

MU
Edition
2013

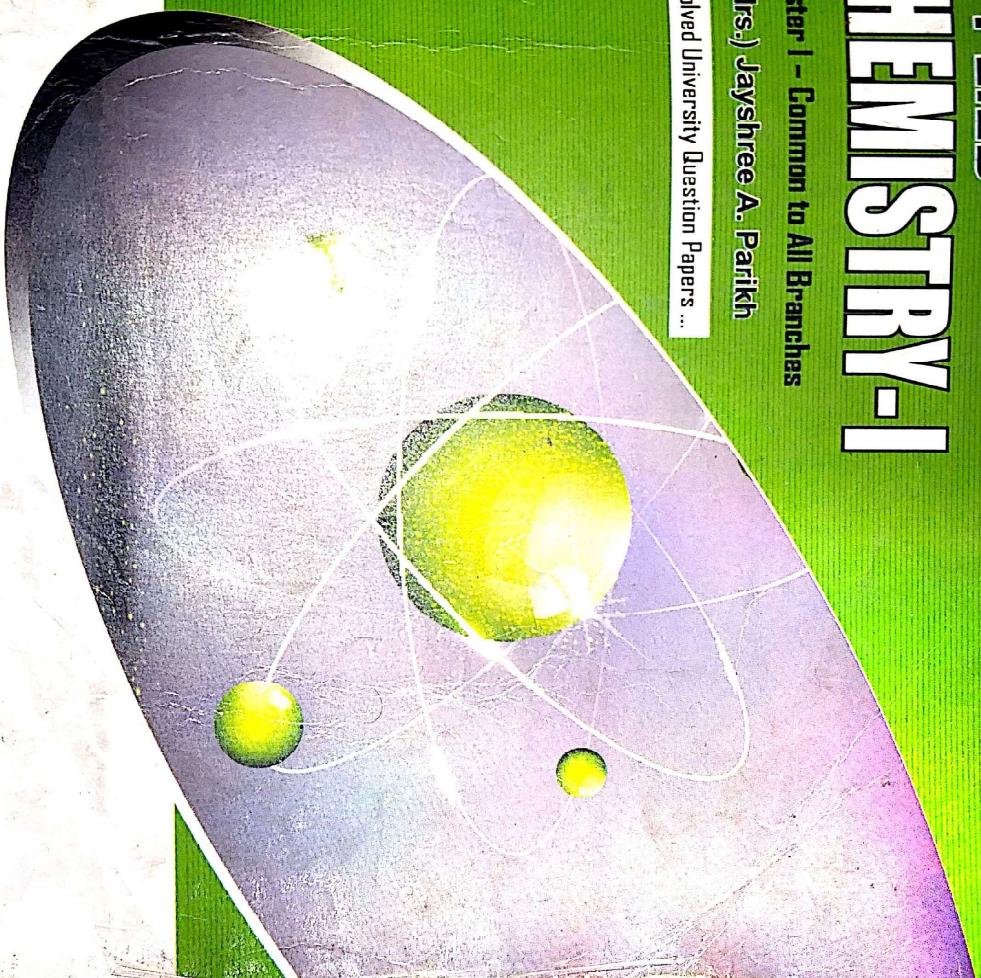
Strictly as per the new revised syllabus w.e.f. academic year 2012-2013

APPLIED **CHEMISTRY-I**

Semester I - Common to All Branches

Dr. (Mrs.) Jayshree A. Parikh

With Solved University Question Papers ...



Syllabus

Module 1 : Water

- Impurities in water, Hardness of water, Determination of Hardness of water by EDTA method and problems. Softening of water by Hot cold lime soda method and problems. Zeolite process and problems. Ion Exchange process and problems.
- Drinking water or Municipal water, Treatments removal of microorganisms, by adding Bleaching powder, Chlorination (no breakpoint chlorination), Disinfection by Ozone, Electrodialysis and Reverse osmosis, ultra filtration.
- **BOD, COD** (def & significance), sewage treatments activated sludge process, numerical problems related to COD. (Refer Chapter 1)

Module 2 : Polymers

- Introduction to polymers, Thermoplastic and Thermosetting plastic.
- Ingredients of the plastic (Compounding of plastic.)
- Fabrication of plastic by Compression, Injection, Transfer, Extrusion molding. Preparation, properties and uses of Phenolformaldehyde, PMMA, Kevlar.
- Effect of heat on the polymers (Glass transition temperatures) Polymers in medicine and surgery.
- Conducting polymers, Industrial polymers.

Rubbers

- Natural rubber (latex), Drawbacks of natural rubber, Compounding of rubber (vulcanization of rubber), Preparation, properties and uses of Buna-S, Silicone and Polyurethane rubber.

(Refer Chapter 2)

Module 3 : Lubricants

- Introduction, Definition, Mechanism of Lubrication, Classification of lubricants, Solid lubricants (graphite & Molybdenum disulphide), Semisolid lubricants (greases Na base, Li base, Ca base, Axle greases), Liquid lubricants (blended oils).
- Important properties of lubricants, definition and significance, viscosity, viscosity index, flash and fire points, cloud and pour points, oiliness, Emulsification, Acid value and problems, Saponification value and problems. (Refer Chapter 3)

Acknowledgement...

I sincerely acknowledge the chairman and Trustee of Suman Educational Trust for their motivational approach towards academic activities.

I sincerely thank my husband Dr. Akshay Parikh, my son Vinit and my daughter Urvi for their support and cooperation without which it would be impossible for me to achieve success at various stages in my academic progress, and especially for this edition, it would be impossible for me to cope up with time line due to my ill health.

This desire of mine to write this book was born from the need to help my students, professional peer, colleagues and well wishers for their active and moral support for writing this book.

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Prof. - Dr. (Mrs.) Jayshree A. Parikh

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Module 4 : Phase Rule

- Gibbs' Phase Rule, Explanation, One Component System (Water), Reduced Phase Rule, Two Component System (PbAg), Limitations of Phase Rule. **(Refer Chapter 4)**

Module 5 : Important Engineering Materials

- **Cement:** Manufacture of Portland Cement, Chemical Composition and Constitution of Portland Cement, Setting and Hardening of Portland Cement, Concrete RCC and Decay. **Refractories** Preparation, properties and uses of Silica bricks, Dolomite bricks, Silicon Carbide (SiC).
- **Nanomaterials,** preparation (Laser and CVD method), properties and uses of CNTS. **(Refer Chapter 5)**

Theory Examination

1. Question paper will comprise of total 6 questions, each of 15 marks.
2. Total four questions need to be solved.
3. Question - 1 will be compulsory and based on entire syllabus wherein sub questions of 2 to 3 marks will be asked.
4. Remaining questions will be mixed in nature (for example suppose Q.2 has part (a) from module 3 then part (b) will be from any module other than module 3)
5. 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. The distribution of marks for term work shall be as follows:
 - Laboratory Work (Experiments and Journal) : 10 marks.
 - Attendance (Practical and Theory) : 05 marks.
 - Assignments : 10 marks.
- Total : 25 marks
- The final certification and acceptance of TW ensures the satisfactory performance of laboratory work and minimum passing in the TW.

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CHAPTER 1

Water and its Treatment

Syllabus

Water

- Impurities in water, Hardness of water, Determination of Hardness of water by EDTA method and problems. Softening of water by Hot cold lime soda method and problems. Zeolite process and problems. Ion Exchange process and problems.
- **Drinking water or Municipal water,** Treatments removal of microorganisms, by adding Bleaching powder, Chlorination (no breakpoint chlorination), Disinfection by Ozone, Electrodialysis and Reverse osmosis, ultra filtration.
- **BOD, COD (def,& significance),** sewage treatments activated sludge process, numerical problems related to COD.

1.1 Introduction

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.

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) Underground water |

- 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/slurries; 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.

- ~~Alkalinity is due to carbonates, bi-carbonates or sulphates.~~
- Hardness is caused due to calcium and magnesium salts. Hardness is of two types :
 - (i) Carbonate hardness

- (ii) 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.

1.4 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".

1.5 Hardness of Water

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What is Hardness of water?

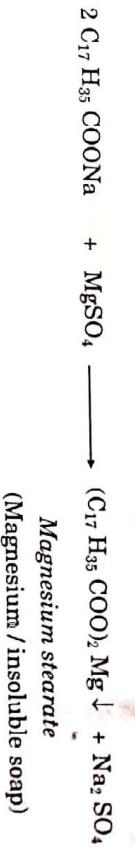
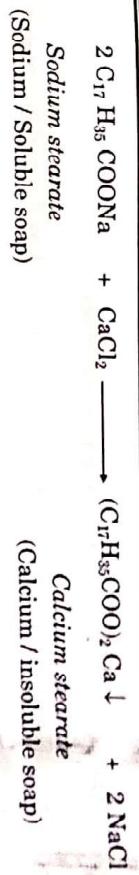
Hardness in water is that characteristic, which prevents the lathering of soap.

- Hardness was originally defined as, "the soap consuming capacity of a water sample."

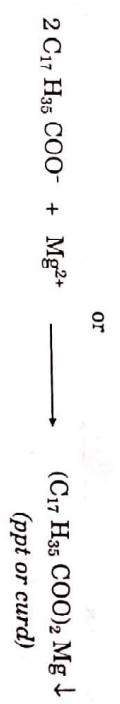
Soaps generally consist of sodium salts of long chain fatty acids such as oleic acid, palmitic acid and stearic acid.

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.



or



- Other metal ions like Fe^{2+} , Mn^{2+} and 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 Ca^{2+} and Mg^{2+} content.

1.6 Types of Hardness

There are two types of hardness, as :

Types of hardness

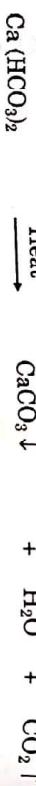
- Temporary or carbonate or alkaline hardness.
- Permanent or non-carbonate or non-alkaline hardness.

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1.6.1 Temporary or Carbonate or Alkaline Hardness

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

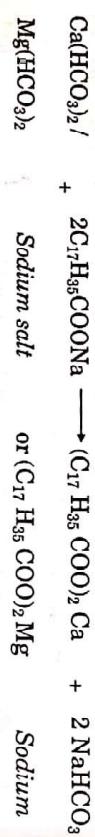
Temporary hardness is mostly removed by mere boiling of water, where bicarbonates are decomposed producing insoluble carbonates or hydroxides.



Calcium bicarbonate
(Insoluble)



Magnesium bicarbonate
Magnesium hydroxide



Bi-carbonates
of stearic acid

Calcium and magnesium (Impurity)
salt of stearic acid

1.7 Factors Influencing Hardness of Water (Causes of Hardness)

There are mainly three causes of hardness

Causes of hardness



- Dissolved minerals
- Dissolved Oxygen
- Dissolved Carbon-di-oxide

1.7.1 Dissolved Minerals

- Dissolved minerals are of *heavy metals*.

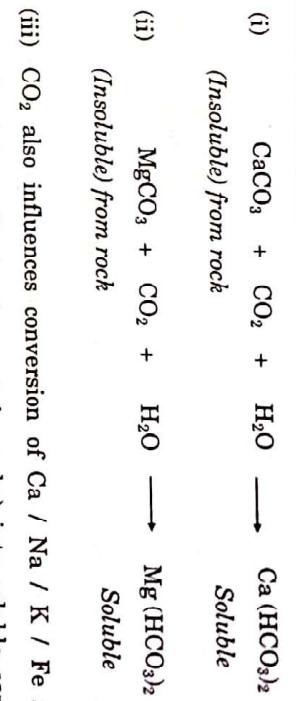
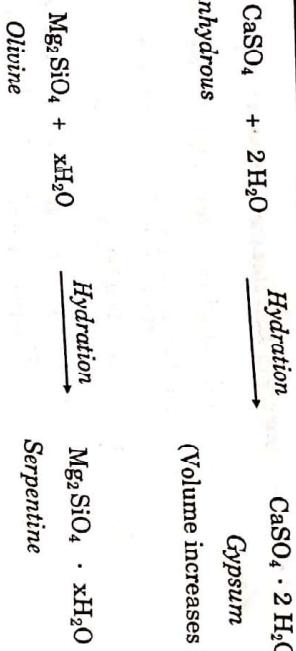
- They get assimilated in water in the form of their soluble salts.

- Thus contact with minerals influences hardness.

- Dissolution is followed by hydration process in which minerals like CaSO_4 (Anhydrite) or Mg_2SiO_4 (Olivine) react with water as,

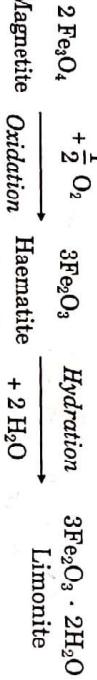


- The Ca / Mg carbonates or hydroxides thus formed being almost insoluble are deposited as a crust or scale at the bottom of the vessel; while CO_2 escapes out in air.



- Dissolved oxygen is also one of the major factor to influence the hardness in water.

D.O. influences oxidation and hydration of metal oxides / sulphides as,



1.8 Measurement of Hardness

- The extent of hardness is measured in terms concentration of ions contributing to hardness.
- It is usually expressed in terms of equivalent amount of CaCO_3 .
- The equivalents of CaCO_3 is convenient precisely because the molecular weight of CaCO_3 is 100 (equivalent weight is 50). The other reason this compound is being formed which gets precipitated during water treatment.

- The pH of water decreases due to dissolution of CO_2 from atmosphere. Due to this the dissolution of other minerals also increases.

- The following reactions are self explanatory that how dissolved CO_2 influences hardness of water,

1.8.1 Calculation of Equivalents of CaCO_3

- The equivalents of CaCO_3 for a hardness causing substance can be calculated by using following formula,

~~Mass of hardness producing substance~~

~~Multiplication factor~~

Equivalent of CaCO_3

~~Mass of hardness producing substance~~

$= \frac{\text{Mass of hardness producing substance} \times (\text{Chemical equivalent of } \text{CaCO}_3)}{\text{Chemical equivalent of hardness producing substance}}$

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

- 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 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 CaCO_3 .

- Table 1.8.1 gives the multiplication factor for converting various substances into equivalents of calcium carbonates.

