \times 10^7 \text{ mg of CaCO}_3 \text{ equivalent} \end{aligned}$$

According to data the water sample has 500 ppm hardness.

i.e. 1 lit. of water contains 500 mgs of CaCO<sub>3</sub> equivalent hardness.

$\therefore x$  lit. of water contains :

$$= 8.547 \times 10^7 \text{ mg of CaCO}_3 \text{ equivalent}$$

**Ans. :** Thus 1,70,940 lit. of water of hardness 500 ppm can be softened.

**Problem 2.18.55:** A zeolite softener was completely exhausted and was regenerated by passing 150 litres of NaCl soln., containing 50 g/litres of NaCl. How many litres of water of hardness 450 ppm can be softened by this container?

(Dec. 2005)

**Solution :**

Let litres of water be x

Regeneration reaction is



Now 50 gm/litre of NaCl solution is used for regeneration.

$$\therefore \text{Quantity of NaCl used} = 150 \times 50$$

$$= 7500 \text{ gm}$$

$$\begin{aligned} \text{From equation } 2 \text{ NaCl} &= \text{CaCl}_2 = \text{CaCO}_3 \\ \therefore \text{NaCl} &= \frac{1}{2} \text{ CaCl}_2 = \frac{1}{2} \text{ CaCO}_3 \end{aligned}$$

i.e. 58.5 mgs NaCl = 50 mgs of CaCO<sub>3</sub> equivalent

$$\begin{aligned} \therefore 7500 \times 10^3 \text{ mgs NaCl} &= \frac{7500 \times 10^3 \times 50}{58.5} \\ &= \frac{75 \times 5 \times 10^6}{58.5} \end{aligned}$$

According to data, the water sample has 450 ppm hardness.

i.e. 1 litre of water contains 450 mgs of  $\text{CaCO}_3$  equivalent hardness.  
 $x$  litre of water contains  $6.410 \times 10^6$  mgs of  $\text{CaCO}_3$  equivalent

$$\therefore x = 14244 \text{ litres}$$

**Ans.:** Thus 14244 litres of water of hardness 450 ppm can be softened.

**Problem 2.18.56:** An exhausted zeolite softener was regenerated by passing 75 litres of NaCl solution having strength 75 g/lit. If hardness of water is 300 ppm, then calculate the total volume of water that is softened by zeolite softener.

(May 2004)

**Solution:**

**Given data :**

Quantity of NaCl solution = 75 litres

Quantity of NaCl in solution = 75 gms/litre

Hardness of water sample = 300 ppm

Total volume of water softened = ?

Sodium chloride solution used for regeneration contain 75 gms/litre of NaCl.

Total amount of NaCl in 75 litres = 75 gms/litre  $\times$  75 litres

$$= 5625 \text{ gms of NaCl.}$$

Now,

$$5625 \text{ gms of NaCl} = 5625 \times \frac{100}{117} \text{ gms CaCO}_3 \text{ equivalent}$$

$$= 5625 \times \frac{100}{117} \times 10^3 \text{ mgs CaCO}_3 \text{ equivalent}$$

$$= 4.8 \times 10^6 \text{ mgs CaCO}_3 \text{ equivalents}$$

Let  $V$  litres of 300 ppm (i.e. 300 mg/l) of water contains  $4.8 \times 10^6$  mgs  $\text{CaCO}_3$  equivalents hardness.

$$\text{i.e. } V \times 300 = 4.8 \times 10^6$$

$$\therefore V = (4.8 \times 10^6) 300 = 1.6 \times 10^4 \text{ litres}$$

$$= 16000 \text{ litres}$$

**Ans.:** Thus 16000 litres of water was softened by zeolite bed.

**Applied Chemistry - I (MU)** 2-146 Water & its Treatment  
**Problem 2.18.57:** 800 litres of raw water was soften by zeolite softener. After it got exhausted required 40 litres of NaCl solution containing 110 gm per liter of NaCl for its regeneration. Calculate the hardness of water. (Dec. 2007, 4 Marks)

**Solution:**

**Given :**

Concentration of NaCl solution:

$$= 110 \text{ gm/liter NaCl}$$

$$= 110 / 1000 \text{ ml.}$$

Volume of Raw water = 800 liter

Volume of NaCl for regeneration = 40 liter

To calculate hardness of water

$\because$  40 liter of NaCl consumed

$$= 40 \times 110 \text{ gm. NaCl}$$

$$= 4400 \text{ gm of NaCl consumed for regeneration.}$$

$$= \frac{4400 \times 50}{58.5} \text{ equivalents of CaCO}_3$$

$$= 3760.7 \text{ gms equivalents of CaCO}_3$$

Thus

$$800 \text{ litres of water} = 3760 \text{ gms CaCO}_3 \text{ equivalents}$$

$$1 \text{ litre of water} = \frac{3760.7}{800} \text{ gms CaCO}_3 \text{ equivalents}$$

$$= 4.7 \text{ gms CaCO}_3 \text{ equivalents}$$

$$= 4700.85 \text{ gms CaCO}_3 \text{ equivalents}$$

Thus hardness of water sample = 4700.85 ppm.

**Ans.:** Hardness of water sample = 4700.85 ppm.

**Review Questions**

- Q. 1 Define temporary hardness and permanent hardness.
- Q. 2 Define hardness of water. How it can be chemically detected?
- Q. 3 How is temporary hardness in water eliminated?
- Q. 4 What is hardness? Name the substances that cause permanent hardness?
- Q. 5 What are scales and sludges? Mention the disadvantages caused by them in boilers.
- Q. 6 Differentiate between hard water and soft water.
- Q. 7 Why is hard water unsuitable for boilers?
- Q. 8 What is meant by "Phosphate Conditioning" of water?
- Q. 9 What is the principle involved in the determination of total hardness?
- Q. 10 What is the principle behind carbonate conditioning?
- Q. 11 What is the function of "Sodium Phosphate" and "Hydrazine" in the treatment of boiler feed water?
- Q. 12 Why it is necessary to carry out internal treatment of water in the boilers in addition to softening of water?
- Q. 13 Write in brief "Disadvantages of hard water in different industries".
- Q. 14 Differentiate between temporary hardness and permanent hardness.
- Q. 15 What are the impurities associated with water? Give their effects if it is used in various industries.
- Q. 16 What is hardness? Explain how would you determine hardness of water using E.D.T.A method?
- Q. 17 With the help of chemical equation explain the principle involved in softening of hard water by lime-soda process.
- Q. 18 Discuss the process of softening of water by using zeolites. What are the limitations of this process?
- Q. 19 Describe the demineralization (Ion-exchange/de-ionisation) process for softening of hard water. Are there any drawbacks of this method?
- Q. 20 When do you recommend only internal treatment for boiler water and completely avoid external treatment?
- Q. 21 Write a brief note on caustic embrittlement.

**2.19 Unsolved Problems**

**Ex. 1 :** Calculate the quantity of lime and soda required for softening 5,00,000 litre of water containing following impurities.

$$\begin{aligned} \text{Ca(HCO}_3)_2 &= 32.4 \text{ ppm;} & \text{CaSO}_4 &= 40.8 \text{ ppm;} \\ \text{Mg(HCO}_3)_2 &= 43.8 \text{ ppm;} & \text{MgCl} &= 5.7 \text{ ppm;} \\ \text{CaCl}_2 &= 22.2 \text{ ppm;} & \text{MgSO}_4 &= 3.6 \text{ ppm;} \end{aligned}$$

[Ans. : Lime = 32.9 kg., Soda = 31.27 kg]

**Ex. 2 :** A sample of water has the following impurities per litre:  
 $\text{Mg(HCO}_3)_2 = 58.4 \text{ mg;} \quad \text{SiO}_2 = 20 \text{ mg;} \\ \text{Ca(HCO}_3)_2 = 32.4 \text{ mg;} \quad \text{Na}_2\text{SO}_4 = 435 \text{ mg}$   
 Calculate the amount of soda required for treatment of 20,000 litres of water.  
**(Hint :**  $\text{SiO}_2$  and  $\text{Na}_2\text{SO}_4$  do not contribute to hardness)

[Ans. : Lime = 1.48 kg., Soda not required.]

**Ex. 3 :** A sample of water contains the following impurities per litre:  
 $\text{Mg(HCO}_3)_2 = 146 \text{ mg;} \quad \text{MgSO}_4 = 12 \text{ mg;} \\ \text{CaCl}_2 = 111 \text{ mg;} \quad \text{Ca (NO}_3)_2 = 16.4 \text{ mg}$

Lime used is 75 % pure while soda used is 85 % pure.  
 Calculate the amount of lime and soda required for softening 10,000 litres of water.  
 20 % excess chemicals are to be used for treatment.

[Ans. : Lime = 2.072 kg., Soda = 1.371 kg.]

**Ex. 4 :** Calculate the amount of lime (81 % pure) required for treatment of 30,000 litres of water whose analysis is as follows:

$$\begin{aligned} \text{Ca(HCO}_3)_2 &= 40.5 \text{ mg/lit.;} & \text{NaCl} &= 58.0 \text{ mg/lit.;} \\ \text{SiO}_2 &= 15 \text{ mg/lit.;} & \text{FeSO}_4 &= 75.9 \text{ mg/lit.;} \\ \text{MgCl}_2 &= 19 \text{ mg/lit.;} & \text{CaCl}_2 &= 55.5 \text{ mg/lit.;} \\ \text{MgCO}_3 &= 84 \text{ mg/lit.} & & \end{aligned}$$

[Ans. : Lime = 8.085 kg., Soda not required.]

**Ex. 5 :** Calculate the amount of lime (80 % pure) and soda (95 % pure) required to soften and soda (95 % pure) required to soften one million litre of water which contains

$$\text{CaCO}_3 = 125 \text{ mg/lit.};$$

$$\text{O}_2 = 65 \text{ ppm};$$

$$\text{CaCl}_2 = 222 \text{ ppm};$$

$$\text{NaHCO}_3 = 33.6 \text{ ppm}.$$

[Hint : Both  $\text{NaHCO}_3$ ,  $\text{CaCO}_3$  are to be considered as temporary hardness.]

[Ans. : Lime = 606.8 kg., Soda = 335.85 kg.]

**Ex. 6 :** Calculate the amount of lime and soda required for softening 10,000 litres of water containing the following dissolved salts.

$$\text{Ca}(\text{HCO}_3)_2 = 162 \text{ mg};$$

$$\text{MgSO}_4 = 136 \text{ mg};$$

$$\text{NaCl} = 585 \text{ mg}$$

[Ans. : Lime = 2.72 kg., Soda = 2.5 kg.]

**Ex. 7 :** A water sample was found to contain the following dissolved salts;

$$\text{Ca}(\text{HCO}_3)_2 = 48.6 \text{ ppm};$$

$$\text{Mg}(\text{HCO}_3)_2 = 29.2 \text{ ppm};$$

$$\text{CaCl}_2 = 3.8 \text{ ppm};$$

$$\text{MgCl}_2 = 3.8 \text{ ppm};$$

$$\text{CaSO}_4 = 54.4 \text{ ppm}.$$

Calculate the cost of chemicals required for softening 1 million litres of water by the lime soda process. Cost of 90 % pure lime is Rs. 62 per kg and that of soda is Rs. 29 per kg.

[Ans. : Lime = 2.72 kg; Cost = Rs. 4038.33,  
Soda = 2.35 kg; Cost = Rs. 58.15.]

**Ex. 8 :** Calculate the quantity of lime and soda for softening 70,000 litres of water containing the following dissolved salts.

$$\text{Ca}(\text{HCO}_3)_2 = 8.1 \text{ mg};$$

$$\text{NaCl} = 66 \text{ mg};$$

$$\text{CaSO}_4 = 13.6 \text{ mg};$$

$$\text{Mg}(\text{HCO}_3)_2 = 7.3 \text{ mg}.$$

[Ans. : Lime = 1.55 kg., Soda = 2.59 kg.]

**Ex. 9 :** Calculate the amount of lime and soda needed for softening water containing the following dissolved salts per litre :

$$\text{Ca}(\text{HCO}_3)_2 = 16.2 \text{ mg};$$

$$\text{Mg}(\text{HCO}_3)_2 = 73 \text{ mg};$$

$$\text{NaCl} = 58.5 \text{ mg}$$

[Ans. : Lime = 88.8 kg., Soda = 116.6 kg.]

**Ex. 10 :** Calculate the amount of lime and soda required to soften 3,00,000 litres of water which contained the following dissolved salts :

$$\text{CO}_2 = 300 \text{ ppm};$$

$$\text{MgCl}_2 = 95 \text{ ppm};$$

$$\text{Mg}(\text{HCO}_3)_2 = 86.7 \text{ ppm};$$

$$\text{Mg}(\text{NO}_3)_2 = 26.9 \text{ ppm};$$

$$\text{MgSO}_4 = 8.4 \text{ ppm};$$

$$\text{H}_2\text{SO}_4 = 16.9 \text{ ppm}$$

[Ans. : Lime = 183.37 kg., Soda = 39.75 kg.]

**Ex. 11 :** A sample of hard water was found to contain :

$$\text{CaCO}_3 = 120 \text{ mg/lit.};$$

$$\text{CaSO}_4 = 8.6 \text{ mg/lit.};$$

$$\text{MgSO}_4 = 60 \text{ mg/lit.};$$

$$\text{MgCl}_2 = 19 \text{ mg/lit.}$$

Calculate the amount of lime and soda required for the softening of 5 million litres of water, if the purity of lime is 90 % and that of soda is 88 %.

[Ans. : Lime = 803 kg., Soda = 483.75 kg.]

**Ex. 12 :** Calculate the amount of lime and soda required to soften 3 million litres of water having following composition.

$$\text{Free CO}_2 = 25 \text{ ppm};$$

$$\text{Mg}(\text{HCO}_3)_2 \text{ as MgCO}_3 = 15 \text{ ppm};$$

$$\text{Ca}(\text{HCO}_3)_2 \text{ as CaCO}_3 = 120 \text{ ppm}.$$

[Ans. : Lime = 530 kg., Soda = 198.76 kg.]

**Ex. 13 :** A sample of water contains the following salts expressed in gm/lit.

$\text{Ca}(\text{HCO}_3)_2 = 0.343;$	$\text{Mg}(\text{HCO}_3)_2 = 0.175;$
$\text{CaSO}_4 = 0.235;$	$\text{MgCl}_2 = 0.147.$

Calculate the amount of pure lime and soda for softening 1000 litres of water.

[Ans. : Lime = 0.449 kg., Soda = 0.348 kg.]

**Ex. 14 :** A sample of hard water contains following dissolved salts.

$$\text{Ca}(\text{HCO}_3)_2 = 48.5 \text{ ppm};$$

$$\text{Mg}(\text{HCO}_3)_2 = 36.5 \text{ ppm};$$

$$\text{CaSO}_4 = 35 \text{ ppm};$$

$$\text{NaCl} = 43 \text{ ppm};$$

$$\text{CaCl}_2 = 27.75 \text{ ppm};$$

$$\text{MgCl}_2 = 50 \text{ ppm}.$$

[Ans. : Lime = 80.66 kg., Soda = 91.16 kg.]

**Ex. 15 :** A water sample on analysis gave the following compositions :

$$\text{Calcium bicarbonate} : 4.86 \text{ mg/lit.};$$

$$\text{Magnesium chloride} : 38 \text{ mg/lit.};$$

$$\text{Calcium chloride} : 333 \text{ mg/lit.};$$

$$\text{Magnesium sulphate} : 54.4 \text{ mg/lit.};$$

**Calcium sulphate :** 54.4 mg/lit.;

**Magnesium bicarbonate :** 29.2 mg/lit.

**Ex. 16:** Calculate the carbonate and non-carbonate hardness of the sample and the amount of lime and soda required to soften 5000 litres, of hard water. The purity of lime is 80 % and that of soda is 75 %.

[Ans. : Lime = 0.4 kg., Soda = 2.71 kg.]

**Ex. 16:** Sample of water was found to contain the following impurities :

$\text{CaCO}_3 = 140 \text{ mg/lit.};$	$\text{CaSO}_4 = 136 \text{ mg/lit.};$
$\text{MgCO}_3 = 8.4 \text{ mg/lit.};$	$\text{MgSO}_4 = 60 \text{ mg/lit.};$
$\text{SiO}_2 = 20 \text{ mg/lit.};$	$\text{MgCl}_2 = 38 \text{ mg/lit.}$

Calculate the quantity of lime (90 % pure) and soda (95 % pure) required for softening 5 million litres of water.

[Ans. : Lime = 904.5 kg., Soda = 892.6 kg.]

**Ex. 17:** The hardness of 30,000 litres of a water sample was completely removed by zeolite. The exhausted zeolite then required 1500 litres of NaCl containing 234 mg of NaCl per litre for regeneration. Calculate the hardness of the water sample.

[Ans. : 10 ppm]

**Ex. 18:** What is the carbonate and non-carbonate hardness of a sample of water which has the following impurities per litre ?

$\text{Ca}(\text{HCO}_3)_2 = 50.25 \text{ mg};$	$\text{Ca}(\text{IO}_3)_2 = 8.2 \text{ mg};$
$\text{CaCl}_2 = 22.2 \text{ mg};$	$\text{KNO}_3 = 20.2 \text{ mg};$
$\text{MgCO}_3 = 16.8 \text{ mg};$	$\text{FeSO}_4 = 3.8 \text{ mg};$
$\text{MgSO}_4 = 6.0 \text{ mg}.$	

Express the results as ppm, Clarke degree and French degree.

[Ans. : Carbonate hardness = 51 ppm or 5.1 °Fr or 3.56 °C]

Non-carbonate hardness = 27.5 p.p.m or 2.75 °Fr or 1.92 °Cl.]

**Ex. 19:** The hardness of  $10^6$  litres of a water sample was completely removed by zeolite softener. The zeolite required 80 litres of NaCl solution, containing 1500 mg/lit of NaCl for regeneration. Calculate the hardness of water sample.

[Ans. : 0.102 ppm]

**Ex. 20:** 0.25 gm of  $\text{CaCO}_3$  is dissolved in dilute HCl and diluted to 250 ml. 25 ml of this solution required 24.0 ml of EDTA using Eriochrome Black-T indicator. 50 ml of a hard water sample required 22.5 ml of the same EDTA. 100 ml of the water after boiling and filtering required 120 ml of the said EDTA. Calculate the hardness in the sample (permanent and temporary).

[Ans. : Total Hardness = 468 ppm,  
Permanent Hardness = 333 ppm,  
Temporary Hardness = 135 ppm]

**Ex. 21:** A water sample on analysis, gave the following data.

$\text{MgCl}_2 = 95 \text{ ppm};$	$\text{MgSO}_4 = 120 \text{ ppm};$
$\text{H}_2\text{SO}_4 = 49 \text{ ppm};$	$\text{CaSO}_4 = 272 \text{ ppm};$
$\text{SiO}_2 = 4 \text{ ppm}.$	

Calculate the amount of lime (95 % pure) and soda (97 %) needed for treating 1 million litres of water.

[Ans. : Lime = 194 gm., Soda = 491.75 gm]

**Ex. 22:** A zeolite softener completely exhausted was regenerated by passing 200 litres of NaCl. How many litres of a sample of a water of hardness 50 ppm can be softened by this softener.

[Ans. : 34,184.03 lit.]

**Ex. 23:** Find carbonate and non-carbonate hardness of a sample of water which has the following impurities per lit.

$\text{CaCO}_3 = 12.5 \text{ mg/lit.};$	$\text{MgCl}_2 = 9.5 \text{ mg/lit.};$
$\text{MgCO}_3 = 15.8 \text{ mg/lit.};$	$\text{CO}_2 = 22 \text{ mg/lit.};$
$\text{CaCl}_2 = 11.1 \text{ mg/lit.};$	$\text{NaHCO}_3 = 13.6 \text{ mg/lit.}$

[Ans. : Carbonate hardness = 32.5 ppm,  
Non-carbonate hardness = 20 ppm.]

**Ex. 24:** A water sample containing following salts,

$\text{MgCl}_2 = 9.5 \text{ ppm};$	$\text{MgSO}_4 = 60.0 \text{ ppm};$
$\text{CaSO}_4 = 27.2 \text{ ppm};$	$\text{H}_2\text{SO}_4 = 4.9 \text{ ppm};$
$\text{SiO}_2 = 0.4 \text{ ppm}.$	

was softened by lime soda process. Calculate the quantity of lime and soda (90 % pure each) required to soften 1 million litres of water.

[Ans. : Lime = 4.1 kg., Soda = 100 kg.]

**Ex. 25:** Calculate the amount of lime (90 % pure) and soda (95 % pure) required for softening of  $10^5$  litres of hard water containing the following constituent.

$\text{Ca}(\text{HCO}_3)_2 = 162 \text{ mg/lit.};$	$\text{HCl} = 73 \text{ mg/lit.};$
$\text{MgCl}_2 = 10 \text{ mg/lit.};$	$\text{CO}_2 = 22.0 \text{ mg/lit.};$
$\text{NaCl} = 117 \text{ mg/lit.};$	$\text{CaCl}_2 = 111 \text{ mg/lit.};$
$\text{Mg}(\text{HCO}_3)_2 = 3 \text{ mg/lit.};$	$\text{MgSO}_4 = 30.0 \text{ mg/lit.}$

[Ans. : Lime = 32 kg., Soda = 37.45 kg.]

**Ex. 26 :** 50 ml of standard hard water containing 1 mg of pure  $\text{CaCO}_3$ ; per ml/ consumed 30 ml of EDTA, 50 ml of water sample consumed 35 ml of EDTA solution using Enochrome Black-T indicator, 50 ml of water sample required 28 ml of EDTA using same indicator. Calculate temporary and permanent hardness.

[Ans. : Temporary hardness = 234 ppm.  
Permanent hardness = 935.2 ppm.  
Total hardness = 1169.2 ppm.]

**Ex. 27 :** What is carbonate and non-carbonate hardness of a sample of water which has the following impurities per litre

$$\begin{aligned}\text{Mg}(\text{HCO}_3)_2 &= 146 \text{ mg/lit.}; & \text{MgCl}_2 &= 95 \text{ mg/lit.}; \\ \text{NaCl} &= 50 \text{ mg/lit.}; & \text{Ca}(\text{HCO}_3)_2 &= 81 \text{ mg/lit.}; \\ \text{CaCl}_2 &= 111 \text{ mg/lit.}; & \text{CaSO}_4 &= 68 \text{ mg/lit.}\end{aligned}$$

Express the results as ppm,  $^{\circ}\text{Cl}$  and  $^{\circ}\text{Fr}$ .

[Ans. : Carbonate hardness = 150 ppm = 15  $^{\circ}\text{Fr}$  = 10.5  $^{\circ}\text{Cl}$ .  
Non-carbonate hardness = 250 ppm = 25  $^{\circ}\text{Fr}$  = 17.5  $^{\circ}\text{Cl}$ .]

**Ex. 28 :** An exhausted zeolite softener was regenerated by passing 200 litres of NaCl solution, having a strength of 200 mg/lit. of NaCl. How many litres of hard water sample, having hardness of 500 ppm can be softened, using this softener ?

[Ans. : 68.376 lit.]

**Ex. 29 :** A water sample on analysis gave the following data :

$$\begin{aligned}\text{Ca}^{2+} &= 40 \text{ ppm}; & \text{CO}_3^{2-} &= 15 \text{ ppm}; \\ \text{Mg}^{2+} &= 72 \text{ ppm}; & \text{K}^+ &= 20 \text{ ppm}; \\ \text{CO}_2 &= 20 \text{ ppm}\end{aligned}$$

Calculate the lime (88 % pure) and soda (89 % pure) required to soften 2 million litres of the water sample.

[Ans.: Lime = 580.99 kg., Soda = 1012.35 kg.]

**Ex. 30 :** What is the carbonate and non-carbonate hardness of a sample of water which has the following impurities per litre ?

$$\begin{aligned}\text{Ca}(\text{HCO}_3)_2 &= 81 \text{ mg/lit.}; & \text{MgCl}_2 &= 95 \text{ mg/lit.}; \\ \text{NaCl} &= 38.5 \text{ mg/lit.}; & \text{CaCl}_2 &= 22.2 \text{ mg/lit.}; \\ \text{Mg}(\text{HCO}_3)_2 &= 58.2 \text{ mg/lit.}; & \text{CO}_2 &= 4.4 \text{ lit.}\end{aligned}$$

Express the results as ppm, Clarke's degree and french degree.

[Ans. : Carbonate hardness = 89.85 ppm = 6.29  $^{\circ}\text{Cl}$  = 8.986  $^{\circ}\text{Fr}$ .]

Non-carbonate hardness = 120 ppm = 8.4  $^{\circ}\text{Cl}$  = 12  $^{\circ}\text{Fr}$ .]

**Ex. 31 :** 0.1 g of  $\text{CaCO}_3$  was dissolved in dil. HCl and diluted to 100 ml. 50 ml of this solution required 40.0 ml of EDTA solution for titration. 50 ml of hard water sample required 25 ml of EDTA solution, 50 ml of same water sample on boiling, filtering required 20 ml of EDTA. Calculate hardness in ppm.

[Ans. : Temporary hardness = 125 ppm.,  
Permanent hardness = 500 ppm.,  
Total hardness = 625 ppm.]

### Problems for Practice

**Ex. 1** A water sample contains the following impurities.

$$\begin{aligned}\text{CaSO}_4 &= 136 \text{ ppm}; & \text{MgCl}_2 &= 95 \text{ ppm}; \\ \text{H}_2\text{SO}_4 &= 49 \text{ ppm}; & \text{MgSO}_4 &= 60 \text{ ppm}; \\ \text{SiO}_2 &= 50 \text{ ppm};\end{aligned}$$

Calculate the amount of lime (90 % pure) and washing soda (100 % pure) required for treating one million litres of water.

**Ex. 2** Calculate the temporary and permanent hardness in water from the following data :

$$\begin{aligned}\text{Mg}(\text{HCO}_3)_2 &= 14.6 \text{ mg/litre}; & \text{Ca}(\text{HCO}_3)_2 &= 8.1 \text{ mg/litre}; \\ \text{Mg}(\text{NO}_3)_2 &= 29.6 \text{ mg/litre}; & \text{MgCl}_2 &= 19.0 \text{ mg/litre}; \\ \text{MgSO}_4 &= 24.0 \text{ mg/litre}.\end{aligned}$$

**Ex. 3** A sample of water was found to contain the following impurities :

$$\begin{aligned}\text{Mg}(\text{HCO}_3)_2 &= 156 \text{ mg/litre}; & \text{H}_2\text{SO}_4 &= 4.9 \text{ mg/litre}; \\ \text{MgCl}_2 &= 23.75 \text{ mg/litre}; & \text{NaCl} &= 5.6 \text{ mg/litre}; \\ \text{SiO}_2 &= 16.2 \text{ mg/litre};\end{aligned}$$

Calculate the amount of lime (90 % pure) and soda (95 % pure) required to soften 50,000 litres of same water.

Atomic weights : Na = 23, Ca = 40, Mg = 24, O = 16, S = 32, Cl = 35.5, N = 14, H = 1, C = 12, Si = 28

**Ex. 4** Calculate the amount of lime (85 % purity) and soda ash (95 % purity) required for softening 10,000 litres of boiler feed water containing the following impurities :

$$\begin{aligned}\text{Ca}(\text{HCO}_3)_2 &= 16.2 \text{ ppm}; & \text{MgSO}_4 &= 6.0 \text{ ppm}; \\ \text{CaSO}_4 &= 6.8 \text{ ppm}; & \text{Mg}(\text{HCO}_3)_2 &= 8.4 \text{ ppm}; \\ \text{CaCl}_2 &= 11.1 \text{ ppm}; & \text{SiO}_2 &= 8.0 \text{ ppm}; \\ \text{NaCl} &= 14.0 \text{ ppm}.\end{aligned}$$

**Ex. 5** Calculate the temporary hardness and total hardness of a sample of water containing following salts :

$$\text{Mg}(\text{HCO}_3)_2 = 7.3 \text{ mg/litre}; \quad \text{Ca}(\text{HCO}_3)_2 = 16.2 \text{ mg/litre};$$

$$\text{MgCl}_2 = 9.5 \text{ mg/litre}; \quad \text{CaSO}_4 = 13.6 \text{ mg/litre};$$

**Ex. 6** A sample of water contains following impurities :

$$\text{Mg}(\text{HCO}_3)_2 = 73 \text{ mg/litre}; \quad \text{CaCl}_2 = 222 \text{ mg/litre};$$

$$\text{MgSO}_4 = 120 \text{ mg/litre}; \quad \text{Ca}(\text{NO}_3)_2 = 164 \text{ mg/litre};$$

The purity of lime is 74 % and soda is 90 %. Calculate the quantity of lime and soda needed for softening 5000 litres of water.

**Ex. 7** Calculate the amount of lime and soda required for softening of 50,000 litres of hard water containing :

$$\text{MgCO}_3 = 144 \text{ ppm}; \quad \text{CaCO}_3 = 25 \text{ ppm};$$

$$\text{MgCl}_2 = 95 \text{ ppm}; \quad \text{CaCl}_2 = 111 \text{ ppm};$$

$$\text{Fe}_2\text{O}_3 = 25 \text{ ppm}; \quad \text{Na}_2\text{SO}_4 = 15 \text{ ppm};$$

$$\text{MgSO}_4 = 10.0 \text{ ppm}; \quad \text{Al}_2(\text{SO}_4)_3 = 36.5 \text{ ppm};$$

$$\text{Mg}(\text{HCO}_3)_2 = 17.1 \text{ ppm}; \quad \text{CaSO}_4 = 20.4 \text{ ppm};$$

$$\text{MgCl}_2 = 19.0 \text{ ppm}; \quad \text{SiO}_2 = 24.0 \text{ ppm}.$$

**Ex. 8** Three water samples A, B and C were analysed for their salt content. Sample A was found to contain 168 mg magnesium carbonate per litre. Sample B was found to contain 82 mg of calcium nitrate and 2 mg of silica per litre. Sample C was found to contain 20 mg of potassium nitrate and 20 mg of calcium carbonate per 500 ml. Determine the hardness in all the above three water samples A, B and C.

**Ex. 9** The hardness of 10,000 litres of a sample of water (containing 341.9 ppm hardness) was completely removed by passing it through a zeolite softener. The zeolite softener was regenerated by passing sodium chloride solution containing 20 gms/lit. of NaCl. How many litres of sodium chloride solution will be required to regenerate zeolite softener?

**Ex. 10** Calculate the quantity of lime needed for softening of 5000 litres of water containing :

$$\text{MgCO}_3 = 8.4 \text{ mg/litre}; \quad \text{CaSO}_4 = 13.6 \text{ mg/litre};$$

$$\text{KNO}_3 = 20.0 \text{ mg/litre}; \quad \text{CaCO}_3 = 5.0 \text{ mg/litre}$$

**Ex. 11** Calculate the hardness of water sample, whose 20 ml required 30 ml of EDTA. 10 ml of calcium chloride solution, whose strength is equivalent to 300 mg of calcium carbonate per 200 ml required 20 ml of EDTA solution.

**Ex. 12** A zeolite softener was completely exhausted and was regenerated by passing 100 litres of sodium chloride solution containing 60 gms/lit. NaCl. How many litres of a sample of water of hardness 400 ppm can be softened by this softener.

**Ex. 13** Calculate the quantity of soda needed to soften 10,000 litres of water containing :

$$\text{Na}_2\text{SO}_4 = 7 \text{ mg/lit.}; \quad \text{CaCO}_3 = 5 \text{ mg/lit.};$$

$$\text{SiO}_2 = 2 \text{ mg/lit.}; \quad \text{CaCl}_2 = 22.2 \text{ mg/lit.};$$

**Ex. 14** The hardness of 50,000 litres of sample of water was completely removed by passing through a permunt softener. The softener required 200 litres of common salt solution containing 200 g/litre of NaCl for regeneration. Calculate hardness of water sample.

**Ex. 15** Calculate the quantity of lime and soda required to soften one million litre of hard water containing following impurities :

$$\text{CaCO}_3 = 10.0 \text{ ppm}; \quad \text{CaSO}_4 = 20.4 \text{ ppm};$$

$$\text{Mg}(\text{HCO}_3)_2 = 17.1 \text{ ppm}; \quad \text{MgCl}_2 = 19.0 \text{ ppm};$$

$$\text{Al}_2(\text{SO}_4)_3 = 36.5 \text{ ppm}; \quad \text{SiO}_2 = 24.0 \text{ ppm}.$$

**Ex. 16** A sample of water contains 16.8 mg of  $\text{MgCO}_3$  and 6.0 mg of  $\text{SiO}_2$  per litre. Find its temporary and permanent hardness.

**Ex. 17** The hardness of 10,000 litres of a hard water sample was completely removed by passing it through a zeolite softener. The zeolite softener requires 5,000 litres of sodium chloride solution containing 1170 mg of NaCl per litre for regeneration. Determine the hardness of water sample.