Table 1.8.1 : 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) CaSO_4	136	68	100 / 136
(c) CaCl_2	111	55.5	100 / 111
(d) 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) MgSO_4	120	60	100 / 120
(c) MgCl_2	95	47.5	100 / 95
(d) MgCO_3	84	42	100 / 84
(e) $\text{Mg}(\text{NO}_3)_2$	148	74	100 / 148

1.9 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)

- One part per million (ppm) is a unit weight of solute per million unit weights of solution.
- In dilute solutions of density ≈ 1 , 1 ppm = 1 mg / litre. It is customary to express hardness in terms of equivalents of CaCO_3 . Hence, all the hardness causing impurities are first converted in terms of their respective weights equivalent to CaCO_3 and the sum total of the same is expressed in ppm.

Equivalent of 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 CaCO_3 equivalent hardness in 10^6 parts of water.

(ii) Milligrams per litre (mg / litre)

- It is the number of milligrams of CaCO_3 equivalent hardness present per litre of water.

Thus, hardness of 1 mg / litre = 1 mg of CaCO_3 equivalent hardness in 1 litre.

$$1 \text{ litre of water} = 1 \text{ kg} = 1000 \text{ g} = 1000000 \text{ mg}$$

$$= 10^6 \text{ mg}$$

$$\therefore 1 \text{ mg / litre} = 1 \text{ mg of } \text{CaCO}_3 \text{ equivalent per } 10^6 \text{ mg of water.}$$

$$\text{or } 1 \text{ mg / litre} = 1 \text{ part of } \text{CaCO}_3 \text{ equivalent per } 10^6 \text{ parts of water.}$$

$$= 1 \text{ ppm}$$

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

$$\text{mg/litre} = \text{ppm} \quad \text{write any same no}$$

conversion factor

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

- It is the number of grains (1 / 7000 lb) of CaCO_3 equivalent hardness per gallon (10 lb) of water or it is the parts of CaCO_3 equivalent hardness per 70,000 parts of water. Thus,

$$1 {}^\circ\text{Cl} = 1 \text{ grain of } \text{CaCO}_3 \text{ equivalent hardness per gallon of water or}$$

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

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

It is the parts of CaCO_3 equivalent hardness per 10^5 parts of water.

Thus,

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

Inter-relationships between various units of hardness :

$$1 \text{ ppm} = 1 \text{ mg / litre} = 0.1 {}^\circ\text{Fr} = 0.07 {}^\circ\text{Cl}$$

$$1 \text{ mg / litre} = 1 \text{ ppm} = 0.1 {}^\circ\text{Fr} = 0.07 {}^\circ\text{Cl}$$

$$1 {}^\circ\text{Cl} = 1.43 {}^\circ\text{Fr} = 14.3 \text{ ppm} = 14.3 \text{ mg / l}$$

$$1 {}^\circ\text{Fr} = 10 \text{ ppm} = 10 \text{ mg / l} = 0.7 {}^\circ\text{Cl}$$

1 mg / litre = 1 ppm	$1 \text{ ppm} = 1 \text{ mg / litre}$
	$1 \text{ ppm} = 0.07 {}^\circ\text{Cl}$
	$1 {}^\circ\text{Fr} = 10 \text{ ppm}$

Water classification on basis of hardness

Hardness (ppm)	Type
< 150	Good
150 to 350	Fair
350 onwards	Bad

1.10 Determination of Hardness of Water

X

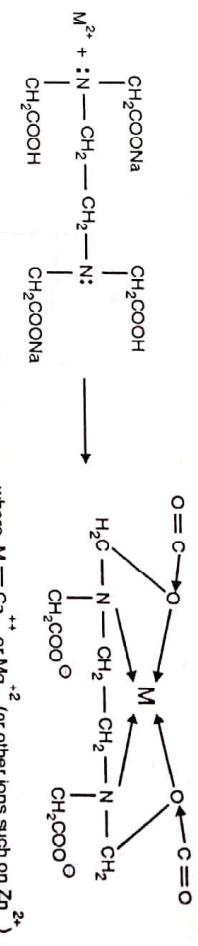
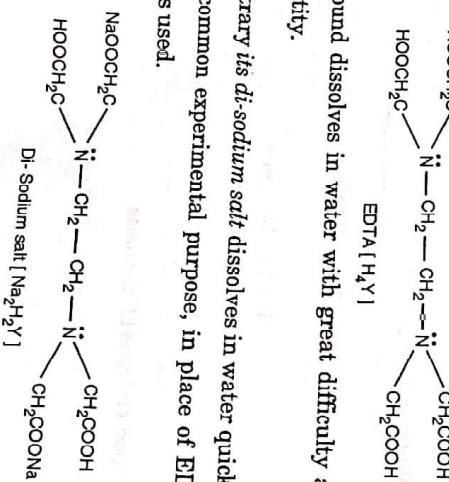
The hardness of water can be determined by following methods :

- (i) EDTA method – Used most widely
- (ii) O'Hehner's method – Not used commonly
- (iii) Soap titration method – Not used commonly

1.10.1 Determination of Hardness by EDTA Method

MU – Dec. 2010

- EDTA is abbreviation of Ethylene diamine tetra acetic acid.
- HOOCCH₂C—N—CH₂—CH₂—N—CH₂COOH
 HOOCCH₂C—N—CH₂—CH₂—N—CH₂COOH
 EDTA [H₄Y]
- 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.



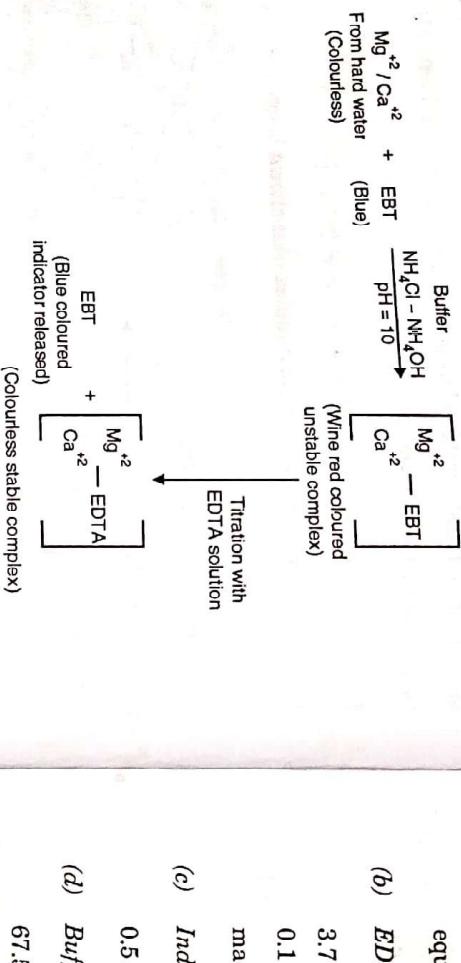
1.10.2 Principle of EDTA Method

MU – Dec. 2008, Dec. 2011

- The di-sodium salt of Ethylene diamine tetra acetic acid (EDTA) forms complexes with Ca²⁺ and Mg²⁺, as well as with many other metal cations, in aqueous solution.
- Thus, in a hard water sample, the total hardness can be determined by titrating Ca²⁺ and Mg²⁺ present in an aliquot of the sample with Na EDTA solution, using NH₄Cl. NH₄OH 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 Ca²⁺/Mg²⁺ 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).

- EDTA is a hexadentate ligand. It binds the metal ions in water i.e. Ca²⁺ or Mg²⁺ to give highly stable chelate complex. (These metal ions are bonded via oxygen or nitrogen from EDTA molecule).
- Therefore, this method is called as complex metric titration.
- The formation and structure of complex is as shown below :

Reaction



Thus noting the colour change, the point of equivalence can be trapped and hardness of water can be determined by using this method.

1.10.3 Procedure for EBT Titration

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

Step 1: Preparation of reagents

Step 2 : Titrations

Step 1: Preparation of reagents

One gram of pure, dry CaCO_3 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

Step 1: Preparation of reagents

The various solutions required can be made as follows:

(a) Standard hard water

One gram of pure, dry CaCO_3 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

Step 2 : Titration

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

(a) Standardization of EDIA 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 described above against EDTA solution (volume of EDTA = V_2 ml).

(c) *Estimation of permanent hardness*

filtered, diluted with distilled water to make 50 ml and titrated as above against EDTA solution. (Volume of EDTA = V_3 ml).

Step 1: Preparation of reagents

The various solutions required can be made as follows :

One gram of pure, dry CaCO_3 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_3 equivalent per ml (1 mg CaCO_3 / ml).

EDTA solution

3.7 grams of pure EDTA (Di-Sodium salt) crystals are mixed with 0.1 gram of $MgCl_2$, and dissolved in distilled water and the solution is made to 1 litre.

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 for calculation is given on page 76)

Advantages of EDTA method

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

1.11 Disadvantages of Hard Water

(F)

Effect of hard water

(1) Domestic purpose

- o Washing
- o Bathing
- o Cooking
- o 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

Since hard water, if used, causes problems, it is essential to soften the water.

There are two different methods softening,

1. Internal treatment
2. External treatment

Internal treatment involves conditioning treatment given to water during its usage in boilers.

In External treatment, hard water is treated with chemicals/resins/UV/UFR to bring down its hardness.

(3) Steam generation purpose : In boilers

1.12 Softening of Water

(F)

"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.

- Soft water is also used in many industries like paper, rayon, textile, ice, laundries, brewing, distilleries, pharmaceuticals, canning etc.

Internal treatment given to water helps to some extent especially to give a correction to the problems associated with use of water containing traces of certain salts. But internal treatment may not be sufficient to overcome the problems due to hard water when concentration of hardness causing salts is high. Under such circumstances softening methods are required to be used.

1. Lime soda process.
2. Zeolite process or permuntit process.
3. Ion-exchange or deionization or demineralisation process
4. Reverse osmosis
5. Ultrafiltration

1.12.1 Hot Cold Lime-Soda Process / Method

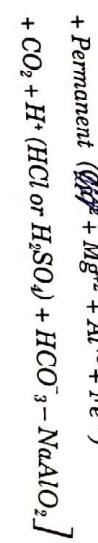
MU - Dec. 2007, Dec. 2010, May 2012, Dec. 2012, May 2013

Principle

In this method hard water is treated with calculated amounts of slaked lime, $[\text{Ca}(\text{OH})_2]$ and soda ash $[\text{Na}_2\text{CO}_3]$ 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,

$$L = \frac{74}{100} \left[\text{Temporary } Ca^{+2} + 2 \times \text{Temporary } Mg^{+2} \right.$$



all in terms of their $CaCO_3$ equivalents.

- Soda required for softening,

$$S = \frac{106}{100} \left[\text{Permanent } (Ca^{+2} + Mg^{+2} + Al^{+3} + Fe^{+3}) \right.$$



all in terms of their $CaCO_3$ equivalents.

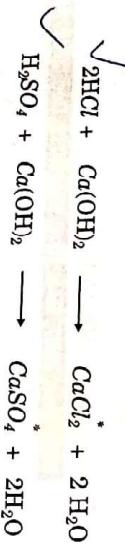
- Normally, about 10 % excess of chemicals are added in the reaction tanks to complete the reactions quickly.

(i) Reactions with lime

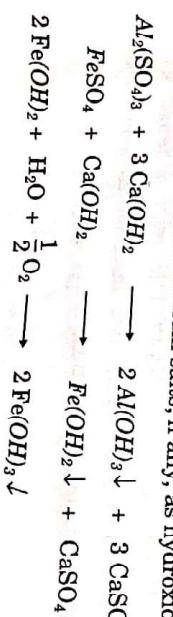
MU – Dec. 2011

Lime reacts in following ways, during softening of water.

- To neutralise any free acid present. For example



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



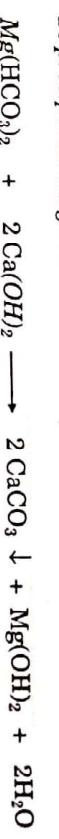
- To precipitate dissolved CO_2 as $CaCO_3$



- To precipitate calcium bicarbonate as $CaCO_3$



- To precipitate magnesium salts as hydroxides.



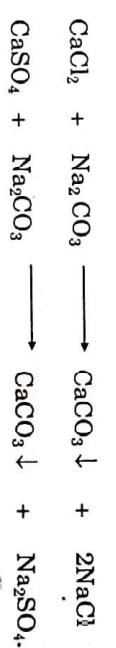
- To convert bicarbonate ions (like $NaHCO_3$, $KHCO_3$, etc) into carbonates.



- * $CaCl_2$ & $CaSO_4$ produced are to be treated as permanent hardness.

(ii) Reactions with soda

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

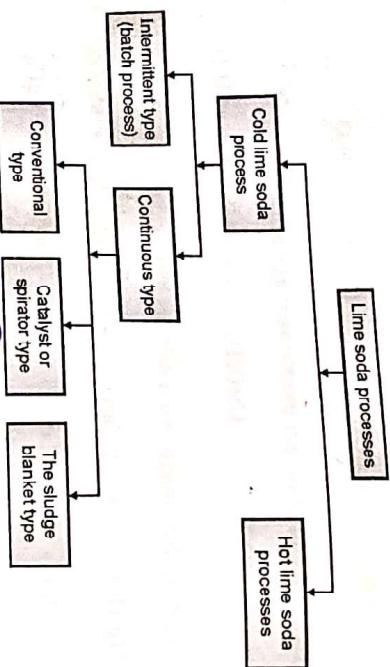


There are two types of lime soda processes as,

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

(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.



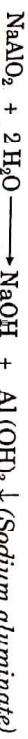
1. Cold lime soda process

- 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)
- (ii) Continuous type.

(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.

(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.

(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.