**Ex. 18** Calculate the quantity of lime and soda needed to soften 20,000 litres of hard water containing the following salts :

$$\text{MgCl}_2 = 9.5 \text{ mg/lit.}; \quad \text{CaCl}_2 = 22.2 \text{ mg/lit.};$$

$$\text{Ca}(\text{HCO}_3)_2 = 81 \text{ mg/lit.}; \quad \text{Mg}(\text{HCO}_3)_2 = 73 \text{ mg/lit.};$$

$$\text{FeSO}_4 = 151.8 \text{ mg/lit.}; \quad \text{MgSO}_4 = 120 \text{ mg/lit.};$$

**2.20 University Questions (Theory)****Dec. 2003****Q. 4 Explain the demineralization of hard water with neat diagram and appropriate equations. (Section 2.13.3)****May 2000****Q. 1 State the limitations of zeolite process. (Section 2.13.2)****Q. 2 Describe with the help of a neat labeled diagram, the hot lime soda process of softening of water. (Section 2.13.1)****Q. 3 How is hardness of water determined by EDTA method ? Write the necessary calculation. (Section 2.10.1, 2.10.2 and 2.10.3)****Q. 4 What is the difference between scale and sludge. (Section 2.17.4)****Dec. 2002****Q. 1 What is hardness of water ? Explain the temporary and permanent hardness. (Section 2.5)****Q. 2 What are the effects of scales in the generation of steam in pressure boilers? (Section 2.12.1)****Q. 3 Explain the effect of sodium aluminate in the softening of water. (Section 2.12.2)****Q. 4 Explain the permalit-zeolite process for softening of water with its advantages and disadvantages. (Section 2.13.2)****Dec. 2003****Q. 1 Write a short note on internal conditioning of boiler water. (Section 2.12.2)****Q. 2 (a) Explain with neat sketch and all chemical reactions taking place, the zeolite-permalt process for softening of water. What are the advantages and disadvantages of this process. (Section 2.13.2)****(b) Write a brief note on "Boiler corrosion". (Section 2.12.4)****Q. 3 What is the difference between scale and sludge. (Section 2.17.4)****Dec. 2004****Q. 1 What are advantages of Hot lime-soda process ? (Section 2.13.1) (20 Marks)****Q. 2 Explain phosphate conditioning as a internal treatment method in case of boilers. (Section 2.12.2) (3 Marks)****Q. 3 Explain : Boiler corrosion. (Section 2.12.4) (5 Marks)****Q. 4 Explain Ion-Exchange resins. (Section 2.13.3) (4 Marks)****Q. 5 What is caustic embrittlement in boilers ? (Section 2.12.3) (5 Marks)****Dec. 2004****Q. 1 Explain with equations role of coagulants in cold lime soda process. (Section 2.13.1)****Q. 2 Why 'Hydrazine' is an ideal chemical employed for degassing water ? (Section 2.12.2)****Q. 3 Discuss calgon conditioning of water. (Section 2.13.2)****Q. 4 Explain with neat sketch and chemical reactions the zeolite-permalt process for softening of water. What are the advantages and disadvantages of this process ? (Section 2.13.2)****July 2003****Q. 1 What is degree of hardness in water ? How is it expressed ? (Section 2.8) (2 Marks)****Q. 2 Explain the theory of Lime-Soda process with special reference to the different functions of lime and soda. (Section 2.13.1) (6 Marks)****Q. 3 What are scales and sludges ? What are their disadvantages ? How can scale be prevented by Phosphate conditioning ? (Section 2.12.1 and 2.12.2) (6 Marks)****Q. 4 What are Zeolites ? Explain theory, procedure and limitations of Zeolite process with the help of neat diagram. (Section 2.13.2) (6 Marks)**

- Q. 1 Why is hot lime soda process better than the cold process ? (Section 2.13.1)**
- Q. 2 Explain phosphate conditioning of water. (Section 2.13.2)**
- Q. 3 What is difference between scale and sludge ? (Section 2.17.4)**

**May 2005**

- Q. 1** Why hydrazine is preferred over  $\text{Na}_2\text{S}$ ,  $\text{Na}_2\text{SO}_3$ ? (Section 2.12.2) (2 Marks)
- Q. 2** How demineralization of water is carried out? (Section 2.13.3) (7 Marks)
- Q. 3** Draw the labelled diagram of Hot Lime Soda Process and give only advantages of the method. (Section 2.13.1) (6 Marks)

**Dec. 2005**

- Q. 1** Name the indicator used in EDTA titration. What is colour change at the end point of titration? (Section 2.10.2 and 2.10.3) (6 Marks)
- Q. 2** Explain Reactions of Lime and Soda used for softening. (Section 2.13.1) (6 Marks)
- Q. 3** Give an account of Phosphate conditioning in case of boilers as internal treatment method. (Section 2.12.2) (4 Marks)

**May 2006**

- Q. 1** What is hardness of water? Distinguish between alkaline and non-alkaline hardness. (Section 2.5) (3 Marks)
- Q. 2** What are Zeolites? Explain theory, procedure and limitations of Zeolite process for softening of water with the help of a neat diagram. (Section 2.13.2) (4 Marks)
- Q. 3** Write short notes on : Caustic-embrittlement. (Section 2.13.2) (3 Marks)
- Q. 4** Write short note on : Phosphate conditioning. (Section 2.12.2) (3 Marks)

**Dec. 2006**

- Q. 1** What is meant by 'phosphate conditioning' of water? (Section 2.12.2) (3 Marks)
- Q. 2** What is pollution? Name of primary air pollutants? (3 Marks)
- Q. 3** Write short note on : Caustic embrittlement. (Section 2.12.3) (3 Marks)
- Q. 4** Write principle and all chemical reactions involved in lime soda process. (Section 2.13.1) (9 Marks)
- Q. 5** Write short note on : BOD and COD (Section 2.14.3) (4 Marks)

**May 2007**

- Q. 6** How hardness of water is determined by EDTA method? Explain with the help of following points :  
 (i) Principle (Section 2.10.2)  
 (ii) Chemical reactions (Section 2.10.1)  
 (iii) Structure (Section 2.10)  
 (iv) Calculations for temporary, permanent and total hardness (Section 2.18.2) (9 Marks)

**Q. 7** Distinguish clearly between : Scale and sludge (Section 2.17.4) (7 Marks)**Dec. 2007**

- Q. 1** Explain phosphate conditioning for internal treatment of water. (Section 2.12.2) (3 Marks)
- Q. 2** Explain boiler corrosion due to dissolved oxygen in water. How can it be prevented? (Section 2.12.4) (3 Marks)
- Q. 3** What is demineralisation? Explain demineralisation with reference to the following points :  
 (i) Principle  
 (ii) Ingredients used  
 (iii) Chemical equations  
 (iv) Advantages and disadvantages (Section 2.13.3) (10 Marks)
- Q. 4** Explain BOD and COD stating its applications. (Section 2.14.3) (5 Marks)
- Q. 5** Principle and reactions involved in the lime-soda method for softening of water. (Section 2.13.1) (5 Marks)

**Dec. 2007**

- Q. 1** What do you mean by hardness of water? Distinguish between alkaline and non-alkaline hardness of water. (Sections 2.5, 2.6.1, 2.6.2) (2 Marks)
- Q. 2** Explain the theory of Lime-soda process with reference to the different functions of lime and soda. (Section 2.13.1) (5 Marks)
- Q. 3** Explain the terms :  
 (i) B.O.D. (Section 2.14.1)  
 (ii) C.O.D. (Section 2.14.2)  
 What is their significance? (3 Marks)

**May 2008**

- Q. 1** Explain theory, procedure and limitations of Zeolite process with the help of a neat diagram.  
(Section 2.13.2) (6 Marks)

- Q. 2** What are carbonate and non-carbonate hardness ? (Section 2.17.1) (3 Marks)

- Q. 3** Give brief account of reverse osmosis. (Section 2.13.4) (3 Marks)

- Q. 4** Write short note on : Activated sludge method to control water pollution  
(Section 2.15.1) (5 Marks)

**2.21 University Questions (Problems)****Dec. 2001**

- Q. 1** Calculate lime (80 % purity) and soda (90 % purity) required to soften 1 lakh litres of water containing the following impurities.

$$\text{Mg}(\text{HCO}_3)_2 = 7.1 \text{ mg/lit.}$$

$$\text{Ca}(\text{HCO}_3)_2 = 8.1 \text{ ppm.}$$

$$\text{Na}_2\text{SO}_4 = 15 \text{ ppm.}$$

(Problem 2.18.37)

(6 Marks)

- Q. 2** A zeolite softener was completely exhausted and was regenerated by passing 1000 litres of sodium chloride solution containing 100 gm.-lit. of sodium chloride. How many lit. of water sample of hardness 500 ppm can be softened by this softener.  
(Problem 2.18.37)

(Problem 2.18.54)

**May 2002**

- Q. 3** Calculate the carbonate and non-carbonate hardness of a sample of water containing :  
 $\text{MgCl}_2 = 95 \text{ ppm}; \quad \text{MgSO}_4 = 48 \text{ ppm};$   
 $\text{Ca}(\text{HCO}_3)_2 = 16.2 \text{ ppm}; \quad \text{KCl} = 12 \text{ ppm};$   
 $\text{Mg}(\text{HCO}_3)_2 = 14.6 \text{ ppm} \quad (\text{Problem 2.18.4})$

(6 Marks)

**May 2003**

- Q. 7** Calculate the quantities of lime and soda (90 % pure each) required for softening 25000 litres of hard water containing following ions/chemicals.

$\text{HCO}_3^- = 12.2 \text{ ppm};$	$\text{CO}_2 = 4.4 \text{ ppm};$
$\text{Ca}^{++} = 30 \text{ ppm};$	$\text{Mg}^{++} = 21.6 \text{ ppm};$
$\text{Fe}_2\text{O}_3 = 15.4 \text{ ppm};$	$\text{H}_2\text{SO}_4 = 4.9 \text{ ppm}$
	(6 Marks)

(Problem 2.18.34)

- Q. 4** Calculate the amount of lime (95 % pure) and soda (80 % pure) for softening 50,000 lit. of water containing :

$$\text{Mg}(\text{HCO}_3)_2 = 14.6 \text{ ppm};$$

$$\text{CaSO}_4 = 6.8 \text{ ppm};$$

$$\text{MgSO}_4 = 12 \text{ ppm};$$

$$\text{SiO}_2 = 12 \text{ ppm}$$

(Problem 2.18.35)

**Dec. 2002**

- Q. 5** 0.23 gm of  $\text{CaCO}_3$  was dissolved in HCl and the solution made upto 1 litre with distilled water. 100 ml of the above solution required 28 ml of EDTA solution. 100 ml of hard water sample required 33 ml of EDTA solution. After boiling 100 ml of this water, cooling and filtering and then titration required 10 ml of EDTA solution. Calculate each type of hardness of water. (Problem 2.18.19) (6 Marks)

- Q. 6** Calculate the quantities of lime (86 % pure) and soda (90 % pure) required for softening 25,000 litres water having following analysis :-

$$\text{HCl} = 12.5 \text{ mgs/lit.};$$

$$\text{CaCO}_3 = 35.2 \text{ mgs/lit.};$$

$$\text{NaSO}_4 = 8.8 \text{ mgs/lit.};$$

$$\text{Al}_2(\text{SO}_4)_3 = 33.3 \text{ mgs/lit.};$$

$$\text{MgCl}_2 = 7.8 \text{ mgs/lit.};$$

$$\text{Fe}_2\text{O}_3 = 18.6 \text{ mgs/lit.}$$

(Problem 2.18.36)

(6 Marks)

(6 Marks)

**Q. 8** The hardness of 75,000 litres of a water sample was completely removed by a permittit. The exhausted permittit then required 1500 litres of NaCl containing 117 mg of NaCl per litre for regeneration. Calculate the hardness of water sample.

(Problem 2.18.53)

**Dec. 2003** (5 Marks)

**Q. 9** Calculate the amount of lime (92 % pure) and soda (95 % pure) required for softening 15,000 litres of hard water containing the following salts.

$$\text{CaCO}_3 = 68.2 \text{ mg/litre}, \quad \text{Mg}(\text{NO}_3)_2 = 29.6 \text{ mg/litre},$$

$$\text{Mg}(\text{CH}_3\text{COO})_2 = 58.4 \text{ mg/litre}, \quad \text{MgSO}_4 = 36.0 \text{ mg/litre},$$

$$\text{MgCl}_2 = 95.0 \text{ mg/litre}, \quad \text{CaSO}_4 = 27.2 \text{ mg/litre},$$

$$\text{Fe}_2\text{O}_3 = 19.3 \text{ mg/litre}. \quad (6 \text{ Marks})$$

**Q. 10** 50 ml of standard hard water containing 1 mg of pure  $\text{CaCO}_3$  per ml consumed 20 ml of EDTA. 50 ml of water sample consumed 25 ml of EDTA solution using Erio-T Indicator. 50 ml of water sample after boiling, filtering etc. consumed 18 ml of EDTA using Erio-T indicator. Calculate the various types of hardness of the sample.

(Problem 2.18.43) (6 Marks)

**May 2004** (5 Marks)

**Q. 11** Calculate the amount of lime and soda required for 50,000 lit. of water sample containing :

$$\text{CaCO}_3 = 10 \text{ ppm}, \quad \text{Mg}(\text{HCO}_3)_2 = 14.6 \text{ ppm},$$

$$\text{CO}_2 = 4.4 \text{ ppm}, \quad \text{CaCl}_2 = 22.2 \text{ ppm},$$

$$\text{MgCl}_2 = 9.5 \text{ ppm}, \quad \text{SiO}_2 = 2.8 \text{ ppm}. \quad (4 \text{ Marks})$$

(Problem 2.18.40)

**Q. 15** Calculate Lime (74 % pure) and soda (90 % pure) required for 5000 lit. of water containing following impurities :

$\text{Mg}(\text{HCO}_3)_2 = 73 \text{ mg/lit.}$        $\text{MgSO}_4 = 120 \text{ mg/lit.}$   
 $\text{CaCl}_2 = 222 \text{ mg/lit.}$        $\text{Ca}(\text{NO}_3)_2 = 164 \text{ mg/lit.}$   
 $\text{SiO}_2 = 15 \text{ mg/lit.}$        $\text{Ca}(\text{NO}_3)_2 = \text{traces}$

(Problem 2.18.40)

**Q. 12** An exhausted zeolite softener was regenerated by passing 75 litres of NaCl solution having strength 75 g/lit. If hardness of water is 300 ppm, then calculate the total volume of water that is softened by zeolite softener. (Problem 2.18.55)

(5 Marks)

**Dec. 2005**

**Q. 16** Calculate total hardness, in ppm, in given water sample :  
(i) 50 ml standard hard water, containing 1 mg pure  $\text{CaCO}_3$  per ml, consumed 20 ml EDTA solution.  
(ii) 50 ml water sample consumed 30 ml EDTA solution using Erio-Black T Indicator.

(Problem 2.18.56) (4 Marks)

**Q. 17** Calculate amount of Lime (90 % pure) and Soda (100 % pure) for 1 million lit. of water containing the following impurities :

$$\text{CaSO}_4 = 136 \text{ ppm}, \quad \text{H}_2\text{SO}_4 = 49 \text{ ppm}, \quad \text{MgCl}_2 = 95 \text{ ppm}, \quad \text{MgSO}_4 = 60 \text{ ppm}, \quad \text{SiO}_2 = 50 \text{ ppm}. \quad (5 \text{ Marks})$$

**Q. 18** A zeolite softener was completely exhausted and was regenerated by passing 150 litres of NaCl soln., containing 50 g/litres of NaCl. How many litres of water of hardness 450 ppm can be softened by this container ? (Problem 2.18.55) (6 Marks)

**May 2006**

**Q. 19** Find out temporary, permanent and total hardness in a sample of water with following impurities

- (i)  $\text{Ca}(\text{HCO}_3)_2 = 81 \text{ ppm}$
- (ii)  $\text{MgCO}_3 = 84 \text{ ppm}$
- (iii)  $\text{CaCl}_2 = 22.2 \text{ ppm}$
- (iv)  $\text{MgSO}_4 = 60 \text{ ppm}$
- (v)  $\text{KCl} = 30 \text{ ppm}$  (Problem 2.18.5)

**Q. 20** A water sample on analysis gave the following data :

- (i)  $\text{MgCl}_2 = 95 \text{ ppm}$
- (ii)  $\text{CaSO}_4 = 272 \text{ ppm}$
- (iii)  $\text{MgSO}_4 = 120 \text{ ppm}$
- (iv)  $\text{H}_2\text{SO}_4 = 49 \text{ ppm}$
- (v)  $\text{SiO}_2 = 4 \text{ ppm}$

Calculate the lime and soda requirement in kg. For the softening of 10,000 litres of water if it is given that lime is 85 % pure and soda is 90 % pure.

(Problem 2.18.38)

(7 Marks)

**Dec. 2006**

**Q. 21** A sample of water has hardness 304 ppm  $\text{CaCO}_3$  equivalent. Find the hardness in terms of degree Clark, degree French and mg/lit. (Problem 2.18.8) (3 Marks)

**Q. 22** Calculate the quantities of lime (85% pure) and soda (95% pure) required for softening one million litres of water if it has analysis as follows :

- (1)  $\text{CaCl}_2 = 49.95 \text{ ppm}$
- (2)  $\text{MgSO}_4 = 42 \text{ ppm}$
- (3)  $\text{NaHCO}_3 = 12.5 \text{ ppm}$
- (4)  $\text{SiO}_2 = 10 \text{ ppm}$
- (5)  $\text{NaCl} = 500 \text{ ppm}$
- (6)  $\text{Mg} (\text{HCO}_3)_2 = 51.1 \text{ ppm}$
- (7)  $\text{CO}_2 = 3 \text{ ppm}$
- (8)  $\text{Fe}^{+2} = 3 \text{ ppm}$
- (9)  $\text{AlCl}_3 = 1.5 \text{ ppm}$  (Problem 2.18.44)

(7 Marks)

**Q. 23** Calculate lime (90% pure) and soda ash (90% pure) to soften 1,00,000 litres of water containing :

$$\begin{aligned}\text{Mg}(\text{HCO}_3)_2 &= 146 \text{ mg/lit} & \text{MgCl}_2 &= 95 \text{ mg/lit} \\ \text{Ca}(\text{HCO}_3)_2 &= 81 \text{ mg/lit} & \text{CaCl}_2 &= 111 \text{ mg/lit} \\ \text{Na}_2\text{SO}_4 &= 15 \text{ mg/lit} & \text{SiO}_2 &= 10 \text{ mg/lit}\end{aligned}\quad (6 \text{ Marks})$$

(Problem 2.18.44(A))

**Q. 24** 50 ml of standard hard water ( $1.2 \text{ g CaCO}_3 / \text{lit}$ ) requires 32 ml of EDTA solution. 100 ml of water sample consumes 14 ml EDTA solution. 100 ml of boiled and filtered water sample consumes 8.5 ml EDTA solution. Calculate temporary hardness of this sample from above experimental data. (Problem 2.18.20(A)) (5 Marks)

**Dec. 2007**

**Q. 25** 800 litres of raw water was soften by zeolite softener. After it got exhausted required 40 litres of NaCl solution containing 110 gm per liter of NaCl for its regeneration. Calculate the hardness of water. (Problem 2.18.57) (4 Marks)

**Q. 26** Calculate lime (90%) pure and soda (95%) pure required for softening of 20000 liters of water containing following impurities :

- (i)  $\text{Ca} (\text{HCO}_3)_2 = 81 \text{ mg per liter}$
- (ii)  $\text{MgCO}_3 = 42 \text{ mg per liter}$
- (iii)  $\text{NaAlO}_2 = 4.1 \text{ mg per liter}$
- (iv)  $\text{HCl} = 3.65 \text{ mg per liter}$
- (v)  $\text{Ca} (\text{NO}_3)_2 = 82 \text{ mg per liter}$
- (vi)  $\text{NaCl} = 4.5 \text{ mg per liter}$

(At Wt. Ca = 40, H = 1, C = 12, O = 16, Mg = 24, Na = 23, Al = 27, Cl = 35.5, N = 14) (Problem 2.18.44(C)) (5 Marks)

**May 2008**

**Q. 27** A water sample contain :

- (i)  $\text{Ca} (\text{HCO}_3)_2 = 32.4 \text{ mg/l}$
  - (ii)  $\text{Mg} (\text{HCO}_3)_2 = 29.2 \text{ mg/l}$
  - (iii)  $\text{CaSO}_4 = 13.5 \text{ mg/l}$
- Calculate temporary, permanent and total hardness (At. wt. C = 40, Mg = 24, H = 1, C = 12, O = 16, S = 32) (Problem 2.18.7(A)) (2 Marks)

**Q. 28** Calculate the amount of limes (85% pure) and soda (90% pure) required for softening of 10,000 litres of boiler-feed water containing following impurities :

- (i)  $\text{Ca}(\text{HCO}_3)_2 \rightarrow 16.2 \text{ ppm.}$
- (ii)  $\text{CaSO}_4 \rightarrow 6.8 \text{ ppm.}$
- (iii)  $\text{CaCl}_2 \rightarrow 11.1 \text{ ppm.}$
- (iv)  $\text{MgSO}_4 \rightarrow 6.00 \text{ ppm.}$
- (v)  $\text{Mg}(\text{HCO}_3)_2 \rightarrow 8.4 \text{ ppm.}$
- (vi)  $\text{SO}_4 \rightarrow 8.00 \text{ ppm.}$

(At. wt. Ca = 40 Mg = 24, S = 32, O = 16, Cl = 35.5, H = 1, Si = 28)

(Problem 2.18.44(B))

(6 Marks)

**Q. 29** A standard hardware contains 15 gm/l calcium carbonate. 20 ml of this water required 25 ml of EDTA solution. 100 ml of sample water required 18 ml of EDTA solution. The same sample after boiling required 12 ml of EDTA solution. Calculate temporary hardness of water. (Problem 2.18.20(B))

(3 Marks)

**Note**

# CHAPTER 3

## Lubricants

### 3.1 Introduction

► [ May 2008 ]

It has been known from ancient times that lubrication helps to reduce wear of solid surfaces.  
*"The substances used to reduce the wear are known as lubricants"*.

- With increasing number of machines in industries, the usefulness of lubrication has been proved in every sector.

The solid surfaces in contact, if in relative motion, give rise to friction. Friction is nothing but, *"the force of resistance to the relative motion of two solid surfaces in contact"* and *co-efficient of friction is, "the ratio of force of friction to the applied force or load"*. Thus,

$$\text{Coefficient of friction} = \frac{\text{Frictional Resistance}}{\text{Applied Force or load}}$$

When the applied force is more than the resistance between two moving surfaces, the *wear* occurs.

- Definition
- Classification
- Characteristic properties
- Problems on acid value and saponification value
- Theories of lubrication.
- Additives for lubricants
- Selection of lubricant.

As a result, use of lubricants to reduce friction also depends upon the type of surfaces in contact. Further, it also depends upon the working conditions of various machines.

- Thus it is a study involving different types of solid surfaces, surface energies, surface roughness, speed of machines, temperature at which machines are operated etc. In fact the surface roughness is not visible with open eyes, if very minute.
- It is quite common that highly polished metal surfaces, if viewed under electron microscope, are found to possess considerable roughness. Due to this, the metal surfaces develop voids giving rise to corrosion.

Subsequently corrosion further enhances roughness and irregularities of the surface. Hence, it is obvious that the lubricants have to be applied to the metal surfaces, even if apparently the surface appears to be smooth, as it is a known fact that *the surfaces of metals are never flat in true sense*.

- This also helps to *reduce maintenance cost* of machines, because a thin film of a lubricant reduces friction and thus controls wear.

### 3.2 Lubricants and Lubrication

► [ May 2003, Dec. 2005, Dec. 2007 ]

- The lubricants are defined as, "the chemical substances which reduce friction between two *sliding / moving metal surfaces and thereby reduce wear and tear of machines.*"

- The lubricant keeps the two surfaces apart, thus the *frictional resistance reduces*. This helps in reducing the destruction of material.

- Lubrication is nothing but "a process by which wear gets reduced, with the use of lubricants."

#### 3.2.1 Functions of Lubricants

(i) Lubricants *reduce friction, wear and tear* of surfaces.

- (ii) Lubricants *reduce wastage of energy*, and thereby *increase efficiency* of machines.

- (iii) Lubricants act as *coolants*, thereby avoiding loss of energy. They reduce the frictional heat, thereby controlling expansion of metals. It helps to maintain shape, size and dimensions of metal parts in contact.

- (iv) Lubricants *reduce the wastage of power*, e.g. in internal combustion engines, the lubricant applied between the piston and the cylinder acts as a coolant.

- (v) Lubricant *acts as a sealant*, as it does not allow the escape of gases from engine under high pressure.

- (vi) Lubricant *prevents the attack of moisture* on machine surface. This helps to control corrosion of the moving machine parts.

- (vii) Lubricants also help as *cleaning agents*, because they have the tendency to wash off solid particles produced due to combustion or wear. Thus with the presence of lubricants such particles are transported away from the sliding surfaces. This helps to control corrosion of the surfaces.

#### 3.2.2 Mechanism of Lubrication

- By and large, the friction between two surfaces occurs when the surfaces come in contact with each other. When one metal surface slides over other metal surface, due to surface roughness, the motion would not be smooth, causing friction.

Friction depends upon,

- The nature of the metal.
- The load on the metal.
- The temperature developed during operation/working.
- The pressure exerted during operation/working.

- If two metal surfaces in contact are different in material, i.e. one metal is harder than the other metal, then if harder metal is sliding over the surface of a less hard (soft) metal, the coefficient of friction is usually small and vice versa.

- The mechanism of lubrication is nothing but, "application of lubricant on sliding/moving surfaces and its action towards reducing frictional resistance".

There are *three types of mechanisms* most widely used under various conditions :

- Fluid film or thick film or hydrodynamic lubrication.
- Thin film or boundary lubrication.
- Extreme pressure lubrication.

#### 3.2.2.1 Fluid Film or Thick Film or Hydrodynamic Lubrication

► [ May 2002, May 2003, Dec. 2003, Dec. 2004, Dec. 2006, May 2007 ]

- In this type of mechanism, a *liquid lubricant with high viscosity* (generally vegetable/mineral or blended oils) is applied in the form of thick film between two moving surfaces. The film is at least  $1000 \text{ } \mu\text{m}$  thick.

- Such film helps to *avoid surface to surface contact* of moving surfaces. The hydrodynamic lubrication helps to reduce the coefficient of friction  $\mu$  to about  $0.001$  to  $0.03$ , which is *much lower* as compared to that for unlubricated surfaces ( $0.5$  to  $1.5$ ).

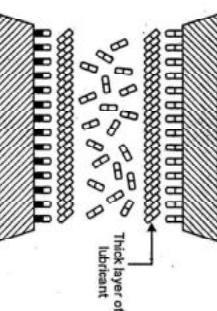
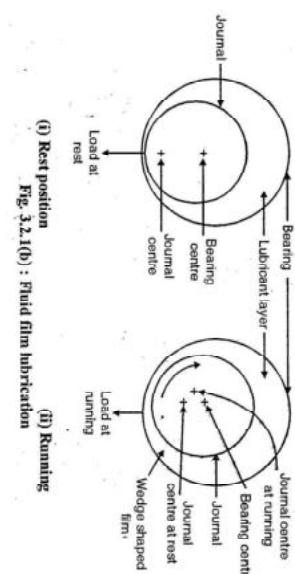


Fig. 3.2.1(a) : Hydrodynamic lubrication or fluid film lubrication

- The mechanism of hydrodynamic lubrication can be better understood by considering the operation of a journal bearing. Refer Fig. 3.2.1(a) and (b). The bearing consists of a shaft rotating at a fair speed, with moderate load.



(i) Rest position

(ii) Running

Fig. 3.2.1(b) : Fluid film lubrication

- The lubricant is applied in annular space. When journal bearing is stationary the two surfaces remain in contact, but as the shaft (journal) begins to rotate, the film of lubricant also rotates between the two metallic surfaces.
- Due to the presence of thick oily layer, all the asperities of the metal surfaces are filled up and a pressure is developed which practically keeps the two surfaces away from each other, thereby reducing wear. The motion is smooth as the resistance to the motion is restricted amongst the particles of lubricant.

- To achieve best results in hydrodynamic lubrication, the lubricants chosen should possess an adequate viscosity, so that an uniform layer of lubricant is always maintained between the two moving surfaces.

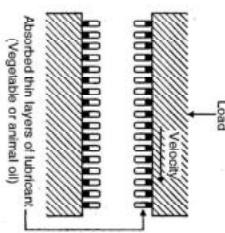


Fig. 3.2.2 : Boundary lubrication

### 3.2.2 Thin Film or Boundary Lubrication

► [ Dec. 2001, Dec. 2007 ]

This type of mechanism is useful under certain working conditions of machines, such as :

- (i) If viscosity of liquid lubricant (oil) is low,
- (ii) The machine is to be operated at comparatively low speed
- (iii) During operation of machine, a shaft starts moving from rest at fixed intervals or
- (iv) The machine is operated under high load.

- A continuous thick film of lubricant cannot persist in between two sliding surfaces under such working conditions. Hence, to reduce friction in such machines a thin film of lubricating oil is introduced in the clearing space of the moving surfaces.

- This film gets adsorbed on metal surfaces due to physical or chemical or both the forces and it is retained there. The coefficient of friction falls to the extent of 0.05 to 0.15 and load on the machine is carried by the adsorbed thin film between the sliding surfaces.

- Intermittently the layer of lubricant is checked, so that the machine surfaces remain protected from friction. The lubricants generally applied are the soaps of vegetable or animal oils, as they possess a great tendency of adsorption on surfaces.

- These soaps get attached to surfaces either by physical forces or by chemical forces and form a very thin film which covers all irregularities of metal surface, thereby reducing the frictional wear.

- The soaps are suitable at moderate temperatures. But at high temperatures, they get decomposed. Hence, these are not suitable to be used in internal combustion engines. In such cases, mineral oils blended with fatty oils or fatty acids are used, because the thermal stability of mineral oils is high.

- Other substitutes are solid lubricants such as, graphite or molybdenum di-sulphides, either alone or their stable suspension in oil, which is also suitable. These suspensions or solids form a thin film on metal surfaces which can bear load as well as high temperatures.

- In short, the lubricants possessing :

- (i) high viscosity index,
- (ii) resistance to oxidation
- (iii) stability at elevated temperature,
- (iv) adequate oiliness, and

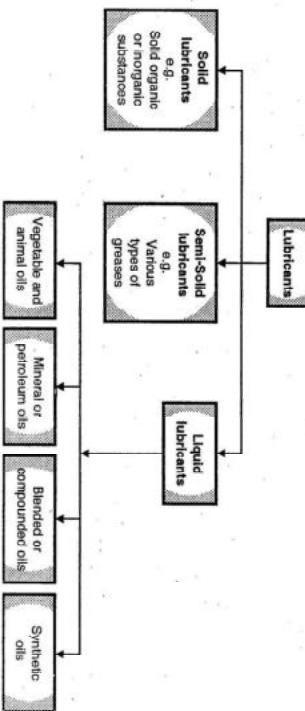
- At working conditions where sliding/moving surfaces are under high pressure and high speed, the machine surfaces normally attain slightly higher temperature.
- Under such working conditions, the liquid lubricant may not stick to the surfaces and it may also decompose at that temperature, losing its lubricating capacity. There might be loss of lubricant due to vaporization.
- To satisfy the requirement of a lubricant under such extreme conditions, generally mineral oils with special additives are used. Such additives used to improve specific characteristics of a lubricating oil are known as extreme pressure additives. The substances under this category should have a tendency to adhere on metal surfaces with greater local forces of attraction to form thicker film which sticks to the metal surfaces and is retained in place for longer duration.

- Such a film of lubricant should be able to withstand high temperature and pressure. Substances such as chlorinated esters, sulphurised oils or phosphates (like tri-cresyl phosphate) are commonly used.
- The metal underlying the film of lubricant reacts with these additives and form metal-chlorides, sulphides or phosphides. Such metal compounds possess very high melting points.
- Hence, the film of lubricant remains on the surface of metal providing adequate lubrication, under such extreme pressure and extreme temperature working condition.
- Such additives give good results on metals like iron, but are not suitable for use on chemically inert metal surfaces, e.g. silver, copper or titanium.

- In addition to these additives, colloidal suspension of solid lubricants in oil or resin have been found most suitable for extreme pressure-temperature lubrication.
- The machines in which E.P.T. lubrication is applied are, cutting tools, rock crushing machines, wire drawing machines etc.

### 3.3 Classification of Lubricants

On the basis of physical state, the lubricants are classified as follows :



#### 3.3.1 Solid Lubricants

Solid lubricants are used in situations such as,

- (1) When heavy machinery is to be operated at high speed and moderate load or at very high load and low speed, the liquid lubricants cannot be useful. This is because, due to high load and low speed, the film of liquid lubricant cannot remain in between sliding surfaces. Due to this the friction increases at selected areas, and so also increases wear and tear.
- (2) When the machine parts are not easily accessible, i.e. if the design is intrinsic, then use of liquid or semisolid lubricant fails.
- (3) When machine is at high working temperature and pressure, and hence under such conditions combustible lubricants (oils) are unsuitable.
- The substances most commonly used as solid lubricants are graphite, mica, Teflon, molybdenum disulfide, chalk, talc, soap stone, etc.
- The solid lubricants, if not manufactured properly, sometimes contain grain particles, which may damage delicate parts/surface of machinery. Hence, under special working conditions as mentioned above, the solid lubricants are to be used which are checked carefully for fineness.

Fig. 3.3.1 : Layer structure of graphite

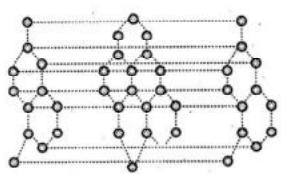
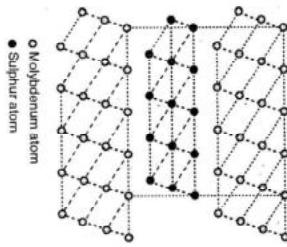


Fig. 3.3.2 : Layer structure of Molybdenum di-sulfide (Sandwich like)



#### Graphite

- Graphite being an allotrope of carbon, consists of meshwork of hexagonal carbon rings arranged on each other. Graphite, when applied between uneven surfaces, fills into valleys, thereby making surfaces more even.
- When machine is in operation, the graphite particles slide over each other with the motion of machine. Each graphite atom consists of carbon atoms which are arranged in regular hexagons in flat parallel layers.
- Each carbon atom is linked by covalent bonds to three other carbon atoms. The distance from the fourth carbon is almost more than double, due to which this fourth valency atom is flexible and keeps moving about, thereby weakening the bonds between different layers. As a result the graphite is soft and has a lubricating property.
- Graphite is non-flammable, sooty to touch, and not oxidized in the presence of air below 375°C temperature. It can be used up to much higher temperature in the absence of air. It can be used in powdered form or in the form of its 'suspension' in water or oil.
- The suspension of graphite in water is known as 'aqua-dag'. This is used in the machinery where lubricant free from oil is necessary, e.g. Food processing industry.

(iii) Machines where *liquid lubricant cannot be maintained in position due to intermittent operations of machine parts such as shaft etc.*

- The suspension of graphite in oil is known as '*oil-dag*'. This is used particularly in I.G. engines.

- Graphite is also mixed with greases to form "*graphite greases*". These are used at *still higher temperatures*.

#### **Molybdenum-di-sulphide**

Molybdenum-di-sulphide possesses a *sand-wich like structure* Fig. 3.3.2 in which a layer of molybdenum atoms lie between two layers of sulphur atoms. Molybdenum di-sulphide also shows lubricating action in similar way due to sliding layers of molybdenum atoms and sulphur atoms.

Molybdenum-di-sulphide possesses very low coefficient of friction and is stable in air upto 400°C. It can be used very easily as lubricant, either by direct sprinkling or applying its dispersion in solvents or greases, known as "*molykotes*".

Both these solid lubricants are particularly valuable because of (i) their stability at very high temperatures and extreme pressures. (ii) their low coefficient of friction below their decomposition temperature.

*These characteristics make the solid lubricants most useful:* in conditions of wide temperature changes, e.g. on surface of moon, the temperature changes are more like 110°C during day and -150°C during nights.

Under such a temperature conditions perhaps graphite may act as a good lubricant. Of course so far any study has not been available in support, which should be taken into account.

Amongst solid lubricants mentioned above, other most commonly used one is *teflon*. It has a very low coefficient of friction. It is used widely in gasoline gear pumps, periscopes, underwater machineries, oxygen valves, brass cartridges etc.

#### **3.3.2 Semisolid Lubricants**

► [ May 2003, Dec. 2004, May 2005, May 2007 ]

- The most widely used semisolid lubricants are *greases and vaselines*. The semisolid lubricants are used under working conditions, such as,
  - t (i) *Low speed and high pressure, and high temperature* (upto 80°C)
  - y (ii) Machineries used in *textile mills, paper and food product manufacturing etc.* where spilling and spurting of lubricant is harmful to the product.

- Machines where *liquid lubricant cannot be maintained in position due to intermittent operations of machine parts such as shaft etc.*

- In places where the bearing has to be sealed against entry of dirt, water, dust and grit.

*Semisolid lubricants (Greases)* are further classified on the basis of soaps used in their manufacture. The characteristics of greases are influenced by the soaps and the properties such as,

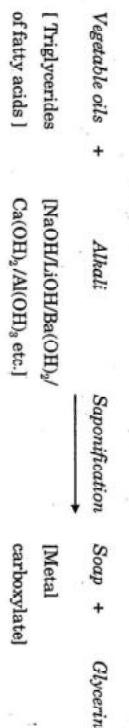
- (a) *Cloud and pour point of greases*, (i.e. determination of the lower temperature upto which the grease can be suitably used) should be as low as possible.
- (b) *Resistance to oxidation*, (i.e. when in contact with water, moisture or oxygen, whether grease is stable) should be as high as possible.
- (c) *Consistency of finished greases*, (the property which determines spreadability of the grease on machine surfaces at room temperature) should not alter to a greater extent at working temperature. This property governs the behaviour of greases under extreme conditions.

The important greases are :

- (i) Calcium soap greases [cup greases]
- (ii) Sodium soap greases.
- (iii) Lithium soap greases.
- (iv) Barium soap greases.
- (v) Aluminium soap greases.
- (vi) Axle greases [sett greases].

- The greases are manufactured by saponification of fatty oil with an alkali such as NaOH [sodal, Ca(OH)<sub>2</sub> [lime], Al(OH)<sub>3</sub> [aluminium] or LiOH [lithium]. *Axle greases* are prepared by mixing lime or other heavy metal oxides with resin.
  - This mixture is allowed to stand for few hours. The stiff mass which separates out on the surfaces is separated. To maintain consistency of the grease, *fillers like talc or mica are mixed*.
  - For manufacture, the fatty oil is mixed with mineral oil to form a homogeneous solution which is then subjected to *saponification with respective alkalies*.
- The greases are named on the basis of the alkalies used in manufacture.

- The consistency of greases is maintained by taking the ingredients in appropriate proportion. Reactions involved can be represented as,



Soaps formed act as *gelling agent* which are treated with synthetic/petroleum oil at high temperature (upto 80°C) with continuous stirring to obtain grease.



#### Properties of greases

- (1) *Calcium soap greases :*
  - (a) They are *cheapest*.
  - (b) They possess *good resistance to oxidation*.
  - (c) They can be used upto 65 °C.
  - (d) These can be used to lubricate *water pumps, tractors etc.*
- (2) *Sodium soap greases :*
  - (a) They possess *high temperature sustainance*.
  - (b) They can be used upto 175 °C.
  - (c) They have *high affinity for water*, which is their *drawback*.
  - (d) They can not be used for *machines/bearings which are exposed to wet conditions*.
- (3) *Aluminium soap greases :*
  - (a) They have *good oxidation stability*.
  - (b) They have *high drop point* as compared to calcium soap greases.
  - (c) They can be used upto 90 °C.
  - (d) These greases are used for machines where *high adhesiveness* is desired; especially where *speed and load is high*.

#### Functions of gelling agent (soap) in greases

The gelling agent i.e. soap in this case possesses properties such as viscosity, oxidation resistance etc. depending upon nature of alkali used. The important functions performed by soaps are:

- (i) *Soaps act as thickener* to provide required thickness/viscosity and also oiliness to finished greases, so that the greases stick to the sliding/moving surfaces firmly.
- (ii) *Nature of soaps governs the temperature* up to which greases can be used under working conditions.
- (iii) *Nature of soaps also governs other properties* of greases such as their consistency, water resistance and oxidation stability.

### 3.3.3 Liquid Lubricants

► [Dec. 2002, Dec. 2003, May 2005, Dec. 2005, May 2006, May 2007, Dec. 2007]

- Liquid lubricants (oils) are classified on the basis of their origin into following four classes :

(i)	Vegetable or animal oils.
(ii)	Mineral oils.
(iii)	Blended oils.
(iv)	Synthetic lubricating oils.

#### (i) Vegetable or animal oils

- Vegetable or animal oils are extracted from plants/animals respectively. These oils are triglycerides of higher fatty acids.
- They possess *high oiliness*. Some examples of these are *tallow*, *lard*, *castor*, *olive*, *coconut*, *palm*, *neem*, *linseed*, *rosin*, *hazel nut*, *whale*, *neat foot*, *codliver* etc. Pure fatty acids such as *oleic acid* etc. are also used as lubricants.
- These oils possess high oiliness due to which oil gets adhered to the machine surface and helps to reduce friction.
- Vegetable/animal oils are very costly*. They tend to undergo oxidation, in the presence of oxygen or moisture, or emulsification with water at working temperature.
- They form *gummy, sticky products* which are *acidic* in nature. These substances acquire *dirt and dust* from surroundings, and *form grit* on the surface of machine. They also get *thickened* or *hardened* in the presence of air thereby increasing friction of machine parts.
- These oils show tendency to get hydrolysed in moist/humid air on prolonged exposure liberating *free acids* which cause corrosion of metal surfaces.

- Due to these disadvantages these oils are rarely used directly as lubricant. On the contrary they are used as *blending agents* with other oils to form a lubricating blend suitable for working conditions of machines.

#### (ii) Mineral oils

- Mineral oils* are obtained by fractional distillation of crude oil. These oils normally have long hydrocarbon chains of 12 to 50 carbon atoms.
- The oils with lower number of carbon atoms show lower viscosity. These oils are most widely used as lubricants because they are abundantly available, stable under working conditions, and are of low cost.
- Their oiliness is low as compared to vegetable/animal based oils. To overcome this, mineral oils are generally made into blends of suitable oiliness, by adding vegetable/animal oils, oleic/stearic acids etc.

#### (iii) Blended oils

- Blended oils* are normally made by using vegetable/animal/mineral oils. The blends can be made in such a way that the characteristics/properties of lubricant get improved to suit the service conditions of machinery.
- Blending* is essential because no single pure lubricant serves satisfactorily. Blending agents are used to improve properties such as viscosity index, oxidation stability, oiliness, pour point, flash point etc.
- Other types of additives are corrosion/abrasion inhibitors, antifoaming agents, emulsifiers etc. In addition to this, certain additives are added so that extreme pressure conditions of machineries can also get suitable lubricants.
- The Table 3.3.1 shows the substances/compounds commonly used to improve the properties of the lubricants i.e. of blend.

Table 3.3.1

Property	Substances/Compounds
Oxidation stability improvers.	Aromatic amine, phenols, organic sulphides / phosphides etc. They retard oxidation of oil, but they themselves get oxidized preferentially e.g. in internal combustion engines where lubricants tend to get oxidised.
Corrosion/ Abrasion stability improvers.	Organic compounds of phosphorous or antimony. They form a layer between the sliding surfaces thereby not allowing contact between the surfaces.

Property	Substances/Compounds
Foam preventors.	Glycols or glycerols. Phenols or compounds of naphthalene. Pour point depressants.
Viscosity index improvers.	High molecular weight organic compounds e.g. hexanol.
Viscosity improvers.	Polystyrenes, polyesters etc. They act as thickeners.
Extreme - pressure / temperature additives	Organic phosphorus / sulphur / chlorine compounds, fatty acids / esters, chlorinated waxes, tricresyl phosphate, Vegetable oils etc.
Oiliness carriers	Vegetable oils, fatty acids / amines.
Cloud / pour point depressants	Waxes, alkylated naphthalenes and phenols
Antisear additives	Substances like tricresylphosphate, Zn-dialkyl dithiophosphate.
Rust inhibitors	Fatty acids, Aminophosphates.

## (iv) Synthetic lubricating oils

- The blended oils satisfy most of the requirements of a suitable lubricant for the working conditions of different machineries.
- But for certain machines which work under *severe extreme conditions*, the blended oils are found to be unsuitable e.g. in aircraft engines. When an aircraft in a cold region is to be taken off, the oil has to be pumped at about 0 to 50 °C depending upon the temperature of the region.
- On the contrary when the same machine/engine is landing in other country where the temperature is high, the engine may get heated to very high temperature.
- This type of working conditions evolve the need of a lubricant which can be useful between very wide range of temperatures such as -50 °C to +150 °C.
- For such lubricants, the *viscosity index* and *flash and fire points* should be as *high as possible* whereas their *pour point* should be as *low as possible*.
- The *resistance to corrosion and oxidation*, should be high and their *oiliness and thermal stability* also should be *very high*.

- All such special requirements of the properties are satisfied by synthetic oils. These oils are specially prepared to suit the requirement of the conditions.
- For example :
  - (i) Chloro-fluoro hydrocarbons
  - (ii) Siliconised oils (silicones)
  - (iii) Derivatives of poly-hydroxy alcohols (glycols)
  - (iv) Organophosphatic esters.
- These oils are *inflammable*, but as their *flash and fire points* are *very high*, and all other properties also are suitable for severe working condition, these are used as lubricants.
- *Disadvantage* of these oils is only their *high cost*. Hence these are generally used only for *special machines* such as *in aircraft and refrigeration industry*. For any other requirements, the hydrocarbon oils blended with blending agents can be successfully used.
- Specific properties of synthetic oils are summarised in Table 3.3.2

Table 3.3.2

(i)	$\text{Poly-alkene-glycols}$ $[\text{HO}-\text{CH}_2-\text{C}(\text{CH}_2\text{OCH}_2)_n-\text{CH}_2-\text{OH}]$	Low pour point, high viscosity index, high flash and fire point, can be used up to 300 °C. e.g. polyethylene glycol / poly propylene glycol.
(ii)	Silicone Oils/Fluids	High viscosity index, low volatility, high/good oxidation stability, moisture resistant, can be used up to 200 °C.
(iii)	Poly ethers	Low pour point, high viscosity index, high flash and fire point can be used at low and high temperature application. At very high temperature, these compounds decompose, but do not leave any residue.
(iv)	Dibasic acid esters	Low pour point, high viscosity index, low volatility, highly stable. Non-toxic, do not get hydrolysed, non-corrosive, can be used from -50°C to +230°C. e.g. Di-2-ethyl hexyl sebacate
(v)	Halogenated hydrocarbons	Low pour point, high viscosity index, high flash and fire points, do not catch fire easily, good thermal stability. At very high temperature, they decompose, form extremely corrosive products.

### 3.4 Testing of Lubricants

The lubricating oils are tested for their physical and chemical properties. Knowledge of these help to choose the appropriate lubricant most suitable under the given working condition.

Generally the oils are tested for their physical and chemical properties.

The Table 3.4.1 and 3.4.2 shows the Physical and Chemical tests normally performed and the methods used for the same.

Table 3.4.1

Sr. No.	Physical Tests	Method Used
1.	Viscosity and viscosity index determination.	Redwood viscometer number 1 and 2.
2.	Flash point and fire point determination.	(a) Abel's flash point apparatus. (b) Pensky-Marten's flash point apparatus.
3.	Cloud point and pour point determination.	Cloud and pour point apparatus.
4.	Volatile matter content.	Vaporimeter.
5.	Oxidation stability.	Slight oxidation test.
6.	Carbon residue.	(a) Conradson's method (b) Ramsbottom method

Table 3.4.2

Sr. No.	Chemical Tests	Method Used
(1)	Acid value	Titrimetry
(2)	Saponification value	Titrimetry
(3)	Aniline point	Aniline point apparatus
(4)	Emulsification	Steam emulsion number (SEN)

### 3.5 Characteristics of an Ideal Lubricant

A lubricant can be an ideal one if it prevents the machine surfaces from wear and tear due to friction under all severe working conditions.

An ideal lubricant should perform functions, such as :

- It should reduce friction, thereby reducing deformation, wear and tear of the machine surfaces, and ultimately the maintenance cost.
- Lubricant should act as a coolant.
- Lubricant should reduce waste of energy, thereby increasing efficiency of the machine.
- Lubricant should also act as a sealant under certain conditions. For example in internal combustion engine, the lubricant layer acts as a seal, between piston and cylinder, thereby preventing the leakage of gases.

If the above mentioned properties are found to be upto the requirement of the working conditions, the lubricant is said to be an ideal lubricant.

Thus an ideal lubricant should have following characteristics,

- Should have high oiliness.
- Viscosity should be adequate whereas the variation in the viscosity (viscosity index) should be to a lower extent i.e. V.I should be as high as possible.
- Flash and fire point of the lubricant should be as high as possible, necessarily must be higher than the working temperature of the machines in which the lubricant is to be used.
- The pour point of the lubricant should be as low as possible. It must be lower than the working temperature of the machine where it is to be used for lubrication.
- Acid value of the lubricant should be very low.
- Saponification value of the lubricating oil should be low.

7. Tendency of the lubricating oil to form stable emulsions should be low i.e. emulsion formed by oil with water should be unstable i.e. it should decompose at working temperatures.

8. Oxidation stability of the lubricating oil should be high.

### 3.6 Properties (Testing) of Lubricating Oils

► [ May 2000, May 2004, May 2006 ! ]

► [ May 2006, May 2008 ! ]

#### 3.6.1 Viscosity and Viscosity Index

- Viscosity can be defined as, the property by virtue of which a liquid or fluid (oil) offers resistance to its own flow.
- Viscosity Index can be defined as rate of change of viscosity with respect to temperature.
- Oils become thin on heating, i.e. their viscosity falls/decreases. If the decrease in viscosity is rapid the oil is said to have a *low viscosity index* and vice versa. A good lubricant should have *high viscosity index*.

Viscosity and viscosity index are related to molecular weight of oils. Generally oils with higher molecular weights show higher viscosity. For an ideal lubricant viscosity should be appropriate.

Measurement of viscosity of an oil is carried out using an apparatus called as viscometer. In commonwealth countries, Redwood viscometers are used while in U.S.A. Saybolt viscometer is used.

- The viscosity of oil is expressed in terms of seconds of the respective apparatus; because the viscosity is measured as time taken for a fixed volume of oil to flow through orifice of the oil cup of the apparatus. Thus if it is a Redwood viscometer, then viscosity is say x Redwood seconds and so on.
- Redwood Viscometers are of two types as *Redwood viscometer number 1* and *Redwood viscometer number 2*, the former is used to determine viscosity of thin oils i.e. which possess low viscosity, while the latter one is used for thicker (viscous) oils.

In our country Redwood viscometer number 1 is commonly used, which is shown in Fig. 3.6.1.

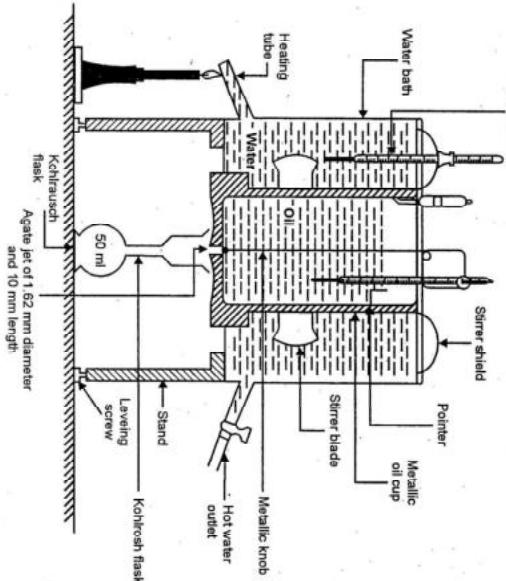


Fig. 3.6.1 Redwood viscometer number 1

#### Construction of Redwood Viscometer :

##### (i) Oil cup

- It is silver plated cylinder, open at top; 90 mm in height 46.5 mm in diameter. The agate jet with bore of diameter 1.62 mm and 10 mm in length is fitted at the bottom of oil cup.
- The jet can be opened or closed with a *value rod*, which is a small silver plated brass ball, fixed to a long stout wire, which helps to use this value rod. The cup at its upper end is fitted with a *pointer*, which indicates the level up to which the cup should be filled with oil.
- The oil cup is provided with a lid having an opening for *thermometer*. This thermometer is used to record the *temperature* of oil.

**(ii) Heating bath**

- Surrounding to the oil cup a cylindrical copper container is fitted. This serves as water/heating bath. The water is to be filled in this cylinder from its opening at top.
- After the use of viscometer hot water is removed from hot water outlet which is attached at the left side of bottom of this container.
- At the right side of bottom, a side tube is provided which is used for heating the oil. Now-a-days electrically heating viscometers are also available.

**(iii) Stirrer**

- Outside the oil cup a stirrer with four blades is provided, so as to heat the water uniformly.
- It is also provided with a shield which prevents the splashing of water during operation. Thus water does not enter the oil cup.

**(iv) Spirit level**

- The lid of oil cup is provided with spirit level for vertical leveling of the jet.

**(v) Levelling screws**

- The three legs of the apparatus are provided with levelling screws. These help to level the apparatus.

**(vi) Kohlrausch flask**

- It is a wide mouth flask measuring definite quantity of oil, (generally 50 ml.) which is shown on its neck as a circular mark.

**Working of Redwood viscometer**

- The oil cup is cleaned and levelled. The oil is filled upto the pointer mark. The agate jet is closed with valve rod. The water bath is filled with water at room temperature.
- A clean Kohlrausch flask is arranged under the agate jet. The temperature of the oil is recorded. The valve rod is shifted to open the agate jet so that oil starts flowing out of oil cup.

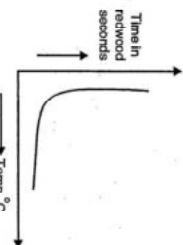


Fig. 3.6.2 : Graph of time (Redwood Seconds) versus temperature

- A burner is arranged under the side tube provided for heating the water bath and the oil. When the thermometer shows that the temperature is  $10^{\circ}\text{C}$  above the room temperature, 50 ml of oil is collected in flask in the similar way as was done at room temperature.

The time in seconds is recorded. Similarly readings of time measurement are taken at  $20^{\circ}\text{C}$ ,  $30^{\circ}\text{C}$ ,  $40^{\circ}\text{C}$ ,  $50^{\circ}\text{C}$ , i.e. at higher temperatures. Similarly with falling temperatures also the procedure can be repeated.

- Then a graph of temperature v/s time (Redwood Seconds) is plotted. Refer Fig. 3.6.2.
- It is a linear curve, because as the oils on heating become thin, their viscosity decreases and hence the time taken for definite quantity of oil to flow out of the agate jet reduces.

**Significance of viscosity and viscosity index:**

- A lubricating oil selected for a job should have viscosity index as high as possible. This helps in achieving desired results to control wear and tear of machine parts. The study also helps to decide about the addition of blending agents to improve the property of lubricating oil.

**3.6.2 Flash and Fire Point**

► [Dec. 2002, Dec. 2005, May 2006, Dec. 2007]

- Flash point can be defined as, *the temperature at which the oil gives out enough vapours that ignite for a moment when a small flame is brought near it.*
- Fire point can be defined as, the temperature at which the oil gives out enough vapours which burn continuously at least five seconds when a small flame is brought near it.

- The flash and fire points are very important properties of an oil, because these help in knowing the highest temperature upto which an oil can be used as a lubricant.

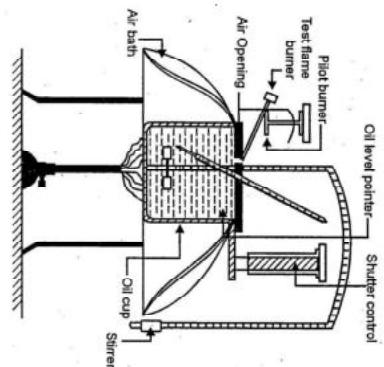


Fig. 3.6.3 : Pensky-Marten's flash point apparatus

- These constants are usually determined by using Pensky-Marten's flash point apparatus.

#### Construction/parts of Pensky-Marten's flash point apparatus

##### (i) An oil cup

- It is about 5 cm in diameter and 5.5 cm deep. The level to which oil is to be filled is marked inside the cup. The cup lid is provided with four openings of standard sizes.
- Through one of these passes a thermometer. Second opening is used for introducing test flame. Through third opening, passes a stirrer carrying two brass blades. The fourth is meant for admission of air.

##### (ii) Shutter

- It is a lever mechanism provided at the top of the cup. By moving the shutter, opening in the lid opens and flame carried by the flame exposure device is dipped into this opening thereby bringing the flame over the oil surface.

##### (iii) Flame exposure device

- It is small flame and this is connected to the shutter by a lever mechanism.

##### (iv) Air bath

Oil cup is supported by its flange over an air bath which is heated by a gas burner.

##### (v) Pilot burner

As the test flame is introduced in the opening, it gets extinguished, but when the test flame is returned to its original position, it is automatically lighted by the pilot burner.

#### Working of Pensky-Marten's flash point apparatus

- Oil under examination is filled upto the mark in the oil cup and it is heated by heating the air bath. Stirrer is worked between tests at a rate of about 1 to 2 revolution per second.
- Heat is applied so as to raise the oil temperature. At every 1°C rise of temperature, flame is introduced for a moment by working the shutter.
- The temperature at which a distinct flash (a combination of a weak sound and light) appears inside the cup, is recorded as the flash point.
- The heating is continued there after and the test flame is applied as before. When the oil ignites and continues to burn for at least 5 seconds, the temperature reading is recorded as the fire point of the oil.

#### Significance of flash and fire point

- A lubricating oil selected for a job should have a flash point which is reasonably above its working temperature. This ensures safety against fire hazards during the storage, transport and use of the lubricating oil.
- It is also useful for identification and detection of contaminants in the oil.

#### 3.6.3 Cloud and Pour Point

► [ May 2004, May 2005, Dec. 2006, Dec. 2007, May 2008 ]

- Cloud point can be defined as the temperature at which the oil becomes cloudy or hazy in appearance.
- Pour point can be defined as, the temperature at which the oil ceases to flow or pour.
- These characteristic physical constants indicate the suitability of oils at lower temperature, or in cold condition. The lubricating oils used in machines working at low temperatures, should have much lower cloud and pour points than the working temperatures.

- Otherwise, the lubricating oil may get solidified at working temperature and this may cause jamming of the machine parts. This may affect the speed of the machine.

The cloud and pour point of oils with impurities are generally high, especially if waxes are present. Hence, it is essential to remove wax like impurities from the oils during their extraction and purification.

- The cloud and pour points for an oil are determined by using a specific apparatus shown in Fig. 3.6.4.

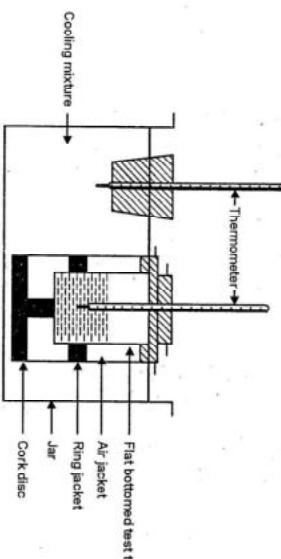


Fig. 3.6.4 : Cloud or pour point apparatus

- Apparatus consists of a broad petridish/jar, which is used as a cold bath. The oil is taken in a flat bottomed hard glass test tube. This test tube is kept in an air jacket as shown in Fig. 3.6.4.

- Two thermometers are suspended, one in oil tube and other in cooling mixture in the jar to note the respective temperatures.

#### Procedure or determination of cloud and pour point

- The oil tube is filled with oil upto the level generally half the length of tube. The jar is filled with the cooling mixture surrounding the air jacket.
- The tube is inserted in the air jacket, the two thermometers are suspended through the wooden corks and temperatures of oil and cooling bath are noted. The oil is subjected to cooling.

- Initially with every 2 °C fall in temperature of oil, the tube is taken out of air jacket, wiped with filter paper from outside and the oil is viewed for checking the transparency. The

temperature at which oil loses its transparency i.e. appears cloudy or hazy is recorded as **cloud point**.

The cooling of oil is continued further. Now with every 1 °C. fall in temperature, the oil tube is taken out and tilted to check the flow of the oil. The temperature at which the oil hardens i.e. ceases to flow along the side of the tube is recorded as **pour point**.

#### Significance of cloud and pour point

- Cloud and pour point of an oil are significant as they help us to know the lowest temperature upto which the oil can be suitable as a liquid lubricant.
- Knowledge of this can help the machines to be prevented from getting jammed in places from cold region or during winter season in some areas in India.

#### 3.6.4 Saponification Value

► [ May 2000, Dec. 2006, May 2007, Dec. 2007 ]

**Saponification value of an oil can be defined as, the number of milligrams of potassium hydroxide required to saponify one gram of oil.**

Saponification value is the characteristic property of vegetable/animal oils, and not of mineral/synthetic oils. This is because mineral/synthetic oils do not undergo saponification.

Saponification is nothing but alkaline hydrolysis of pure oil giving soap and glycerol. The vegetable/animal oils are triglycerides of mixed fatty acids. The fatty acids normally found present in these oils are from  $C_4$  to  $C_{20}$  and many oils have even higher fatty acids. The mixed fatty acids are of saturated as well as unsaturated nature. For example, capric ( $C_{10}$ ), caprylic ( $C_8$ ), caproic ( $C_6$ ), lauric ( $C_{12}$ ), myristic ( $C_{14}$ ), palmitic ( $C_{16}$ ), stearic ( $C_{18}$ ), etc are saturated fatty acids. The general empirical formula of these acids is  $C_nH_{2n}O_2$ .

The most common unsaturated fatty acids are oleic [ $C_{18}, 1$ ] linoleic [ $C_{18}, 2$ ], linolenic [ $C_{18}, 3$ ] acids. All these fatty acids are present in oils in the form of their triglycerides. During saponification, on treatment of oil with aqueous alkali (KOH), the soaps are formed and the potassium salt of glycerol is released.

#### Determination of saponification value of an oil

A known quantity (W gms) of oil is mixed with known excess of alcoholic KOH solution (0.5 N). The mixture is shaken very vigorously and allowed to stand for nearly 24 hours at room temperature. Alternatively the mixture is refluxed for about 2 hours, on water bath, using water condenser.

- The fatty acids form potassium salts (soaps) and glycerol is released.



In the above reaction the oil consumes KOH. At the end, the unreacted KOH is titrated using dil. HCl (0.5 N). The blank reading is taken which can be used in knowing the quantity of alc.KOH reacted/consumed.

The amount of unreacted KOH is known from amount of HCl consumed, thereby the quantity of KOH consumed can be calculated. Saponification value is calculated using formula,

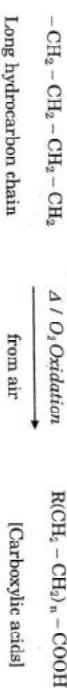
$$\text{Saponification value} = \frac{\text{Amount of KOH consumed (Blank - Back)}}{\times \frac{\text{Normality of KOH (0.5 N)} \times 56}{\text{Weight of oil taken (W gms.)}}}$$

The saponification value is expressed as milligrams of KOH.

#### Significance of Saponification value

- The knowledge of saponification value helps to know the stability of oil in aqueous/alkaline medium if in case machine parts face any such conditions.
- Further it also signifies the composition of vegetable/animal oils, thereby helps to check the suitability of oils for lubrication purposes. Drying property of oils which is harmful during lubrication can also be checked.

e.g.



*Unsaturated part of veg/animal oil*



#### 3.6.5 Acid Value

- Acid value is defined as the number of milligrams of KOH required to neutralize free fatty acids present in one gram of oil.

- It is essential to determine the content of *free acids* in an oil because, these acids if present even in small quantity, *harm machines during lubrication*. The lubricating oils, mineral or vegetable/animal based, generally possess long hydrocarbon chains or fatty acids as glycerides.

- The mineral oils on prolonged exposure to O<sub>2</sub> from air or continuous rise and fall of temperature in working conditions undergo cleavage and get oxidised by air.
- The vegetable/animal based oils contain fatty acids in combined form as triglycerides of mixed fatty acids. The unsaturated sites in fatty acids tend to absorb oxygen on exposure to air, and form carboxylic acids.
- Thus the absorption of O<sub>2</sub> and thereby formation of carboxylic acids affects the quality of oil. Such an oil becomes unsuitable for lubrication, because acids affect the machine parts. Thus ideally acid value should be minimum, to make oil suitable.

#### Determination of acid value of an oil

- The oil sample is weighed (W gms, ideally 1 gm) and mixed with absolute alcohol (50 ml for 1 gm of sample ideally). The mixture is warmed for 10-15 minutes on water bath.
- The free fatty acids separate out from oil. The mixture is then titrated against standard 0.1 N KOH solution, using phenolphthalein indicator. The quantity of KOH solution is noted as  $\chi$  ml. The acid value is then calculated as,

$$\text{Acid value} = \frac{\text{Quantity of KOH } (\chi \text{ ml}) \times \text{normality of KOH} \times 56}{\text{Weight of oil (W gms)}}$$

Unit of acid value is mgs of KOH

#### Significance of acid value

- The determination of the acid value can help us know the suitability of the lubricating oil. Higher the acid value, more the corrosion of machine surfaces, more wear and tear, more maintenance cost for machines.

► [ May 2000, Dec. 2004, May 2008 ! ]

### 3.7 Solved Problems

#### 3.7.1 Problems based on Saponification Value

**Problem 3.7.1:** 5 gms of a vegetable oil was saponified using excess of alcoholic KOH (0.5 N). The mixture required 15.0 ml. of 0.5 N HCl while blank titration required 45.0 ml. of same HCl. Find the saponification value of the oil.

**Solution :**

Given  
Weight of oil = 5 gms.

Blank titration reading = 45 ml. 0.5 N HCl.

Back titration reading = 15 ml 0.5 N HCl

Thus, volume of 0.5 N KOH required by the oil for saponification in terms of 0.5 N HCl = 45 - 15 = 30 ml.

$$\text{Saponification value} = \frac{\text{Volume of KOH consumed} \times \text{Normality of KOH} \times 56}{\text{Weight of oil in gms.}}$$

$$= \frac{30 \times 0.5 \times 56}{5}$$

= 168 mg. KOH.

**Ans. : Saponification value of oil = 168 mgs KOH**

**Problem 3.7.2:** An oil sample of saponification value 180 mgs. KOH, was saponified using 0.4 N alcoholic KOH solution. The blank titration reading was 50 ml. of 0.4 N HCl solution. Find the quantity of alcoholic KOH consumed by the oil per gram.

**To find:** Saponification value of oil.

**Solution :**

Given Saponification value of oil = 180 mg. KOH

Normality of alcoholic KOH = 0.4 N.

Normality of HCl = 0.4 N

Blank titration reading = 50 ml.

Weight of oil = 1 gm.

**To find**

Quantity of 0.4 alcoholic KOH required by 1 gm of oil.

**Problem 3.7.4:** 2.5 gms of an oil was saponified by alcoholic KOH (0.25 N). The blank reading with 0.5 N HCl was 40 ml while back was 20 ml of same HCl. Find saponification value of oil.

**Solution :**

Given

$$\text{Weight of oil} = 2.5 \text{ gms}$$

$$\text{Blank titration reading} = 40 \text{ ml } 0.5 \text{ N HCl}$$

$$\text{Back titration reading} = 20 \text{ ml } 0.5 \text{ N HCl}$$

$$\text{Normality of KOH} = 0.25 \text{ N}$$

To find : Saponification value of oil.

∴ Strength of alcoholic KOH and HCl are given as, 0.25 N and 0.5 N respectively,

∴ Point of equivalence in titration would reach as,

$$2 \text{ ml } 0.25 \text{ N KOH} = 1 \text{ ml } 0.5 \text{ N HCl.}$$

Thus quantity of KOH added to oil (blank) = 80 ml.

and quantity of KOH unreacted (back) = 40 ml.

$$\text{Saponification value} = \frac{\text{Volume of alcoholic KOH} \times \text{N}_{\text{KOH}} \times 56}{\text{Weight of oil in gms}}$$

$$\therefore \text{S.V.} = \frac{[\text{Blank} - \text{Back}] \times \text{N}_{\text{KOH}} \times 56}{\text{Weight of oil}}$$

$$\therefore \text{S.V.} = \frac{(80 - 40) 0.25 \times 56}{2.5}$$

$$\therefore \text{S.V.} = \frac{40 \times 0.25 \times 56}{2.5} \text{ mg. KOH}$$

$$\therefore \text{S.V.} = 224 \text{ mg. KOH}$$

**Ans. : Saponification value of oil = 224 mg. KOH**

**Problem 3.7.5:** 5 gms of oil was saponified using 50 ml alcoholic KOH (1.4 gms per 50 ml solution). The mixture required 10 ml. 0.5 N HCl while blank titration reading was 40 ml of same HCl. Find the saponification value of oil.

**Solution :**

Given

$$\text{Weight of oil} = 5 \text{ gms}$$

$$\text{Strength of alcoholic KOH} = 1.4 \text{ gm per 50 ml.}$$

**Problem 3.7.6:** 6 gms of an oil was saponified with 50 ml 0.5 N alcoholic KOH. After refluxing for 2 hrs. the mixture was titrated by 25 ml of 0.5 N HCl. Find saponification value of oil.

(Dec. 2002)

**Solution :**

Given

$$\text{Weight of oil} = 6 \text{ gms}$$

To find : Saponification value,

$$\text{S.V.} = \frac{\text{Volume of alcoholic KOH} \times \text{N}_{\text{KOH}} \times 56}{\text{Weight of oil in gms.}}$$

$$\therefore \text{S.V.} = \frac{[\text{Blank} - \text{Back}] \times \text{N}_{\text{KOH}} \times 56}{\text{Weight of oil}}$$

$$\therefore \text{S.V.} = \frac{(40 - 25) 0.5 \times 56}{5} \text{ mg. KOH}$$

$$\therefore \text{S.V.} = \frac{30 \times 0.5 \times 56}{5} \text{ mg. KOH}$$

$$\therefore \text{S.V.} = 168 \text{ mg. KOH}$$

**Ans. : Saponification value of oil = 168 mg. KOH.**

**Problem 3.7.7:** 1.5 gm of an oil is saponified with 26 ml of N/2 alcoholic KOH. After refluxing the mixture, it requires 15 ml of N/2 HCl. Find saponification value of oil.

(Dec. 2003, 3 Marks)

**Solution:****Given**

$$\text{Wt. of oil} = 1.55 \text{ gm}$$

$$\text{Normality of KOH} = \frac{N}{2} = 0.5 \text{ N}$$

$$\text{Amt. of KOH} = 26 \text{ ml.}$$

$$\text{Normality of added HCl} = \frac{N}{2} = 0.5 \text{ N}$$

$$\text{Amount of HCl consumed} = 15 \text{ ml}$$

$$\text{Saponification value} = \frac{\text{Amount of KOH consumed} \times \text{Normality} \times 56}{\text{Wt. of oil}}$$

$$= \frac{(26 - 15) \times 0.5 \times 56}{1.55}$$

$$= \frac{11 \times 0.5 \times 56}{1.55}$$

$$= 198.7 \text{ mgs of KOH}$$

**Ans. : Saponification value = 198.7 mgs of KOH****Problem 3.7.8 :** In determination of saponification value of vegetable oil 5 gm of oil sample was refluxed with 50 ml of alcohol and 50 ml of 0.5 N alcoholic KOH solution.

To get the end point 20 ml of 0.5 N HCl was required. The blank reading was 52 ml. Find the saponification value of oil.  
(Dec. 2004, 4 Marks)

**Given**

$$\text{Wt. of oil} = 5 \text{ gm}$$

$$\text{Normality of KOH} = 0.5 \text{ N}$$

$$\text{Amount of HCl} = 31.5 \text{ ml}$$

$$\text{Saponification value} = 192 \text{ mgs}$$

$$\% \text{ Cottonseed oil} = ?$$

**To find :** % Cottonseed oil in blend

$$\therefore 50 \text{ ml KOH} = 45 \text{ ml } 0.5 \text{ N HCl}$$

$$\therefore N_1 V_1 = N_2 V_2$$

$$N_1 \times 50 = 0.5 \times 45$$

$$\therefore N_1 = \frac{0.5 \times 45}{50}$$

$$= 0.45 \text{ N}$$

$$\therefore \text{Normality of KOH} = 0.45 \text{ N}$$

$$\therefore \text{Weight of blended oil} = 16 \text{ gm}$$

$$\therefore \text{Weight of cottonseed oil} = 16 - x \text{ gm}$$

$$\text{Now, Saponification value} = \frac{(\text{Blank} - \text{Back}) \times N \times 56}{(16 - x)}$$

Blended oil contains castor oil and petroleum oil.

**Problem 3.7.9 :** 16 gm of blended oil was heated with 50 ml KOH. This mixture then required 31.5 ml of 0.5 N HCl .50 ml KOH required 45 ml 0.5 N HCl. Find % cottonseed oil, if saponification value = 192 mg. (Dec. 2005, 6 Marks)**Solution:****Given**

$$\text{Weight of blended oil} = 16 \text{ gm}$$

$$\text{Amount of KOH} = 50 \text{ ml}$$

$$\text{Normality of HCl} = 0.5 \text{ N}$$

$$\text{Amount of HCl} = 31.5 \text{ ml}$$

$$\text{Saponification value} = 192 \text{ mgs}$$

$$\% \text{ Cottonseed oil} = ?$$

**To find :** % Cottonseed oil in blend

$$\therefore 50 \text{ ml KOH} = 45 \text{ ml } 0.5 \text{ N HCl}$$

$$\therefore N_1 V_1 = N_2 V_2$$

$$N_1 \times 50 = 0.5 \times 45$$

$$\therefore N_1 = \frac{0.5 \times 45}{50}$$

$$= 0.45 \text{ N}$$

$$\therefore \text{Normality of KOH} = 0.45 \text{ N}$$

$$\therefore \text{Weight of blended oil} = 16 \text{ gm}$$

$$\therefore \text{Weight of cottonseed oil} = 16 - x \text{ gm}$$

$$\text{Now, Saponification value} = \frac{(\text{Blank} - \text{Back}) \times N \times 56}{(16 - x)}$$

Blended oil contains castor oil and petroleum oil.