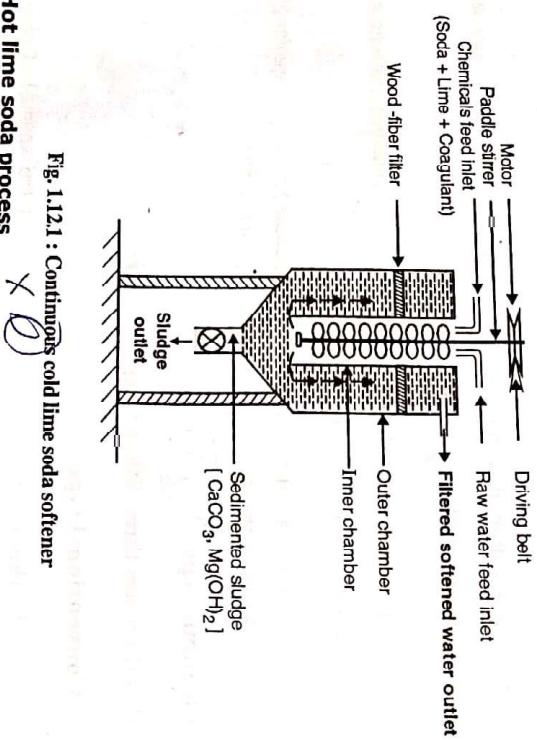


Fig. 1.12.1 : Continuous cold lime soda softener

2. Hot lime soda process

- When the chemicals are added at *higher temperature* (80 °C to 150 °C), the process is known as *Hot lime soda process*.
- This process is preferred as cold one because, at higher temperature
 - The reactions are fast
 - Precipitation is more complete
 - Settling rate and filtration rates are increased.

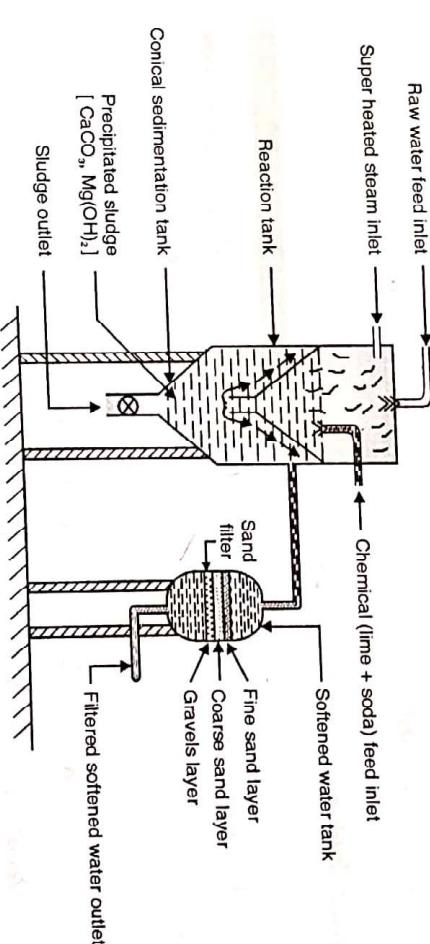


Fig. 1.12.2 : Continuous hot lime soda process

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.

- 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.

Construction :

- Hot lime soda plant essentially consists of three parts.
- A *conical sedimentation vessel* in which sludge settles down and thoroughly mixed.
- A *sand filter* which ensures complete removal of sludge from the softened water.

1. A *reaction tank* in which raw water, chemicals and steam are

thoroughly mixed.

2. A *conical sedimentation vessel* in which sludge settles down and

3. A *sand filter* which ensures complete removal of sludge from the

softened water.

- 3. To a certain extent, iron and manganese are also reduced.
- 4. Certain quantity of minerals are reduced from water.
- 5. Alkaline nature of water reduces pathogenic bacteria present in water to considerable extent.
- 6. Less amount of coagulants are required.

Disadvantages of lime soda process

MU - Dec. 2009

1. 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.
2. Careful operation and skilled supervision are required for economical and efficient softening.
3. Disposal of large quantity of sludge formed during process is a problem.

1.12.2 Zeolite or Permutit Process

MU - May 2008, May 2012, Dec. 2012

- The name zeolite (Greek : Zein-boiling, lithos-stone) means boiling stone. The chemical formula of sodium zeolite may be represented as,



(Zeolite = hydrated sodium alumino silicate)

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

- (i) Natural zeolites
- (ii) 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.

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

MU - Dec. 2009

a.	Thomsonite	: $(\text{Na}_2\text{O}, \text{CaO})$	$\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\frac{1}{2}\text{H}_2\text{O}$
b.	Natrolite	: Na_2O	$\text{Al}_2\text{O}_3 \cdot 4\text{SiO}_2 \cdot 2\text{H}_2\text{O}$
c.	Laumontite	: CaO	$\text{Al}_2\text{O}_3 \cdot 4\text{SiO}_2 \cdot 4\text{H}_2\text{O}$
d.	Harmotome	: $(\text{BaO}, \text{K}_2\text{O})$	$\text{Al}_2\text{O}_3 \cdot 5\text{SiO}_2 \cdot 5\text{H}_2\text{O}$
e.	Stilbite	: $(\text{Na}_2\text{O}, \text{CaO})$	$\text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2 \cdot 6\text{H}_2\text{O}$
f.	Brewsterite	: $(\text{BaO}, \text{SrO}, \text{CaO})$	$\text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2 \cdot 5\text{H}_2\text{O}$
g.	Ptilolite	: $(\text{CaO}, \text{K}_2\text{O}, \text{Na}_2\text{O})$	$\text{Al}_2\text{O}_3 \cdot 0\text{SiO}_2 \cdot 5\text{H}_2\text{O}$

(ii) Synthetic zeolites

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

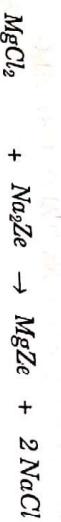
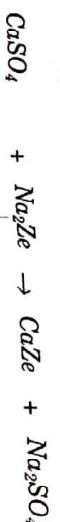
- (a) China clay, felspar and soda ash and granulating the resultant mass after cooling.
 - (b) Solutions of sodium silicate, aluminium sulphate and sodium aluminate.
 - (c) Solutions of sodium silicate and aluminium sulphate.
 - (d) Solutions of sodium silicate and sodium aluminate.
- Synthetic zeolites have higher exchange capacity per unit weight.

Principle of zeolite-permutit process

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

- sodium salts are released which remain in water. When zeolite gets exhausted it is regenerated and can be used again for softening water.

Reactions taking place during the softening process are :

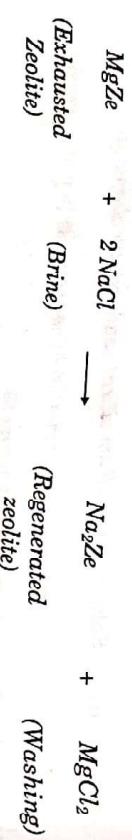


Iron and manganese present in small quantities are also removed as follows:



Regeneration of zeolite - permuntit 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 CaCl_2 and 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 Ca^{+2} and Mg^{+2} are retained in zeolite bed and soft water rich in Na^+ salts 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.

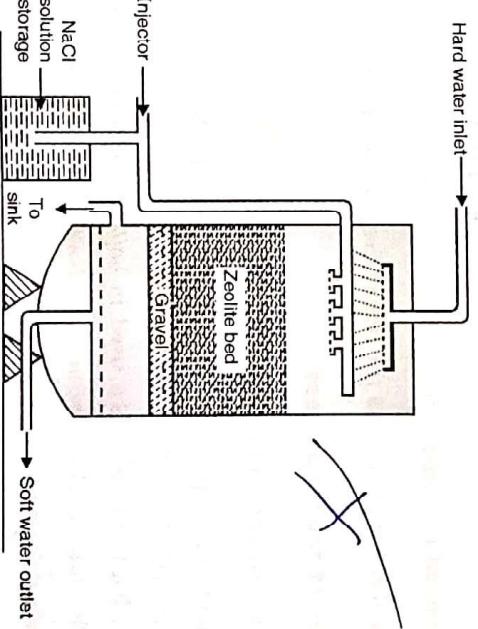


Fig. 1.12.3 : Zeolite Softner

Limitations of zeolite process

1. Turbid water (containing suspended impurities) can not be admitted to the zeolite bed, otherwise it will block the pores of zeolite and make zeolite inactive. Hence, suspended impurities must be removed before passing water through.
2. If the water contains coloured ions such as Fe^{2+} , they must be removed first, because these ions produce iron zeolite which cannot be easily regenerated.
3. Mineral acids if present in water, destroy the zeolite bed and therefore they must be neutralized with soda before water being entered into zeolite plant.

Advantages of zeolite process

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

Disadvantages of zeolite process

1. The treated water contains more sodium salts.
2. The method only replaces Ca^{2+} and Mg^{2+} ions by Na^+ ions, but leaves all acidic ions (HCO_3^- and CO_3^{2-}) in soft water. Such soft water containing (NaHCO_3 , Na_2CO_3) etc. when used in boilers, NaHCO_3 decomposes to give CO_2 which causes boiler corrosion and Na_2CO_3 hydrolyses to NaOH , causing caustic embrittlement.

1.12.3 Ion Exchange Process / Demineralization Process

MU - May 2009, Dec. 2009, May 2010, May 2013

- 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
 - (a) Polycondensation and
 - (b) 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 ($-\text{COOH}$, $-\text{SO}_3\text{H}$, 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 ($\text{R}'(\text{OH})$)

- The resin containing *basic functional groups* (e.g. $-\text{NH}_2$, $=\text{NH}$, 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 :



- Resins available for water treatment are listed in tabular form as,

Types of ion-exchange	Functional groups
(1) Cation-exchangers	
(a) Strongly acidic	SO_3^{H}
(b) Weakly acidic	COOH or $-\text{OH}$

Types of ion-exchange	Functional groups
(2) Anion-exchangers	
(a) Strongly basic	NR_3^+ , $-\text{CH}_3$, $\equiv\text{P}^*$ etc.
(b) Weakly basic	$-\text{NH}_2$, $-(\text{C}_2\text{H}_4)_x$, $(\text{NH})_y^-$

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,



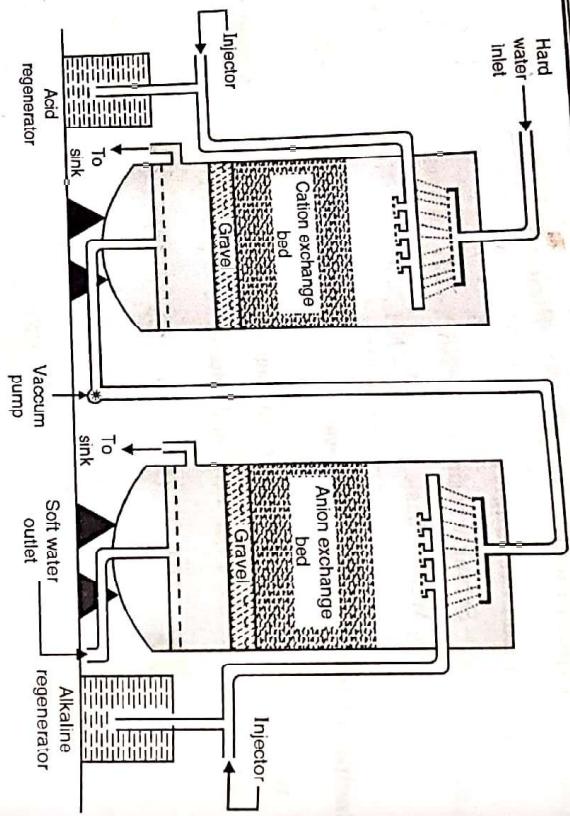


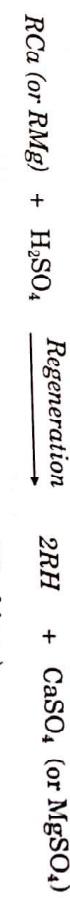
Fig. 1.12.4 : Demineralization of water

- Thus, the water coming out from anion exchange bed becomes *free of cations as well as from anions.*
- The resulting ion-free water is *deionized water* or *demineralised water*.
- The water is finally freed from dissolved gases by passing it through a degasser, 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 H₂SO₄ solution.



Process of ion-exchange/demineralisation

- The hard water is first passed through cation exchange column and then through anion exchange column (Fig. 1.12.4).
- 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 ppm.)

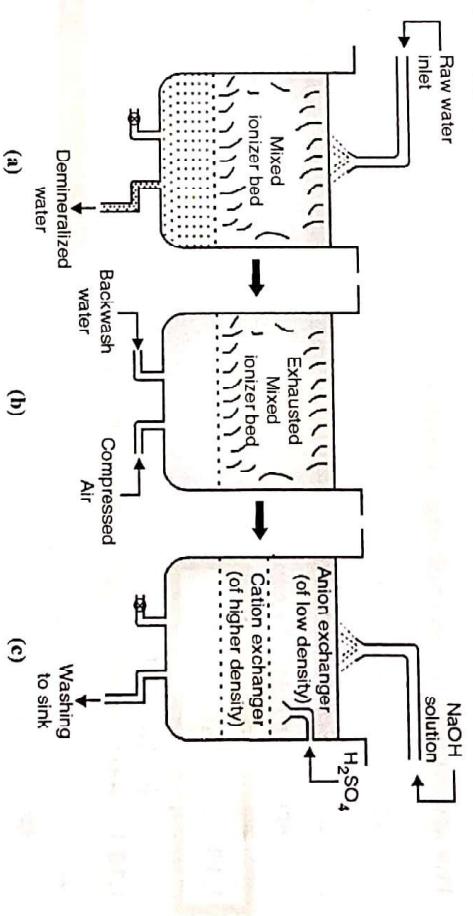
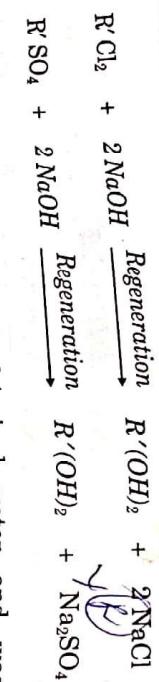


Fig. 1.12.5 : Regeneration of mixed ion exchange

- The exchange bed is washed with deionised water and washings (containing Ca²⁺, Mg²⁺, and Cl⁻ or SO²⁻) are passed to sink or drain.

- The exhausted anion exchanger is regenerated by treating it with a dilute NaOH solution.



- The exchanger bed is washed with deionised water and washings (containing NaCl or Na₂SO₄) are passed to sink or drain.
- The regenerated ion-exchange 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 ppm.