$\therefore$  petroleum oil has saponification value always zero.

$\therefore$  Let us calculate saponification value of the blended oil.

$$\begin{aligned}\text{Saponification-value} &= \frac{\text{Volume of KOH} \times N_{\text{KOH}} \times 56}{\text{Weight of Blend}} \\ &= \frac{13.5 \times 0.45 \times 56}{16} \\ &= 36 \text{ mgs of KOH}\end{aligned}$$

$\therefore$  Saponification-value of blend = 21.26 mgs of KOH

$$\% \text{ castor oil} = \frac{\text{Saponification value of blend}}{\text{Saponification value of castor oil}} \times 100$$

$$\begin{aligned}&= \frac{21.26}{192} \times 100 \\ &= 11.074 \%\end{aligned}$$

Ans.: % of castor oil in blend = 11.074 %

**Problem 3.7.9(A):** 1.55 gram of an oil is saponified with 20 ml of  $\frac{N}{2}$  alcoholic potassium hydroxide solution. After refluxing the mixture, it requires 15 ml of  $\frac{N}{2}$  HCl solution. Find saponification value of oil. (May 2008, 3 Marks)

**Solution:**

Given data:

$$\begin{aligned}\text{Wt. of lubricant} &= 3 \text{ gm.} \\ \text{Blank titration reading} &= 36 \text{ ml.} \\ \text{Back titration reading} &= 12 \text{ ml.} \\ \text{Normality of HCl} &= 0.5 \text{ N}\end{aligned}$$

To calculate saponification value,

$$\begin{aligned}\text{Sap. Value} &= \frac{\text{Vol. of KOH consumed} \times 28}{\text{Wt. of Oil}} \text{ mgs of KOH} \\ &= \frac{(36 - 12) \times 28}{3} \text{ mgs of KOH} \\ &= \frac{24 \times 28}{3} \\ &= (8 \times 28) \text{ mgs of KOH} \\ &= 224 \text{ mgs of KOH}\end{aligned}$$

**Ans.** Saponification Value = 224 mgs of KOH

### 3.7.2 Problems based on Acid Value

**Problem 3.7.10:** 2.5 gm of an oil sample required 2.5 ml of  $N/100$  KOH to neutralise fatty acids in oil. Find the acid value.

**Solution:**

$$\text{Saponification Value} = \frac{\text{Volume of KOH consumed} \times N_{\text{KOH}} \times 56}{\text{weight of oil}}$$

$$\begin{aligned}&= \frac{(20 - 15) \times 0.5 \times 56}{1.55} \\ &= \frac{5 \times 0.5 \times 56}{1.55} \\ &= \frac{2.5 \times 56}{1.55}\end{aligned}$$

To find: Acid value,

= 90.32 mgs of KOH

**Ans.: Saponification value = 90.32 mgs of KOH**

**Solution:**

**Problem 3.7.9(B):** 3 gm of liquid lubricant was saponified with potassium hydroxide solution. After saponification the mixture was titrated against 0.5 N HCl solution. The burette reading was found to be 12 ml. If blank titration burette reading was 36 ml, calculate the saponification number of the lubricant. (Dec. 2007, 4 Marks)

(Dec. 2007, 4 Marks)

Given data:

$$\begin{aligned}\text{Wt. of lubricant} &= 3 \text{ gm.} \\ \text{Blank titration reading} &= 36 \text{ ml.} \\ \text{Back titration reading} &= 12 \text{ ml.}\end{aligned}$$

Normality of HCl = 0.5 N

To calculate saponification value,

$$\begin{aligned}\text{Sap. Value} &= \frac{\text{Vol. of KOH consumed} \times 28}{\text{Wt. of Oil}} \text{ mgs of KOH} \\ &= \frac{(36 - 12) \times 28}{3} \text{ mgs of KOH} \\ &= \frac{24 \times 28}{3} \\ &= (8 \times 28) \text{ mgs of KOH} \\ &= 224 \text{ mgs of KOH}\end{aligned}$$

**Ans.** Saponification Value = 224 mgs of KOH

### 3.7.3 Problems based on Saponification Value

**Problem 3.7.11:** 2.5 gm of an oil sample required 2.5 ml of  $N/100$  KOH to neutralise fatty acids in oil. Find the saponification value.

**Solution:**

$$\text{Saponification Value} = \frac{\text{Volume of KOH consumed} \times N_{\text{KOH}} \times 56}{\text{weight of oil}}$$

$$\begin{aligned}&= \frac{(20 - 15) \times 0.5 \times 56}{1.55} \\ &= \frac{5 \times 0.5 \times 56}{1.55} \\ &= \frac{2.5 \times 56}{1.55}\end{aligned}$$

To find: Acid value,

$$\text{Acid value} = \frac{\text{Volume of KOH} \times N_{\text{KOH}} \times 56}{\text{Weight of oil in gms}}$$

$$\text{Acid value} = \frac{2.5 \times 0.01 \times 56}{2.5}$$

$$= 0.56 \text{ mg/gm.}$$

Ans.:

$$\text{Acid value of oil} = 0.56 \text{ mgs KOH}$$

**Problem 3.7.11:** A vegetable oil was tested for its acid value. 10 gms of oil required 0.2 ml of KOH. Find its acid value. ( $N_{\text{KOH}} = 0.02 \text{ N}$ )

**Solution:**

$$\text{Given} \quad \text{Weight of oil} = 10 \text{ gms}$$

$$\text{Normality of KOH} = 0.02 \text{ N.}$$

$$\text{Volume of KOH} = 0.2 \text{ ml.}$$

**To find:** Acid value,

$$\text{Acid value} = \frac{\text{Volume of KOH} \times N_{\text{KOH}} \times 56}{\text{Weight of oil in gms.}}$$

$$\text{Acid value} = \frac{0.2 \times 0.02 \times 56}{10}$$

$$= 0.0224 \text{ mg/gm.}$$

Ans.:

$$\text{Acid value of oil} = 0.0224 \text{ mgs. KOH}$$

**Problem 3.7.12:** An oil blend used was analysed for its acid value. 5 ml of oil required  $\frac{N}{100}$  KOH. Find its acid value. State whether the blend can still be useful for lubrication. (density of oil = 0.89).

**Solution:****Given**(Weight = Volume in ml  $\times$  Density)

$$\text{Weight of oil} = 5 \text{ ml} \times 0.89 = 4.45 \text{ gms.}$$

$$\text{Normality of KOH} = 0.01 \text{ N}$$

$$\text{Volume of KOH} = 2.5 \text{ ml.}$$

$$\text{To find : Acid value}$$

$$\therefore \text{Volume of oil} = 5 \text{ ml}, \quad \text{Volume of KOH} = 2 \text{ ml}$$

$$\text{Density of oil} = 0.92, \quad \text{Normality of KOH} = 0.01 \text{ N}$$

$$\text{To find weight of oil,}$$

$$\text{Density} = \frac{\text{Mass}}{\text{Volume}} \quad \text{or} \quad \text{Mass} = \text{Density} \times \text{Volume}$$

$$= 0.92 \times 5$$

$$\therefore \text{weight of oil} = 4.60 \text{ g}$$

$$\text{Acid value} = \frac{\text{Volume of KOH required} \times \text{normality of KOH} \times 56}{\text{Weight of oil (gm)}}$$

$$\text{Hence acid value} = \frac{2 \times 0.01 \times 56}{4.60} = 0.243 \text{ mg}$$

Ans.:

$$\text{Acid value} = 0.243 \text{ mg of KOH.}$$

**Problem 3.7.14:** 9 ml oil is taken from machine and it requires 1.5 ml of 0.04 N KOH. Find acid value (density of oil = 0.81 g/ml.) (May 2004)

**Solution :****Given**

$$\text{Volume of oil} = 9 \text{ ml}$$

$$\text{Density of oil} = 0.81 \text{ g/ml}$$

$$\text{Normality of KOH} = 0.04 \text{ N}$$

$$\text{Amount of KOH} = 1.5 \text{ ml}$$

**To find :** Acid value

$$\begin{aligned} \text{Wt of oil} &= \text{Volume} \times \text{density} \\ &= 9 \times 0.81 \\ &\approx 7.29 \text{ gm} \end{aligned}$$

**Step II :**

$$\begin{aligned} \text{Amount of 0.04 N KOH} &= 1.5 \text{ ml} \\ \text{Amount of 0.1 N KOH} &= \frac{0.1 \times 1.5}{0.04} \\ &= \frac{0.15}{0.04} = 3.75 \text{ ml} \end{aligned}$$

**Ans. : Acid value = 2.88 mgs of KOH**

$$\text{Acid value} = \frac{\text{Amount of KOH consumed} \times \text{Normality} \times 56}{\text{Wt. of oil in grams}}$$

$$\begin{aligned} &= \frac{3.75 \times 0.1 \times 56}{7.29} \\ &= 2.88 \text{ mgs of KOH} \end{aligned}$$

**Ans. : Acid value = 2.88 mgs of KOH****Problem 3.7.15 :** 20 ml. of a lubricating oil was dissolved in alcohol. Solution was titrated against 0.1 N KOH solution. At the end point burette reading was found to

2.5 ml. Calculate the acid value of the oil. (density of oil = 0.86 gm/ml)

(May 2006)

**Solution :**

Given :

Volume of oil = 20 ml

Density of oil = 0.86 gm/ml

Normality of KOH = 0.1 N

Amount of KOH = 2.5 ml

Acid value = ?

**To find :** Acid value

$$\begin{aligned} \text{Weight of oil} &= \text{Volume} \times \text{density} \\ &= 20 \times 0.86 \\ &= 17.20 \text{ gm} \end{aligned}$$

$$\begin{aligned} \text{Acid value} &= \frac{\text{Amount of KOH} \times \text{N}_{\text{KOH}} \times 56}{\text{Weight of oil}} \\ &= \frac{2.5 \times 0.1 \times 56}{17.20} \\ &= 0.814 \text{ mgs of KOH} \end{aligned}$$

**Ans. : Acid value = 0.814 mgs of KOH****Problem 3.7.16 :** Find acid value of 3 gm of oil which required 0.2 ml of 0.025 N KOH to neutralise free acids present. (May 2005, 8 Marks)**Solution :**

Given :

Weight of oil = 3 gm

Quantity of KOH = 0.2 ml

Normality of KOH = 0.025 N

Acid value = ?

**To find :** Acid value

$$\text{Acid value} = \frac{\text{Volume of KOH consumed} \times \text{N}_{\text{KOH}} \times 56}{\text{Weight of oil}}$$

$$\begin{aligned} &= \frac{0.2 \times 0.025 \times 56}{3} \\ &= 0.0933 \text{ mgs of KOH} \end{aligned}$$

**Ans. : Acid value = 0.0933 mgs of KOH****Problem 3.7.17 :** Find acid value of a used oil sample whose 7 ml required 3.8 ml of  $\frac{N}{20}$  KOH during titration. (density of oil = 0.88). State whether oil is proper for lubrication or not from acid value. (Dec. 2006, 3 Marks)

**Solution :**

**Given:**

$$\text{Weight of oil} = 7 \text{ ml}$$

$$\text{Quantity of KOH} = 3.8 \text{ mL}$$

$$\text{Normality of KOH} = \frac{N}{20} = 0.05 \text{ N}$$

$$\text{Acid value} = ?$$

**To find :** Acid value

$$\text{Weight of the oil} = \text{volume} \times \text{density}$$

$$= 7 \times 0.88$$

$$= 6.16 \text{ gms}$$

$$\begin{aligned}\text{Acid value} &= \frac{\text{Volume of KOH consumed} \times \text{N}(\text{KOH}) \times 56}{\text{Weight of oil}} \\ &= \frac{3.8 \times 0.05 \times 56}{6.16}\end{aligned}$$

$$\text{Acid value} = 1.72 \text{ mgs of KOH}$$

**Ans. : Acid value = 1.72 mgs of KOH**

### 3.8 Selection of Lubricant

The main factors to be taken into account for proper selection of a lubricant are,

- (i) Temperature
  - (ii) Load condition
  - (iii) Speed.
- The lubricant selected should possess suitable characters for the operating system and should not change its properties. Properties of lubricants required for different types of machinery are summarised as below:

Type of machinery	Operating conditions	Properties required in lubricant
1. Internal combustion engine	High temperature, Low to high speed, low to high pressure	<ul style="list-style-type: none"> <li>(i) High thermal stability.</li> <li>(ii) Non corrosive.</li> <li>(iii) High viscosity index.</li> <li>(iv) Good oiliness.</li> <li>(v) Should act as seal between piston rings and cylinder wall, against high pressure combustion gases.</li> <li>(vi) Oxidation stability.</li> <li>(vii) Moderate viscosity, e.g. petroleum oils blended with above 'property improvers'.</li> </ul>
2. Spindles	Low load, high speed	<ul style="list-style-type: none"> <li>(i) Low to moderate viscosity.</li> <li>(ii) Oxidation resistance.</li> <li>(iii) Should contain corrosion inhibitor.</li> <li>(iv) Nonvolatile, e.g. Thin petroleum oil blended with corrosion inhibitor.</li> </ul>
3. Refrigeration	Low temperature, Moderate load	<ul style="list-style-type: none"> <li>(i) Low pour point, below - 40°F.</li> <li>(ii) Moderate viscosity.</li> <li>(iii) Low cloud point.</li> <li>(iv) naphthenic base oil.</li> </ul>
4. Circulating system (turbine, hydraulic)	Water or steam contact, high temperature	<ul style="list-style-type: none"> <li>(i) High oxidation resistance.</li> <li>(ii) Antifoaming character.</li> <li>(iii) Antirusting character.</li> <li>(iv) Medium viscosity.</li> <li>(v) High viscosity index.</li> </ul>

Type of machinery	Operating conditions	Properties required in lubricant
		(vi) Minimum emulsification property. e.g. petroleum oils blended with antirust, antifoaming, viscosity index improving additives.
5. Gears	High pressure, high temperature low to high speeds	(i) High oiliness. (ii) Proper viscosity (medium to high). (iii) Oxidation resistance high. (iv) High viscosity index. (v) Good antifoam property. (vi) No dissolution effect on rubber seals. e.g. (a) Proper viscosity petroleum oils blended with antifoam, antioxidant, V.I. and oiliness improvers. (b) Greases.
6. Cutting / drilling	Very high pressure, high temperature, (function to cool and lubricate the tool and job)	(i) Low viscosity. (ii) High oiliness. (iii) Anticorrosive nature. (iv) Coolant. (v) Extreme pressure additive in it. e.g. Cutting oils (emulsion of vegetable oil in water medium with emulsifier) mixed with antioxidant, extreme pressure additive.
7. Transformers		Insulation, heat transfer, higher temperature in on load condition

Type of machinery	Operating conditions	Properties required in lubricant
7. Transformers	Insulation, heat transfer, higher temperature in on load condition	(i) Low viscosity. (ii) High dielectric property. (iii) High oxidation resistance. (iv) Good chemical stability. e.g. Highly refined petroleum oil without any trace of dirt and moisture.
8. Extreme pressure - low speed (tractor, roller, lathe, concrete mixer, rail track joint, crane pulleys)	Extreme pressure, high temperature low speed	(i) Very high thermal stability. (ii) Non-inflammable. (iii) Soft. (iv) Reactive on metal surface to form inorganic compounds film of soft nature. e.g. (a) Solid lubricant like graphite, $\text{MoS}_2$ , soaps, etc. in the form of suspension in oil or water. (b) Petroleum oil blend with extreme pressure additive
9. Delicate instruments	Low load, high speed.	(i) Low to moderate viscosity. (ii) Nonvolatile. (iii) Low pour point. e.g. (a) Vegetable oils (b) Animal oils (c) Low viscosity petroleum oils.
10. Steam engine cylinder	Steam contact, high temperature, high pressure	(i) High oiliness. (ii) Less emulsification with water. (iii) High viscosity index.

**Review Questions**

**Q. 1** What are lubricants ? Give their important functions.

**Q. 2** How are lubricants classified ? Explain with examples.

- Q. 3** Define grease. Under which situation it is used as a lubricant ?
- Q. 4** Explain the term flash and fire point. Give their significance.

**Q. 5** Define :

(a) Acid value

(b) Saponification value

**Q. 6** Define :

(a) Viscosity

(b) Viscosity Index

**Q. 7** What is oiliness ? What is its importance in lubrication ?

**Q. 8** Define 'saponification value'. How does it help in assessing the quality of lubricant ?

**Q. 9** What is cloud point and pour point ? Give their importance.

**Q. 11** Mention the essential qualities of a good lubricant.

**Q. 12** What is lubricant ? Mention its functions. Explain in brief fluid film lubrication.

**Q. 13** With the help of neat diagram, explain working of Redwood viscometer.

**Q. 14** Explain in brief the mechanism of lubrication.

**Q. 15** What is extreme pressure lubrication ? Discuss with suitable examples.

**Q. 16** What are the different mechanisms of lubrication ? Explain the boundary film lubrication.

**Q. 17** What is viscosity ? Explain in brief how would you determine the viscosity of lubricating oil.

**Q. 18** Define and explain the importance of the following :

- (a) Viscosity  
(b) Viscosity index  
(c) Cloud and pour point  
(d) Fire and flash point  
(e) Acid value

**Q. 19** Define flash point. Describe any one method of determining flash point.

**Q. 20** How are lubricants classified ? Give their examples.

**Q. 21** How are lubricants obtained and refined from crude petroleum ?

**Q. 22** Give a short account of selection of lubricants.

**3.9 Unsolved Problems**

**Ex. 1** Find acid value of a vegetable oil and its suitability for lubrication, if 5 gms of oil required 0.03 ml. of  $\frac{N}{40}$  KOH for neutralization of free fatty acids.

[Ans. : (i) 0.0672 mgs KOH, (ii) suitable for lubrication.]

**Ex. 2** A sample of vegetable oil required 15 ml of  $\frac{N}{50}$  alcoholic KOH for complete saponification. Find its saponification value if weight of oil analysed is 3 gms.

[Ans. : 140 mgs KOH]

**Ex. 3** Alcoholic KOH was prepared by dissolving 2.8 gms in 100 ml solution. 1.5 gm of an oil sample required 10 ml of this solution to get saponified completely. Find its saponification value.

[Ans. : 186.6 mgs KOH]

**3.10 University Questions (Theory)****May 2003**

- Q. 1** Define grease. Under which situation it is used as a lubricant ? (Section 3.3.2)  
**Q. 2** Write a note on solid lubricants. (Section 3.3.1)

- Q. 3** Define lubrication. Explain boundary line lubrication. (Section 3.2 and 3.2.2.1)  
**Q. 4** How quality of mineral oil be improved ? (Section 3.3.3)

- Q. 5** Write a note on fluid-film lubrication. (Section 3.2.2.1)  
**Q. 6** Write a note on solid lubricants. (Section 3.3.1)

**May 2000**

- Q. 1** Describe how do you determine neutralization number and saponification value of lubricant. (Section 3.6.4 and 3.6.5)  
**Q. 2** How would you determine viscosity of a lubricating oil using Redwood viscometer ? (Section 3.6.1)  
**Q. 3** Name a few solid lubricants. Under which conditions a solid lubricant is used ? (Section 3.3.1)

**Dec. 2001**

- Q. 1** What are the various functions of lubricants ? (Section 3.2.1)

- Q. 2** Explain cloud and pour point of oil. (Section 3.6.3)

- Q. 3** Explain boundary film and extreme pressure lubrication. (Section 3.2.2.2)

**May 2002**

- Q. 1** Write a short note on selection of lubricants. (Section 3.8)

- Q. 2** Distinguish between fluid film and extreme pressure lubrication. (Section 3.2.2.1 and 3.2.2.3)

- Q. 3** Describe the mechanism of thick film and boundary lubrication. (Section 3.2.2.1)

**Dec. 2002**

- Q. 1** What is neutralization number ? How is it helpful in assessing the quality of lubricant ? (Section 3.5) (2 Marks)  
**Q. 2** Explain the mechanism of lubrication which is provided for delicate instruments and machine. (Section 3.2.2.1) (4 Marks)  
**Q. 3** Give brief account of Semi-Solid lubricants. (Section 3.3.2) (4 Marks)

- Q. 3** Define flash and fire point of lubricants and their significance. (Section 3.6.2)

**May 2005****Q. 4** Write short note : Semi-solid Lubricant (Section 3.3.2) (4 Marks)**Q. 1** What are Blended oils ? (Section 3.3.3) (2 Marks)**Q. 2** Give four functions of good quality lubricant. (Section 3.2.1) (4 Marks)**Q. 3** Where are the solid lubricants used ? Explain only with one example. (Section 3.3.1) (5 Marks)**Q. 4** Explain Extreme Pressure Lubrication. (Section 3.2.2.3) (5 Marks)**Q. 5** Explain : Cloud point and pour point. (Section 3.6.3) (2 Marks)**Dec. 2005****Q. 3** What is lubricant ? Explain different types of lubricants. (Section 3.2) (9 Marks)**Q. 1** Define :

- (i) Cloud point (Section 3.6.3)
- (ii) Pour point (Section 3.6.3)
- (iii) Saponification value (Section 3.6.4)

**Q. 2** Write short note on : Fluid film lubrication. (Section 3.2.2.1) (3 Marks)**Q. 3** (4 Marks)**Q. 1** Fatty oils are no more used as lubricants on the large scale. Why ? (Section 3.3.3) (2 Marks)**Q. 2** Which TYPE of film/lubrication required for HIGH SPEED, LOW LOAD Machines ? (Section 3.2.2.3) (4 Marks)**Q. 3** Define flash point of lubricant. How is it determined by Pensky-Marten's Apparatus ? (Section 3.6.2) (5 Marks)**May 2006****Q. 1** What are blended oils ? How are they better than animal or vegetable oils ? (Section 3.3.3) (3 Marks)**Q. 2** (3 Marks)**Q. 2** Explain extreme pressure lubrication. (Section 3.8) (3 Marks)**Q. 3** Explain hydrodynamic or thickfilm lubrication with the help of a diagram. (Section 3.2.2.1) (5 Marks)**Q. 4** What is saponification number ? How is it experimentally determined ? State its significance. (Section 3.6.4) (5 Marks)**Q. 5** (5 Marks)**Q. 1** What are blended oils ? How are they superior to vegetable and mineral oils ? (Section 3.3.3) (3 Marks)**Q. 2** Write short note on : Boundary layer lubrication. (Section 3.2.2.3) (3 Marks)**Q. 3** Explain following properties of lubricant :

- (i) Viscosity and viscosity index (Section 3.6.1)
- (ii) Flash point and fire point temperature (Section 3.6.2)
- (iii) De-emulsification (Section 3.6)

**Dec. 2007****Q. 1** What are blended oils ? How are they superior to vegetable and mineral oils ? (Section 3.3.3) (2 Marks)**Q. 2** (2 Marks)**Q. 2** What are lubricants ? Explain the mechanism of thin film lubrication in detail. (Sections 3.2, 3.2.2) (4 Marks)**Q. 3** (4 Marks)

What are their importances ?

**Q. 3** Explain any two of the following properties of lubricants :

- (i) Flash point and fire point temperature (Section 3.6.2)
- (ii) Cloud point and pour point temperature (Section 3.6.3)
- (iii) Saponification number. (Section 3.6.4)

**May 2008**

**Q. 1** What are lubricants ? List different functions of lubricants.

(Sections 3.1, 3.2.1)

**Q. 2** Explain any two of the following properties of lubricants :

- (i) Oilliness (Section 3.6)
- (ii) Acid value (Section 3.6.5)

(3 Marks)

(3 Marks)

**Q. 3** Write short note on : Solid lubricant (Section 3.3.1)

(5 Marks)

### 3.11 University Questions (Problems)

**Dec. 2003**

**Q. 1** 1.55 gm of an oil is saponified with 26 ml of N/2 alcoholic KOH. After refluxing the mixture, it requires 15 ml of N/2 HCl. Find saponification value of oil. (Problem 3.7.7)

(3 Marks)

**Dec. 2004**

**Q. 2** 9 ml oil is taken from machine and it requires 1.5 ml of 0.04 N KOH. Find acid value (density of oil = 0.81 gm/ml) (Problem 3.7.14)

(6 Marks)

**May 2008**

(3 Marks)

**Q. 4** Find acid value of 3 gm of oil which required 0.2 ml of 0.025 N KOH to neutralise free acids present. (Problem 3.7.16)

(6 Marks)

**Dec. 2005**

**Q. 5** 16 gm of blended oil was heated with 50 ml KOH. This mixture then required 31.5 ml of 0.5 N HCl .50 ml KOH required 45 ml 0.5 N HCl. Find % cottonseed oil, if saponification value = 192 mg. (Problem 3.7.9)

(6 Marks)

**May 2005**

**Q. 6** 20 ml. of a lubricating oil was dissolved in alcohol. Solution was titrated against 0.1 N KOH solution. At the end point burette reading was found to 2.5 ml. Calculate the acid value of the oil. (density of oil = 0.86 gm/ml) (Problem 3.7.15)

(3 Marks)

**May 2004**

**Q. 7** Find acid value of a used oil sample whose 7 ml required 3.8 ml of  $\frac{N}{20}$  KOH during titration. (density of oil = 0.88). State whether oil is proper for lubrication or not, from acid value. (Problem 3.7.17)

(3 Marks)

**May 2006**

(3 Marks)

**Q. 8**

3

Sc

fc

n

**Dec. 2007****Note**

- Q. 8** 3 gm of liquid lubricant was saponified with potassium hydroxide solution. After saponification the mixture was titrated against 0.5 N HCl solution. The burette reading was found to be 12 ml. If blank titration burette reading was 36 ml, calculate the saponification number of the lubricant. (*Problem 3.7.9(B))*) (4 Marks)

**May 2008**

- Q. 9** 1.55 gram of an oil is saponified with 20 ml of  $\frac{N}{2}$  alcoholic potassium hydroxide solution. After refluxing the mixture, it requires 15 ml of  $\frac{N}{2}$  HCl solution. Find saponification value of oil. (*Problem 3.7.9(A))*) (3 Marks)

# CHAPTER 4

## Energy

### 4.1 Introduction

- The term 'energy' has been known to us for ages. In simple words, the term 'energy' can be defined as 'capacity to do work'. The first law of thermodynamics and other two laws are well known to us which definitely explain the significance of energy for different areas, may be transport, communication etc.
- Thus in all industrial operation, the input of energy is a must to obtain an output from the industry. Energy is consumed in various forms such as heat, electricity etc.
- Over the years due to rapid industrialization and also population escalation the usage of energy has been increased manifold. It is also known that the usage of Fossil fuels as compared to other energy sources is maximum, which is unsustainable. More so, during their use the other environmental issues also have been encountered. Overall view of this situation has made man more and more aware and concerned for making maximum use of renewable sources of energy such as solar, wind, tidal etc.
- In this chapter, we are to discuss the development of technology to use non-conventional sources of energy maximally, so that the environmental issues get sorted out considerably and so also the conventional sources of energy do not face threat of near extinguishment state.

### 4.2 Classification

► [Dec. 2007]

Energy sources are classified into following two categories

#### Sources of Energy

- (i) Primary energy sources
  - Conventional (Non-renewable) sources
    - e.g. Fossil fuels – coal, coke, nuclear fuels
  - Non conventional (renewable) sources
    - e.g. solar energy, wind energy etc.
- (ii) Secondary energy sources
  - e.g. petrol or gasoline hydrogen from electrolysis of water

### 4.3 Examples, their Source and Uses

Example	Source	Use
1. Solar Energy	Electromagnetic radiation from sun.	For domestic and industrial uses.
2. Hydro Power	Falling water	Turbines, mill wheels
3. Wind Power	Moving air	Wind mills
4. Tidal Power	Rise and fall of tidal water	To generate electricity.
5. Geothermal Power	Rocks beneath the earth's surface	To generate electricity
6. Nuclear Fuels	Fission or Fusion reaction of radioactive elements	Nuclear power generation
7. Fossil Fuels	Crude oil, Coal, Lignite, Natural gas.	Domestic and industrial uses.

### 4.4 Solar Energy

► [May 2008 !]

- The estimated amount of solar flux reaching the upper atmosphere of earth is approximately 1400 watts/m<sup>2</sup>/mn and that of heat equivalent is  $2.68 \times 10^{24}$  Joules /year.
- The eco system on the surface of earth utilises about 0.2 to 0.5 % of the total amount of solar energy recd.
- Thus, very small fraction of solar energy is actually used for life on earth, especially the ecosystem.
- It is indicated clearly that large amount of solar energy gets wasted, which otherwise can be of immense use for satisfying energy needs of humans.
- The use of solar energy is advantageous as,
  - (i) It is non-polluting and non depletable.
  - (ii) It is renewable source of energy.
  - (iii) It does not alter the biosphere.
- In spite of these most important advantages, the use of solar energy on large scale is still not in practice, which may be accounted due to the reasons such as,
  - (i) Difficulties faced in economical collection of solar energy, its conversion into other form of energy which can easily stored, transported and/or used for work output in different equipments.
  - (ii) Non-availability of intense sunlight in all areas throughout the year. Hence, the technology has to be developed to tackle these problems.
- Thus now the world has accepted solar energy as a main source for all human requirements which is economically feasible, and sustainable for healthy, non-polluted environment, and therefore use of solar energy is gaining wider uses year by year.

#### 4.4.2 Application of Solar Energy

- These radiations are resulted from the thermonuclear fusion reactions which take place in the sun.
- Sunrays fall on the surface of earth, giving energy to the planet, which is partly absorbed by earth and remaining is emitted back to the space.
- All the radiations from sun are not in same wavelength range. Almost 92% lie in the range of 315 nm to 1400 nm.
- The surface of earth absorbs almost 45% of these which lie in the (visible region) wavelength range i.e. 400 nm to 700 nm.
- The absorption of radiation by surface of earth is in visible region whereas emission of the radiation is in IR region.

#### 4.4.2.2 Indirect Use of Solar Energy

- (i) Hydropower
- (ii) Wind power
- (iii) Biomass energy.
- (iv) Ocean energy.

Other non-conventional sources of energy are,

- (i) Geothermal energy.
- (ii) Tidal power.

Details of above applications are discussed in this chapter.

#### Heating

Solar energy is used for heating water, or space.

- The cold countries on earth, face severe problem of maintaining warmth in space generally in temperature range around 20°C and that to have hot water at about 50-60°C.
- Conventionally this was done by using oil or electricity. But it proved to be wastage of efficiency of respective material/ source to be used for getting output of so low temperature.
- For such applications, solar energy has proved to be the best alternative, because it is economical.
- The device used for heating is known as "Flat-plate solar collector".

#### Flat plate solar collector (Solar heater)

- The device works on principle of "perfect black body" in which heat absorbing capacity and tendency of a black surface is exploited to achieve benefits for humans.
- "Perfect black body" can be defined as, "the surface which can absorb all the radiations incident on it, without reflecting or transmitting a portion of it".
- The coefficient of absorption for perfect black body is unity.
- The coefficient of reflection and transmission for PBB is zero.

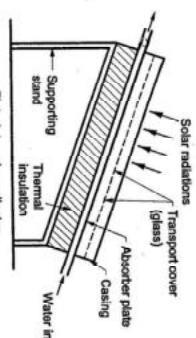


Fig. 4.4.1 : Flat plate solar collector

#### Construction

- It consists of black surface to absorb all radiant heat form sunlight.
- The black surface is covered by plastic or glass serving as insulator, preventing the escape of heat. Thus it increases efficiency of device.
- There are tubes embedded in the black surface, carrying water, which get heated due to the heat absorbed.
- The air passing through the area between black surface and plastic/glass cover also gets heated, which is utilised in raising the temperature of surrounding, creating warmth and comfort in winter/cold countries.
- Thus at almost negligible cost, the hot water can be made available and also space warming is fulfilled.

These devices are now very common in colder countries, which has solved the problem of environmental pollution and also of the expenditure on any other energy source.

#### Applications

- The flat plate solar collectors are highly useful for low temperature heating.
- Such solar heating system, beyond the collector can be of two types,
  - (i) Active system
  - (ii) Passive system.
- Active system involves use of pumps or blowers to circulate the heated air/water through the location near/far from the collector. Thus the solar energy is been used on wider area economically though initial installation cost of such circulation system, is comparatively high.
- Passive system involves the fulfillment of need in the place of collector, e.g. in a building or society etc. Thus passive system are cheaper and maintenance free.

**Recent developments**

- As awareness for use of solar energy is increasing day by day, the architecture of newly constructed buildings is modified.
- During construction, the building is made to act as a collector of solar energy, through more number of large windows thereby absorbing more radiant heat during day time.
- During night in winter/colder countries the drapes (curtains) help retain the warmth inside the building.
- Similarly in summer drapes help to prevent the absorption of heat during day making human comfortable.

**4.4.3 Draw Backs of Solar Heating System**

The only draw back of the system is that storage of energy is not being done.

**4.4.3.1 Advantages of Solar Energy**

- The solar energy proves to be a reliable source for clean energy which is
- Non-polluting
  - No hazardous waste generation.
  - Inexhaustible and infinitely renewable.

**4.4.4 Solar Energy for Production of Electricity**

► [May 2008 1]

Electricity can be produced using solar energy. The following two techniques are commonly used to generate electricity using solar energy.

- Solar thermal collector.
- Photovoltaic cells

**(i) Solar thermal collector**

- It is device designed to absorb heat from sunlight hence the word thermal collector is used.
- There are different types of thermal collectors,

- Solar parabolic trough.
- Solar power tower.
- Flat plate - for water heating.
- Box type - domestic common solar cooker.

**Solar parabolic trough (dish)**

- It looks similar to dish antenna for receiving transmission.
- This is most powerful of all collectors. Because the parabolic shape enables the concentration of sunlight on a single focal point.
- The concentration is adjusted in such way by using one or more parabolic dishes.
- These dishes are arranged in similar way as that in telescope used to focus starlight or as in dish antenna for waves.

**Power tower**

- It is a large tower having heliostats around it.
- Heliostats are nothing but small size rotating mirrors.
- The arrangement of these mirrors is such that they can get aligned with each other to focus sunlight on one point on tower.
- At this point on tower a powerful receiver is fitted which is on top of tower.
- A power station is located below the tower where the collected heat gets transformed into electricity.

**Solar pyramids**

- In this type of collector the shape is like pyramid.
- The working of it involves the absorption of air inside and it gets heated with solar energy.
- The hot air then moves through turbines so as to generate electricity.
- In our country such solar pyramids are now getting developed for use.

**Advantages of solar thermal collectors**

- (a) Very high temperatures can be reached if sunlight is sufficient.
- (b) Electricity can be generated even by conventional methods like steam turbine etc.
- (c) The modification in design of collectors can help to generate more electricity most economically which would prove cheaper than using even solar cells
- (d) The use of mirrors is cheaper than solar cells and it can also cover large area.
- (e) Large structures like building can be provided with electricity by redirecting the concentrated light via optical fiber cable.

**Disadvantages of solar thermal collectors**

- (a) More open area/land is required to have perfect concentrating systems because the focus of sunlight at collector can be maintained by dual axis sun tracking.
- (b) Diffused sunlight does not give power, where in solar cells prove to be better.

**(ii) Photovoltaic cells (Solar cells)**

- These are the devices designed for use to convert the available sunlight into electrical energy.
- This type of conversion does not involve any chemical reactions or moving parts in the device.
- Primarily development of the concept came into light, way back in 1839.
- French physicist, A.C. Becquerel, while working with electrodes in electrolytic medium, observed development of voltage when electrode faced light. This effect was named as photovoltaic effect.
- The first typical solar cells was constructed by Charles Fritts in 1877 almost 50 years later. In his work he used concept of semiconductors silicon coated by almost transparent film of gold. This device could not work with efficiency, as it could convert almost 1% of sunlight into electrical energy.
- Following few years the solar cells faced many modification such as,
- Year 1927 : Semiconductor junction with copper-copper oxide was developed.
- Year 1930 : Selenium cells and copper oxide cell were used in light sensitive devices [Efficiency < 1%].

Year	Event	Description
Year 1941	:	Russel Ohl developed solar cell using silicon (Semiconductor).
Year 1954	:	American researchers group G.L. Pearson et. al. modified silicon solar cell (Efficiency > 6%) which was used under direct sunlight.
Year Late 1980s	:	Silicon cells to Ga-As cells in use. (Efficiency $\approx$ 20%)
Year 1989	:	"Concentrator solar cells" concept developed. (Efficiency $\approx$ 37%)

**Structure or construction of modern Solar cells**

- These are based on principle of semiconductor physics.
- These cells basically consists of P-N junction photodiodes, which have very large light sensitive area.
- There are three layers called as "energy convention layers" where "photovoltaic effect" occurs which converts sunlight into electrical energy.
- (a) Top junction layer (made of N-type semiconductor)
- (b) Middle absorber layer (core of the device) i.e. P-N junction where energy is absorbed.
- (c) Back junction layer (made of p-type semiconductor).
- Thus such photodiodes (PD) are P-N junctions designed specifically to possess optimum photosensitivity which are used in photovoltaic cells (PV cells).

**Photovoltaic effect - Explanation**

- Sunlight is composed of tiny energy packets known as "photons".
- When sunlight falls on solar cells, the photons with high frequency get readily absorbed.
- The light energy present with photon is transferred to the semiconductor (eg. Silicon atom) particularly to electron in the atom.
- If electron receives sufficient energy, it escapes from its normal position, causing a hole (i.e. an empty dot/spot where electron would be).
- This phenomenon proceeds causing one hole with one photon, as it can strike only one electron.
- Since both electron/hole are mobile, they are capable to carry current, which is nothing but "photo voltaic effect".

**Working of PV cell / Solar cell**

- The three layers present in PV cell work simultaneously for absorption of sunlight, photovoltaic effect to occur, and conversion of heat into electrical energy as explained below.
- The unique characteristics of semiconductor to act as good conductors when supplied with light or heat and otherwise act as insulators at low temperature is been used effectively in solar cells.

The top junction layer is N-type made up using electron deficit material and lower or back junction layer is P-type.

The electropositive metals possessing only one valence electron are used to form lower layer because they can lose electron easily leaving behind hole.

- When sun light falls on the absorbing surface, the photons are absorbed and electrons from lower layer are replaced (freed) to form hole.
- The free electrons move towards upper (top) layer where it can be accepted because of electron deficit material.
- This process continues involving flow of electrons to holes in the PV cell creating a potential difference, at the P-N junction. Hence, current is generated at junction.
- The electric field is thus created at junction.

**Factors influencing efficiency of PV cells**

- Thus for high efficiency of PV cells, the P type semiconductor layer should be of such material which has high conductance so that maximum photons are absorbed, which frees that many number of electrons.
- Other important precaution required is not to allow free electrons escape the cell. This is achieved by designing PV cell in such a way that the surface where the electrons are to be freed is as close as possible to junction.
- These precaution maximise efficiency of PV cells.
- e.g. silicon cells, Cadmium sulphide-copper sulphide, Ga-As-indium phosphide are few other type of solar cells.

**Advantages of PV cells**

- Clean technology.
- Can be used nearly for 20 years as there is no movement in cell. Hence no wear.

- (3) Maintenance minimal.  
 (4) Environment pollution issues do not arise.  
 (5) Can be used for domestic purposes, in industries automobiles etc.

**Limitations of PV cells**

- Initial cost is high.
- More number of cells in battery are required for higher supply.
- Use is mainly in instrument which require low energy e.g. calculators etc.
- In automobiles, engine efficiency decreases due to high weight of batteries.
- Modification/further development in battery technology is in progress.

**Recent advances in PV cells**

- The use of nanoparticles to improve efficiency.
- The use of cadmium telluride to reduce cost to PV cells.
- The organic solar cells (using polymers) and thin layer PV cells can be manufactured more easily at low cost of materials.

**4.5 Hydropower****Factors influencing efficiency of Hydropower**

- The word indicates clearly that it is energy generated from water [Hydro = Water Power = Energy].
- Water stored in reservoir through dams, is made to flow on turbines/paddle wheels, to generate mechanical energy which is then converted into electrical energy.
- Hydropower is renewable energy source and non-polluting, clean energy.

**Hydropower plant**

- It is also known as hydroelectric power plant, used to obtain mechanical and electrical energy from stored water, by making it flow with force/pressure over turbine wheels.
- The plant is simple and can be operated practically anywhere, if source of water is available.

**Principle**

The "potential energy of stored water is converted into mechanical energy using hydraulic turbines, which is then used to run the electrical generator converting it into electrical energy", is the basic principle of Hydro electric power plant.

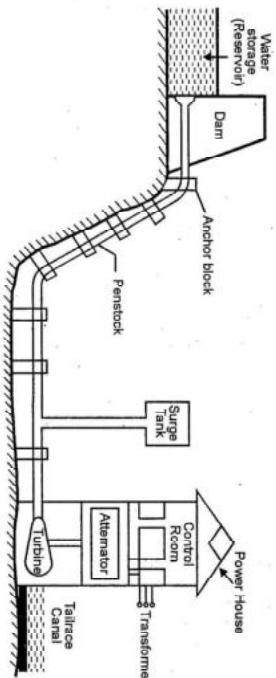
**4.5.1 Hydroelectric Power Plant**

Fig. 4.5.1

As shown in Fig. 4.5.1. The hydroelectric power plant essentially consists of following parts/ components.

**(1) Water reservoir**

The water is stored at higher level. The reservoirs are of various sizes depending upon the requirement.

If water reservoir is the stored natural water, i.e. river, pond or lake, then it is supported with dam, which is used to release water flow as required.

**(2) Penstock**

The large diameter PVC pipes used for carrying water from reservoir to the turbine wheels are named as "penstocks".

In large size power plants, all penstocks are supported by concrete structures called as "Anchor blocks". This is essential because when water is released from reservoir through dam, it flows with high pressure and velocity, which may damage the penstock.

**(3) Surge Tanks**

To handle such situation, an additional small tank is also connected to penstock which stores excess water, if released due to natural force. Thus the penstocks are protected such additional tank is called as "surge tanks".

**(4) Turbine wheels**

These are metal wheels situated in power house and are rotating at high speed. The shaft of wheel is coupled with an electrical generator.

**(5) Power house**

It is a building where the energy transformation occurs. The operation of plant is controlled from the "control room" situated at the top of this building.

**4.5.2 Advantages of Hydro-electric Power Plant**

- (1) Electrical energy is generated at very low cost as,
- (a) No fuel is required
- (b) Operating cost is low
- (c) Maintenance cost is low
- (2) The time required to generate power is small.
- (3) The plants do not produce green house gases, thus no air and water pollution.

**4.5.3 Disadvantages of Hydro-electric Power Plant**

- (1) Installation cost is high.
- (2) Plants can be set up only where plenty of rainfall occurs.
- (3) Long length transmission lines are required for distribution of power. Hence it adds to cost and also maintenance.

**4.5.4 Limitations of Hydroelectric Power Plant**

- (1) Construction of dams cause destabilization of population in near by areas.

- (2) Ecobalance is disturbed.
- (3) Fertility of land surrounding the river area is decreased.
- (4) Earthquakes may be caused due to concentration of high hydrostatic pressure in certain selected areas.
- (5) High humidity in the area of dam increases the corrosion of various metallic structures in surrounding area.

#### 4.6 Wind Power

- Wind can be defined as the air in high speed motion.
- The motion of air varies every moment because of uneven heating of surface of earth, by sun rays.
- The air above land gets heated faster during the day as compared to the air over water i.e. ocean, river water surfaces.
- The hot air rises upward due to expansion and its place is taken by cool air, which we call as wind.
- During night, exactly reverse process is observed due to faster cooling of hot air on earth surface as compared to that on water surfaces.
- The energy associated with wind is used to generate electricity.
- Wind energy is also renewable because it would be continuously available till sunlight is available.

#### Wind machines

- The machines used to convert kinetic energy of wind into mechanical and then after electrical energy are called as wind machines e.g. wind mill, wind turbine etc.
- These machines are consists of air foil shaped blades. The blades rotate at high speed when wind blows.
- These blades are connected to a drive shaft which turns on electric generator to produce electricity.
- Wind turbines are used which are of two types, based on direction of the rotating shaft.

- (a) Horizontal axis machines  
 (b) Vertical axis machines

#### (b) Vertical axis machines

- These are not used commonly as compared to horizontal machines.
- They are similar to horizontal machines except in the direction of blades which are going vertically down.
- A typical machine generally is 100 feet tall and 50 feet wide.

#### 4.6.1 Advantages of Wind Energy

- Wind is ever available free.
- By ways of wind farms, it is possible to satisfy the need of electrical energy for large cities.
- 4.6.2 Disadvantages**
- Installation requires open land. Thus cost is high especially in developing countries.
- Wind is produced due to heating done by sun hence it is indirect use of solar energy. Therefore solar energy as well can be used directly.
- As shown in Fig. 4.6.1 such machine have three blades similar to the propellers of airplanes.
- Different size machines are available.
- The choice of size depends upon the area for which the electricity is generated.

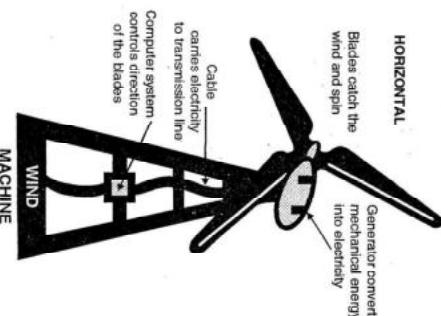


Fig. 4.6.1

- Totally dependent on speed of wind and plant needs to be equipped to sustain storm like condition.

## 4.7 Biomass Energy from Biotechnology

### Introduction / overview

- Biomass is nothing but biological natural (waste) material, which can be used to obtain energy.

e.g. Dead trees, unused crops if any, wood chips, lawn cuttings, household waste etc.

When all such materials are burnt the energy produced is known as "biomass energy".

• It is evident that the biomass thus available is basically plant or plant derived material, where the energy is accumulated due to photosynthesis which once again is dependent on sunlight.

- But unlike wind energy, biomass energy is the best source of alternative energy because production of energy from biomass solves the problem of solid waste management, which otherwise needs concern.

### 4.7.1 Biotechnology

Typically any biomass if burnt produces energy.

- Recent advances in biotechnology enables the use of microbes to carry out chemical process on biomass, generating energy feels.

This has proved to be better process than simple burning.

- Microbes can convert biomass, hydrocarbon to useful energy products without producing green house gases such as  $\text{CO}_2$ .

Biomass can be used directly as solid fuel or can be converted into liquid or gaseous form which can be used to generate electric energy, chemicals, heat, fuel etc.

Such conversions into different useful products involve various conversion processes.

- A single conversion centre where all different processes are made to work is a new concept in recent years known as "Biorefinery".
- To obtain energy from biomass, the choice of pathway / process depends upon "Types of biomass".
- The biomass is of two types,

### Power plants / Crops

The crops grown specifically for production of energy are called as "Energy Crops" or "Power Crops".

Such crops can be grown in farms like any other food crops.

In different regions, as per type of soil, climate, rainfall and other environmental conditions, the suitable native crops are grown.

Energy crops examples are,

- (1) Corn, which is grown easily.
- (2) Trees like sweet gum, eucalyptus etc.
- (3) Grasses like sorghum.
- (4) Oil plants like Soyabean, Sunflower.

### Natural residues

Naturally generated residual biomass comes from various sources.

Comes from various sources,

- (a) Forestry
- (b) Agriculture residues : From harvesting and processing
- (c) Cities :
  - (i) Domestic : Organic waste
  - (ii) Industries : Food and drink manufacture.

## 4.7.2 Conversion of Biomass into Bioenergy

► [Dec. 2007 1] Energy

### Applications of combustion

#### (I) In co-generation, which is simultaneous generation of heat and electricity.

Recent development also involves refrigeration process as well simultaneously known as "Tri-generation".

This is called as CHP i.e. "Combined heat and power".

CHP is mostly advisable in case,

(a) Space heating requirement exists near the generator.

(b) Local areas require low temperature water for use.

(2) In co-firing which is a process of replacing fossil fuel partially (when fed into any power station or boiler) with any other alternative renewable (e.g. Carbon lean) source

This application is used only in coal fired power station.

More development in the technology of co-firing is in progress.

### (I) Thermal conversion by combustion

- Combustion is a process in which any flammable material undergoes burning in the presence of air or oxygen.
- Basically combustion is nothing but 'oxidation'.
- The heat generated can be used directly for the output.
- e.g. Water heating.

**Combustion of biomass** specifically involves the elements such as carbon, hydrogen, which undergo combustion to form  $\text{CO}_2$  to  $\text{H}_2\text{O}$ .

e.g. Cellulose, Hemicellulose etc.

Biomass, may contain other elements such as, Sulphur (S), Phosphorous (P), Nitrogen (N), Potassium (K), Sodium (Na), Silicon (Si), Heavy metals, Alkali metals etc.

- All these metals, being active, participate in combustion, forming their respective compounds.
- Such products draw concern as, these might contribute to pollution. Hence are required to be treated further for removal.

- Thermochemical processes
  - Combustion
  - Gasification
  - Pyrolysis
- Chemical processes
  - Various chemical processes
    - e.g. Transesterification of oil to get biodiesel
- Biochemical processes
  - Anaerobic digestion
  - Fermentation
  - Composting

### (II) Thermal conversion by Gasification

When a carbon source like biomass (or coal or natural gas) is broken into the products like  $\text{H}_2$ ,  $\text{CO}_2$ , CO and /or  $\text{CH}_4$  by subjecting it to partial oxidation, the process is named as "Gasification".

### Types of Gasification

There are two types of gasification,

(a) Low temperature gasification ( $700\text{-}1000^\circ\text{C}$ )

This process gives the product gases where high % hydrocarbons are present.

(b) High temperature gasification ( $1200\text{-}1600^\circ\text{C}$ )

This process gives the product gases where high % of CO and  $\text{H}_2$  are present.

### Application

Gasification can be used for

- Generating steam.
- Heating water for different processes.

### (III) Thermal conversion using pyrolysis

Pyrolysis is a process of thermal decomposition in the absence of oxygen. The products obtained can be gaseous or liquid.

It is temperature dependent and there are following two types of pyrolysis.

- (a) Low temperature pyrolysis
- (b) High temperature pyrolysis

Low temperature pyrolysis i.e.  $\approx 400^{\circ}\text{C}$ , proceeds slowly, about  $\approx 500$

High temperature pyrolysis i.e.  $\approx 500$  or above, proceeds fast.

Unique feature of this process, is, if temperature kept around  $500^{\circ}\text{C}$  and vapour residence time is maintained low i.e. 1 second or less, the product is bio-oil, followed by other gaseous products.

Bio-oil obtained is,

- (a) Dark brown in colour,
- (b) Optimum viscosity for oil to be mobile
- (c) Low heating value (as compared to conventional fuel oil).

Bio-oil thus obtained can

- (i) Directly burned
- (ii) Modified to match properties to other fuel oils,
- (iii) Gasified or co-fired.

### (II) Chemical conversion

There are many chemical processes to get biomass converted into energy source. e.g. Transesterification of vegetable oils to give biodiesel.

Vegetable oils, though combustible, pose problem in their direct use as fuel.

This is because of their chemical composition where fatty acids are in triglyceridic form, i.e. one molecule of glycerol is combined to three molecules of fatty acid chain.

They are highly viscous as compared to mineral oils, and hence need to be modified to make them suitable for use as fuel in vehicles etc.

Hence, vegetable oils or animal fats are transesterified.

In this process, the oil is reacted with ethanol or methanol to convert the triglyceridic esters to monoesters each with one fatty acid chain known as fatty acid methyl esters which itself is "Biodiesel"

- The suitability of the process depends upon,
  - (a) % of standard Fatty acids.
  - (b) Melting point of Fatty acids etc.
- Few oils such as palm oil, soyabean oil, rape seed oil are found suitable for modification by this method.
- Biodiesel thus produced can be used directly or as blend with petroleum (generally 5% biodiesel, 95% fossil diesel).

### (III) Biochemical conversion

This technology makes use of enzymes or bacteria and other micro-organism to break down bio-mass.

The technique involves,

- (a) Anaerobic digestion.
- (b) Fermentation
- (c) Composting.

### Biochemical conversion : By Anaerobic digestion

In Anaerobic digestion, as term indicates, anaerobic bacteria are used, which attack organic matter of biomass, thereby breaking it to form mainly a gaseous product.

This gas is known as 'biogas'. Main chemical component of 'biogas' is methane ( $\text{CH}_4$ ). Where as in low proportion  $\text{CO}_2$  is produced.

This process is used to process sewage since very long time, where apart from above gases, solid residue similar to compost, and some liquid product are also given out, which are suitably used as fertilizer.

In marshy places, such a process automatically also occurs, producing foul smelling gas which is commonly called as "Marsh gas" or "Landfill gas".

Methane gas produced can be used

- (a) Directly for producing heat
- (b) In electricity generation.

**Biochemical conversion by Fermentation**

- Fermentation is a process known for decades, commonly used for brewing and wine making, involving conversion of sugar to alcohol (ethanol).
- From biomass, bioethanol is obtained, using enzymatic hydrolysis of biomass to convert into saccharides (which are fermentable).
- Bioethanol produced can be used as blend with fossil petrol in range of 5 to 10%, as fuel.

**Biochemical conversion by Composting**

- It is similar to Anaerobic digestion, where the only difference lies in,

- In AD slurry is used
- In composting dry material is used.

**Hydrogen as a fuel**

Hydrogen is one of the best secondary source of energy.

- It is obtained by splitting the molecule of water by using other energy such as nuclear or solar.
- It is also be obtained by electrolysis.

**4.8 Hydrogen as a Fuel**

Hydrogen is one of the best secondary source of energy.

- It is obtained by splitting the molecule of water by using other energy such as nuclear or solar.
- It can also be obtained by electrolysis.
- Hydrogen has to be produced, (usually by splitting water  $H_2O$  to get the hydrogen) because it does not occur free in nature in useful quantities.

**4.9 Fuel Cells**

► [Dec. 2007, May 2008 II]

- Fuel cells convert the chemical energy produced by a chemical reaction into usable electric power/electrical energy.
- Fuel cells produce electricity as long as fuel (hydrogen) is supplied, and the charge is not reduced/lost.
- Fuel cells produce direct current (DC) power, not alternating current (AC) power similar to a battery.

**4.9.1 Operation of Fuel Cells**

► [Dec. 2007 II]

**Characteristics of Hydrogen**

- Hydrogen is the lightest of the elements.
- Its atomic weight is 1.0.
- Liquid hydrogen has a density of 0.07 g/cc. Density of water is 1.0 g/cc and that of gasoline about 0.75 g/cc.

**Principle**

- A fuel cell is an electro-chemical device in which the chemical energy of fuel is continuously converted into electric energy. This conversion of energy takes place at constant pressure and temperature.
- The important feature of a fuel cell is that the fuel and the oxidant are combined in the form of ions.

e.g. hydrogen ( $H_2$ ) – Oxygen ( $O_2$ ) called hydrox fuel cell.

The main components of a fuel cell are :

1. Anode comprising of fuel.
2. Cathode comprising of an oxidant, (Which is also a fuel material)
3. An electrolyte (a solution of  $H_2SO_4$  for acidic fuel cell and KOH for alkali fuel cells).
4. Container with inlets and outlets for  $H_2$  to  $O_2$ .
5. Separators.
6. Sealing material.

Fig. 4.9.1 represents the schematic diagram of an alkaline fuel cell, using

- (i) Hydrogen as fuel,
- (ii) Oxygen as oxidant, and
- (iii) Alkaline solution of KOH as electrolyte.

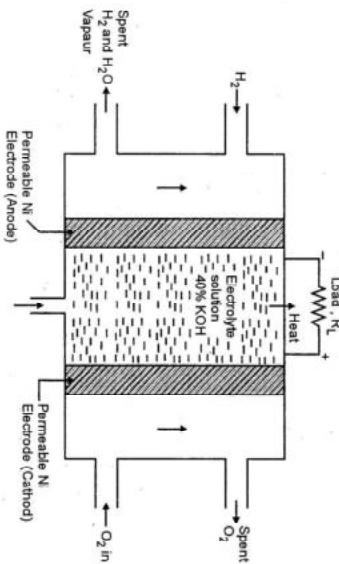


Fig. 4.9.1 : A hydrox ( $H_2$  –  $O_2$ ) fuel cell (Alkaline Fuel Cell)

### Construction

It consists of

- (i) Two *permeable nickel electrodes* as anode and cathode.
- (ii) These electrodes are immersed in an electrolyte of good conductivity.
- (iii) In alkaline fuel cell, solution of KOH is used (and for acidic fuel cell solution of  $H_2SO_4$  is used)

- (iv) The porous fuel electrode as anode (negative pole) and the other porous oxidant electrode as cathode (positive pole) both are separated by a gas barrier called separator (which is not shown in Fig. 4.9.1.).

### Working

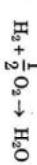
- The electrodes are connected through an external circuit as shown in Fig. 4.9.1.
  - The anode is supplied with  $H_2$  gas as fuel at a certain pressure and the cathode is supplied with  $O_2$  as oxidant at same pressure.
  - These gases pass through the respective electrodes and bubble through the electrolyte solution.
  - The electrochemical reactions take place between gases, electrodes and electrolyte to come in contact.
  - The *electro-chemical reactions being generally slow*, it is a common practice to use a catalyst to accelerate the reaction.
  - *Platinum* is the best catalyst but costly. Other less expensive catalysts like *nickel* and *silver* are used.
  - The catalytic electrochemical reactions in this type of cell take place as,
- At anode
- $$H_2 \xrightarrow{\text{catalytic dissociation}} 2H$$
- (7)
- At cathode
- $$\frac{1}{2}O_2 + H_2O + 2e^- \rightarrow 2OH^-$$
- (8)
- At
- $$2H + 2OH^- \rightarrow 2H_2O + 2e^-$$
- (9)
1. Each hydrogen molecule gets dissociated to two hydrogen atoms on the surface of electrode, due to catalytic property of electrode.
  2. The H atoms thus generated enter into electrolyte solution and form two  $H^+$  ions and electron.
  3. The electron travel to positive (cathode) electrode through external circuit,
  4. At cathode
  5.  $\frac{1}{2}O_2 + H_2O + 2e^- \rightarrow 2OH^-$
  6. At cathode water molecule reacts with supplied oxygen taking up the electrons and form hydroxyl ions.

- The hydroxyl ion thus formed at cathode, migrate to anode through the electrolyte.

- Thus  $H^+$  (from anode) and  $OH^-$  (from cathode) get into reaction in electrolyte to form a molecule of water as,



- Overall electrochemical reaction can be represented as,



#### Physical characteristics of $H_2 - O_2$ fuel cell

- Highly efficient and free from pollution. The efficiency of fuel cells is approximately 70-75% higher than conventional cells.
- These are operated between the temperature range of 100-200°C.
- Single fuel cell can ideally produce emf of 1.23V at 25°C and pressure 760 mm.
- The emf decreases with increasing temperature.
- Generally the life of these fuel cells is ten thousand hours.
- The overall average (rated) voltage given as 0.7 to 0.8V.
- They can give desired value of voltage (higher value) by connecting in series.
- They serve as continuous source of energy so long as fuel is available.

#### Applications of fuel cells

Fuel cells have variety of application few are listed below :

- These are used to supply power to
  - All types of devices, such as hand held to portable generators.
  - All types of vehicles, such as trucks, buses, marine transport etc.
  - Space programmes.
- Fuel cells as, "Stationary Power Stations".
- Stationary fuel cells can be used for *backup power*, power for *remote locations*, distributed power generation, and cogeneration (in which excess heat released during electricity generation is used for other applications).

#### 4.9.2 Advantages of Fuel Cells Over Conventional Power Plants

- Simple in operation and less polluting*, as the by-product is pure water.
  - Space requirement is much less.
  - Cooling water is not needed.
  - Energy conversion efficiency is higher, especially for  $H_2$ -powered fuel cells,
  - Heat generated is rejected directly to atmosphere, the process being *isothermal* almost 3 times of traditional combustion technology.
  - Fuel cells can be installed at the point of use thus *reducing power losses during the transmission and distribution*.
  - By using series - parallel combination of fuel cells, the output power rating at any voltage and current can be obtained.
  - The capacity can be increased as the demand grows.
  - It has *long life*.
  - Fuel cells operate quietly, have fewer moving parts and are well suited for a variety of applications.
  - Batteries are the devices to convert chemical energy into electrical energy.
- Batteries**
- (i) Primary (Disposable)  
 (ii) Secondary (Rechargeable)
- Types of batteries :** There are two types of batteries as shown above.
- #### Primary
- Primary batteries are those which carry out chemical reaction to supply electrical power.
  - These type of batteries become dead over a period of time and the chemical reaction stops.
  - They can not be recharged again, hence are disposed.
- For example, Dry batteries, mercury cell etc.
- Downloaded from **FaadooEngineers.com**
- Downloaded from **FaadooEngineers.com**

**Secondary**

- This type of batteries can be recharged by passing direct current through them.
- They can be used again and again for many hours.

Eg. lead storage battery or lead Acid Battery or Lead Accumulator.

Nickel – Hydrogen battery

Nickel – Cadmium battery

Nickel – Iron battery

Rechargeable alkaline storage cell. (battery)

**Lead Acid Battery / Lead Accumulator**

This battery consists of six voltaic cells connected in series.

- The anode in each cell is of cathode is of a grid of lead packed with lead oxide ( $PbO_2$ ).
- The electrolyte is an acid (aqueous solution of  $H_2SO_4$ ) 38% by mass.
- The cell and the reactions of the battery can be represented as shown in Fig. 4.10.1

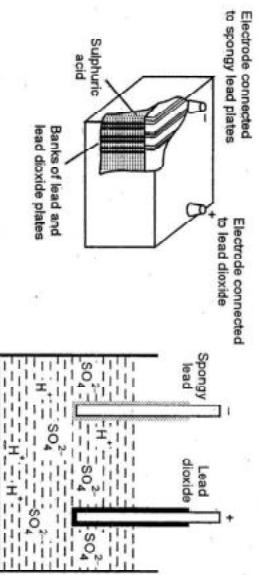


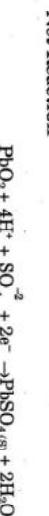
Fig. 4.10.1

The cell can be represented as,

**Reactions****Primary**

- This type of batteries can be recharged by passing direct current through them.
- They can be used again and again for many hours.

Eg. lead storage battery or lead Acid Battery or Lead Accumulator.

**Net Reaction****Discharging****Recharging****Construction**

- It contains an outer jacket to hold electrolyte solution anode and cathode plates and also outlet points to supply electrical energy to the engine.
- The anode and cathode plates are arranged in alternating manner and they are separated by sheets of insulating material.
- The anode and cathode plates are connected with each other separately as shown in Fig. 4.10.2.

Fig. 4.10.2

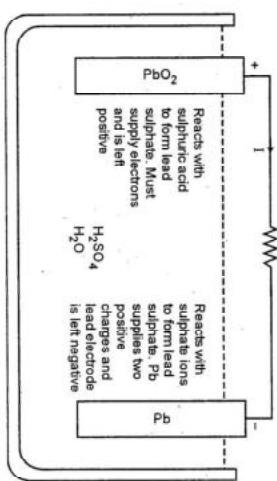


Fig. 4.10.2 : Lead accumulator in use for car-(discharging)

**Working**

- As the automobile starts the cell starts working the concentration of  $H_2SO_4$  decreases, because sulphate ions are consumed to form  $PbSO_4$  as shown in Fig. 4.10.2
- With decreasing concentration of  $H_2SO_4$  density of the electrolyte also decreases.

- Hence by measurement of density of solution, condition of battery can be checked easily.
- On continuous use the battery gets discharged.
- It is recharged by supplying higher potential, so as to reverse the reaction as shown in Fig. 4.10.3.

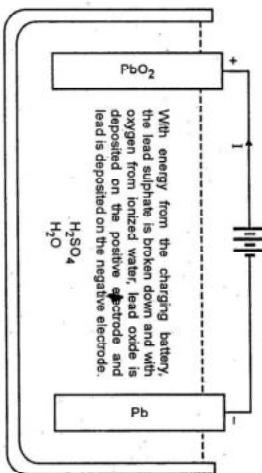


Fig. 4.10.3 : Lead accumulator - recharging

**Advantages**

- This battery is very low priced.
- Available in different size.
- High current density is produced
- Easily recycled
- Tolerant to over charging.
- Potential does not depend on size. But only on acid concentration.

**Disadvantages**

- Charging is slow .
- Very heavy and bulky
- In has to be stored carefully due to use of acid.

**Uses**

- Used in laboratories power station, motors, cars, trains etc.
- Also used in radio sets, electric clocks, telephone / telegraphs etc.

**► [Dec. 2007]**  
**4.11 Rechargeable Alkaline Storage Batteries**

Alkaline storage batteries are secondary batteries in which potassium hydroxide (alkaline electrolyte solution) is used as the main electrolyte.

Most of these battery systems use nickel oxyhydroxide ( $\text{NiOOH}$ ) as the positive active material because of

- Superior charge-discharge cycle characteristics and
- Long life.

**Example :** Nickel cadmium (Ni-Cd) system, Nickel-metal hydride (Ni-MH) based batteries, Ni-Hydrogen, Nickel-Iron battery.

There are two types of alkaline storage batteries presently in use.

- (i) "open" type which permit gases to be exchanged with the medium,
- (ii) "sealed" type which have a valve and no exchange with the outside medium in normal operation. e.g. Nickel-cadmium and Nickel-metal hydride storage batteries.
- These are small, light weight and provide high output densities and are capable to boost charging and high-current discharging
- They used as power sources for various devices and apparatuses both in portable and industrial.
- e.g. cellular phones and notebook computers, electric cars, or hybrid vehicles.
- These are highly immune to overcharging and overdischarging. It has therefore been used for electronic products in which a large storage capacity and high charge/discharge efficiencies are required.
- Their excellent capacity and reliability, nickel metal hydride batteries are considered to be most promising for electric power sources of electric tools and electric vehicles which require charging and discharging at high rate.

**Construction**

- An alkaline storage battery consists of
  - (i) A positive electrode configured with a nickel oxide or a nickel hydroxide,
  - (ii) A negative electrode configured with a hydrogen storage alloy (capable of electrochemically absorbing and desorbing hydrogen in a reversible manner) an oxide or a hydroxide of cadmium, iron or zinc or the like, and
  - (iii) An electrolyte prepared with an alkaline aqueous solution.
- A separator is installed between a positive electrode and a negative electrode to separate them from each other and prevent a short-circuit.
- The separator can hold an electrolyte to thereby smoothly carry out an electromotive reaction.
- The separator is required to have an erosion resistance to an electrolyte, such as potassium hydroxide.
- A closure cap covers an opening of the external casing. A gasket usually made of nylon, is inserted between the closure cap and the external casing to seal the opening.

**Working**

- The positive electrode is comprised of Nickel hydroxide. It is used as active material of alkaline storage batteries but it has a very low electric conductivity. Hence, it is converted to a trivalent nickel oxyhydroxide which has a somewhat higher conductivity. The conversion is brought about by charging.
- Negative electrode comprises of hydrogen absorbing alloy.
- It produces hydride by absorbing hydrogen electrochemically while charging.
- Later during discharging, it absorb hydrogen and forms back the initial alloy.
- The performance of a nickel-hydrogen battery depends on the activity of a hydrogen-absorbing alloy which is serving as a negative-electrode active substance.
- Therefore, in alkaline secondary batteries fine powder of the hydrogen-absorbing alloy, is used, thereby increasing efficiency.

- The fine powder of the hydrogen-absorbing alloy helps to the electrochemical reaction to be more complete due to its large surface area. Hence battery capacity, increases..
- The electrical conductivity of nickel hydroxide, also depends upon the oxidation number of nickel.
- The oxidation of nickel hydroxide (during charging process of a battery) proceeds smoothly, but the reduction (in discharging process) does not proceed smoothly.
- This is due to the lowered electrical conductivity in the terminal stage of discharging process.
- This causes an insufficient discharge.
- To enhance the electrical conductivity in the positive electrode and to get the sufficient discharge a conductive agent, such as a cobalt compound, is added to the active material.
- In a sealed type alkaline storage battery, the discharge capacity of a negative electrode plate is adjusted larger than that of a positive electrode plate.
- This helps to restrain hydrogen gas generated from the negative electrode plate at charging and to absorb oxygen gas generated from the positive electrode plate.
- This in turn helps to restrain an increase of internal pressure of the battery.

- In order to increase internal volumetric efficiency of equipment using storage batteries, a rectangular alkaline storage battery has been developed as a replacement for a cylindrical alkaline storage battery having a group of spiral electrodes into which positive and negative electrode plates are coiled spirally with separators sandwiched between them.

**4.11.1 Nickel Iron Batteries (Edison cells)**

- The nickel-iron battery is a storage battery having.
  - (i) Nickel(II) oxide-hydroxide cathode (more commonly nickel oxide,  $\text{Ni}_2\text{O}_3$ )
  - (ii) An iron anode,
  - (iii) Electrolyte used is potassium hydroxide (KOH).
- The active materials are held in *nickel-plated steel tubes* or *perforated pockets*

**Advantages**

- (i) Very robust.
- (ii) Withstands overcharge and over-discharge, thermal shocks or short circuiting.
- (iii) Accepts high depth of discharge - deep cycling.
- (iv) Can remain discharged for long periods without damage, whereas a Lead Acid battery needs to be stored in a charged state.
- (v) Lifetime of 20 years possible.

**Disadvantages**

- (i) Low cell voltage (about 1.2 V).
- (ii) Very heavy and bulky.
- (iii) Gets charged slowly and vice versa.
- (iv) Low coulombic efficiency, typically less than 65%
- (v) Steep voltage drop off with state of charge/poor charge retention.
- (vi) Low energy density/low specific energy.
- (vii) High self discharge rate.

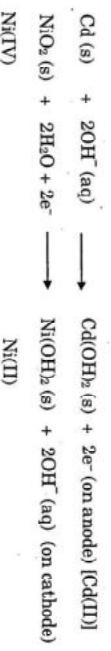
**Applications**

- (i) In heavy duty work like mining operations.
- (ii) In modern electrical application.
- (iii) Wind and solar power systems.

**4.11.2 Nickel-Cadmium Battery**

- The *nickel-cadmium battery* (commonly called as "nye-cad") is a popular type of *rechargeable battery* in which
  - (i) Nickel hydroxide is used as, positive active material.
  - (ii) metallic cadmium (Cd) as the negative active material.
  - (iii)  $\text{MnO}_2$  and KOH as electrolytes.