1.13 BOD and COD

Biological Oxygen Demand (BOD)

MU – Dec. 2008, Dec. 2011

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



- 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.

$$\therefore BOD = (DO)_1 - (DO)_2$$

Where (DO)₁ = Dissolved oxygen of diluted water sample immediately after its preparation.

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

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

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

Significance of BOD :

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

1.13.2 Chemical Oxygen Demand (COD)

MU - 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 :

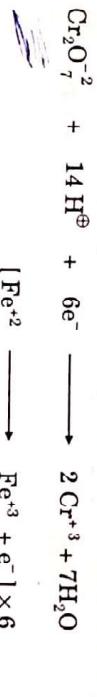
- A known volume of sample is refluxed with a known excess of $K_2Cr_2O_7$ solution in 50% H_2SO_4 , in the presence of Ag_2SO_4 (Catalyst), and $HgSO_4$.
- $K_2Cr_2O_7$ is strong oxidizing agent, in acidic medium. It oxidizes the organic matter into CO_2 and H_2O .

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 ($FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6 H_2O$) using ferroin as indicator. At end point blue colour changes to wine red.



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.

1.13.3 Difference between BOD and COD

MU - Dec. 2012, May 2013

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 $K_2Cr_2O_7$ and 50% H_2SO_4 and then titrating the unreacted $K_2Cr_2O_7$ solution against FAS solution.

$$4. BOD = \frac{(DO)_1 - (DO)_2}{x} ppm$$

$$COD = \frac{(V_2 - V_1) \times N \times 8 \times 1000}{V} ppm$$

- (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.

Sr. No.	BOD	COD
Where,	Where	
$(DO)_1 = DO \text{ in blank titration}$ $(DO)_2 = DO \text{ of the sample after}$ $x = \frac{\text{Volume of sample}}{\text{Total volume to which it was diluted}}$	$V_1 = \text{Volume of FAS for sample titration}$ $V_2 = \text{Volume of FAS for blank titration}$ $V = \text{Volume of sample taken for the test}$	$N = \text{Normality of FAS solution}$

1.14 Sewage Treatment

MU - Dec. 2009, May 2010

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.

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.*

- There are anaerobic and aerobic biological treatments. The former one is slow and in the absence of oxygen, thus commonly used for waters with higher concentrations of pollutants.
- During treatment, some useful materials may be recovered, thereby collecting water of better quality either for reuse or safe disposal.
- Biological waste water treatment involves conversion of colloidal and dissolved solids into settleable solids by microorganisms under favourable environmental conditions.

- The aerobic biological method is fast, in the presence of oxygen, which is described as *activated sludges process and trickling filters*.

Activated sludge process for sewage treatment

MU - May 2008, Dec. 2008, May 2009, Dec. 2009, May 2010, Dec. 2010, Dec. 2011

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 treated for the following reasons :

- 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.
- 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.
- To prevent the destruction of fish and other aquatic life.
- 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.

1.14.1 Broad Outline of Sewage Treatment by Activated Sludge Process

MU-Dec. 2012

- 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 :

- Preliminary treatment
- Primary treatment
- Secondary or biological treatment
- Disinfection.

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.

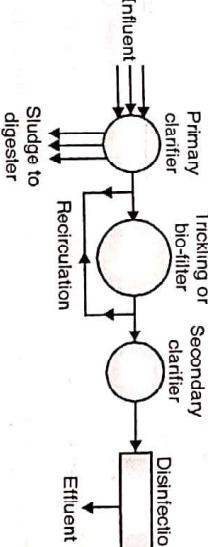


Fig. 1.14.1 : Stages in sewage treatment

- 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.
- 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.
 - 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. 1.14.1.

- o Trickling filters consists of circular beds, 2 - 5 m high, filled with porous lumpy materials, e.g. hard coke.
 - o The waste water is poured on the filter bed with the help of a rotatory sprinkler.
 - o As the waste water percolates the filter bed, the aerobic bacteria grow using the organic matter in the sewage as their food.
 - o It is necessary to maintain *highly aerobic condition*.
 - o 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.
 - o The process is comparatively *very fast*, if the aerobic condition is maintained.
 - o 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.
- Disinfection**
- o After the secondary or biological treatment the effluent free from sludges is subjected to *disinfection*.
 - o It is *chlorinated* to kill the bacteria which may remain in the effluent of sewage.
 - o 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.
 - o 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.
 - o If the water is only to be safely disposed off, then the treatment steps are chosen accordingly and vice versa.

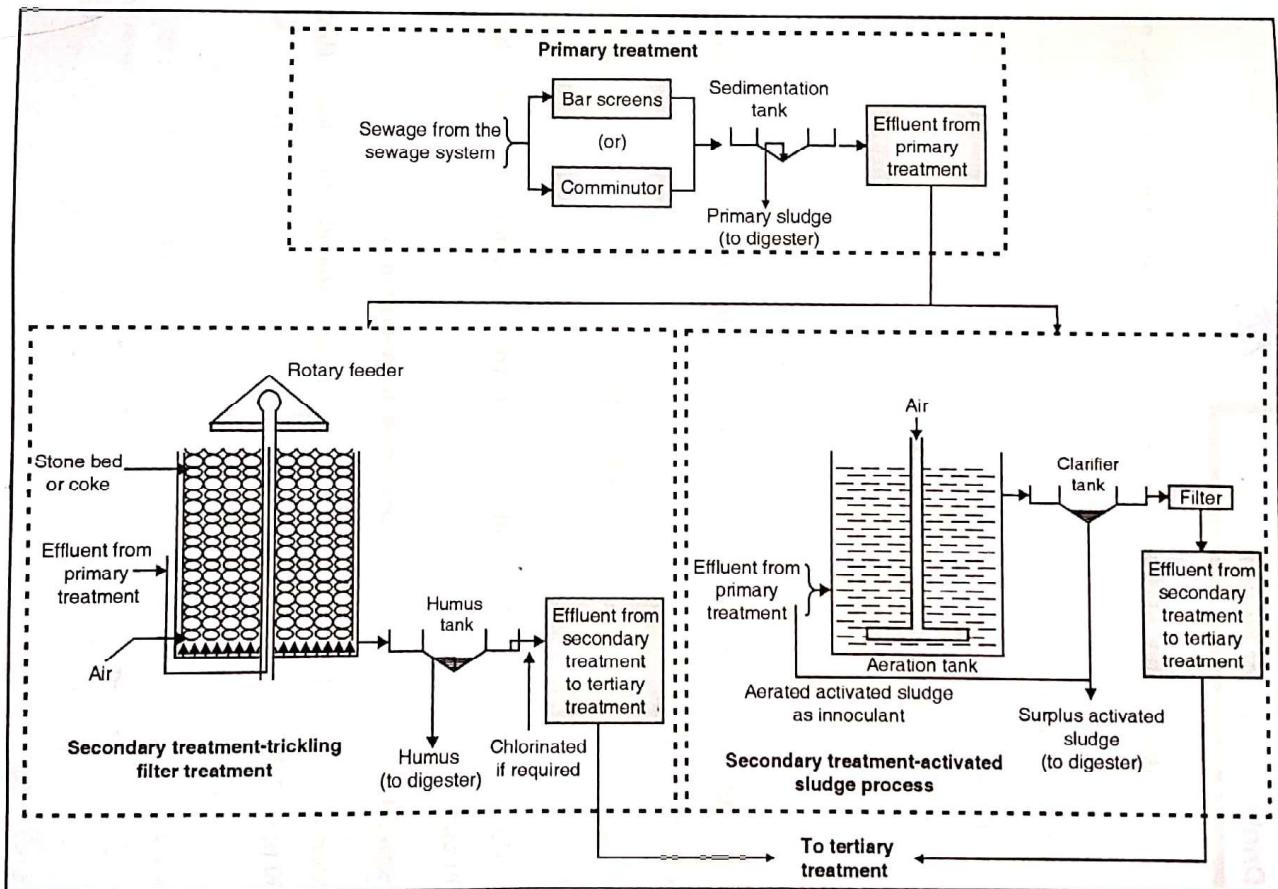


Fig. 1.14.2 : Schematic diagram activated sludge process

1.15 Drinking Water or Municipal Water

The following table summarises water quality standards :

Table 1.15.1 : Standards for municipal water or drinking water

- The municipal supply of water should have following characteristics, or specific standards :
- It should be colourless and odourless,
 - It should be good in taste,
 - It should not be hot,
 - Its turbidity should be less than 10 ppm,
 - It should be free from objectionable dissolved gases like H_2S ,
 - It should be free from objectionable minerals such as lead, arsenic, chromium and manganese salts,
 - Its alkalinity should not be high. pH should be in the range of 7.0 – 8.5.
 - It should be reasonably soft, total hardness should be less than 500 ppm.
 - It should be free from disease-producing micro-organisms.
 - Chloride, Fluoride and sulphate contents should be less than 250 ppm, 1.5 ppm and 250 ppm respectively.

Sr. No.	Characteristics/Impurities	Specified/Recommended standard
		ISI (mg/L) WHO (mg/L)
1.	Colour, Odour and Taste	Colourless, Odourless and Tasteless
2.	pH	6.9
3.	Total dissolved solids	–
4.	Dissolved oxygen	3.0
5.	Chloride	600
6.	Sulphate	1,000
7.	Nitrate	–
8.	Cyanide	0.01
9.	Fluoride	3.0
10.	Chromium	0.05
11.	Lead	0.1
12.	Arsenic	0.2
		0.05

As discussed above, the water being an important commodity is required to be in pure form, for different uses. Hence it is important to analyse the water for various impurities. Different tests done are to test, hardness, chloride, alkalinity, DO, COD, BOD etc.

In any town, village or city the water supply has been monitored by municipality of the respective area. The most common sources of water are river, lake, wells etc. But the water getting accumulated in these is not fit to be used directly, especially for drinking purposes and also cooking purposes. Hence, the water is required to be treated to make it 'potable'.

Treatment of water

The combination of treatment methods depends upon the nature and extent of impurities present in water. The Table 1.15.2 gives broad idea about the choice of technique employed for particular category of impurities existing in the water.

Table 1.15.2 : Techniques for treating impurities in water

Sr. No.	Type of impurity	Technique
1.	Floating matter (e.g. wood pieces, leaves, flowers, fruits etc.)	Screening or filtration.
2.	Suspended impurity (e.g. clay, sand, dust etc.)	Sedimentation
3.	Fine suspended inorganic matter (e.g. silica, mica, fine dust etc.)	Sedimentation with coagulation.
4.	Colloidal impurities.	Filtration or ultra filtration.
5.	Micro organisms.	Disinfection and/or sterilisation.
6.	Pathogenic Bacteria.	Disinfection and/or sterilisation.
Each of the technique is described in brief,		

Screening or filtration

In this process, raw water is passed over screens / sieves of larger size holes, to remove large size floating matter present in water.

Sedimentation

In this process, the water free from floating matter, is collected in tanks and allowed to stand undisturbed for about 2-10 hours. The suspended particles settle down at the bottom of tank, due to gravitational force. The water is decanted and collected in other tank leaving behind the settled matter.

By this process, water is free from the medium size suspended matter (almost 75%).

Sedimentation with coagulation

Coagulation accompanied with sedimentation is essential under conditions where only 'sedimentation' does not remove the impurities.

e.g. Fine silica, clay or organic matter do not settle down easily, thus making 'sedimentation' alone as unsuccessful technique. In such cases if coagulants like Alum $[K_2SO_4, Al_2(SO_4)_3, 24H_2O]$ or sodium aluminate ($NaAlO_2$) is added to water, impurities settle down at faster rate. This is because the coagulant, when added to water, gets hydrolysed and forms gelatinous precipitate of $Al(OH)_3$. This ppt of $Al(OH)_3$ is insoluble, and is flocculant in nature. Hence, as it descends in water to settle down, traps fine impurities, forms larger flocs and thus settle down with impurities, faster. These coagulants are pH sensitive and adjusting pH in particular range, the best results can be obtained.

e.g. Alum : Ideal pH range \rightarrow 6.5 - 8.5

$FeSO_4$: Ideal pH range \rightarrow > 8.5

$Na AlO_2$: Ideal pH range \rightarrow 5.5 - 8.0

Filtration

This is the last stage of purification process, where settled precipitates are removed. By and large sand filters are used where beds of fine and coarse sand and gravels is used for filtration.

The uppermost layer is of fine sand, followed by coarse sand, fine gravels and lastly coarse gravels.

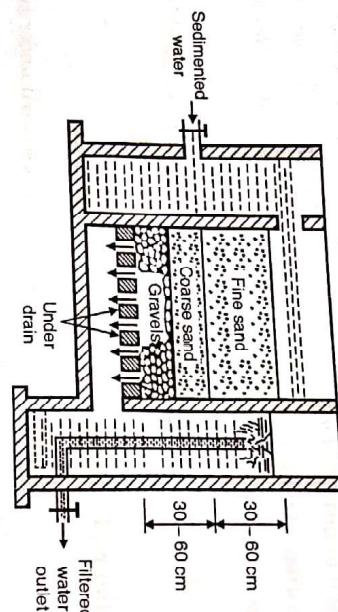


Fig. 1.15.1 : Sand filter

Through inlet, the sedimented water is allowed to enter the tank. It gets percolated due to gravitational force, leaving its impurities on fine sand layer. Intermittently, the top layer is changed with new one whereas the used one is cleaned, dried and reused.

The method is simple, fast, economic and hence used widely.

1.15.1 Removal of Micro-organism

Followed to removal of all solid impurities, the disease causing pathogenic bacteria are removed / destroyed. This is highly important especially for water to be potable.

"Process of destroying micro-organism / bacteria is known as dis-infection." But dis-infection may not destroy all the bacteria. Therefore, when totally pure form of water is desired e.g. during epidemics, the process of dis-infection is replaced by "sterilisation".

Sterilisation is a process which completely destroys the bacteria and micro-organisms.

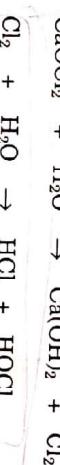
Water can be sterilised by boiling for a period of time as required, and then used. But sterilisation in this way is feasible for small scale requirements. For municipal supply of water to larger population, this method does not help.

Water is disinfected by

- (i) Addition of bleaching powder.
- (ii) Chlorination.

1.15.2 By adding Bleaching Powder

Bleaching powder reacts with water as,



Hypochlorous acid



Nascent oxygen

In these reactions above, the HOCl deactivates the enzymes present in the cells of micro-organism.

Thus the metabolic activity of micro-organism gets affected, thereby making the micro organism inactive. Finally it dies.

Disadvantages of Bleaching powder are,

- (i) If used in excess, imparts bad smell and taste to treated water.
- (ii) It produces excess calcium thereby making water more hard.

1.15.3 Chlorination

The reaction of chlorine is as,



With very small concentration of chlorine, HOCl thus formed destroys the bacteria, as it is a powerful germicide.

The apparatus used for chlorination is called as 'chlorinator'. Application of Cl_2 can be as gas or concentrated solution in water.

The raw water and concentrated chlorine solution ($0.3 - 0.5$ ppm Cl_2) is passed through the chlorinator. The water and Cl_2 solution get mixed thoroughly in the chlorinator due to baffle plates, and sterilised water is collected using outlet.

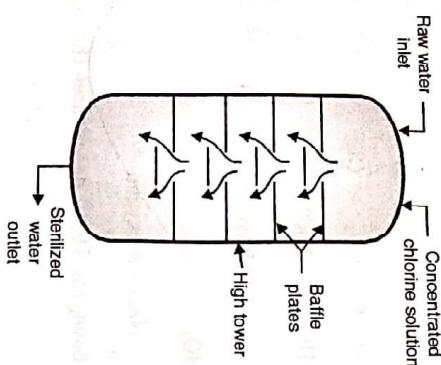


Fig. 1.15.3 : Chlorinator

The dis-infection is governed by nature of substances used, and sterilisation by chlorination is governed by temperature of (i) water, (ii) time of contact (iii) pH of water.

Characteristics of an ideal disinfectant

1. Should not be toxic to humans.
2. Should be economic.
3. Should act at Room Temperature killing all micro-organisms.

4. Should retain the treated water quality during storage and / or transport.

The process of dis-infection is not very popular as it cannot prevent contamination of water during storage or transportation. Hence, sterilisation is preferred.

Factors affecting efficiency of chlorine

- (i) Temperature of water : The efficiency increases with rise in temperature.
- (ii) Time of contact : With time, efficiency goes on decreasing.
- (iii) pH of water : At lower pH values (between 5-6.5) the efficiency is higher.

Advantages of using chlorine as disinfectant

- (i) The use of chlorine is more effective and economical,
 - (ii) It is stable, requires small space for storage and does not deteriorate on keeping,
 - (iii) It can be used at high as well as low temperatures,
 - (iv) It does not introduce any impurity in treated water.
- To sum up, chlorine is the most ideal disinfectant.

Disadvantages of using chlorine as disinfectant

- (i) If excess of chlorine is added, it produces bad taste and disagreeable odour.
(As a result of chlorination of phenols, leading to the formation of chlorophenols, water acquires a peculiar odour).
 - (ii) Excess chlorine produces irritation on mucous membrane,
 - (iii) It is not effective at higher pH values.
- "The treated water should not contain more than 0.1-0.2 ppm of free chlorine."

Disinfection by other substances
Other substances or methods such as chloramine, ozone, potassium permanganate, UV light etc. are also used for the disinfection of water for municipal purposes.

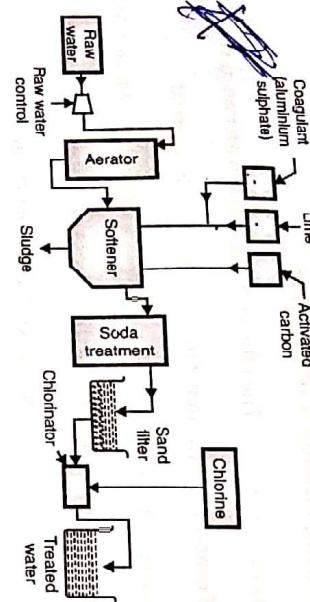
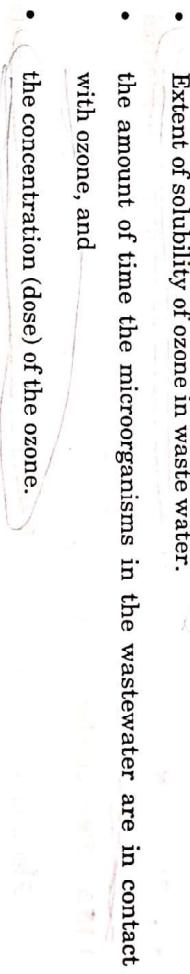


Fig. 1.15.3(A) : Flow sheet diagram showing municipal water treatment

1.15.4 Disinfection by Ozone

One common method of disinfecting wastewater is ozonation (also known as ozone disinfection). Ozone is an unstable gas that can destroy bacteria and viruses. It is formed when oxygen molecules (O_2) collide with oxygen atoms to produce ozone (O_3).



Ozone is generated by an electrical discharge through dry air or pure oxygen and is generated onsite because it decomposes to elemental oxygen in a short amount of time. After generation, ozone is fed into a down-flow contact chamber containing the wastewater to be disinfected. From the bottom of the contact chamber, ozone is diffused into fine bubbles that mix with the downward flowing wastewater.

Ozone disinfection process diagram

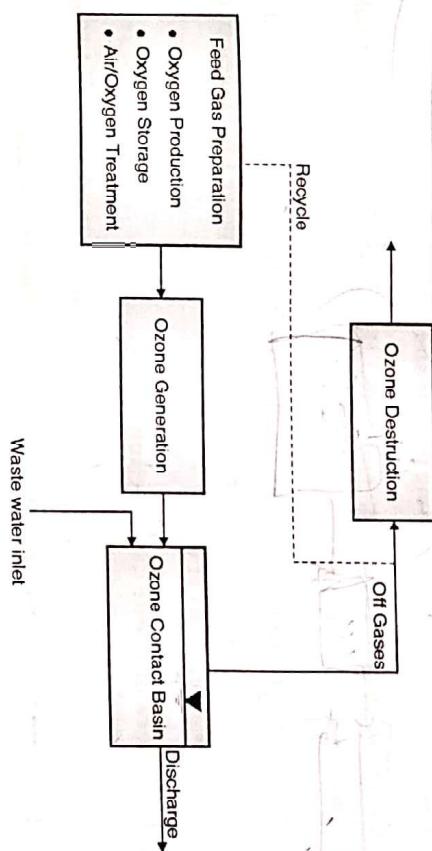


Fig. 1.15.4 : Ozone disinfection process diagram

Factors influencing ozone disinfection :

The effectiveness of the ozonation process depends on :

- how susceptible the bacteria, viruses, and other microorganisms are to the ozone,

- Extent of solubility of ozone in waste water.
- the amount of time the microorganisms in the wastewater are in contact with ozone, and
- the concentration (dose) of the ozone.

Advantages of ozone disinfection

- Ozone is more effective than chlorine in destroying viruses and bacteria.
- The wastewater needs to be in contact with ozone for just a short time (approximately 10 to 30 minutes).
- Ozone decomposes rapidly, and therefore, it leaves no harmful residual that would need to be removed from the wastewater after treatment.

- There is no regrowth of microorganisms after ozonation, unlike the sterilization by using bleaching powder and chlorine disinfection.
- Ozone is generated onsite, and thus, there are fewer safety problems associated with shipping and handling.
- Ozonation increases the dissolved oxygen (DO) concentration of the discharged wastewater. The increase in DO can improve the oxygen content of the receiving body of water.

Disadvantages of ozone disinfection

- Low dosages may not effectively inactivate some viruses, spores and cysts.
- Ozonation is more complex than other disinfection technologies.
- Ozone is very reactive and corrosive, thus requiring corrosion-resistant material, such as stainless steel.
- Ozonation is not economical for poor quality (poorly treated) wastewater.
- Ozone is extremely irritating and possibly toxic, so off-gases from the contactor must be destroyed to prevent worker exposure.
- The cost of treatment is relatively high, being both capital and power intensive.
- There is no measurable residual to indicate the efficacy of ozone disinfection.

1.15.5 Electrodialysis (ED)

Electrodialysis (ED) is an electrochemical process in which ions migrate through ion-selective semipermeable membranes as a result of their attraction to two electrically charged electrodes. ED is able to remove most charged dissolved ions.

Contaminants treated by ED

ED is useful for making water free from metals such as barium, selenium, nitrates and nitrites, and TDS.

Description of process

Pretreatment

Initially, scale inhibitor is added to prevent scaling and reduce the concentrate LSI below 2.1 in the concentrate stream,

Residual chlorine concentration of 0.5 mg/L is maintained to prevent biological growth, and H₂S is removed using a cartridge filter (10-20 μm) or air stripping ED/EDR.

Principle

Electrodialysis is a process that depends on the principle that most dissolved salts are positively or negatively charged and they will migrate to electrodes with an opposite charge. Thus ED uses selective membranes which are able to allow the passage to either anions or cations in an alternating fashion to create concentrate and product streams.

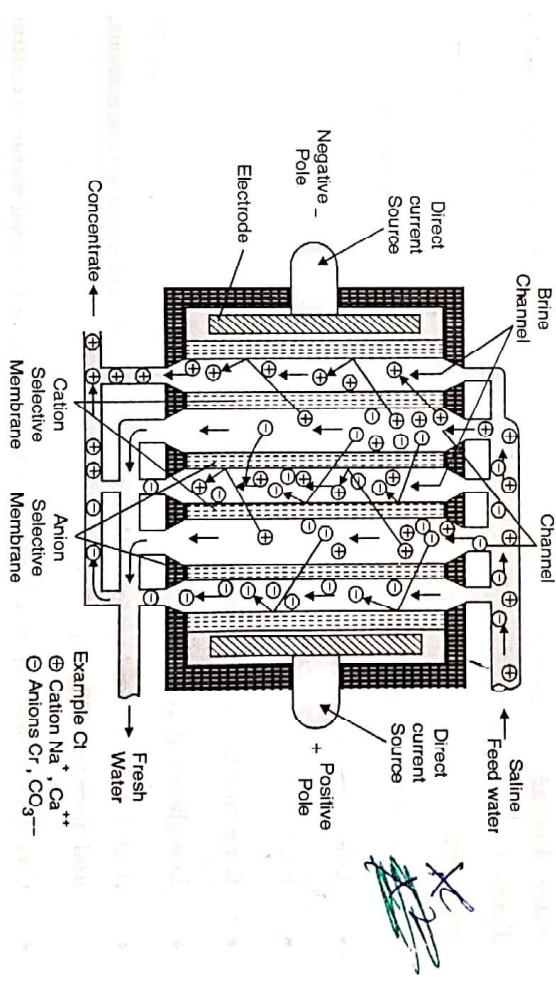


Fig. 1.15.5 : shows movement of ions in ED

- The anions are able to pass through the anion-selective membrane, but are not able to pass by the cation-selective membrane, which blocks their path and traps the anions in the brine stream (Figure 1.15.5).
- Similarly, cations move in the opposite direction through the cation-selective membrane under a negative charge and are trapped by the anion-selective membrane.
- A typical ED system includes a membrane stack with a number of cell pairs, each consisting of a cation transfer membrane, a demineralized flow spacer, an anion transfer membrane, and a concentrate flow spacer. Compartments for the electrodes are at opposite ends of the stack. The electrodes are continually flushed to reduce fouling or scaling.
- Waste Disposal** The concentrate waste stream, electrode cleaning flows, and residuals from the pretreatment process will be a part of a typical waste stream flow and will require disposal. Common disposal methods include: surface water discharge, evaporation ponds, etc. Spent membranes will also require disposal.
- Benefits**
- ED can operate with minimal fouling or scaling, or chemical addition.
 - Low pressure requirements.
 - ED facilities are quieter than RO.
 - Long membrane life expectancy.
 - Low chemical usage for pretreatment.
 - Ability to treat feed water with higher SDI, TOC and silica concentrations, and more turbidity than RO.
 - Can operate with up to 0.5 ppm of free chlorine in the feed water to control the biological matter in the feed water.

1.15.6 Reverse Osmosis (RO)

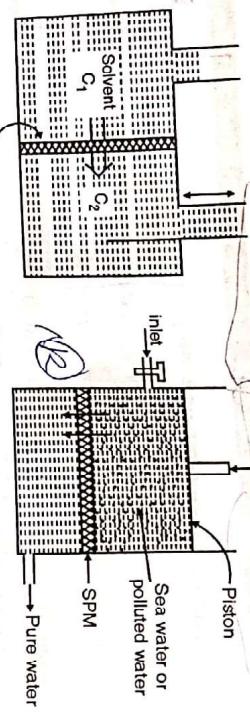
MU – May 2008, Dec. 2008, Dec. 2010, May 2011, Dec. 2011, May 2012

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. 1.15.6, 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.



(a) Osmosis
Semipermeable
membrane
 C_2 Conc. $>$ C_1 Conc.

(b) Reverse osmosis cell

Fig. 1.15.6

Method :

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_2O 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
• Rinse Waters	• Biomedical Applications
• Laboratory Applications	• Photography
• Pharmaceutical Production	• Kidney Dialysis
• Water used in chemical processes	• Cosmetics
• Animal Feed	• Hatcheries
• Restaurants	• Greenhouses

Metal Plating Applications	• Wastewater Treatment
Boiler Water	• Battery Water
Semiconductor production	• Hemodialysis

1.15.7 Ultrafiltration

MU – May 2009, May 2011

- Ultrafiltration, is a cross-flow separation process.

Principle

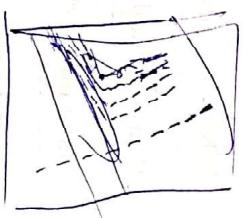
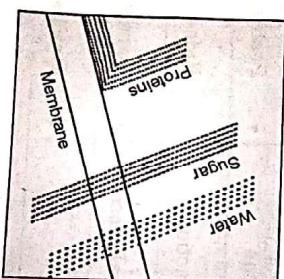
- Here liquid stream to be treated (feed) flows tangentially along the membrane surface, thereby producing two streams. The stream of liquid that comes through the membrane is called *permeate*.