The nickel-cadmium battery utilizes the following reactions:



Ni(IV)

Ni(II)

**Advantages**

1. Internal resistance is low.
2. Charge and discharge rate can be increased as required.
3. Useful in wide temperature range (Up to 70°C) almost over 500 cycles.
4. Charging is fast, ranging 15 mins to 2 hours.
5. The sealed nickel-cadmium cell can be stored in the charged or discharged state without damage.
6. Available in different sizes and capacities

**Disadvantages**

1. A major drawback of this technology is its susceptibility to memory effect.
2. NiCad batteries are also prone to damage by overcharging.
3. Low cell voltage of 1.2 Volts compared with primary alkaline cells 1.5 Volts.
4. Affects environmental safety, hence not used widely.

**Applications of NiCd batteries**

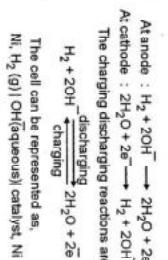
1. Sealed NiCd cells may be used individually, or assembled into battery packs containing two or more cells.
2. Small NiCd dry cells are used for portable electronics and toys.
3. Specialty NiCd batteries used in cordless and wireless telephones, emergency lighting, power tools, boats and cars, camera flash units etc.
4. Larger flooded cells are used for aircraft starting batteries, electric vehicles, and as standby power.

## 4.12 Nickel Hydrogen Batteries

- Ni-H and NiMH batteries are based on fuel cell technology.

In this rechargeable battery, the hydrogen electrode is reversible when properly catalysed and  $H_2$  can be generated from  $H_2O$ , in the cell during charging.

The negative electrode is the limiting electrode so that  $O_2$  is not evolved in the charging process. Reaction in the stainless steel case cell during discharging are,



- Since the reactions of nickel with  $H_2$  is slow, such cells are more useful for short delays, between charging and discharging and short discharge times.
- The specific energy of this battery is high (good for space applications). The cell needs stainless steel vessel to bear the  $H_2$  pressure of 200bar. The charging and discharging of this can be more than 40,000 times.

### Uses

- This cell is best suited for low orbit earth satellite (10 cycles of charge-discharge per day).

- The cell can also be used for civilian or military purposes.

## 4.13 Rechargeable Lithium Batteries

### Characteristics of lithium

- Lithium is the lightest of metals and it floats on water. It also has the greatest *electrochemical potential* which makes it one of the most reactive of metals. These properties give lithium the potential to achieve very high energy and power densities in high power battery applications such as automotive and standby power.

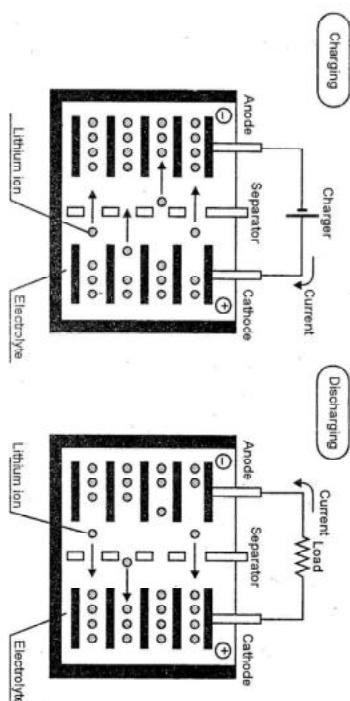


Fig. 4.13.1

### Working of battery

- The operating principle of a lithium ion rechargeable battery is shown in the Fig. 4.13.1. When the battery is charged, lithium ions in the cathode material move in between the layers of the anode, which is of carbon material, thus charging the battery.
- During discharging, the lithium ions move from the anode to the cathode, and a discharge current flows. In this way, the lithium ion rechargeable battery is charged and discharged only through the movement of lithium ions.

### Advantages

- Lithium batteries is almost the perfect cell chemistry.
- Existing since last 3 decades i.e. from 1970's, and they are now modified and in low power applications such as mobile phones, laptops, cameras and other consumer electronic products.

- Ideal for higher power applications such as automotive and standby power.
- High cell voltage of 3.6 Volts (One Lithium cell can replace three NiCad or NiMH cells which have a cell voltage of only 1.2 Volts).
- No liquid electrolyte and hence no leakage.
- Very high energy density (about 4 times better than Lead acid). For example a 3.5 ton electric powered LDV light van uses 750 Kg of Lead acid batteries.

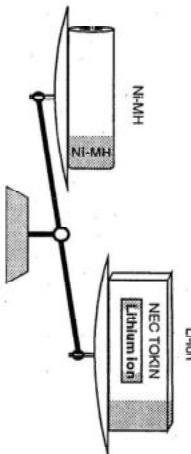


Fig. 4.13.2

#### Very high power density.

- Low weight
- Can be optimised for capacity or rate.

#### Individual cells from 500 Ah to 1000Ah capacity available.

- Fast charge* possible.
- Very low self discharge rate.* Can retain charge for up to ten years.

- Very high coulombic efficiency (Capacity discharged over Capacity charged) of almost 100%.
- Thus very little power is lost during the charge/discharge cycles.

#### Costs

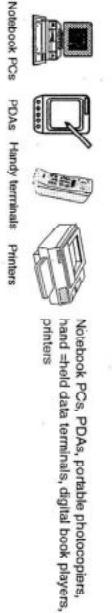
- Lithium ion rechargeable battery has no "memory" effect,
- Long cycle life. Tolerates microcycles
- Can be tuned for specific applications.

#### Applications

- Rechargeable Lithium cells are used a wide range of consumer products including cameras, camcorders, electric razors, toothbrushes, calculators, medical equipment, communications equipment, instruments, portable radios and TVs, pagers and PDA's.
- They are *fast replacing Nickel Metal Hydride* cells as the preferred power in mobile phones. Laptop computers almost exclusively use Lithium batteries.
- Now high power versions of up to 1000Ah capacity and more are becoming available for use in traction applications in electric and hybrid vehicles as well as for standby power.

#### Applications of lithium ion rechargeable battery

- Lithium ion rechargeable battery used as the main power supply for mobile devices PCs, MP<sub>3</sub> players, Digital cameras etc.

**Communication devices****Information devices****Notebooks**

Notebooks, PDAs, Handy terminals, Printers

**Camcorders**

Camcorders, MP3 Players, Digital still cameras

**MP3 Players**

Digital still cameras, LCD TVs, compact cameras

**Digital still cameras**

Digital still cameras, LCD TVs, compact cameras

**Measuring equipments**

Measuring equipments, wireless conferencing system, Portable video games, Blue tooth, other new applications

**Portable video games**

Portable video games, Blue tooth, other new applications

**Exercise**

Fig. 4.13.3

- Q. 1** Discuss the use of solar energy for space heating, water heating and for production of electricity.
- Q. 2** Write informative notes on any two of the following :
- Flat plate solar collectors
  - Photovoltaic cells
  - Solar trough collectors

**Q. 3** Write short notes on :

- Wind power
- Biomass energy
- Tidal power.

**Q. 4** Discuss the use of Indirect solar energy for generation of electrical power.

**Q. 5** Discuss the principle involved in producing hydropower and the advantages and environmental consequences involved in hydropower generation.

**Q. 6** Write informative notes on any two of the following :

- Wind power
- Biomass energy
- Tidal power.

**Q. 7** Discuss the principles involved in Ocean Thermal Energy Conversion (OTEC). Discuss its merits, disadvantages.

**Q. 8** How is Geothermal energy used for generation of electrical power ? Discuss its advantages and disadvantages.

**Q. 9** Write short notes on the following :

- Conservation of energy
  - Problems associated with the use of fossil fuels.
- Q. 10** Explain how hydrogen can be used as a source of energy.
- Q. 11** What is a fuel cell ? Explain with the help of a diagram hydrox fuel cell.
- Q. 12** State the advantages of fuel cells over conventional power plants.
- Q. 13** State the applications of fuel cells.
- Q. 14** What are alkaline storage batteries what are the types available.
- Q. 15** Explain the working and advantages of lithium ion batteries.
- Q. 16** Explain Nickel hydrogen batteries with the help of reactions.

**4.14 University Questions (Theory)****Dec. 2007****Note**

- Q. 1** Name the different renewable and non-renewable sources of energy. Distinguish between conventional and non-conventional energy. (Section 4.2) (2 Marks)
- Q. 2** What is fuel cell ? Explain the principle and working of hydrogen-oxygen fuel cell. (Sections 4.9 and 4.9.1) (5 Marks)
- Q. 3** Write short note on : Alkaline batteries (Section 4.11) (3 Marks)
- Q. 4** Give the composition of biogas. Describe the method for production of biogas from animal waste. (Section 4.7.2) (6 Marks)

**May 2008**

- Q. 1** What are fuel cells ? List the advantage of fuel cells over conventional power plants. (Section 4.9) (2 Marks)
- Q. 2** What is solar energy ? Explain the working of solar heating system using flat plate collectors. (Section 4.4) (6 Marks)
- Q. 3** Write short note on : Photovoltaic cell (Section 4.4.4) (5 Marks)

□□□

# CHAPTER 5

## Phase Rule and Steels

### 5.1 Introduction

- Phase rule is an important generalization given by Willard Gibbs (1874) which deals with the behaviour of heterogeneous systems in the state of equilibria.
- In general, with the application of phase rule, it has been possible to predict qualitatively (by means of a diagram) the effect of changing temperature, pressure and concentration on a heterogeneous system in equilibrium. Such a diagram is known as 'phase diagram.'
- This heterogeneous system containing two or more different phases which exist in equilibrium with each other is studied with the help of generalization called phase rule. This rule was deduced on the basis of principles of thermodynamic by an American physicist Willard Gibbs to explain the equilibria existing in heterogeneous system.

### 5.2 Gibb's Phase Rule

► [Dec. 2007]

- o Gibbs Phase Rule
  - o One Component System : Water.
  - o Two Component System : Iron - Carbon Equilibrium Diagram with Microstructures
  - o Limitations and Application of Phase Rule
  - o Plain Carbon Steel
  - o Limitations
  - o Introduction to Alloy Steels
  - o Special steels
  - o Principles of shape memory effect and its application.
- The following terms are involved in phase rule,
- (i) Phase
  - (ii) Components
  - (iii) Degrees of Freedom (variance)
- Let us discuss each term with examples.

### 5.2.1.1 Phase

A phase is defined as any homogeneous, physically distinct and mechanically separable portion of a system, which is separated from other such parts of the system by definite boundary surfaces.

#### Examples

1. In water system, at freezing point of water, an equilibrium exists where ice, water and water vapours are the three phases, each of which is physically distinct and homogeneous, and with definite boundaries between ice, water and water vapours, as,



2. All gases mix freely to form homogeneous mixtures. Therefore, any mixture of gases, say O<sub>2</sub> and N<sub>2</sub> and H<sub>2</sub> forms one phase only.

3. Two completely miscible liquids yield an uniform solution. Thus, a solution of alcohol and water is a one phase system.

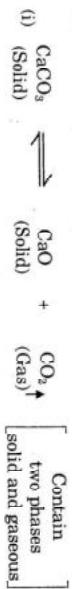
4. A mixture of two non-miscible liquids on standing forms two separate layers. Thus, a mixture of an oil and water constitutes a two phases system.

5. An aqueous solution of a solid substances like salt (NaCl) or sugar is uniform throughout. Therefore, it is a one phase system.

6. Each solid substance makes a separate phase except in the case of solid solutions.

e.g. Allotropic forms of Sulphur or Carbon, though all exist together, but are all separate phases.

7. Equilibria given below,



(Two phases exist in equilibrium)

### 5.2.1.2 Components

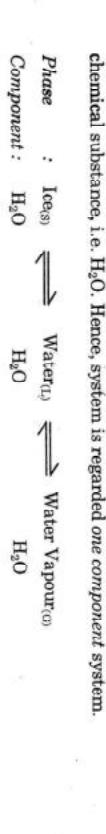
► [ May 2008 ]

#### Definition

The term component is defined as, "the smallest number of independently variable constituents taking part in the state of equilibrium by means of which the composition of each phase can be expressed directly or in the form of chemical equation".

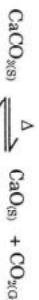
#### Examples

1. In water system, we have three phases, i.e. ice (Solid), water (Liquid) and water vapour (Gaseous) in equilibrium. Each of these phases are different physical forms of the same chemical substance, i.e. H<sub>2</sub>O. Hence, system is regarded one component system.



2. In sulphur system, there are four phases, i.e. rhombic sulphur, monoclinic sulphur, liquid sulphur and sulphur vapour. The composition of all four phases can be expressed by one chemical individual sulphur (S). Hence, sulphur system is regarded as one component system.

3. When calcium carbonate is heated in a closed vessel, the following reaction takes place.



From the above reaction, it comes to know that, there are three phases CaCO<sub>3(s)</sub>, CaO<sub>(s)</sub> and CO<sub>2(g)</sub>. Thus, the decomposition of CaCO<sub>3</sub> gives CaO<sub>(s)</sub> and CO<sub>2(g)</sub>, i.e. system is two component system. Although this system has three different constituents, it is considered as two component system because the composition of each of the above phase can be expressed in terms of any two of the three constituents present.

This can be understood from following illustration,

If only CaCO<sub>3</sub> and CaO are considered as components, then composition of each can be given as:



Thus it is a two component system.

4. In the equilibrium, for reaction between iron metal and steam,



the composition of each phase can be expressed in terms of the components Fe, H<sub>2</sub>O and H<sub>2</sub>. Hence, it is a *three component system*.

5. In the dissociation of NH<sub>4</sub>Cl in a closed vessel, which can be represented as,



In this case if proportions of NH<sub>3</sub> and HCl are equivalent, then the system is one component system; this is because the composition of both can be expressed in terms of NH<sub>4</sub>Cl alone. But if NH<sub>3</sub> or HCl is in excess, the system becomes a two component system.

6. Saturated solution of NaCl in water, contains solid salt, salt solution and water vapour. The chemical composition of all the three phases can be expressed in term of NaCl and H<sub>2</sub>O. Hence, it is a *two component system*.

7. Dissociation reaction, as,



[Two component system : CuSO<sub>4</sub> and H<sub>2</sub>O].

### 5.2.1.3 Degree of Freedom (Variance)

► [May 2008]

#### Definition

Term degree of freedom is defined as, "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".

#### Examples

1. In case of *water system*:

- (a) If all the three phases are in equilibrium, then no condition need to be specified because the three phases can be in equilibrium only at particular *temperature and pressure*,



The system is *no degree of freedom or invariant or zero variant or non-variant*.

- (b) If condition like temperature or pressure is altered, three phases will not remain in equilibrium and one of the phase disappears.

For the following system :



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

(c) For a system consisting of water in vapour phase only we must state the values of both, the temperature and pressure in order to describe the system completely. Hence, the system has *two* degree of freedom or system is *bivariant*.

- 2. For mixture of gases, degree of freedom is two because a system containing a mixture of two or more gases e.g. N<sub>2</sub> + H<sub>2</sub> is completely defined when its temperature and pressure are specified. If pressure and temperature are specified, the composition, i.e. *third variable* could be automatically definite. Since, it is necessary to specify two variable to define a system completely. Hence, the system is a *bivariant*.

- 3. A system containing saturated solution of sodium chloride in equilibrium with a solid sodium chloride and water vapour is



completely defined if the temperature is specified. Hence, the system has *one* degree of freedom. The other two variables, i.e. composition of NaCl solution and vapour pressure have definite value at a fixed temperature.

#### 5.2.2 Derivation of the Phase Rule

Let us consider a *heterogeneous system in equilibrium* consisting of 'C' components distributed in 'P' phases. As has been already defined, the number of degrees of freedom of a system in equilibrium is that number of variable factors (such as temperature, pressure and composition) that must be arbitrarily fixed to define the system completely.

- Obviously, the number of such variables is given by the total number of variables of the system minus the number of variables which are defined automatically by virtue of the system being in equilibrium.

When a system is in equilibrium, there can be only one temperature and one pressure hence, the total of these variables is two only.

However, the number of concentration (or composition) variables can be more. In order to define the composition of each phase, it is necessary to specify only  $(C - 1)$  composition variables because the composition of the remaining component can be obtained by difference.

- Since there are  $P$  phases, the total number of composition or concentration variables will be  $P(C - 1)$ . On adding the temperature and pressure variables, the total number of variables of the system are  $P(C - 1) + 2$ .

- On the basis of thermodynamic considerations, when a heterogeneous system is in equilibrium, at a constant temperature and pressure, the chemical potential,  $\mu$  of a given component must be same in every phase.

Thus, if there is one component in three phases (say  $\alpha$ ,  $\beta$  and  $\gamma$ ) and one of these (say  $\alpha$ ) is referred to as standard phases, then, this fact must be expressed in the form of the following two equations.

$$\mu_\alpha = \mu_\beta$$

$$\mu_\alpha = \mu_\gamma$$

- Thus, for each component in equilibrium in 3 phases, 2 equations are possible. Hence for each component in  $P$  phase,  $(P - 1)$  equations can be written. If there are  $C$  component the number of equations or variables possible from the conditions of equilibrium are  $C(P - 1)$ .
- Since chemical potential is a function of temperature, pressure and concentration, each equation must represent one variable.
- Hence, the number of possible variables of degree of freedom can be given as,

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

$$\therefore F = C - P + 2$$

3

### 5.3 Application of Phase Rule to One Component System

In one component system, the equilibrium conditions may be represented with the help of diagrams taking *pressure* and *temperature* as the two axes. This diagram is called as *pressure-temperature (p-t) diagram*.

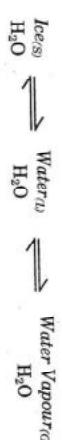
In this diagram any *line* or *curve* represents an *univariant* system, because the equilibrium conditions at any point on line could be completely defined by just fixing either *temperature* or *pressure*. All areas represents *bivariant* systems, because to define the system completely at any point in the area, both *temperature* and *pressure* should be fixed.

In the diagram where all the three phases are in contact with each other at a specific point called as *triple point* represents zero *variant* system because system is completely defined by itself.

#### 5.3.1 Water System

► [Dec. 2007, May 2008]

The water system under normal condition is of *three phases and one component system*. The system involved three phases are *solid - ice*, *liquid - water*, and *gas - water vapour*. All these phases can be represented by one *chemical entity*  $H_2O$ , hence it is one component system.



Let us apply the phase rule to one component, i.e. water system. Substitute the value of component ( $C$ ) = 1, in the phase rule equation, then the equation is

$F = C - P + 2$

$F = 1 - P + 2$

$F = 3 - P$

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

$\therefore F = C - P + 2$

From the above value of degree of freedom ( $F$ ), we can say that, *the degree of freedom (F) depends on the number of phases present at the equilibrium*.

- Therefore, the following three different cases are possible, (Explained with the help of phase diagram, refer Fig. 5.3.1).

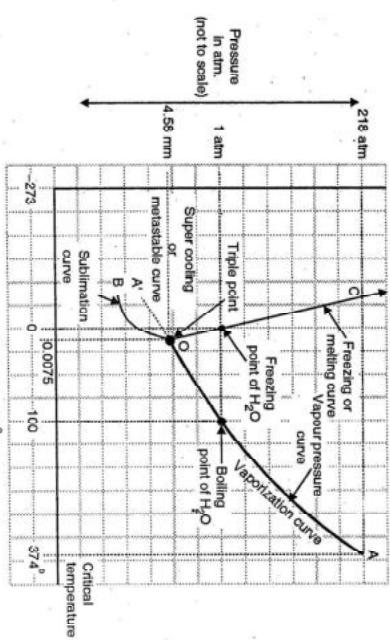


Fig. 5.3.1 : Phase diagram of water system

Hence when,

$$\begin{aligned} P = 1, & \quad \text{then } F = 2 \quad \dots \quad \text{System is Bivariant} \\ P = 2, & \quad \text{then } F = 1 \quad \dots \quad \text{System is Monovariant} \\ P = 3, & \quad \text{then } F = 0 \quad \dots \quad \text{System is Zero variant} \end{aligned}$$

- From the above equation it is clear that, *for any one component system, the maximum number of degree of freedom is two* and most convenient variables are *pressure and temperature*. In the above phase diagram of water system following salient features are observed :

1. The curves OA, OB and OC.
2. The areas AOC, AOB and BOC.
3. The triple point 'O' and
4. The metastable curve (OA')

1. **The curves OA, OB and OC.**  
These three curves meet at the point 'O' (called as triple point) and divide the diagram in to three areas. Therefore, these three curves are known as *boundary lines*.

#### Curve OA (Vapour Pressure Curve)

- The curve OA terminates at A, the critical point 218 atm. and 374° temperature.
- It represents the vapour pressure of liquid water at different temperatures.
- The two phases *water* and *water vapour* coexist in equilibrium along this curve. Here, are two phases ( $P = 2$ ) and one component ( $C = 1$ ), therefore

$$F = 1 - 2 + 2 = 1$$

Hence, system is monovariant or univariant or having one degree of freedom. When the vapour pressure is equal to one atmosphere, the corresponding temperature C as shown in figure is the boiling point of water, i.e. 100°C.

#### Curve OB (Sublimation curve)

- The curve OB terminates at B, the absolute zero, i.e. - 273° temperature. It shows the vapour pressure of solid ice at different temperature.
- The two phases *solid-ice* and *water-vapour* coexist in equilibrium along this curve. Therefore, degree of freedom for this system is also one and system is monovariant.

#### Curve OC (Fusion curve)

- The curve OC terminates at C, the critical pressure. The two phases *solid-ice* and *liquid-water* coexist in equilibrium.
- This curve indicates that the melting point of ice decreases with increase of pressure.
- The one atmosphere (1.0 atm.) line meets the fusion (freezing/melting) curve at 0°C which is the normal melting point of ice. Again, along the curve OC, there are two phases in equilibrium and system is of one component.

Therefore, the system is monovariant.

- From the above discussion, we can say that, along the curves OA, OB and OC there are *two phases* in equilibrium and *one component*. Therefore,

$$F = C - P + 2$$

$$F = 1 - 2 + 2$$

$$F = 1$$

## 2. The areas AOC, AOB and BOC

- The regions or areas between the curves show the conditions of temperature and pressure under which a single phase, i.e. ice, water or water vapour is capable of stable existence. Thus

1. Area AOC represents conditions for liquid phase, i.e. water.

2. Area AOB represents conditions for gaseous phase, i.e. water vapour.

3. Area BOC represents conditions for solid phase, i.e. ice.

- In all the three areas, there being 'one phase' and 'one component'. Therefore,

$$F = C - P + 2$$

$$F = 1 - 1 + 2$$

$$F = 2$$

- Hence, each system has two degree of freedom, i.e. system is **bivariant** or **divariant**.

## 3. Triple point

- All the three curves, OA, OB and OC meet at the point O called as triple point, where all the three phases solid, liquid and vapour are simultaneously in equilibrium.

- This triple point occurs at  $0.0075^\circ\text{C}$  and 4.558 mm Hg pressure. Since, there are *three phases and one component*, therefore

$$F = C - P + 2$$

$$F = 1 - 3 + 2$$

$$F = 0$$

- The system at triple point is zero **variant** or **nonvariant**. Thus, **neither** pressure nor temperature can be altered.

- Even slightly changed three phases would not exist if one of the phase disappears.

## 4. Metastable curve (curve OA')

- This curve is also known as *supercooling* (water/vapour) curve. This is the extension of curve OA, i.e. vapour pressure curve. That is water can be supercooled by eliminating solid particles carefully which includes crystallization.

- The *supercooled water system is unstable, i.e. metastable*. It at once reverts to the stable system ice or vapour on the slightest disturbance.

- The metastable vapour pressure of super cooled water is higher than vapour pressure of ice.

### 5.3.2 Condensed or Reduced Phase Rule

► [May 2008]

- When a single phase is present in a *two component system*, then the degree of freedom ( $F$ ) is represented by following equations;

$$F = C - P + 2$$

$$F = 2 - 1 + 2$$

$$F = 3$$

- From the values of  $F$  ( $F = 3$ ) we can say that, three variables must be specified in order to describe the condition of phase, i.e. *in addition to temperature and pressure the concentration of one of the component has to be given*.

## 5.4 Two Component Systems

### General characteristics of two-component systems

- (1) The maximum number of phases in a two-component system will be four.

$$P = C - F + 2 = 2 - 0 + 2 = 4$$

(Maximum number of phases exist when degrees of freedom = 0. Negative degree of freedom cannot exist).

- (2) The maximum number of degrees of freedom in a two-component system will be three (i.e. when the system exists as a single phase)

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

- (3) The system will have *three variables* namely, *temperature, pressure and concentration*.

- (4) The composition of all the individual phases of the system can be expressed by means of *not less than two components*.

- (5) For constructing a phase diagram of a two-component system, a three dimensional space model is required using the three variables (viz., temperature, pressure and concentration) as its coordinates.

**Phase rule for two component alloy systems**

- In two-component system, when  $p = 2$ , degree of freedom ( $F$ ) has the highest value, i.e., 3.

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

- Consequently, three variables – temperature, pressure and concentration of one of the two components must be specified in order to describe the system completely.

- Since the maximum number of degrees of freedom in a two-component system is three, the phase behaviour of a binary system may be represented by a three-dimensional diagram of pressure, temperature and composition or space models, which cannot be conveniently shown on paper.

- 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 or a system in which vapour phase is not considered, is known as condensed system.

- Since pressure is kept constant (at 1 atmosphere).

- 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 phase rule having two variables, namely, temperature and concentration (or composition) of the constituents.

- Therefore, solid-liquid equilibria are represented on temperature-composition ( $T-C$ ) diagrams and such diagrams are called **isobaric**.

- Similarly,  $P-C$  diagrams at constant temperature are called **isothermal** and  $P-T$  diagrams at constant composition are called **isoplethal**.

**Thermal analysis**

- The shape of the freezing point curves for any system, especially those involving metals, can be determined by thermal analysis.

- So thermal analysis is defined as a method involving a study of the cooling curve of various compositions of a system, during solidification.

- The form of the cooling curve indicates the composition of the solid.

**Principle of thermal analysis**

The principle of the method can be understood from the following considerations :

- |     |   |
|-----|---|
| (1) | Fusing pure substance / cooling liquid slowly |
| (2) | Fused solid solutions cooled slowly           |

**(1) Fusing pure substance / cooling liquid slowly**

- When a pure substance in the fused or liquid state is allowed to cool slowly and the temperature noted at definite times. The graphic representation of the rate of cooling will be continuous curve (See Fig. 5.4.1(a)).

- When the freezing point is reached and the solid makes its appearance, it is indicated by a break in the continuity of the cooling curve and the temperature will remain constant, until the liquid is completely solidified.

- Therefore, the fall in temperature will again become continuous.

**(2) Fused solid solutions cooled slowly**

- 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 (or 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 does not remain constant, as in the previous case of cooling of a pure substance.
- The temperature decreases continuously, but at a different rate and it forms an eutectic mixture, the fall of temperature continues, till the eutectic point is reached.

- The system now becomes *invariant* from the point of view of the phase rule and the temperature remains constant, until solidification is complete (See Fig. 5.4.1(b)).
- Therefore, the *fall of temperature* becomes *uniform*, but the *rate of fall* is quite *different* from the previous one.

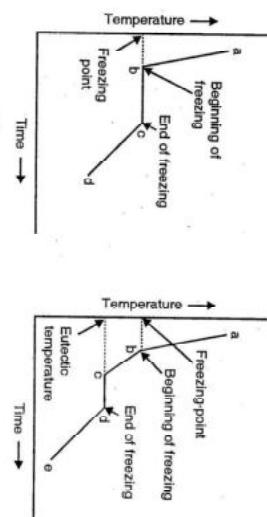


Fig. 5.4.1 : Cooling curves

From the cooling curve for any mixture of a definite composition, it is possible to obtain its :

- freezing point, and
- eutectic temperature

(a) *The freezing point varies with the composition of the system but the eutectic point remains constant for a given system.*

- (b) Nearer the composition of the system to the eutectic, the shorter is the portion bc and the more prolonged is the part cd.
- (c) 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.
- Procedure for thermal analysis method**
- Initially the cooling curves of a series of alloys of *known composition* are worked out and their freezing points are noted. By plotting freezing against composition, a T-C curve is obtained for the alloy system. However, in order to complete the diagram it is necessary to know that the freezing point of the pure components also.
  - 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.

- The *Thermal Analysis* is a procedure which can also be used to derive the phase diagram of any two component system.

### 5.5 Lead Silver System

- This system has two component and four phases. The phases are :
  - Solid silver
  - Solid lead
  - Solution of molten silver and lead and
  - Vapour

*But the boiling points of silver and lead being considerably high, the vapour phase is practically absent.*

Since the pressure has nearly no effect on equilibrium so the system can be conveniently represented by a *temperature-concentration diagram* (see Fig. 5.5.1), at a constant and one variable pressure which is neglected, the condensed form of the phase rule :

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

will be applicable.

When system containing two phases and two components like solid and liquid, then solid-liquid equilibrium has practically no *gas phase* and the effect of pressure is very small that is negligible. Then, it is necessary to take into account the remaining variables, viz. temperature and concentration. Such a solid-liquid system with the gas phase is absent is called a *condensed system*.

- The experimental measurements of temperature and concentration in condensed systems are usually carried out under atmospheric pressure.
  - Since, the degree of freedom in such case is reduced by one, therefore, it can be also termed as *reduced phase rule* and represented by the equation.
- $$F = C - P + 1$$
- The reduced phase rule is more convenient to apply to solid-liquid two components condensed system. Example Pb - Sb, Ag - Pb or Zn - Cd system.

- The complete Temperature - Concentration ( $T$ - $C$  Phase) phase diagram of the system Silver - Lead (Ag - Pb) is shown in Fig. 5.5.1.

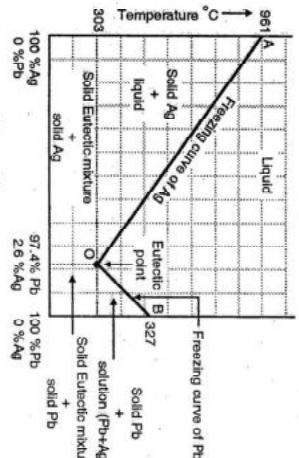


Fig. 5.5.1 : The phase diagram of Pb-Ag system

In the phase diagram shown in Fig. 5.5.1 of Pb-Ag system, following salient features are observed.

- (1) **Curve AO (Freezing curve of Ag)**
    - It shows the effect on freezing point of Ag on addition of lead in small quantities.
    - The curve starts from A (961°C) the melting point of Ag, where pure Ag coexists as solid and liquid (vapour being neglected).
    - This curve, indicates that the melting point of Ag falls gradually on adding Pb, along AO, till the lowest point O (303°C) is reached, where the solution gets saturated with respect to lead. At O, no more lead can go in solution and consequently, the melting point does not fall any further, and if any lead is added, it separates as the solid phase.
    - Along this curve, solid Ag and solution (vapour being negligible) coexist; and hence, according to reduced phase rule equation :
- $$F = 3 - P = 3 - 2 = 1$$
- (2) **Curve BO (Freezing curve of Pb)**
    - It represents the effect on freezing point of Pb on gradual addition of small amounts of Ag to it. Point B is the melting point of pure lead (327°C).
    - Along BO, the melting point gradually falls on the addition of Ag, till lowest point O is reached.
    - At this point the solution gets saturated with respect to Ag and the melting point of lead does not fall any more.
    - On cooling the whole mass (having eutectic composition) crystallizes out. The system is univariant like AO.
  - (3) **Point O (Eutectic point)**
    - The two curves AO and BO meet at O, where three phases-solid Ag, solid Pb and their solution coexist and according to condensed phase rule, the system will be invariant ( $F = 3 - P = 3 - 3 = 0$ ).
    - The point O (303°C) represents a fixed composition of  $Ag = 2.6\% : Pb = 97.4\%$  and is called eutectic composition temperature.
    - At the eutectic composition point, the temperature remain constant, until the whole of the melt solidifies in block to become solid of eutectic composition.*
    - However, further cooling results in the simultaneous crystallization of a mixture of Ag and Pb in relative amounts corresponding to eutectic point O.
    - Below the temperature line of the eutectic temperature, we have two regions in the diagram viz.
      - (i) Region marked as *eutectic + solid Ag*, in which crystalline silver and solid eutectic are stable, and
      - (ii) Region marked *eutectic + Pb*, in which crystalline lead and solid eutectic are stable.

**(4) Area AOB**

- It represents solution of Pb-Ag. If a sample of lead containing *less than 2.6 % Ag* is taken, at an arbitrary point on curve. On allowing the mass to cool, the temperature gradually falls without any change in composition till this point is reached on the curve BO (point may be 'P').
- On lowering the temperature, lead begins to separate out and the composition varies along PO till point O is reached.
- On further cooling the whole mass solidifies in block to the eutectic composition (2.6 % Ag : 97.4 % Pb).

**5.5.1 Application to Pattinson's Process**

- The above principle is utilized in the Pattinson's process of *desilverization of lead*.
- If a sample of *argentiferous lead*, containing less than 2.6 % Ag, is allowed to cool gradually, lead will separate out and the solution will become progressively richer in Ag, till the percentage 2.6 of Ag is reached; and on further cooling, the whole mass will solidify as such.
- On the other hand, if lead-silver alloy containing Ag greater than 2.6 % is allowed to cool, then pure silver separates along the curve AO, till the eutectic composition at O is reached.

**Problem 1:** An alloy of tin and lead contains 73 % tin. Find the mass of eutectic in 1 kg of solid alloy, if the eutectic contains 64 % of tin.

**Solution :**

1 kg of alloy contains 730 g tin and 270 g lead.

In the eutectic composition, tin is 64 % and lead is 36 %. Therefore, corresponding to 270 g of lead the mass of tin in eutectic.

$$= \frac{270 \times 64}{36} = 480 \text{ g}$$

Total mass of eutectic in alloy

$$= 270 + 480 \text{ g} = 750 \text{ g}$$

**5.5.2 Eutectic System**

A *binary system consisting of two substances which are miscible in all proportions 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 point represents the lowest or limiting temperature at which a liquid phase can exist in the system.
- No other mixture containing the two components will have a melting point lower than the eutectic temperature.
- Eutectic point has precise values of temperature and composition and it represents an invariant system.
- If the liquid is cooled is just below the eutectic point, both the components of the eutectic simultaneously solidify without any change in the composition or temperature of the liquid phase.
- An eutectic system can maintain its temperature constant over long periods.
- When the liquid is cooled below the eutectic point, the components solidify in the form of small crystals intimately mixed with each other. These small crystals fill in the spaces between the larger crystals of the pure components which are already separated out. Eutectic mixtures appreciably contribute towards the strength of the solid structures in case of alloys.
- Recent electron microscopic studies show that eutectics are mixtures of the components but not their compounds.

**5.5.4 Uses of Eutectic Systems**

- Eutectic mixtures are used in preparing "solders" used for joining two metal pieces together. Ex: Pb-Sn solders.
- They are used in "safety fuses" used in buildings to protect them against fire hazards. Ex: Woods metal, which is an alloy containing (50 % Bi + 25 % Pb + 12.5 % Sn + 12.5 % Cd). This alloy melts at 65 °C, and is used for plugging water sprayers in buildings. In case of accidental fire in the building, the plug made of the eutectic melts and the water forces out as a spray to put off the fire.

## 5.6 Iron Carbon System

► [May 90, Dec. 92]

The iron-carbon system is the theoretical basis for ferrous alloys (metallurgy). Fig. 5.6.1 shows the phases of system, till the formation of  $\text{Fe}_3\text{C}$  is completed; i.e. pure iron reacts with carbon to form this compound known as Iron carbide or cementite.

There are following different modifications of pure iron,

- (i) Stable crystalline form upto  $910^\circ\text{C}$  called  $\alpha$ -iron. (BCC lattice)
- (ii) At  $910^\circ\text{C}$  transition of  $\alpha$ -iron takes place to form  $\gamma$ -iron (FCC lattice)
- (iii) At  $1401^\circ\text{C}$   $\gamma$ -iron transforms back to  $\delta$ -iron (BCC lattice).