- The type and amount of species left in the permeate will depend on

- characteristics of the membrane
- operating conditions
- quality of feed.

Process

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



- 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.*

Advantages

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

Disadvantages

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

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.*

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.

Fig. 1.15.7

1.16 Comparisons

1.16.1 Temporary Hardness and Permanent Hardness OR
Alkaline and Non Alkaline Hardness OR
Carbonate and Non Carbonate Hardness

MU – Dec. 2007, May 2008

Table 1.16.1

Sr. No.	Temporary Hardness	Permanent Hardness
1.	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.
2.	It is due to bicarbonates, carbonates hence also known as carbonate hardness.	It is due to other salts, hence known as non-carbonate hardness.
3.	It is due to dissolved bicarbonates of Ca ⁺² , Mg ⁺² , Fe ⁺² etc.	It is due to other dissolved salts of Ca ⁺² , Mg ⁺² , Fe ⁺² etc. such as chlorides, sulphates and nitrates.
4.	This is known as alkaline hardness.	This is known as non-alkaline hardness.
5.	Temporary hard water can be softened by	Permanent hard water can be softened by treating with soda.
	1. Only boiling. 2. Treating only with lime.	

1.16.2 Zeolite Process and Lime Soda Process

Table 1.16.2

Sr. No.	Zeolite Process	Lime Soda Process
1.	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.
2.	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.
3.	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.

Sr. No.	Zeolite Process	Lime Soda Process
4.	The size of the softening plant depends upon the hardness of the water. Hence, plant is <i>compact and occupies less space</i> .	The size of softening plant depends upon <i>quantity</i> of hard water to be softened. Hence, <i>size is not compact</i> , but increases with quantity of water and thus <i>occupies more space</i> .
5.	This process cannot be used for <i>hot water, acidic water, turbid water</i> and <i>water with suspended impurities</i> .	This process <i>does not have</i> any such restrictions.
6.	The process is <i>simple and efficiency is high</i> .	The process is <i>not simple</i> , as it involves settling coagulation and filtration, and hence <i>efficiency is low</i> .
7.	Process is <i>disadvantageous</i> because temporary hardness forms bicarbonates of sodium.	Process is <i>advantageous</i> , because temporary hardness gets completely removed as precipitates of CaCO_3 and $\text{Mg}(\text{OH})_2$.
8.	The soft water obtained by this process creates problems in boilers because it contains bi-carbonates which lead to the formation of NaOH and CO_2 at high temperature which cause <i>caustic embrittlement</i> .	The soft water obtained does not create <i>problems of caustic embrittlement</i> in boilers because the resultant products such as CaCO_3 and $\text{Mg}(\text{OH})_2$ are removed by filtration.

1.16.3 Ion-Exchange Process and Zeolite Process

Table 1.16.3

Sr. No.	Ion-Exchange Process	Zeolite Process
1.	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.
2.	The resultant water is <i>suitable for all types of boilers, especially high pressure boilers</i> .	The resultant water is <i>not suitable for use in high pressure boilers</i> . Water can be used <i>only in low or medium pressure boilers</i> .
3.	The cation and anion exchange beds used are <i>more expensive</i> . Hence, capital cost is high.	Zeolite softener is comparatively cheap, hence capital cost is lower.
4.	The softening plant is <i>not compact</i> , hence occupies <i>more space</i> .	The softening plant is <i>compact</i> . Hence occupies <i>less space</i> .
5.	The process effectively removes <i>all the hardness causing substances</i> . It can also remove alkali metals such as Na or K, as chlorides or sulphates completely.	This process can remove only Ca^{+2} , Mg^{+2} , Fe^{+2} and Mn^{+2} ions. Hence, softened water contains salts like NaCl , NaHCO_3 , Na_2SO_4 etc. in dissolved form.
6.	This process is <i>useful for acidic as well as alkaline water</i> .	This process is <i>not useful for highly acidic water</i> as acids affect zeolite bed, because zeolites get dissolved in.

Sr. No.	Ion-Exchange Process	Zeolite Process
7.	Soft water obtained does not cause caustic embrittlement in boilers and is suitable for boilers as it is free from Na^+ ions.	Soft water obtained is not suitable for boilers, due to the presence of NaHCO_3 , which subsequently forms NaOH , causing thereby caustic embrittlement in boilers.

1.17 Solved Problems

1.17.1 Problems based on Carbonates and Non Carbonates Hardness (Total Permanent, Temporary Hardness) ~~X~~ (P)

Problem 1.17.1: A sample of water has hardness 304 ppm CaCO_3 equivalent.

Find the hardness in terms of degree Clark, degree French and mg/lit.A.

Solution:

Given : Hardness of water = 304 ppm

Hardness in term of ${}^\circ\text{Cl}$:

$$\therefore 0.07 {}^\circ\text{Clarke} \equiv 1 \text{ ppm}$$

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

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

Hardness in term of ${}^\circ\text{Fr}$:

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

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

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

Hardness in term of mg/lit

$$\because 1 \text{ ppm} \equiv 1 \text{ mg/lit}$$

$$\therefore 304 \text{ ppm} \equiv 304 \text{ mg/lit}$$

$$\text{Ans. : Hardness of water } 304 \text{ ppm} \equiv 21.28 {}^\circ\text{Clarke}$$

$$\text{Ans. : } 21.28 \div 2 = 10.64 {}^\circ\text{Fr}$$

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

Problem 1.17.2: Convert the total hardness of water samples in ppm from ${}^\circ\text{Cl}$ and ${}^\circ\text{Fr}$. (i) 2.42 ${}^\circ\text{Clarke}$ (ii) 3.6 ${}^\circ\text{Fr}$.

Solution :

$$(1) \quad \because 0.07 {}^\circ\text{Clarke} \equiv 1 \text{ ppm}$$

$$\therefore 2.42 {}^\circ\text{Clarke} \equiv \frac{2.42}{0.07} \text{ ppm}$$

$$= 34.57 \text{ ppm}$$

$$(ii) \quad \because 0.1 {}^\circ\text{Fr} \equiv 1 \text{ ppm.}$$

$$\therefore 3.6 {}^\circ\text{Fr} \equiv \frac{3.6}{0.1} \text{ ppm}$$

$$= 36 \text{ ppm}$$

Ans. : Hardness of water

$$2.42 {}^\circ\text{Clarke} \equiv 34.57 \text{ ppm}$$

$$3.6 {}^\circ\text{Fr} \equiv 36 \text{ ppm}$$

Problem 1.17.3: 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) $\text{CaSO}_4 = 13.6 \text{ mg/l}$

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

(May 2008, 2 Marks)

Solution :

Calculation of CaCO_3 equivalents

Impurity/ies	Quantity	Multiplying factor	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
CaSO_4	13.6 mg/l	$13.6 \times \frac{100}{136}$	10

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

$$= 20 + 20$$

$$= 40 \text{ ppm}$$

Permanent hardness = CaSO_4

$$= 10 \text{ ppm}$$

Total hardness = temporary + permanent

$$= 40 + 10$$

$$= 50 \text{ ppm}$$

Ans.:

Temporary Hardness = 40 ppm

Permanent Hardness = 10 ppm

Total Hardness = 50 ppm

Problem 1.17.4: A water sample contains:

- (i) $\text{Mg}(\text{HCO}_3)_2 = 14.6 \text{ ppm}$ (ii) $\text{Mg}(\text{NO}_3)_2 = 29.6 \text{ ppm}$.
- (iii) $\text{Ca}(\text{HCO}_3)_2 = 8.1 \text{ ppm}$ (iv) $\text{MgCl}_2 = 19 \text{ ppm}$.

Calculate the temporary and permanent hardness of water sample.

(At. wt. C = 12, Mg = 24, H = 1, O = 16, S = 32)

$$\text{N} = \sqrt{Q} \propto \sqrt{C} = 35 \text{ ppm}$$

Solution :

Conversion in CaCO_3 equivalents

Salt	Quantity ppm	Multiplication factor	CaCO ₃ equivalent ppm	Type of hardness
$\text{Mg}(\text{HCO}_3)_2$	14.6	$\frac{100}{146}$	10	Temporary
$\text{Mg}(\text{NO}_3)_2$	29.6	$\frac{100}{148}$	20	Permanent
$\text{Ca}(\text{HCO}_3)_2$	8.1	$100/162$	5	Temporary
MgCl_2	19	$100/95$	20	Permanent
MgSO_4	24	$100/120$	20	Permanent

Now, temporary hardness is due to $\text{Ca}(\text{HCO}_3)_2$ and $\text{Mg}(\text{HCO}_3)_2$

$$\therefore \text{Temporary hardness} = 05 + 10$$

$$= 15 \text{ ppm}$$

Permanent hardness is due to $\text{Mg}(\text{NO}_3)_2$, MgCl_2 and MgSO_4 .

$$\therefore \text{Permanent hardness} = 20 + 20 + 20$$

$$= 60 \text{ ppm}$$

Ans.: Temporary hardness = 15 ppm

Permanent hardness = 60 ppm

Problem 1.17.5: Calculate temporary and total hardness of a water sample containing:

$$\begin{aligned} \text{Mg}(\text{HCO}_3)_2 &= 7.3 \text{ mg/l}, \text{ Ca}(\text{HCO}_3)_2 = 16.2 \text{ mg/l}, \\ \text{MgCl}_2 &= 9.5 \text{ mg/l}, \text{ CaSO}_4 = 13.6 \text{ mg/l}. \end{aligned}$$

(Dec. 2009, Dec. 2012, 3 Marks)

Solution :

Conversion in CaCO_3 equivalents.		Multiplication Factor	CaCO_3 equivalent	Type of Hardness
Salt	Quantity in ppm or mg/L			
$\text{Mg}(\text{HCO}_3)_2$	7.3	$7.3 \times \frac{100}{146}$	05	Carbonate or Temporary
$\text{Ca}(\text{HCO}_3)_2$	16.2	$16.2 \times \frac{100}{162}$	10	Carbonate or Temporary
MgCl_2	9.5	$9.5 \times \frac{100}{95}$	10	Non-Carbonate or Permanent
CaSO_4	13.6	$13.6 \times \frac{100}{136}$	10	Non-Carbonate or Permanent

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

$$= 05 + 10$$

$$= 15 \text{ ppm}$$

Permanent Hardness = $\text{MgCl}_2 + \text{CaSO}_4$

$$= 10 + 10$$

$$= 20 \text{ ppm}$$

Total Hardness = Temporary Hardness + Permanent Hardness.

$$= \text{Mg}(\text{HCO}_3)_2 + \text{Ca}(\text{HCO}_3)_2 + \text{MgCl}_2 + \text{CaSO}_4$$

$$= 05 + 10 + 10 + 10 = 35 \text{ ppm}$$

Ans. : Temporary Hardness = 15 ppm

Total Hardness = 35 ppm

Problem 1.17.6:

A water sample on analysis has been found to contains :

$$\text{MgCl}_2 = 19 \text{ mg/lit},$$

$$\text{Ca}(\text{HCO}_3)_2 = 29.5 \text{ mg/lit},$$

$$\text{CaSO}_4 = 13 \text{ mg/lit}.$$

Calculate temporary, permanent and total hardness.

Solution :

Constituents	Amount present	Multiplication factor	CaCO_3 equivalents	Type of Hardness
Mg Cl_2	19 Mg/lit	$19 \times \frac{100}{95}$	20 ppm	Permanent
CaCO_3	5 Mg/lit	$5 \times \frac{100}{100}$	5 ppm	Temporary
$\text{Ca}(\text{HCO}_3)_2$	29.5 Mg/lit	$29.5 \times \frac{100}{162}$	18.2 ppm	Temporary
CaSO_4	13 Mg/lit	$13 \times \frac{100}{136}$	9.56 ppm	Permanent

$$\therefore \text{Temporary Hardness} = 5 + 18.2$$

and

$$\text{Permanent Hardness} = 20 + 9.56$$

$$= 29.56 \text{ ppm}$$

$\therefore \text{Total Hardness} = \text{Temporary hardness} + \text{permanent hardness}$

$$= 23.2 + 29.56$$

$$= 52.76 \text{ ppm}$$

Problem 1.17.7: Hardness of 4,500 liters of water was removed completely by zeolite softener. This zeolite required 30 liters of 100 gm/lit of NaCl to regenerate.

Calculate the hardness of water.

(Dec. 2010, 4 Marks)

Solution :

Using regeneration reaction,



(May 2011, 5 Marks)

$2(58.5) \text{ gms} \equiv 111 \text{ gms} \equiv 100 \text{ gm of CaCO}_3$

Now,

Quantity of NaCl in regeneration,

$$= 30 \times 100$$

$$= 3000 \text{ gms NaCl}$$

Thus,

$$(2 \times 58.5) \text{ gms NaCl} \Rightarrow 100 \text{ gms CaCO}_3$$

$$\therefore 3000 \text{ gm NaCl} = \frac{3000 \times 100}{2 \times 58.5} = \frac{3000 \times 100}{117}$$

$$= 2564.102 \text{ gms of CaCO}_3$$

$$= 2564.102 \text{ mgs of CaCO}_3$$

$\because 4500 \text{ litres of hard water} = 2564.102 \text{ mgs CaCO}_3$

$$\therefore 1 \text{ litre of hard water} = \frac{2564.102}{4500} \text{ mgs of CaCO}_3$$

$$= 56.98 \text{ mgs of CaCO}_3 = 56.98 \text{ ppm}$$

Solution :
Hardness of water sample = 56.98 ppm

Problem 1.17.8: Classify the following impurities into temporary, permanent and non-hardness causing impurities.

$\text{Ca}(\text{HCO}_3)_2$, MgSO_4 , CaCl_2 , CO_2 , HCl , $\text{Mg}(\text{HCO}_3)_2$, CaSO_4 and NaCl .

How many grams of CaCl_2 dissolved per litre gives 150 ppm of hardness?