This system is very interesting, because it has allotropes which are stable at constant pressure, both below and above a certain range of temperature. The solid solutions of carbon in iron structure are known as **ferrites**.

The important features of three allotropic forms are shown in Table 5.6.1.

Sr. No.	Name	Lattice pattern	Temperature Range	% solubility of carbon	Magnetic properties
1.	$\alpha$ -iron	BCC	Upto $910^\circ\text{C}$	Nil	Magnetic
2.	$\gamma$ -iron	FCC	$910$ to $1400^\circ\text{C}$	2%	Non-magnetic
3.	$\delta$ -iron	BCC	$1401$ to $1525^\circ\text{C}$	0.1%	Non-magnetic

Pure iron melts at  $1539^\circ\text{C}$  and the liquid iron boils at about  $3000^\circ\text{C}$ .

The solid solutions of carbon in the various forms of iron are interstitial solutions. They have the same crystal form as the iron; but the carbon atoms fit between the iron atoms in the lattice instead of replacing them. The various important micro-constituents are as follows :

- **Austenite** is the solid solution of carbon in  $\gamma$ -iron. The maximum solubility of carbon is 2.06 % at  $1147^\circ\text{C}$ . Austenite does not exist in equilibrium below  $723^\circ\text{C}$ , as it decomposes on cooling.

• **Cementite** is the name given to the compound  $\text{Fe}_3\text{C}$ . It exists at all temperatures studied from 0 to  $1800^\circ\text{C}$ . It undergoes only a magnetic change at  $200^\circ\text{C}$ . It is hard, brittle and water-resistant.

• **Ferrite** is the solution of carbon in  $\alpha$ -iron. The solubility of carbon is very small, maximum being 0.035 % at  $723^\circ\text{C}$  and the solubility at room temperature is only 0.007 %. Ferrite is often considered to be practically pure  $\alpha$ -iron but even by this minute amount of dissolved carbon, some of its properties (particularly its magnetism) are strongly affected.

• **Perlite** is the eutectoid of ferrite and cementite formed by the decomposition of austenite. It contains 0.8 % carbon. It is a fine-grained mixture of ferrite and cementite and normally has a lamellar structure.

• **Martensite** is the transformed form the austenite. It consists of a supersaturated solution of carbon (or  $\text{Fe}_3\text{C}$ ) in highly stressed  $\alpha$ -iron. It is magnetic. It has needle like structure. Next to cementite, it is the hardest constituent of case iron and steel.

• **Troostite** is formed when the martensite is tempered in the range  $230$  to  $400^\circ\text{C}$ . It consist of finely dispersed aggregate of superfine particles of cementite and ferrite. It is softer but tougher than martensite.

• **Bainite** is the transformed form of austenite in the temperature range of  $260$  to  $540^\circ\text{C}$ . It has a ferrite matrix in which cementite is embedded. It is magnetic, moderately ductile and harder than pearlite and tougher than martensite.

• **Sorbite** is formed when martensite is tempered at  $400$  to  $600^\circ\text{C}$ . It is an important constituent in some special steels such as rails. It consists of ferrite and globules of iron carbide. Its properties are intermediate between those of pearlite and troostite.

### 5.6.1 Iron-Carbon Equilibrium Diagram with Microstructures

The iron carbon system provides the most prominent examples of heat treatment and property alteration based on polymorphic transformation and ejection decomposition.

Iron carbon equilibrium diagram (Please refer Fig. 5.6.1) indicates :

1. Phase changes which occur during heating and cooling.
2. The nature and the amount of structural components that exist at any temperature.
3. A correlation between the microstructure and properties of steel and cast iron.

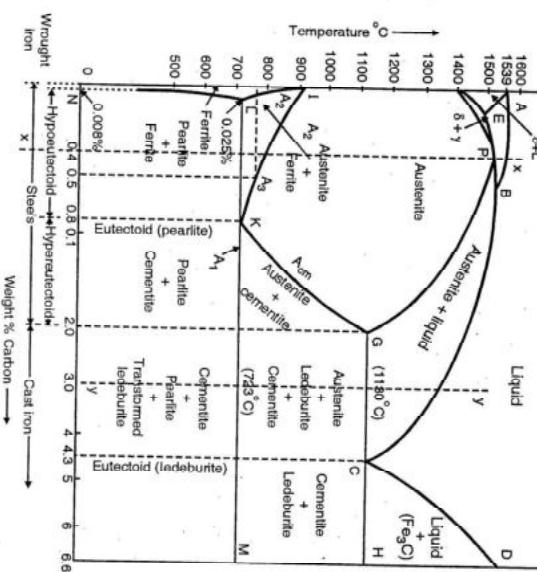
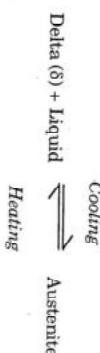


Fig. 5.6.1 : Iron-carbon system

The effect of heat treatment (shown in Fig. 5.6.1) are discussed as given below:

- Pure iron melts at 1525°C and as carbon is dissolved in it, the melting point drops along the line ABC till the lowest melting point is 1130°C, which is eutectic temperature, at which % of carbon arrives to 4.3%.
- As the carbon content further increases upto 6.67%, the melting point rises along the line CD. The region BCD indicates liquid phase.
- The curve ABGECA indicates the completion of solidification. The region between the ABCD and ABGECH line indicates various iron carbon compositions which are completely solid.
- If liquid alloys containing 0 to 0.55 % of carbon are cooled, solid solution of carbon in  $\delta$  iron is obtained.
- If alloys containing 0.55 to 4.3 % of carbon are cooled, solid solution of carbon in  $\gamma$  iron or austenite is produced.



- Austenite exists in the region AEC or EC represents solidus.
- When alloy containing upto 4.3 % carbon is cooled, the conditions are shown as solidus.
- Liquid alloy containing more than 4.3 % carbon after cooling gives solid crystals of cementite on curve CD (liquid). These get solidified on curve CF (solid).
- The alloy containing 4.3 % carbon is the eutectic alloy. It completely solidifies at 1130 °C.
- Iron carbon alloys containing upto 1.7 % (less than 2.06%) carbon are classified as steels. Those containing over are called as cast iron.

#### Micro constituents of iron and steel

- The solid solutions of carbon in the various forms of iron are interstitial solutions. They have same crystal form as the iron, but the carbon atoms fit between the iron atoms in the lattice instead of replacing them.
- The various important micro constituents are as follows :

• Austenite	• Cementite
• Ferrite	• Pearlite
• Martensite	• Troostite
• Bainite	• Sorbite

#### Austenite

- It is the solid solution of carbon in  $\gamma$ -iron.

- The maximum solubility of 2.06 % carbon.
- It does not exist in equilibrium below 723 °C, as it decomposes on cooling.

#### Cementite

- Compound Fe<sub>3</sub>C is known as cementite.
- It exists at all temperatures from 0 to 1800 °C.
- It undergoes only a magnetic change at 200 °C.
- It is hard, brittle and wear-resistant.

#### Ferrite

- It is solution of carbon in  $\alpha$ -iron.
- The solubility of carbon is very small, maximum up to 0.035 % at 723 °C.
- The solubility of carbon at room temperature is 0.007 %.

- (iv) It is often considered to be practically pure iron.  
 (v) Minute amount of dissolved carbon, strongly affects its properties (particularly magnetism).

**Pearlite**

- (i) It is the eutectoid of ferrite and cementite formed by the decomposition of austenite.
- (ii) It contains 0.8 % carbon.
- (iii) It is finely – grind mixture of ferrite and cementite.
- (iv) It has a lamellar structure.

**Martensite**

- (i) It is the transformed form of austenite.
- (ii) It consists of a super saturated solution of carbon in highly stressed α-iron.
- (iii) It is magnetic.
- (iv) It has needle like structure.
- (v) It is the hardest constituent of cast iron and steel.

**Troostite**

- (i) It is formed when martensite is tempered in the range  $230^{\circ}\text{C}$  to  $400^{\circ}\text{C}$ .
- (ii) It consists of finely dispersed aggregate or superfine particles of cementite and ferrite.
- (iii) It is softer but tougher than martensite.

**Bainite**

- (i) It is the transformed form of austenite in the temperature range of  $260^{\circ}\text{C}$  to  $540^{\circ}\text{C}$ .
- (ii) It has a ferrite matrix in which cementite is embedded.
- (iii) It has magnetic property.
- (iv) It is moderately ductile and harder than pearlite and tougher than martensite.

**Sorbite**

- (i) It is formed when martensite is tempered at  $400^{\circ}\text{C}$  to  $600^{\circ}\text{C}$ .
- (ii) It is an important constituent in some special steels such as rails.
- (iii) It consists of ferrite and globules of iron-carbide.
- (iv) Its properties are intermediate between pearlite and troostite.

**5.7 Applications of Phase Rule**

1. It applies to physical as well as chemical phase reaction.
2. It provides a convenient basis for classification of equilibrium states of systems with the help of phases, components and degree of freedom.
3. It applies to microscopic systems.
4. It indicates that different systems having the same degrees of freedom behave in a similar fashion.
5. It helps in predicting the behaviour of a system under different conditions of the governing variables.
6. It helps in deciding whether the given number of substances together would exist in equilibrium under a given set of conditions or whether some of them will have to be inter converted or eliminated.
7. Phase rule does not take any cognizance of the nature of the amounts of substances present in the system.

**5.7.1 Limitations of Phase Rule**

- [Dec. 2007]
1. Phase rule can be applied for systems in equilibrium only.
  2. It is not of much help in case of systems which attain the equilibrium state very slowly.
  3. It applies only to a single equilibrium state. It does not indicate the other possible equilibria in the system.
  4. Phase rule considers only the number of phases but not their quantities. Even a minute quantity of the phase, when present, accounts towards the number of phases. Hence, care has to be taken in deciding the number of phases existing in the equilibrium state.
  5. All the phases of the system must be present under the same conditions of temperature, pressure and gravitational forces.
  6. The solid, liquid phases should not be so finely sub-divided as to bring about deviation from their normal values of vapour pressure.

## 5.8 Alloy Steels

► [Dec. 2007]

### Introduction

- Metals possess many useful properties, such as high malleability, ductility, luster, good electrical conductivity being a few to mention. But, in nature metals are not available in pure state.
- When metals are extracted from their natural sources – i.e. minerals or ores, some impurities are carried along with the pure metals.
- Hence, to get pure metal, further purification has to be done by various different methods. But after all this processing, the pure metal obtained from its ore, loses some vital characteristics and becomes practically useless for engineering purposes.
- Some of such characteristics are, its tensile strength, corrosion resistance and hardness.
- The pure metals are very soft, highly chemically reactive, highly malleable and ductile. Thus changes in these vital properties, reduce shock and wear resistance of metals. The high chemical reactivity makes pure metal susceptible to corrosion.
- The properties of pure metals can be improved by alloying the pure metal with another suitable metal/non-metal, e.g. iron in pure state can be alloyed to get steel, which shows the desired properties such as hardness, toughness, high corrosion resistance etc. Here, steel is an alloy of iron with carbon (non-metal), chromium/manganese (metals) etc.
- An *alloy* is a solid mixture of two or more metals or non-metals. Alloy must have necessarily,
  - at least one metal (base metal)
  - at least one additional metal or non-metal.
- The properties of given metal (base metal) can be improved by alloying it with other metals or elements like carbon, phosphorus etc.
- When two or more metals are mixed in their molten state and when this mixture is cooled, the two metals remain in intimate mixture without separation, thus forming a solid mixture.
- This solid homogeneous mixture of two metals is called as alloy. *Thus, an alloy is a substance / material formed by solidification of metallic solution of two or more metals / elements.*
- Alloy can also be defined as, a solid solution where the solutes are the alloying elements whereas the solvent is the element in excess proportion (base or main metal).

### 5.8.1 Principle of Alloying

- It is observed that *the properties of an individual metal or non-metal may be totally or partially improved in combination with other metal or non-metal in the form of mixture of their solid solutions*. This may be because, to prepare an alloy of two different elements each of them are melted and the two different melts are mixed together by slowly adding the low melting element into high melting one.
- The addition is continued till the eutectic temperature of mixture is reached. For various combinations of the mixtures, the eutectic temperatures are constant.
- The eutectic point or temperature is a physical constant of the homogeneous mixture of two different elements. It signifies that the percentages of two different elements making homogeneous mixture composition gets disturbed.
- The fix percentages of two elements at eutectic point is known as *eutectic composition*, e.g. Pb/Ag system, at 303°C while composition is Pb : Ag = 97.5 : 2.5 which is eutectic composition.
- Thus, the alloying elements in solid mixture improve/ change their original properties.*

### 5.8.2 Purpose of Alloying

- Metals are used as a basic material in making various machines, used in industries or household articles or in other areas like making ships, railways, bridges, buildings etc.
- During metallurgical processes involved in extraction of pure metal from its ores, the most important characteristics of metal are been lost/reduced, as discussed above. This affects the performance of metals during operation under given service conditions in engineering uses.
- The *undesirable changes* in the malleability, ductility, tensile strength, elastic limits, hardness have to be improved to make the metal suitable for its uses, which are affected by mixing the metals with other suitable elements. Thus alloy formation, basically helps in getting the desired performance in the given service conditions economically.
- The following *properties of metals* are generally *modified/improved* by alloying the metal, i.e. the purpose of alloying the metal is to improve,
  - Hardness
  - Tensile strength

- (iii) Corrosion resistance
  - (iv) Castability
  - (v) Colours
  - While to decrease,
    - (vi) Melting point
    - (vii) Malleability and ductility
    - (viii) Chemical reactivity
- The Table 5.8.1 shows different examples indicating the improvements in the characteristics of main element on alloying with others.

Table 5.8.1

Sr. No.	Characteristic	Main metal	Alloying elements	Modification in properties of main metal
1.	Hardness	Pure lead	Arsenic (0.5%)	Hardness of lead improves and it is used to make bullets.
	Pure gold	Copper		Ornaments of gold are prepared as hardness of gold improves.
	Pure iron	Carbon (upto 1.5%)	To make steels with greater hardness	
	Pure copper	Tin		Alloy is harder than pure copper.
	Pure copper	Zinc		
2.	Tensile strength	Pure iron	Carbon (1%)	Ten times increase in tensile strength of iron.
3.	Corrosion resistance	Pure iron	Chromium, nickel	The alloy (stainless steel) does not get corroded, not only by moisture but even in acids, whereas pure iron gets corroded easily by the attack of atmospheric gases, moisture etc.

Sr. No.	Characteristic	Main metal	Alloying elements	Modification in properties of main metal
4.	Castability	Pure lead	Tin, Antimony	Castability of this alloy improves and hence it is used in making 'printing type'.
5.	Colours	Silver (white)	Gold (yellow)	The alloy is purple coloured.
	Copper (red)	Zinc	(slivery white)	The alloy is yellow coloured.
	Aluminium (silvery white)	Zinc	(slivery white)	The alloy is golden yellow in colour.
6.	Melting point	Pure iron	M.P. = 1539°C	Carbon (2%) M.P. of alloy is decreased to 1130°C.
	(Bi) Bismuth M. P. = 271°C	Cd (321°C)	Pb (337°C)	The alloy (wood's metal) has M.P. of only 71°C, which is very low as compared to alloying elements.
		Sn (232°C)		
7.	Malleability and ductility	Copper	Zinc	The alloy (brass) is less ductile as compared to copper.
	Gold	Copper		The malleability of gold is reduced.
8.	Chemical activity	Iron	Chromium Nickel	The alloy (stainless steel) has very low reactivity as compared to pure iron.

Thus, from Table 5.8.1, the purpose of making alloys is understood clearly, as each example indicates the modifications/improvements in specific property (drawbacks) of pure metal. *The alloying helps in enhancing the utility of metals for engineering purposes.*

### 5.8.3 Classification of Alloys

- Alloys can be classified on the basis of following criteria,
- (i) Based on microstructure
- (ii) Based on the presence or absence of iron,
- e.g. Ferrous alloys
- Non-ferrous alloys
- (iii) Based on principal metals (constituents) in alloy,

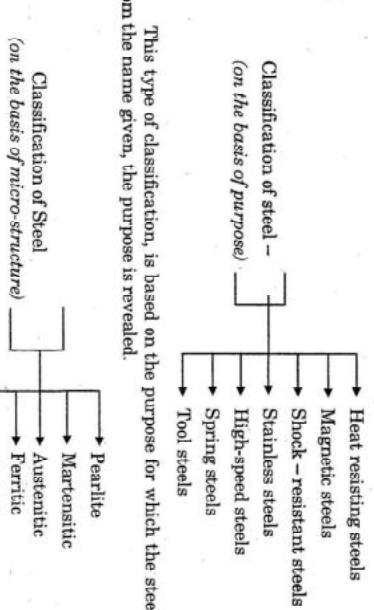
e.g. Alloys of copper with zinc  
– Brasses

Alloys of copper with tin  
– Bronzes

Alloys of aluminium  
– Duralumin

### 5.9 Plain Carbon Steels

► [ May 2008 ]



This type of classification, is based on the purpose for which the steel is used and generally from the name given, the purpose is revealed.

Table 5.9.1 : Composition and properties of plain – carbon steels

Sr. No.	Variety of steel	Carbon content/composition	Properties	Uses
1.	Hypoeutectoid (low carbon steels) (Mild steels)	0.008%– 0.2%	Dark bluish coloured with fibrous structure, soft, ductile, easily weldable, having low tensile strength. They are shock-resistant, but not corrosion resistant; an also not susceptible to heat treatment.	They are used to make boiler plates / tubes, gear wheels, nails, wires, screws, rivets, bolts, etc.

The alloys of iron with other metal(s) or/and non-metal are known as *ferrous alloys*. These are commonly known as *alloy steels*. The metal iron generally forms alloys by mixing with carbon, and any other element (metal) such as either nickel alone or nickel and chromium both. Based on this, the alloy of iron and carbon (i.e. steels – widely known as plain carbon steels) are either,

- (a) Three components i.e. (Fe, C, Ni)
- or (b) Four components i.e. (Fe, C, Ni, Cr)

Since these steels essentially contain iron and carbon, are known as *plain carbon steels*. The percentage of carbon in steels ranges from 0.008% to 2%. The plain carbon steels are further classified/named on the basis of its carbon content as,

Sr. No.	Variety of steel	Carbon content/composition	Properties	Uses
2.	Hypoeutectoid (medium carbon steels)	0.2% – 0.5%	Tougher, harder than low carbon variety, good machinability, good tensile strength, low shock resistance, on heating gets hardened.	They are used for making various machine parts, turbine motors, railway axles, wheels, gears, shafts, hydraulic fittings, spindles, automobile engine parts etc.
3.	Hypo-eutectoid (high carbon steels) (Hard steels)	0.5% – 0.8%	Low weldability or can be welded with care, can be adjusted for desired hardness.	These are used to make wheels for railway bogies, cushion springs, etc.
4.	Hyper-eutectoid – very hard steels	0.8% – 2.0%	These are wear resistant, have good weldability, high tensile strength, can be hardened, toughened and tempered easily.	These are used for making various types of tools, such as cutting tools, engraving tools, drills, hammers, lathe tools, planning tools, slotting and shaping tools, blades, chisels, files, knives, ball-bearings, springs, wire dies etc.

### 5.9.1 Limitations of Plain Carbon Steels

- The *alloy steels/ plain carbon steels*, discussed above necessarily contain iron and carbon.
- In addition to these two elements, *other elements are mixed* in plain carbon steels to impart special or specifically desirable characteristics.
- This is because, properties of iron by alloying with carbon, can be improved to some extent. But if the carbon content is increased beyond a certain limit it is not desirable. Thus the plain carbon steels also have certain drawbacks, which have to be overcome by adding some other elements.
- To understand the effect of other elements on the properties of alloy steels, we shall first discuss the *drawbacks of plain carbon steels*, which are as,

- With increasing percentages of carbon, the *ductility decreases and brittleness increases*.
- Plain carbon steels cannot be deep hardened* on heat treatment, because due to effect of heat, only surface of steel gets hardened while the inner layers of steel remains soft.
- During the use, the *mechanical properties* of plain carbon steels get *deteriorated at higher temperature*. Thus the uses of plain carbon steels to make/manufacture various machine parts has limitation of temperature.
- The *corrosion resistance of plain carbon steels is very low*. As a result, this steel has limited use in manufacturing various machine parts, though strength and welding characteristics may be suitable.

### 5.10 Special Steels

► [Dec. 2007]

- The drawbacks of plain carbon steels make unfit for engineering purposes under the working atmosphere where temperature is *high, corroding environment persists etc.*
  - Hence, it becomes necessary to make further modifications, so as to *make the plain carbon steels more useful*. Thus the addition of various different elements has been taken up with plain carbon steels. Such steels are known as "*special steels*".
  - It is found that, every element has some special effect on the properties of plain carbon steels.
  - The commonly added elements are aluminium, boron, chromium, cobalt, copper, lead, manganese, molybdenum, nickel, niobium, phosphorus, silicon, sulphur, titanium, tungsten, vanadium etc.
- The special effects of these elements on alloy steels is given in Table 5.10.1.

Table 5.10.1

Element	Special effects
Aluminium	Acts as a deoxidiser, restricts growth of austenite grain.
Boron	Enhances hardenability of steel.
Chromium	Enhances hardenability, corrosion and oxidation resistance, increases high-temperature strength. In high carbon steels, it increases abrasion resistance.
Cobalt	Contributes to hardness of steel.
Copper	Enhances resistance to atmospheric corrosion.
Lead	Enhances machinability of alloy steels.
Manganese	Improves hardenability of alloy steels moderately, so also increases the strength of ferrite and reduces susceptibility of alloy steel to heat treatment.
Molybdenum	Enhances, <ul style="list-style-type: none"> <li>(i) Resistance to softening in tempering.</li> <li>(ii) Tensile and creep strengths at high temperatures.</li> <li>(iii) Hardenability.</li> <li>(iv) Corrosion resistance of stainless steels especially in chloride environment.</li> <li>(v) In austenite the grain coarsening temperature.</li> <li>(vi) Resistance to susceptibility to embrittlement during tempering.</li> </ul>
Nickel	Along with other elements, renders moderate to high hardenability ; enhances strength of unhardened steels by solid solution effect ; enhances toughness in pearlitic - ferritic steels.
Niobium	Increases strength of steels at high temperatures, retards tempering, imparts a fine grain size.
Phosphorus	Increases, <ul style="list-style-type: none"> <li>(i) Machinability</li> <li>(ii) Corrosion resistance</li> </ul>

Element	Special effects
	(iii) Strength and hardness
	(iv) Susceptibility of medium carbon steels to temper embrittlement
Silicon	Decreases ductility and notch impact toughness
Sulphur	Improves oxidation stability, increases strength of ferrite without any effect on ductility.
Titanium	It helps to fix carbon as inert particles.
Tungsten	Prevents formation of austenite in high chromium steels.
Vanadium	It helps to form hard and abrasion resisting carbide film in tool steels.
	Imparts high temperature hardness in tempered steels.
	It enhances creep strength in some high temperature steels.
	Increases hardenability.

- The improvements in properties of alloy steels due to special effect of certain metals makes the steels more useful for engineering purposes.
- The most commonly used alloys where the effect of alloying element has made the alloy suitable for multiple purposes are,
  - (a) Nichrome
  - (b) Stainless steel
- The composition, properties and uses of these two alloys are discussed here. Both of these alloys are ferrous alloys.

### 5.10.1 Shape Memory Effect

- The shape memory effect was first discovered in 1932 in a silver-cadmium alloy.
- The **Shape Memory Effect** is the ability of some materials to bend, stay bent, then after some signal, return to its original shape.

- It allows materials possessing shape memory properties to return to their original shape after having suffered some form of deformation after they are heated to temperatures above their transformation temperature.
- It is possible to have a transformation temperature below ambient, in which case the alloy will behave like a spring.

At the phase transformation temperature, the alloy undergoes a crystalline reversible solid state phase change from martensite to austenite. It should be noted that both phases have different properties.

#### Shape Memory Alloy

- Shape memory alloys or SMA's are metals that exhibit shape memory properties.
- Shape memory alloys use **atomic rearrangement** to "remember" their original shape.
- Special symmetry in the atomic arrangement, called "**twins**" allows the material to change shape easily, and change back after given a signal.

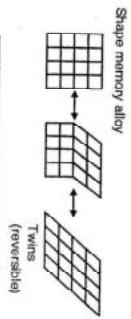


Fig. 5.10.1

- Over a range of temperatures, starting at the transformation temperature, the alloy undergoes a reversible solid state transformation. The transformation temperature is influenced by composition and other factors.
- Shape memory alloys can recover from large amounts of bending and torsional deformations as well as small amounts of strain. Provided the deformations are within recoverable ranges, the process of deformation and shape recovery can be repeated millions of times.

#### Metals exhibiting shape memory characteristics

Commercially available shape memory alloys include:

- Nickel/Titanium alloys such as Nitinol and Timel
- Copper/Zinc/Aluminum Alloys
- Copper/Aluminum/Nickel Alloys

Other alloys that are known to display shape memory properties are:

- Silver/Cadmium Alloys
- Gold / Cadmium alloys
- Copper / Tin alloys
- Copper / Zinc alloys
- Indium / Titanium alloys
- Nickel / Aluminum alloys
- Iron / Platinum alloys
- Manganese / copper alloys
- Iron / Manganese / Silicon alloys

#### Applications for shape memory alloys

The medical and aerospace and marine industries are the largest consumers of shape memory components. Some of their applications are outlined below, together with some less well known application areas:

#### Medical Industry

- Stents**  
A device used to treat coronary disease. It would be inserted in the deformed shape and would expand upon reaching body temperature to open arteries and increase blood flow.

#### Vena-Cava Filters

A device used to trap blood clots. Inserted as a small cylinder, it reverts to an umbrella shaped filter to trap small blood clots and prevent them from travelling to parts of the body where they may have a detrimental effect.

#### Dental and Orthodontic Archwires

These work similar to a spring. They apply a continuous and gentle force correcting misaligned teeth, as opposed to the periodic and uncomfortable tightening required by stainless steels.

#### Aerospace and Marine

- Fluid Fittings - SMA couplings are available that seal metal to metal with large radial clamping forces.

- Supplied in cold couplings are simply placed over the pipe to be connected and they shrink as they warm up.

#### Other areas of Application

Other areas where shape memory alloys are used include:

- Spectacle frames
- Underwired brassieres
- Pipe jointing systems
- Temperature control systems

#### Review Questions

- Q. 1 State Gibb's phase rule with equation.
- Q. 2 Explain the term 'condensed' or 'reduced' phase rule.
- Q. 3 What is Tripple point ?
- Q. 4 Explain the term 'Degree of Freedom' with examples.
- Q. 5 What do you understand by the term "Phase" and "Component".
- Q. 6 Explain the term "Eutectic" and "Eutectoid" point.
- Q. 7 State Gibb's phase rule and explain the various terms involved in it with examples.
- Q. 8 What is phase rule ? Explain the application of phase rule to "One Component" or "Water System".
- Q. 9 Write a brief iron condensed (Reduced) phase rule with example.
- Q. 10 Discuss in brief Iron-Carbon equilibrium with diagram.
- Q. 11 Discuss Iron-Carbon diagram and explain the phase changes that occur when hypoeutectoid steel is cooled from its molten condition.
- Q. 12 State limitations of phase rule.
- Q. 13 What are plain carbon steels ?
- Q. 14 What are characteristics of eutectic point ?

#### 5.11 University Questions and Answers

Dec. 2007

- Q. 1 Give the elements of phase rule. (Section 5.7.1)

- Q. 2 State and explain phase rule. Discuss the application of phase rule to one component water system. (Sections 5.2, 5.3.1)

- Q. 3 What are alloy steels ? (Section 5.8)

(2 Marks)

- Q. 4 What are the effects of following alloying elements on alloy steels :
- (i) Nickel (Section 5.10)
  - (ii) Chromium (Section 5.10)
  - (iii) Cobalt (Section 5.10)
  - (iv) Tungsten (Section 5.10)

(5 Marks)

**May 2008****Note**

- Q. 1** What is triple point in phase diagram ? Explain it with reference to one component water system phase diagram. (Section 5.3.1) (2 Marks)

- Q. 2** Explain any two of the following terms :

- (i) Phase (Section 5.2.1.1)  
(ii) Components (Section 5.2.1.2)  
(iii) Degrees of freedom (Section 5.2.1.3) (6 Marks)
- Q. 3** State and explain condensed phase rule. (Section 5.3.2) (3 Marks)
- Q. 4** What are plain carbon steels ? How can they be classified on the basis of carbon contents ? (Section 5.9) (3 Marks)

# CHAPTER 6

## Nanomaterials

### 6.1 Introduction

The word nanotechnology was used for the first time in 1974 by Prof. Nan'o of Tokyo Science University while explaining the silicon machined down to the small particle, smaller than one micron.

Nano science can be defined as, the study of phenomena and manipulation of materials at atomic, molecular and macromolecular scales, where properties differ significantly from those at a larger scale.

Nanotechnology can be defined as, "the design, characterisation, production and application of structures, devices and systems by controlling shape and size at the nanometre scale."

Materials comprising of particles with a size between  $1$  to  $100$  nm (i.e.  $10^{-9}$ m) are normally considered as *nano materials*.

One nanometre (nm) is  $10^{-9}$ m i.e. one thousand millionth of a metre which is about the size of  $6$  carbon atoms in a line or  $10$  hydrogen atoms in a line.

These objects are too small to see without very powerful electron microscope.

Nanomaterials can be of different shapes such as like rod, plate or any other complex geometry.

The spherical particles which are less than 10 nm are called as clusters.

Particles at nanoscale (100-0.2 nm) show variation in the properties of materials from those at a larger scale (Normal sizes).

*Below 100 nm with every lower value the properties like melting point, colour, i.e. wavelength of optical transition, ionisation potential, hardness, catalytic activity and selectivity, magnetic properties vary.*

These are the same properties in materials which remain almost constant, when particles are not in nano scales.

Due to their remarkably reduced size, such materials provide challenging usage in the various field.

### Nanowires

### Nanocones

### Haeckelites. Their electronic and mechanical properties

### Production methods for CNTs

### Applications of nano materials in

#### i) Medicine

##### ii) Catalysis

##### iii) Environmental Technologies

##### iv) Electronics and related fields.

##### v) Mechanics.

Table 6.1.1 : The sizes of nanoscale objects

Object	Diameter
H-Hydrogen atom	0.1 nm
C <sub>60</sub> -Buckminsterfullerene	0.7 nm
Carbon nanotube (single wall)	0.4 – 1.8 nm
6 carbon atoms aligned	1 nm
DNA	2 nm
Proteins	5–50 nm
CdSe Quantum Dot	2–10 nm
Ribosome	25 nm
Virus	75–100 nm
Semiconductor Chip Features	90 nm * or above
Mitochondria	500–1000 nm
Bacteria	1000–10000 nm
Capillary (diameter)	3000 nm
White blood cell	10000 nm

\*Currently the semiconductor chips are being reduced to 20 nm by a technique *nanolithography*.

## 6.2 Nanomaterials

Nano-materials can be manufactured either of the following methods (nodes)

- (i) Top to bottom
- (ii) Bottom up

- *Top to bottom* method involves milling bulk material with normal size particles bulk to small particles (nanosize).
- At 3 nm 50% of its atoms.

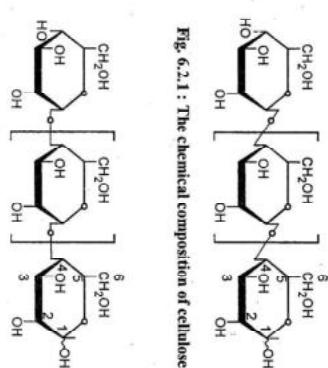


Fig. 6.2.1 : The chemical composition of cellulose

Thus *extraordinary properties* shown by nanomaterials are due to the difference in the arrangement of simple materials.

The properties of materials can be different at the nanoscale for two main reasons.

1. Increase in relative surface area, and
2. Quantum effects.

These factors can change or enhance properties such as reactivity, strength and electrical characteristics.

- With decrease in size of particle, a greater number of atoms are found at the surface as compared to those inside.
- For example, a particle of size 30 nm has 5% of its atoms on its surface,
- At 10 nm 20% of its atoms,
- At 3 nm 50% of its atoms.

- Thus nanoparticles have a much greater *surface area per unit mass* as compared with larger particles.

The catalytic chemical reactions occur mainly on surfaces. Thus given mass of material in nanoparticulate form will be much more reactive than the same mass of material made up of larger particles.

**Example :** U.S. silver dollar

The silver dollar contains 26.96 grams of coin silver, has a diameter of about 40 mm, and has a total surface area of approximately 27.70 square centimeters.

If the same amount of coin silver were divided into tiny particles – say 1 nanometer in diameter – the total surface area of those particles would be 11,400 square meters.

Thus the surface area increases by 4,115 million times than the surface area of the silver dollar, when not in nanosize.

In other materials such as crystalline solids, as the size of their structural components decreases, there is much greater interface area within the material; this can greatly affect both *mechanical* and *electrical* properties.

Most metals are made up of *small crystalline grains*; the boundaries between the grain slow down or arrest the propagation of defects when the material is stressed, thus giving it strength.

If these grains can be made very small, or even nanoscale in size, the *interface* area within the material greatly increases, which enhances its *strength*.

For example, nanocrystalline *nickel* is as strong as *hardened steel*.

Understanding *surfaces* and *interfaces* is a key challenge for nanomaterials.

The known allotropes of carbon are, (i) Graphite (ii) Diamond. But Nanotechnology has helped to get the third allotrope of carbon, Fullerenes or  $C_{60}$ .

- (When graphite was vaporised with a short-pulse, high-power *laser*) it turned into Fullerene –  $C_{60}$ .

**6.3 Graphite**

- Allotrope of carbon i.e. graphite acts as a *lubricant*. It also forms a carbon *fiber* material used in *tennis rackets* and *bicycles*.

- These varied uses of graphite are been mainly due to its structure as shown in Fig. 6.3.1.

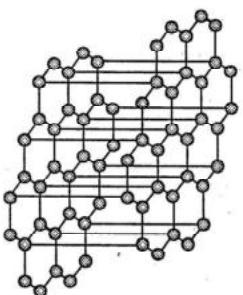


Fig. 6.3.1 : Molecular model of graphite

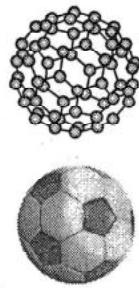
- Each of the carbon atoms is bound to three other carbon atoms in the *same plane*, at a molecular level.
- The *planar* surfaces do not have covalent links and are therefore free to move relative to one another, which gives graphite its *lubricant* properties.
- Because of the structural uniqueness, graphite has slippery movement in molecular form.

**6.4 Fullerene**

► [Dec. 2007 !]

- The fullerenes can be considered, after graphite and diamond, to be the third well-defined allotrope of carbon.
- Fullerenes were first isolated in 1990, in considerable quantity.
- The molecule was named after R. Buckminster Fuller, the inventor of geodesic domes, which conform to the same underlying structural formula.
- A hollow, pure carbon molecule in which the atoms lie at the vertices of a polyhedron with 12 pentagonal faces and any number of hexagonal faces.
- (When graphite was vaporised with a short-pulse, high-power *laser*) it turned into Fullerence –  $C_{60}$ .

- But this was *not a practical method* for making large quantities.



**Fig. 6.4.1: Chemical structure of Buckminsterfullerene-C<sub>60</sub>**

- Each carbon is bound to three other carbons in a pseudo-spherical arrangement consisting of alternating pentagonal and hexagonal rings, in the manner of a soccer ball. Hence its nickname, *buckyball*.

Every carbon is equivalent. NMR spectrum of C<sub>60</sub> reveals a single line.

- Buckminsterfullerene is a beautiful thing it was found as a byproduct of soot formation.
- Scrape the inside of the chimney and you will get few buckyballs on the finger.