(Dec. 2011, 5 Marks)

Solution :

Salts causing respective

Hardness are

Temporary : $\text{Ca}(\text{HCO}_3)_2$, $\text{Mg}(\text{HCO}_3)_2$

Permanent : Mg SO_4 , CaCl_2 , CaSO_4

Non-hardness causing = CO_2 , HCl , NaCl .

To calculate gm of CaCl_2 / litre to give 150 ppm hardness.



M.W. 100 [1 mole] M.W. 111 [1 mole]

If 1 gm CaCO_3 generates 1.11 gm of CaCl_2 . Which when dissolved in 1 litre water gives 1 ppm hardness. Thus to get 150 ppm hardness, CaCO_3 should be taken 150 gm, whereas 166.5 gm CaCl_2 gives 150 ppm hardness.

$$1 \text{ g. CaCO}_3 / \text{litre} \equiv 1000 \text{ mgs / 1000 ml.} = 1 \text{ ppm.}$$

Problem 1.17.9: 15,000 litres of hard water was passed through a zeolite softener. The exhausted zeolite required 120 litres of NaCl having 30 g / litre of NaCl. Calculate the hardness of water.

(Dec. 2011, 5 Marks)

Solution :

Let the hardness of the water sample be $x \text{ mg/l}$

Now, 1 litre of NaCl contains 30 g of NaCl = 30000 mg NaCl

$\therefore 120 \text{ litres of NaCl contains } 120 \times 30000 = 3600000 \text{ mg of NaCl}$

58.5 mg of NaCl = 50 mgs of CaCO_3 equivalent hardness

$$= 3600000 \times \frac{50}{58.5}$$

$$= 30,76,923 \text{ mgs of CaCO}_3 \text{ equivalents hardness}$$

But the total quantity of the water sample = 15,000 litre

$\therefore 15000 \text{ lt. of water} \equiv 30,76,923 \text{ mgs of CaCO}_3$

$$\therefore 1 \text{ lt. of water} = \frac{3076923}{15000} \text{ mgs of CaCO}_3$$

$$= 205 \text{ mg/l of CaCO}_3$$

$$= 205 \text{ ppm CaCO}_3$$

Ans. : Hardness of water sample = 205 ppm

Water & its Treatment

1.17.2 Problems based on Calculation of Hardness by EDTA Method

Method of calculation

- Titrations carried out in this method are :
 1. 50 ml standard hard water (SHW) [containing 1 mg/ml 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 CaCO_3 equivalent. (Since SHW contains 1 mg/ml CaCO_3 equivalent hardness)

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

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

Thus, total hardness in 50 ml = $\left[V_2 \times \frac{50}{V_1} \right]$ mgs. CaCO_3 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.

Thus, permanent hardness of water in 50 ml sample = $\left[V_3 \times \frac{50}{V_1} \right]$ mgs of CaCO_3 equivalent hardness.

$$\therefore \text{permanent hardness of water per litre} = \left[\frac{V_3}{V_1} \times 1000 \right] \text{ mgs/lit}$$

From above two equations we can calculate temporary hardness as

Temporary hardness = Total hardness – Permanent hardness

$$= \left[\frac{V_2}{V_1} \times 1000 \right] - \left[\frac{V_3}{V_1} \times 1000 \right] \text{ mgs/lit of } \text{CaCO}_3 \text{ or ppm}$$

$$= \frac{1000}{V_1} (V_2 - V_3) \text{ mgs/lit of } \text{CaCO}_3 \text{ or ppm.}$$

Problem 1.17.10: Calculate total hardness, in ppm, in given water sample :

- 50 ml standard hard water, containing 1 mg pure CaCO_3 per ml, consumed 20 ml EDTA solution.
- 50 ml water sample consumed 30 ml EDTA solution using Eriob Black T indicator.

Solution :
Given data

$$\text{Quantity of std. hard water} = 50 \text{ ml}$$

$$(1 \text{ mg/ml } \text{CaCO}_3 \text{ equivalent})$$

$$\text{Quantity of EDTA solution consumed by SHW} = 20 \text{ ml}$$

$$\text{Quantity of water sample} = 50 \text{ ml}$$

$$\text{Quantity of EDTA solution consumed by sample} = 30 \text{ ml}$$

Standardisation of EDTA

$$\therefore 20 \text{ ml EDTA solution} \equiv 50 \text{ ml SHW}$$

$$\therefore 1 \text{ ml EDTA solution} \equiv \frac{50}{20} \text{ ml SHW.}$$

$$\therefore 1 \text{ ml EDTA solution} \equiv \frac{50}{20} \times 1 \text{ mgs } \text{CaCO}_3 \text{ equivalent}$$

Calculation of total hardness

$$\therefore 50 \text{ ml HW} \equiv 30 \text{ ml EDTA solution}$$

$$\therefore 1 \text{ ml HW} \equiv \frac{30}{50} \text{ ml EDTA solution}$$

= 330 mgs of CaCO_3 equivalent hardness

$$= \frac{30}{50} \times \frac{50}{20} \text{ mgs. } \text{CaCO}_3 \text{ equivalent}$$

$$\therefore 1000 \text{ ml. HW} = \frac{30}{50} \times \frac{50}{20} \times 1000 \text{ mgs. } \text{CaCO}_3 \text{ equivalent}$$

$$\therefore \text{Total hardness} = 1500 \text{ ppm}$$

Ans.: Total hardness = 1500 ppm

Problem 1.17.11: 0.28 gm of 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.

Solution: Here 0.28 g of CaCO_3 is dissolved and made up to 1000 ml

$$\therefore \text{Concentration of standard hard water} = 0.28 \text{ mg/ml}$$

$$\therefore 100 \text{ ml SHW} = 28 \text{ mgs of } \text{CaCO}_3 \text{ equivalents.}$$

$$\therefore 100 \text{ ml of standard hard water} = 28 \text{ ml of EDTA}$$

$$28 \text{ ml of EDTA} = 28 \text{ mgs of } \text{CaCO}_3 \text{ equivalents}$$

$$\therefore 1 \text{ ml of EDTA} = 1 \text{ mg of } \text{CaCO}_3 \text{ equivalents}$$

Now 100 ml of unknown hard water requires 33 ml of EDTA

i.e. 100 ml of unknown hard water contains = 33×1 mgs of CaCO_3 equivalents

$$= 33 \text{ mgs of } \text{CaCO}_3 \text{ equivalent hardness}$$

$$\therefore 1000 \text{ ml of unknown hard water contains} = \frac{33 \times 1000}{100}$$

= 330 mgs of CaCO_3 equivalent hardness

$$\therefore \text{Total hardness i.e. } H_{\text{Total}} = 330 \text{ mg/L}$$

Now, 100 ml of boiled water required 10 ml EDTA

$$\text{i.e. } 100 \text{ ml of boiled water contains} = 10 \times 1 \text{ mg } \text{CaCO}_3$$

$$= 10 \text{ mg of } \text{CaCO}_3 \text{ equivalent}$$

Ans.: Permanent hardness i.e. $H_{\text{Permanent}} = 100 \text{ mg/L}$

$$\text{Now, } H_{\text{Temporary}} = H_{\text{Total}} - H_{\text{Permanent}}$$

$$= 330 - 100 = 230 \text{ mg/L}$$

$$\text{hardness}$$

Ans.: Total hardness of water = 330 mg/L

Permanent hardness of water = 100 mg/L

$$\text{Temporary hardness of water} = 230 \text{ mg/L}$$

Ans.: Now 100 ml of unknown hard water requires 33 ml of EDTA

i.e. 100 ml of unknown hard water contains = 33×1 mgs of CaCO_3 equivalents

$$= 33 \text{ mgs of } \text{CaCO}_3 \text{ equivalent hardness}$$

$$\therefore 1000 \text{ ml of unknown hard water contains} = \frac{33 \times 1000}{100}$$

Solution :

Given data

$$\text{Concentration of SHW} = 1.2 \text{ g/lit}$$

$$\text{Quantity of SHW. (1.2 g CaCO}_3/\text{lit}) = 50 \text{ ml}$$

$$\text{Quantity of EDTA consumed by 50 ml SHW} = 32 \text{ ml} = V_1$$

$$\text{Quantity of Hard water sample} = 100 \text{ ml}$$

$$\text{Quantity of EDTA consumed} = 14 \text{ ml} = V_2$$

$$\text{Quantity of EDTA consumed after boiling} = 8.5 \text{ ml} = V_3$$

$$\text{Hardness} = ?$$

Standardization of EDTA
Standard hard water has 1.2 g i.e. $1.2 \times 1000 = 120 \text{ mg. of CaCO}_3 \text{ equivalent H per lit.}$

H per lit.

$$= 120 \text{ mgs/lit.}$$

$$= \frac{120}{1000} = 0.12 \text{ mg/ml CaCO}_3 \text{ equivalent H}$$

$$\therefore 50 \text{ ml SHW} = 50 \times 0.12 \text{ mg CaCO}_3 \equiv 6.0 \text{ mgs CaCO}_3$$

$$\therefore 32 \text{ ml EDTA} = 50 \text{ ml SHW} \equiv 6.0 \text{ mgs CaCO}_3$$

$$\begin{aligned} 1 \text{ ml EDTA} &= \frac{6.0}{32} = 0.15 \text{ mgs of CaCO}_3 \text{ equivalent H} \\ &\quad \boxed{V_0.1575} \end{aligned}$$

Calculation of total Hardness

$$100 \text{ ml H.W sample} = 14 \text{ ml EDTA}$$

$$= 14 \times 0.15 \text{ mgs of CaCO}_3 \text{ per 100 ml of HW}$$

$$= 2.1 \text{ mgs of CaCO}_3$$

$$\therefore \text{Total H per litre} = 21 \text{ mgs of CaCO}_3 = 21 \text{ ppm}$$

$$\text{Volume of EDTA for sample} = 18 \text{ ml} = V_2$$

Calculation of permanent hardness

$$\therefore 100 \text{ ml of boiled water} \equiv 8.5 \text{ ml of EDTA}$$

$$= 8.5 \times 0.15 \text{ mgs of CaCO}_3 \text{ in 100 ml}$$

$$= 1.275 \text{ mgs of CaCO}_3$$

$$\text{Hence per litre} = 12.75 \text{ mgs of CaCO}_3$$

$$\text{H temporary} = \text{H total} - \text{H permanent}$$

$$= 21 - 12.75$$

$$= 8.25 \text{ mgs of CaCO}_3$$

$$\therefore \text{Temporary hardness} = 12.75 \text{ ppm}$$

$$\therefore \text{Permanent hardness} = 8.25 \text{ ppm}$$

Problem 17.13: A standard hard water 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.

(May 2008, 6 Marks)

Solution :
Given : Concentration of SHW = 15 g/lit

$$\begin{aligned} &= 15000 \text{ mg / 1000 ml} \\ &= \boxed{15 \text{ mg/ml}} \end{aligned}$$

$$\text{Volume of std hard water} = 20 \text{ ml}$$

$$\text{Volume of EDTA for SHW} = 25 \text{ ml} = V_1$$

$$\text{Volume of water sample} = 100 \text{ ml}$$

$$\text{Volume of EDTA for sample} = 18 \text{ ml} = V_2$$

Volume of water sample (after boiling) = 100 ml
Volume of EDTA solution required for titration = 50 ml
Volume of EDTA for sample (after boiling) = 12 ml = V₃
Volume of EDTA for sample (after boiling) = 12 ml = V₃
∴ 20 ml SHW = 25 ml EDTA soln. ≡ 300 mgs of CaCO₃ Equivalent Hardness

$$\therefore 1 \text{ ml EDTA} = \frac{300}{25} \text{ mgs of CaCO}_3 \text{ Equivalent Hardness}$$

$$\equiv 12 \text{ mgs of CaCO}_3 \text{ Equivalent Hardness}$$

Now,

$$100 \text{ ml water sample} \equiv 18 \text{ ml EDTA solution}$$

$$\equiv [18 \times 12] \text{ mgs of CaCO}_3 \text{ Equivalent Hardness}$$

$$\equiv 216 \text{ mgs of CaCO}_3 \text{ Equivalent Hardness}$$

$$\therefore \text{per litre} \equiv 2160 \text{ mgs of CaCO}_3 \text{ Equivalent Hardness}$$

$$\therefore \text{Total hardness} \equiv 2160 \text{ ppm.}$$

100 ml. water sample (after boiling) ≡ 12 ml. EDTA solution

Now,

$$100 \text{ ml. water sample (after boiling)} \equiv 12 \text{ ml. EDTA solution}$$

$$\equiv [12 \times 12] \text{ mgs of CaCO}_3 \text{ Equivalent Hardness}$$

$$\equiv 144 \text{ mgs of CaCO}_3 \text{ Equivalent Hardness}$$

$$\therefore \text{per liter} \equiv 1440 \text{ ppm.}$$

$$\therefore \text{permanent Hardness} \equiv 1440 \text{ ppm.}$$

$$\therefore \text{Temporary Hardness} \equiv 2160 - 1440 = 720 \text{ ppm.}$$

Ans.

$$\text{Total Hardness} = 2160 \text{ ppm.}$$

$$\text{Permanent Hardness} = 720 \text{ ppm.}$$

$$\text{Temporary Hardness} = 1440 \text{ ppm.}$$

Solution :

$$\text{Concentration of S.H.W.} = 0.5 \text{ gm CaCO}_3 / 500 \text{ ml D.W.}$$

$$= 500 \text{ mgs in 500 ml water}$$

$$= \boxed{1 \text{ mg/ml}}$$

$$\text{Now, } 50 \text{ ml SHW required} \equiv 48 \text{ ml EDTA solution} \equiv 50 \text{ mgs CaCO}_3$$

$$\text{i.e. } 48 \text{ ml EDTA solution} \equiv 50 \text{ mgs CaCO}_3 \text{ equivalent hardness}$$

$$\therefore 1 \text{ ml EDTA solution} \equiv \boxed{\frac{50}{48}} \text{ mgs CaCO}_3 \text{ equivalent hardness}$$