#### Properties and applications

- Fullerenes are *spheroidal* organic molecules. Following are the *physical and chemical* properties of fullerenes,
- Fullerenes and its derivatives show *superconductivity* and *ferro-magnetism*.
- The fullerenes are used in *synthetic, pharmaceutical, and industrial* applications, as *inhibitor* of the *HIV protease*, to make new drugs or proteins.
- C<sub>60</sub> fullerene are used in cosmetics preparation applicable in *halting* the process of *aging*.
- The other type of fullerene C<sub>80</sub> can act as a very good *MRI contrast agent*.
- They can be useful in light emitting diodes (LED), molecular electronics and computing, as *lubricants, rocket fuel etc.*
- Fullerene C<sub>80</sub>, shows *odd* magnetic and electronic *properties* due to its *shape* being intermediate between a sphere and a disk.

#### 6.5 Quantum Dots and Quantum Wells

- *Quantum dots* are *crystals* so small that their properties are subject to quantum effects. They are also called as *zero dimensional objects*.
- The size of Quantum dot is larger than an atom though the difference is negligible. The smallest such quantum dot contains only 3 atoms like water.
- Same quantum dots are made up of *virtual matter* composed of confined electrons.
- Such quantum dots exist in crystal format though their mass is very low.
- Quantum dot is a nanoparticle with *unusual properties*.
- Quantum well are formed when the *electrons are trapped* in an island of *conducting* and *semiconducting* material which is surrounded entirely by an insulator. These *traps* are called as *quantum wells*.
- The traps are of very thin layers similar to computer chips – nanometer thick.
- It was found that electrons can move freely only in *two dimensions*.
- The distance they travel in the third dimension was found to be smaller than the wavelength of electrons.

► May 2008 11

#### 6.6 Carbon Nanotubes (CNT's)

- Carbon particles as *graphene sheets* are made into tubular forms called as *Carbon nanotubes*.
- They have diameters of few nanometers and their lengths are up to several micrometers.
- They were discovered in 1991 by Iijima.
- Carbon nanotubes have very important *future applications*.
- Each nanotube is made up of a *hexagonal network* of covalently bonded carbon atoms.

- Carbon nanotubes are of two types:
  - single-walled
  - multi-walled
- A single-walled carbon nanotube (*SWNT*) consists of a single graphene cylinder whereas a multi-walled carbon nanotube (*MWNT*) consists of several graphene cylinders which are arranged in concentric form.
- Due to such structures, these CNTs show electronic, mechanical, optical and chemical characteristics, thermal conductivity, density, and lattice structure, which make them highly useful for many application.
- The intrinsic properties of CNTs depend on the diameter.

## 6.7 Methods of Preparation for CNTs and Fullerenes

There are five methods for preparation of CNTs, and Fullerenes.

- Arc method
- Laser method
- Chemical Vapour Deposition (CVD)
- Ball milling
- Flame synthesis

### 6.7.1 Arc Method

This is the first method for producing CNTs and fullerenes in reasonable quantities.

- In this method, an electric current is applied across two carbonaceous electrodes in an inert gas atmosphere. This is called *plasma arc*.
- The carbon arc discharge method, has been initially used for producing  $C_{60}$  fullerenes.
- It is the most common and perhaps easiest way to produce CNTs, as it is rather simple.
- It involves the evaporation of one electrode as cations followed by deposition at the other electrode. This plasma-based process is similar to *electroplating* process.

### 6.7.2 Laser Method

► [Dec. 2007 !]

- In 1996 CNTs were first synthesized using a dual-pulsed laser and achieved yields of >70 wt% purity.
- In this method the samples were prepared by laser vaporization of graphite rods with a 1 : 1 catalyst mixture of Cobalt and Nickel at 1200°C in flowing argon, followed by heat treatment in a vacuum at 1000°C to get the  $C_{60}$  and other fullerenes.
- The use of two successive laser pulses minimizes the amount of carbon deposited as soot.
- The second laser pulse breaks up the larger particles ablated by the first one, and feeds them into the growing nanotube structure.
- The material produced by this method appears as a mat of "ropes", 10-20nm in diameter and up to 100μm or more in length.
- Each rope is found to consist primarily of a bundle of single walled nanotubes, aligned along a common axis.
- By varying the temperature, the catalyst composition, and other process parameters, the average nanotube diameter and size distribution can be varied.
- Arc-discharge and laser vaporization are currently the principal methods for obtaining small quantities of high quality CNTs.

**Drawbacks of Arc and laser method**

- Both methods involve evaporating the carbon source. Hence to increase *production* to the *industrial level* using these approaches, is difficult.
- Both methods produce CNTs in highly *tangled forms*, mixed with unwanted forms of carbon and/or metal species.
- Hence, CNTs produced are *difficult to purify, manipulate, and assemble* for building nanotube-device architectures for practical applications.

**6.7.3 Chemical Vapor Deposition [CVD]**

- In this method, hydrocarbon such as acetylene is subjected to chemical vapour deposition catalytically using metal catalyst, such as cobalt or iron.
- Method is established* for last 20 years and has been in use for producing various carbon materials such as *carbon fibers, filaments etc.*
- Hydrocarbon used are, acetylene, ethylene, methane etc.

Table 6.1 : Some of the sources, catalyst, temperatures are as follows :

Carbon source	Temp	Catalyst	Product
Ethylene	545°C 900°C	Ni/Fe/CO	SWCNT and MWCNT
H <sub>2</sub> /CH <sub>4</sub>	1000°C catalytic decomposition	CO/Ni/Fe on MgO	High yield of SWCNT
Acetylene	≈ 600°C	Cobalt	SWCNT MWCNT
Carbon source with oxide solid solution (Reducible to non-reducible oxides with one or more transition metal oxide)	> 800°C	H <sub>2</sub> /CH <sub>4</sub> atmosphere, any metal catalyst	Composite powders containing CNT
CH <sub>4</sub>	> 500°C Decomposition	Metal catalyst	CWCNT (main) MWCNT (minor quantity)
Any carbon source, e.g. acetylene	> 600°C	C/zeolite catalyst	[Fullerene +] + SWCNT + Few MWCNT

**6.7.4 Ball Milling**

- Ball milling and subsequent annealing is a *simple* method for the production of CNTs.
- CNTs of carbon and boron nitride can be produced from their respective powders by thermal annealing.
- These CNTs are fully nanoporous microstructures. Method consists of placing *graphite powder* into a stainless steel container containing four hardened *steel balls*. The container is purged, and *argon* is introduced.
- The milling is carried out at *room temperature* for up to *150 hours*. On completion of milling, the powder is *annealed* under an *inert gas flow* at temperatures of *1400°C* for *six hours*.
- The mechanism of this process is not known, but by using the ball milling process *nanotube nuclei* are formed, and by using *annealing* process growth of nanotube is activated.
- It is observed that this method produces *more multi walled nanotubes* (MWCNT) and *few single walled nanotubes* (SWCNT).

**6.7.5 Other Methods**

- CNTs can also be produced by diffusion flame synthesis, electrolysis, use of solar energy, *heat treatment of a polymer*, and *low-temperature solid pyrolysis*.
- In flame synthesis, combustion of a portion of the hydrocarbon gas provides the elevated temperature required, with the remaining fuel conveniently serving as the required hydrocarbon reagent.
- Thus the flame constitutes an efficient source of both energy and hydrocarbon raw material.
- Combustion synthesis can be used for high-volume *commercial production*, by modifying various parameters of process.

**6.8 Properties of Carbon Nanotubes****a) Electrical Conductivity**

- CNTs can be highly *conducting*, and hence can be said to be metallic.
- Their conductivity has been shown to be a function of (1) *chirality*, (2) *degree of twist* (3) *diameter*.
- CNTs can be either *metallic* or *semi-conducting* in their electrical behavior. Conductivity in MWN's is quite complex.

- (4) The resistivity of the SWCNT ropes is found to be of the order of  $10^{-4} \text{ ohm}\cdot\text{cm}$  at  $27^\circ\text{C}$ . Thus SWCNT ropes are the most conductive carbon fibers known.
- (5) They are able to sustain much higher stable current densities, as high as  $10-13 \text{ A/cm}^2$ .
- (6) It has been reported that individual single walled nanotubes may contain *defects*. These defects allow the single walled nanotubes to act as *transistors*. Likewise, joining CNTs together may form transistor-like *devices*.
- (7) A nanotube with a natural junction (where a straight metallic section is joined to a chiral semiconducting section) behaves as a *rectifying diode* – that is, a half-transistor in a *single molecule*.
- (8) It has also recently been reported that single walled nanotubes can route electrical signals at speeds up to 10 GHz when used as interconnects on semi-conducting devices.

#### b) Strength and Elasticity

- (1) The carbon atoms of a *single sheet* of graphite form a planar *honeycomb lattice*, in which each atom is connected via strong chemical bond to three neighboring atoms.
- (2) Because of these strong bonds, the basal plane *elastic modulus* of graphite is one of the largest of any known material.
- (3) For this reason, CNTs are expected to be the ultimate high-strength fibers. Single walled nanotubes are *stiffer than steel*, and are *very resistant to damage from physical forces*.
- (4) Pressing on the tip of a nanotube will cause it to *bend*, but *without damage* to the tip. When the force is removed, the nanotube *returns* to its *original state*.
- (5) This property makes CNTs very useful as *probe tips* for very high-resolution scanning probe microscopy.
- (6) The current Young's modulus value of single walled nanotubes is about 1 TeraPascal, but this value has been widely disputed, and a value as high as  $1.8 \text{ Tpa}$  has been reported.
- (7) Young's modulus depends on the size and chirality of the single walled nanotubes, ranging from  $1.22 \text{ Tpa}$  to  $1.28 \text{ Tpa}$ .
- (8) They have calculated a value of  $1.09 \text{ Tpa}$  for a generic nanotube.

#### d) Field Emission

- (1) When electrons from a metal tip are tunneled into vacuum, under application of a strong electric field.
- (2) Field emission is resulted the small diameter and high aspect ratio of CNTs is very favorable for field emission.
- (3) Even for moderate voltages, a strong electric field develops at the free end of supported CNTs because of their sharpness.
- (4) This phenomenon was observed by de Heer and co-workers at EPFL in 1995.
- (5) These field emitters are found to be superior to conventional electron sources and hence they find their way into all kind of applications, most importantly flat-panel displays.
- (6) It is remarkable that after only five years Samsung actually realized a very bright color display, which will be shortly commercialized using this *technology*.
- (7) Studying the field emission properties of multi walled nanotubes, Bonard and co-workers at EPFL observed that together with electrons, *light is emitted* as well. This *luminescence* is induced by the electron field emission, since it is not detected without applied potential. This light emission occurs in the visible part of the spectrum, and can sometimes be seen with the naked eye.

**e) High Aspect Ratio**

- (1) CNTs represent, high aspect ratio about 1000 : 1.
- (2) The high aspect ratio indicates that a *lower loading* of CNTs is needed compared to other conductive additives to achieve the same *electrical conductivity*, such as carbon black, chopped carbon fiber or stainless steel fiber.
- (3) Due to low loading of CNTs the toughness, of polymer resins<sup>3</sup> is presented especially at low temperatures, as well as maintaining other key performance properties of the matrix resin.
- (4) CNTs have proven to be an *excellent additive* to impart *electrical conductivity in plastics*.

**f) Highly Absorbent**

- (1) The large surface area gives high absorbency to CNTs which make them ideal for use in *air, gas, and water filtration*.
- (2) *Replacing activated charcoal* with CNTs in certain ultra high purity applications, has been successful.

**6.9 Applications of Carbon Nanotubes**

The most important application of carbon nanotubes are :

- As catalyst support
- In batteries Fuel Cells: H<sub>2</sub>, Li storage
- As field emitters for instrumentation . capacitors
- As electrodes in electrochemistry
- In microscopy
- As nanotube sensors
- As diodes, transistors and capacitors
- As nanoscale reactors, ion channels
- As membranes for molecular transport
- As filling materials in polymer composites

**6.10 Nanowires**

- A *nanowire* is an extremely *thin wire* with a diameter of the order of a few nanometers (nm) or less, where 1 nm = 10<sup>-9</sup> meters.
- Nanowires are like ordinary wires with an abnormally less *thickness 10 atoms diameter*, length can be longer even up to 1000 nm i.e. 1  $\mu\text{m}$ .
- Nanowires are synthesized gradually just like crystal growth.
- Nanowires of various combinations of materials which not only *carries current* but also *information* are not only synthesized but are being manufactured.

**Manufacture**

- There are two processes in *nanotechnology* by which nanowires can be manufactured are

- (i) suspension
- (ii) deposition.

**Suspension**

- In this method a suspended nanowire is held by its ends in an evacuated chamber, and then is chemically *etched* or *bombarded* with high-speed atoms or molecules to *reduce its diameter*.
- Another method involves indenting the surface of a wire in the center of a suspended span, *raising the temperature*, and then *stretching* the wire while it is near its *melting point*.

**Deposition**

- In this method deposited nanowire is *fabricated on* a surface consisting of some non-conducting substance such as *plastic* or *glass*.

- The process is *similar* to that by which semiconductor *chips* are grown, except that the result is a linear (one-dimensional) structure rather than a flat (two-dimensional) or solid (three-dimensional) structure.

**Application**

- Nanowires can be used in field effect transistors (*FETs*), *light emitting diodes (LEDs)*, *nanolasers*, *solar cells*, *thermoelectric devices*, *optical detectors*, *chemical and biological sensors*.
- Fields expected to benefit from nanotechnology include *water purification*, *sanitation*, *agriculture*, *alternative energy (particularly photovoltaics)*, *home and business construction*, *computer manufacturing*, *communications*, and *medicine disease detection and intervention*.
- As filling materials in polymer composites

### 6.11 Nanocoones

- Carbon nanocoones, were discovered in 1994 which are the most simple example of the *nanstructured carbon*.

They are made, of the *hexagonal plane* with a different number of *pentagonal defects*, more precisely, from one to five.

- Each cut, or the pentagonal disclination, has the angle  $2\pi/6$ .

- The fivefold (or positive disclination) could be stable, but the most stable configuration for more than one defect is the *configuration*, where they are *separated by hexagons*.

► [Dec. 2007]

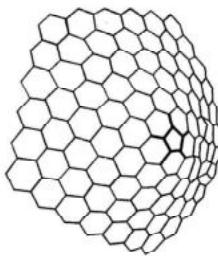


Fig. 6.11.1 : The carbon nancone.

The nanocones are produced by:

- Carbon condensation* on a graphite substrate
- Pyrolysis* of heavy oil.
- Laser ablation* of graphite targets.

In laser ablation, graphite surface is heated with intensive short laser pulse.

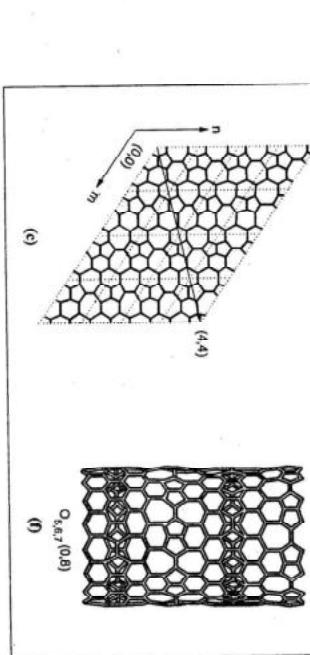
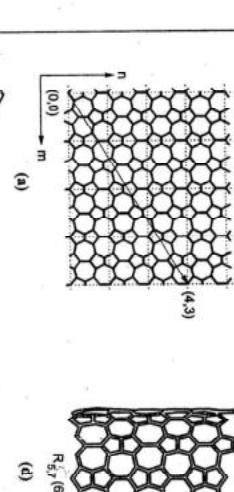
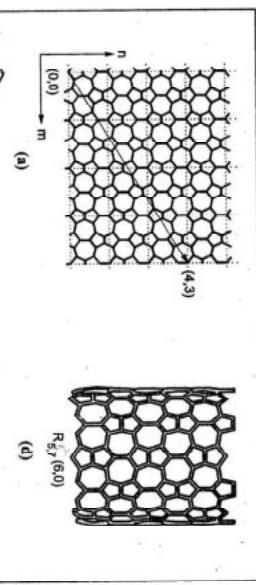
The graphite *evaporates* some number of atoms from the graphene sheet, and other atoms *rearrange* into the *conical surface* as shown above.

The growth of nanocones is yet under study.

### 6.12 Haeckelites

► [Dec. 2007]

- The presence of defects such as *pentagons* and *heptagons* in *fullerenes* modifies the electronic properties.



(a) Rectangular Haeckelite sheet (R) (b) Hexagonal Haeckelite sheet (H) (c) Oblique Haeckelite sheet (O)  
 (d)-(f) are the corresponding Haeckelite tubes.  
 Fig. 6.12.1 : Haeckelites (All Haeckelites are metallic sheets and tubes)

- These arrangements are now called 'Haeckelites' in honour of *Ernst Haeckel*, a German zoologist who produced a beautiful drawing of radiolaria (micro-skeleta of zoo-plankton), in which *heptagonal*, *hexagonal* and *pentagonal* rings were observed.

### Properties

They show metallic behaviour.

- Thus, it is possible to roll up Haeckelite sheets to form nanotubes, which will be *conductors*, *independent* of the diameter and chirality.

- Another property* of Haeckelite tubes retain stiffness of classical CNTs, composed of only hexagons; (the Young's modulus of Haeckelite tubes is around  $1.0 \text{ TPa}$ .)

- In addition, Haeckelites also exhibit local rugosity due to the local curvature introduced by the presence of heptagons and pentagons (Fig. 6.12.1).

### 6.13 Applications of Nanomaterials

Some important current and potential short and long-term applications of nanomaterials are as follows.

#### 6.13.1 Nanomechanics

- Molecules can change conformation due to change in temperature, pH, light, electrontransfer etc.

- Recently nanoscale electromechanical rotor of size 300 nm rectangular blade mounted on multiwall nanotube was functionalised.

- Using electron microscopy it is shown that as a voltage is applied to the stator electrode, the metal blade orientation changes.

- Thus further developments in this area can be *deflectable mirrors*, detection of motion of *microTdrive system* etc.

- Single molecule *nanojar*, thermally driven, with fullerene based wheel like motion is also reported.

- Mechanical applications are mainly dependent on the very strong *carbon nanotubes* which are as *stiff* and *hard* as diamond but *highly flexible*.

- These tubes are *semi-conducting* or metallic. The composite textile material containing carbon nanotubes and polymer polyvinyl alcohol are being produced.

- The nanotubes with  $30 \mu\text{m}$  in diameter and tensile strength of  $1.4$  to  $1.8 \text{ GPa}$  are reported to be produced and have future applications in *helmets*, *protective textiles*, *bullet proof cloths* etc.

- Cutting tools* made of nanocrystalline materials, such as tungsten carbide, tantalum carbide and titanium carbide, are more wear and erosion-resistant, and last longer than their conventional (large-grained) counterparts.

- Drills* used to bore holes in circuit boards.

- Living cells are described as living machines. Nanotechnology builds up the tiny machines through these biological systems, DNA-RNA, self assembly etc. resulting in more *efficient machines*.

- In chemical reactions e.g. when small amount of tin are deposited on Cu (111) single crystal at  $290 \text{ K}$ , it is observed that tin crystal proceed *spontaneously* in a systematic fashion leaving behind bronze alloy.

#### Lubricants

- Nanospheres of inorganic materials could be used as lubricants, in essence by acting as *nanosized 'ball bearings'*.

- The controlled shape make them more durable than conventional *solid lubricants* and *wear additives*.

- These nanoparticles reduce *friction* between metal surfaces, particularly at *high normal loads*.

#### 6.13.2 Medicine

► [May 2008 !]

- Nanomaterials are of the size  $1 \times 10^{-9} \text{ m}$ . Hence they are comparable or even smaller than a single cell  $10 - 100 \mu\text{m}$  and virus  $20 - 450 \text{ nm}$ , protein  $5 - 50 \text{ nm}$ . Thus the materials can freely move through tissues, they can also bind to a biological system.

- Endothelial layers* of fast growing tumour tissues are porous thus these nanoparticles can pass through them bringing out a specialised effect as a *medicine*.

- Drug delivery* is done through self assemblies like *phospholipids* or through block polymers. The drugs molecules can be interrelated in lipophilic wall which acts like a cell membrane.

- Liposome* protects the drug from being *assimilated* during digestion or metabolised in certain environments. Hydrophobic character of the *liposome* dissolves *drug* and allows it to pass through blood, brain, unaffected.

- When it arrives at a specific targetted site the drug is released due to *temperature* or *pH* at the site inflamed of the organ or the concentration at the site liposomes have *pH 4 - 5* and

- tumour tissues also have PH 4 – 5. Thus lysosomes open up at PH 4 – 5 allowing the drug to be released.

Magnetic components like  $\text{Fe}_3\text{O}_4$  magnetite or  $\text{Fe}_3\text{O}_8$  are coated with  $\text{SiO}_2$  and then with biocompatible polymer.

This polymer has *attachment point* for the attachment with *toxic drugs* or *anti bodies*. A magnet is placed outside the body near the target site to capture the magnetic particles, flowing in a circulatory system.

Similarly the action of cytostatic anticancer drugs is localised there by reducing side effects on the patients body especially arthritis, dextrane coated with iron oxides are used and are extracted via liver treatment.

For *localised destruction* of cancer cells this technique is used. It is called as *artificially induced hyperthermia*. *Magnetic particles* are *dispersed* through out the target tissue.

An alternating magnetic field of sufficient strength  $0 - 15 \text{ KA M}^{-1}$  and frequency  $0.05 - 1.2 \text{ MHz}$  is applied to heat up the deceased area and maintained at  $42^\circ\text{C}$  for 30 mins, thus *destroying cancer tissues*, retaining healthy tissues intact.

Magnetic particles are also used for *tagging* the specific biological entities like lung cancer cells, certain bacteria, urological cancer cells and also red blood cells thus making it possible to remove these cells through magnetic separation through fluid flow.

Magnetic particles are also used as contrast enhancing agents in the *MRI*. This shortens the relaxation time  $T_1$  and  $T_2$  for the tissue.

Larger particles of 30 nm are rapidly collected at liver, spleen where as particles  $< 10 \text{ nm}$  are collected in the *reticuloendothelial* cells through out the body i.e. lymph nodes bone marrow etc.

*Tumour cells* do not have reticuloendothelial system of healthy cells. Thus by contrast the site with these particle tissue can be located in *MRI*.

Thus making it easier accurate to detect brain tumour, liver tumour and lymph nodes.

Thus *coating* of *incompatible metallic* material with ceramic type of coating or interface formed by self assembly of monomolecular layers play an important role in medical field giving *biocompatibility* and *application*.

Nanomaterials due to their specific size interface grain boundaries possess unique properties. e.g. *hydrophobic* and *dirt repelling* molecules – reflecting the lotus effect triggered as a function of temperature or light exposure.

### 6.13.3 Catalysts

► [May 2008 : 1]

- In general, nanoparticles have a *high surface area*, and hence provide higher catalytic activity.

Nanotechnologies are enabling changes in the degree of control in the production of nanoparticles, and the support structure on which they reside.

It is possible to synthesise metal nanoparticles in solution in the presence of a *surfactant* to form highly ordered monodisperse films of the catalyst nanoparticles on a surface.

This allows more uniformity in the size and chemical structure of the catalyst, which in turn leads to greater catalytic activity and the production of fewer byproducts.

It may also be possible to *engineer* specific or *selective activity*.

These more active and durable catalysts could find early application in *cleaning up waste streams*.

This will be particularly beneficial if it reduces the demand for *platinum-group metals*, whose use in standard catalytic units is starting to emerge as a problem, given the limited availability of these metals.

### 6.13.4 Applications in Environmental Technology

- At present the use of nanomaterials in environmental technology is not yet explored but is on the way to be in use:
- Nanoporous *aluminosilicates* (*zeolites*) are being used in radio nuclides and poisonous transition metals removal from *waste water* due to their high *adsorption*.
- Nanoporous *membranes polymer membranes* with definite, desired adjustable pore size are used as *microfilters* for dust particles from air and water.
- This technology invites for future applications like *potable water* and *separation of viruses* and *bacteria*.
- Gold nanoparticles are used for degradation of toilet odour.  $\text{TiO}_2$  is used as a tunnel light shield coating it converts deposited carbon to  $\text{CO}_2$  thus keeping the shield transparent. Nano  $\text{ZnO}$  is used for degradation of chlorinated phenols.
- Futuristic use of a *nano-coating* on the *swimming pool walls* by photocatalytically active material can lead to activation of oxygen, forming *hydroxyl ions* which are antibacterial (alkaline) and also *degrade organic compounds*.

- Nanobased sensors, metal sensors, polymer sensors are used to analyse gas mixtures by measuring solubility of gases, vapour pressure, melting point etc. biosensors will be used in future as a lab on chip by chemists, biochemists, physicians, engineers etc.
- The potential of nanoparticles to react with pollutants in soil and groundwater and transform them into harmless compounds is being researched.
- In one pilot study the large surface area and high surface reactivity of iron nanoparticles were exploited to transform chlorinated hydrocarbons (some of which are believed to be carcinogens) into less harmful end products in groundwater.
- It is also hoped that they could be used to transform heavy metals such as lead and mercury from biowavailable forms into insoluble forms.

### 6.13.5 Applications in Electronics

#### ► May 2008 1

To increase the speed at which electric charges work, the distance between them needs to be decreased. Thus number of transistors per unit area increases every year. But there is a limit for this growth. A time at which the space to store one bit becomes about 4 nm, the things happen at quantum level heat will be developed, neighbourings bits would interact.

At present atomic scale memory is possible. A bit is encoded by the pres/abs of -Si atom inside  $5 \times 4 = 20$  atoms. Thus 19 atoms prevent or absorb the heat energy. Thus storage capacity of hard disks is increased. Thin films of organic materials emitting light (OLED) are known. Thin film transistors TFT and thin film organic photovoltaic cells are known.

The deposition at a reasonable cost is possible because of organo inorganic metallic compounds which are normally the soft assembled, nanomaterials. They can form thin films by simple techniques the spray, spin cooling vapour deposition, inkjet printing etc.

#### a) Displays

- The huge market for large area, high brightness, flat-panel displays, as used in television screens and computer monitors, is driving the development of some nanomaterials.
- Nanocrystalline zinc selenide, zinc sulphide, cadmium sulphide and lead telluride synthesized by sol-gel techniques (a process for making ceramic and glass materials, involving the transition from a liquid 'sol' phase to a solid 'gel' phase) are candidates for the next generation of light-emitting phosphors. CNT's are being investigated for low voltage field-emission displays; their strength, sharpness, conductivity and inertness make them potentially very efficient and long-lasting emitters.

#### b) Batteries

- With the growth in portable electronic equipment (mobile phones, navigation devices, laptop computers, remote sensors), there is great demand for lightweight, high-energy density batteries.
- Nanocrystalline materials synthesized by sol-gel techniques are candidates for separator plates in batteries because of their foam-like (aerogel) structure, which can hold considerably more energy than conventional ones.
- Nickel-metal hydride batteries made of nanocrystalline nickel and metal hydrides are envisioned to require less frequent recharging and to last longer because of their large grain boundary (surface) area.

#### c) Magnetic Materials

- It has been shown that magnets made of nanocrystalline yttrium-samarium-cobalt grains possess unusual magnetic properties due to their extremely large grain interface area (high coercivity can be obtained because magnetization flips cannot easily propagate past the grain boundaries). This could lead to applications in motors, analytical instruments like magnetic resonance imaging (MRI), used widely in hospitals, and microsensors
- Overall magnetisation, however, is currently limited by the ability to align the grains' direction of magnetisation.
- Nanoscale-fabricated magnetic materials also have applications in data storage.
- Devices such as computer hard disks depend on the ability to magnetize small areas of a spinning disk to record information. If the area required to record one piece of information can be shrunk in the nanoscale (and can be written and read reliably), the storage capacity of the disk can be improved dramatically. In the future, the devices on computer chips which currently operate using flows of electrons could use the magnetic properties of these electrons, called spin, with numerous advantages.
- Recent advances in novel magnetic materials and their nanofabrication are encouraging in this respect.

**6.13.6 General Applications**

a) Clays	b) Composites
c) Coatings and Surfaces	d) Sunscreens and Cosmetics
e) Paints	f) Fuel Cells
g) Fuel Additives	h) Carbon Nanotube Composites
i) Ceramics	j) Water Purification
k) Military Battle Suits	

**a) Clays**

- (1) Clays containing naturally occurring nanoparticles have long been important as construction materials and are undergoing continuous improvement.

- (2) Clay particle based composites – containing plastics and nano-sized flakes of clay – are also finding applications such as use in car bumpers.

- (4) A range of enhanced textiles, such as breathable, waterproof and stainresistant fabrics, have been enabled by the improved control of porosity at the nanoscale and surface roughness in a variety of polymers and inorganics.
- (2) Recently developed applications include the *self-cleaning window*, which is coated in highly activated *titanium dioxide*, engineered to be highly *hydrophobic* (water repellent) and *antibacterial*, and coatings based on *nano particulate oxides* that *catalytically destroy* chemical agents.
- (3) Wear and scratch-resistant hard coatings are significantly improved by nanoscale intermediate layers (or multilayers) between the hard outer layer and the substrate material. The intermediate layers give good bonding and graded matching of elastic and thermal properties, thus improving adhesion.

**d) Sunscreens and Cosmetics**

- (1) Nanosized *titanium dioxide* and *zinc oxide* are currently used in some sunscreens, as they *absorb* and *reflect* ultraviolet (UV) rays and yet are *transparent* to visible light and so are more appealing to the consumer.
- (2) Nanosized *iron oxide* is present in some *lipsticks* as a pigment but it is our understanding that it is not used by the European cosmetics sector.
- (3) The use of nanoparticles in cosmetics has raised a number of concerns about consumer safety.

**e) Paints**

- (1) Incorporating nanoparticles in paints could improve their *performance*, for example by making them *lighter* and giving them different properties. *Thin film* paint coatings ('lightweighting'), used for example on aircraft, would reduce their weight, which could be beneficial to the environment. However, the whole life cycle of the aircraft needs to be considered before overall benefits can be claimed.
- (2) It may also be possible to substantially *reduce solvent content* of paints, with resulting environmental benefits.
- (3) New types of *fouling-resistant marine paint* could be developed and are urgently needed as alternatives to *tributyl tin (TBT)*, now that the ecological impacts of TBT have been recognised.

(4) *Anti-fouling* surface treatment is also valuable in process applications such as *heat exchange*, where it could lead to *energy savings*. If they can be produced at sufficiently low cost, fouling-resistant coatings could be used in routine duties such as piping for domestic and industrial water systems.

(5) It remains speculation whether very effective anti-fouling coatings could reduce the use of biocides, including chlorine. Other novel, and more long-term, applications for nanoparticles might lie in paints that *change colour* in response to *change in temperature* or *chemical environment*, or paints that have reduced infra-red absorptivity and so *reduce heat loss*.

(6) Concerns about the health and environmental impacts of nanoparticles may require the need for the *durability* and *abrasion* behaviour of nano-engineered paints and coatings to be addressed, so that abrasion products take the form of coarse or microscopic agglomerates rather than individual nanoparticles.

#### f) Fuel Cells

(1) Engineered surfaces are essential in fuel cells, where the *external surface properties* and the *pore structure* affect performance.

(2) The hydrogen used as the immediate fuel in fuel cells may be generated from hydrocarbons by catalytic reforming, usually in a reactor module associated directly with the fuel cell.

(3) The potential use of nano-engineered *membranes* to *intensify catalytic processes* could enable higher-efficiency, small-scale fuel cells. These could act as distributed sources of *electrical power*.

(4) It may eventually be possible to *produce hydrogen* locally from sources other than hydrocarbons, which are the feedstocks of current attention.

#### g) Fuel Additives

Research is underway into the addition of nanoparticulate *ceria (cerium oxide)* to *diesel fuel* to improve fuel economy by *reducing the degradation* of fuel consumption over time.

#### h) Carbon Nanotube Composites

(1) CNTs have exceptional mechanical properties, particularly high tensile strength and light weight. An obvious area of application would be in *nanotubereinforced composites*, with performance beyond current carbon-fibre composites.

#### i) Ceramics

(1) Ceramics are hard, brittle and *difficult to machine*. However, with a reduction in grain size to the nanoscale, ceramic *ductility* can be *increased*. Zirconia, normally a hard, brittle ceramic, has even been rendered *superplastic* (for example, able to be deformed up to 300% of its original length).

(2) Nanocrystalline ceramics, such as *silicon nitride* and *silicon carbide*, have been used in such automotive applications as *high-strength springs*, *ball bearings* and *valve lifters*, because they can be easily formed and machined, as well as exhibiting excellent chemical and high-temperature properties. They are also used as components in high-temperature furnaces. Nanocrystalline ceramics can be pressed into complex net shapes and sintered at significantly lower temperatures than conventional ceramics.

#### j) Water Purification

(1) Nano-engineered membranes could potentially lead to more *energy-efficient* water *purification* processes, notably in *desalination* by *reverse osmosis*.

(2) Again, these applications would represent incremental improvements in technologies that are already available. They would use fixed nanoparticles, and are therefore distinct from applications that propose to use free nanoparticles.

**k) Military Battle Suits**

- (1) Enhanced nanomaterials form the basis of a state-of-the-art 'battle suit' that is being developed by the Institute of Soldier Nanotechnologies at MIT.
- (2) A short-term development is likely to be *energy-absorbing* materials that will withstand *blast waves*; longer-term are those that incorporate sensors to detect or respond to chemical and biological weapons (for example, responsive nanopores that 'close' upon detection of a biological agent).
- (3) There is speculation that developments could include materials which monitor *physiology* while a soldier is still on the battlefield, and uniforms with potential medical applications, such as *splints* for broken bones.

**Exercise**

- Q. 1** Define nanomaterials.
- Q. 2** State the size of H atom, C<sub>60</sub>, C nanotubes, DNA molecule etc. on nanometer scale.
- Q. 3** Why the properties of nanomaterials are different than the conventional materials.
- Q. 4** State the structural details of graphene.
- Q. 5** State the structural details of graphite.
- Q. 6** State the structural details of fullerene.
- Q. 7** What are carbon nanotubes what are their types.
- Q. 8** List the methods for production of carbon nanotubes.
- Q. 9** Explain any one method for the preparation of carbon nanotubes with the advantages of and limitations of this method over the other methods.
- Q. 10** What are nanotubes, how are they made and what are their applications?
- Q. 11** How and why nanotubes and nanowires are interesting materials? Describe their structures.
- Q. 12** Explain the use of nanomaterials in
- (i) Medicine
  - (ii) Electronics
  - (iii) Environment pollution control
  - (iv) Mechanics

**6.14 University Questions (Theory)****Dec. 2007****Q. 1** Explain the structure, properties and uses of fullerene. (Section 6.4) (2 Marks)**Q. 2** What are (i) SWCNT and (ii) MWCNT ? Describe the production of SWCNT by LASER method. (Section 6.7.2) (6 Marks)**Q. 3** Write short notes on, any two the following :  
(i) Nanocones (Section 6.11)  
(ii) Hackelite (Section 6.12) (6 Marks)**May 2008****Q. 1** What are carbon-nanotubes ? Explain different types of carbon-nanotubes. (Section 6.6) (2 Marks)**Q. 2** Explain the use of nano materials in the field of any two of the following :  
(i) Medicine (Section 6.13.2)  
(ii) Electronics (Section 6.13.5)  
(iii) Catalysis (Section 6.13.3) (6 Marks)

Q1. Explain with examples how nanomaterials can be used in the following fields  
i) Medicine ii) Electronics iii) Environment pollution control iv) Mechanics