Now,

$$50 \text{ ml water sample} \equiv 15 \text{ ml EDTA solution}$$

$$\therefore \text{Hardness of sample} \equiv \left[15 \times \frac{50}{48} \right] \text{ mgs CaCO}_3 \text{ equivalent for 50 ml}$$

sample

$$\therefore \text{Hardness per litre of sample} \equiv \left[15 \times \frac{50}{48} \right] \times \frac{1000}{50} \text{ mgs/lit.}$$

$$= \boxed{\left[\frac{750}{48} \right]} \times 20 \text{ mgs lit.}$$

$$\therefore \text{Total hardness} \equiv 312.50 \text{ ppm}$$

$$\text{Now, } 50 \text{ ml water sample after boiling} \equiv 10 \text{ ml EDTA solution}$$

$$\therefore \text{Permanent hardness} \equiv \left(10 \times \frac{50}{48} \right) \text{ mgs CaCO}_3 \text{ equivalent for 50 ml}$$

Problem 17.14: 0.5 gm of CaCO₃ was dissolved in HCl and the solution made upto 500 ml with distilled water. 50 ml of the solution required 48 ml of EDTA solution for titration. 50 ml of hard water sample required 15 ml of EDTA and after boiling and filtering required 10 ml of EDTA solution. Calculate temporary hardness of water. (May 2009, 5 Marks)

Permanent hardness of one litre sample = $\left(10 \times \frac{50}{48}\right) \times \frac{1000}{50}$ mgs/lit.

$$= \left(\frac{500}{48}\right) \times 20 \text{ mgs lit.}$$

$$\therefore \text{Permanent hardness of sample} = 208.33 \text{ ppm}$$

$$\therefore \text{Temporary hardness} = \text{Total hardness} - \text{Permanent hardness}$$

$$= 312.50 - 208.33$$

$$\therefore \text{Temporary hardness of sample} = 104.17 \text{ ppm}$$

$$\text{Ans. : Total hardness} = 312.50 \text{ ppm}$$

$$\text{Permanent hardness} = 208.33 \text{ ppm}$$

$$\text{and Temporary hardness} = 104.17 \text{ ppm}$$

Problem 1.17.14(a): 0.5 g of CaCO_3 was dissolved in dilute HCl and diluted to 500 ml, 50 ml of this solution required 45 ml of EDTA solution for titration. 50 ml of hard water sample required 15 ml of EDTA solution for titration. 50 ml of same water sample on boiling, filtering requires 10 ml EDTA solution. Calculate the temporary, permanent and total hardness in ppm.

Solution: (May 2013, 6 Marks)

$$\text{Concentration of SHW} = 0.5 \text{ gm } \text{CaCO}_3/500 \text{ ml}$$

$$= 500 \text{ mgs } \text{CaCO}_3/500 \text{ ml}$$

$$\boxed{= 1 \text{ mg/ml}}$$

$$\text{Now } 50 \text{ ml SHW required} = 45 \text{ ml EDTA}$$

$$\equiv 50 \text{ mgs } \text{CaCO}_3$$

$$\text{i.e. } 45 \text{ ml EDTA solution} \equiv 50 \text{ mgs } \text{CaCO}_3 \text{ eq. H}$$

$\therefore 1 \text{ ml EDTA solution} = \left(\frac{50}{45}\right) \text{ mgs CaCO}_3 \text{ eq. H}$

$$\text{Now } 50 \text{ ml water sample} \equiv 15 \text{ ml EDTA solution}$$

$$\therefore \text{Hardness of water sample} = \left(\frac{50}{45} \times 15\right) \text{ mgs } \text{CaCO}_3 \text{ eq. H}$$

$$\therefore \text{per litre} = \left(15 \times \frac{50}{45} \times \frac{1000}{50}\right) \text{ mgs } \text{CaCO}_3 \text{ eq. H}$$

$$\therefore \text{Total Hardness} = 333.33 \text{ ppm}$$

$$\text{Now } 50 \text{ ml sample after boiling} \equiv 10 \text{ ml EDTA solution}$$

$$\therefore \text{Hardness of sample} = \left(10 \times \frac{50}{45}\right) \text{ mgs } \text{CaCO}_3 \text{ eq. H}$$

$$\therefore \text{Per litre} = \left(10 \times \frac{50}{45} \times \frac{1000}{50}\right) \text{ mgs } \text{CaCO}_3 \text{ eq. H}$$

$$\therefore \text{Permanent Hardness} = 222.22 \text{ ppm}$$

$$\therefore \text{Temporary Hardness} = \text{Total H} - \text{Permanent H}$$

$$= 333.33 - 222.22 = 111.11$$

$$\text{Ans. : Total Hardness} = 333 \text{ ppm}$$

$$\text{Permanent Hardness} = 222.22 \text{ ppm and Temporary Hardness} = 111.11$$

Problem 1.17.15: 1gm of CaCO_3 was dissolved in 1 liter of distilled water, 50ml of this solution required 45ml of EDTA solution for titration.

50ml of hard water required 25ml of EDTA for titration. The same sample of water after boiling consumed 15ml of EDTA for titration. Calculate the hardness of water.

(Dec. 2010, 5 Marks)

Solution:

$$\text{Given data: Concentration of SHW} = 1 \text{ g/lit}$$

$$\text{Quantity of SHW (1g/lit)} = 50 \text{ ml}$$

$$\text{Quantity of EDTA consumed by 50 ml SHW} = 45 \text{ ml}$$

$$\text{Quantity of hard water sample} = 50 \text{ ml}$$

$$\text{Quantity of EDTA consumed} = 25 \text{ ml}$$

Quantity of EDTA consumed after boiling = 15 ml
Hardness = ?

Standardization of EDTA:

Standard hardwater has 1g i.e. $1 \times 1000 = 1000$ mg of CaCO_3 equivalent hardness per lit

$$\begin{aligned} &= 1000 \text{ mgs / lit} \\ &= \frac{1000}{1000} = 1 \text{ mg / ml } \text{CaCO}_3 \text{ equivalents hardness} \\ \therefore & 50 \text{ ml SHW} = 50 \times 1 \text{ mg } \text{CaCO}_3 = 50 \text{ mgs } \text{CaCO}_3 \\ \therefore & 45 \text{ ml EDTA} = 50 \text{ ml SHW} = 50 \text{ mgs } \text{CaCO}_3 \\ 1 \text{ ml EDTA} &= \frac{50}{45} = 1.11 \text{ mgs of } \text{CaCO}_3 \text{ equivalent hardness} \end{aligned}$$

Calculation of total hardness:

$$\begin{aligned} 50 \text{ ml H.W. sample} &= 25 \text{ ml EDTA} \\ &= 25 \times 1.11 \text{ mgs of } \text{CaCO}_3 \text{ per 50 ml} \end{aligned}$$

Calculation of permanent hardness:

$$\begin{aligned} \therefore 50 \text{ ml of boiled water} &= 15 \text{ ml of EDTA} \\ &= 15 \times 1.11 \text{ mgs of } \text{CaCO}_3 \text{ in 100 ml} \\ &= 16.65 \text{ mgs of } \text{CaCO}_3 \end{aligned}$$

Hence per litre = 333 mgs of CaCO_3

$$\text{Temporary} = \text{H}_\text{total} - \text{H}_\text{permanent}$$

Solution :
Data given :

- ∴ Total hardness = 555 ppm
- ∴ Permanent hardness = 333 ppm
- Temporary hardness = 222 ppm

Problem 1.17.16:

EDTA for titration. After boiling and filtration the same volume required 4 ml of EDTA. Calculate each type of hardness.

(May 2011, 5 Marks)

$$\text{As } \frac{1}{20} \text{ EDTA Solution} = \frac{N}{20} = 0.05 \text{ N}$$

∴ 50 g CaCO_3 diluted to 1000 ml makes 1 normal CaCO_3 solution.
i.e. 1000 ml 1 N CaCO_3 solution = 50 g CaCO_3

$$\therefore 1 \text{ ml of } \frac{N}{20} \text{ CaCO}_3 \text{ correspond to } 0.0025 \text{ gm of } \text{CaCO}_3$$

Now, 50 ml of hard water correspond to 7.2 ml of $\frac{N}{20}$ EDTA.

i.e. correspond to $0.0025 \times 7.2 = 0.018$ gms of CaCO_3 = 18 mgs CaCO_3

∴ 1000 ml of hard water correspond to

$$= (18 \times 20) \text{ mgs } \text{CaCO}_3/\text{lit}$$

$$\text{Ans. : Hardness of water} = 360 \text{ ppm}$$

Problem 1.17.17: 20 ml of standard hard water containing 1.2 g CaCO_3 per litre required 35 ml of EDTA. 50 ml of hard water sample required 30 ml of the same EDTA. 100 ml of hard water sample after boiling required 25 ml of the same EDTA.

Calculate the various hardnesses.

(Dec. 2011, 5 Marks)

Weight of CaCO_3 = 1.2 gm / litre
Volume of SHW = 20 ml.
Volume of EDTA solution for SHW (V_1) = 35 ml.
Volume of EDTA (V_2) = 30 ml. (for 50 ml sample)
Volume of EDTA (V_3) = 25 ml. (for 100 ml sample)

To calculate all types of hardness.

$$\therefore 20 \text{ ml. SHW} = 35 \text{ ml. EDTA}$$

X doubt A

and Concentration of SHW = 1.2 g/lit

$$= 1200 \text{ mg/l} / 1000 \text{ ml.}$$

$$= 1.2 \text{ mg/l ml.}$$

$$\text{Ca } (\text{HCO}_3)_2 = 162$$

$$\text{CaCl}_2 = 22.2$$

$$\text{Mg Cl}_2 = 95$$

$$\text{NaCl} = 20$$

(May 2013, 3 Marks)

Solution :

$$\therefore 20 \text{ ml. SHW} \equiv 20 \times 1.2 \text{ mgs hardness}$$

$$\equiv 24.0 \text{ mgs}$$

Thus 35 ml. EDTA = 24 mgs equivalent CaCO_3 equivalent hardness

$$\therefore 1 \text{ mL. EDTA} \equiv \frac{24}{35} \text{ mgs equivalent } \text{CaCO}_3 \text{ equivalent hardness}$$

$$\therefore \text{Total hardness per } 50 \text{ mL.} = \left(V_2 \times \frac{24}{35} \right) \text{ mgs of } \text{CaCO}_3 \text{ equivalent hardness}$$

$$= \left(30 \times \frac{24}{35} \right) \text{ mgs of } \text{CaCO}_3 \text{ equivalent hardness}$$

$$= 20.57 \text{ mgs of } \text{CaCO}_3 \text{ equivalent hardness}$$

$$\therefore \text{per litre} = \left(20.57 \times \frac{1000}{50} \right) = 411.4 \text{ ppm.}$$

∴ Permanent hardness per 100 mL = $\left(V_3 \times \frac{24}{35} \right)$ mgs of CaCO_3 equivalent hardness

$$= \left(25 \times \frac{24}{35} \right) \text{ mgs of } \text{CaCO}_3 \text{ equivalent hardness}$$

$$= 17.14 \text{ mgs}$$

$$\therefore \text{per litre} = \left(17.14 \times \frac{1000}{100} \right) = 171.4 \text{ ppm.}$$

Ans. : Total Hardness of sample = 220 ppm.

1.17.3 Problems based on Lime Soda Process

Hints for solving numerical problems based on lime soda process.

Ans. :

$$\text{Total H.} = 411.4 \text{ ppm.}$$

$$\text{Permanent H.} = 171.4 \text{ ppm.}$$

$$\text{Temporary H.} = 240.0 \text{ ppm.}$$

3. CaCO_3 or 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.
4. The quantity of $\text{Mg}(\text{HCO}_3)_2$ in terms of CaCO_3 equivalents to be taken double, for calculations.
5. If NaHCO_3 or KHCO_3 is present in water, then their CaCO_3 equivalents per litre should be added in Lime calculations and subtracted from soda calculations.
6. Coagulants like sodium aluminate, aluminium chloride, aluminium sulphate etc. if used, their CaCO_3 equivalents per litre should be calculated and taken into account as,

For NaAlO_2 : Subtract from lime

For $\text{AlCl}_3, \text{Al}_2(\text{SO}_4)_3$: Add in lime and soda both

Table 1.18.1

Sr.No	Salt	Reactions	Need
1.	$\text{Ca}(\text{HCO}_3)_2$ (Temp. Ca^{2+})	$\text{Ca}(\text{HCO}_3)_2 + \text{Ca}(\text{OH})_2 \rightarrow 2\text{CaCO}_3 \downarrow + \text{H}_2\text{O}$	L
2.	$\text{Mg}(\text{HCO}_3)_2$ (Temp. Mg^{2+})	$\text{Mg}(\text{HCO}_3)_2 + 2\text{Ca}(\text{OH})_2 \rightarrow 2\text{CaCO}_3 \downarrow + \text{Mg}(\text{OH})_2 + 2\text{H}_2\text{O}$	2L
3.	Mg^{2+} (Perm. Mg from MgCl_2 or $\text{Mg}(\text{NO}_3)_2$)	$\text{Mg}^{2+} + \text{Ca}(\text{OH})_2 \rightarrow \text{Mg}(\text{OH})_2 \downarrow + \text{Ca}^{2+}$ $\text{Ca}^{2+} + \text{Na}_2\text{CO}_3 \rightarrow \text{CaCO}_3 \downarrow + 2\text{Na}^+$	L + S
		$\text{MgCl}_2 + \text{Ca}(\text{OH})_2 \rightarrow \text{Mg}(\text{OH})_2 \downarrow + \text{CaCl}_2$ $\text{CaCl}_2 + \text{Na}_2\text{CO}_3 \rightarrow \text{CaCO}_3 \downarrow + 2\text{NaCl}$	L + S
		$\text{MgSO}_4 + \text{Ca}(\text{OH})_2 \rightarrow \text{Mg}(\text{OH})_2 \downarrow + 2\text{NaCl}$ $\text{CaSO}_4 + \text{Na}_2\text{CO}_3 \rightarrow \text{CaCO}_3 \downarrow + 2\text{Na}_2\text{SO}_4$	L + S

Note : Aluminium and iron salts may be present in water and they contribute to the permanent hardness or they may be added as coagulants.

		1-91	Water & its Treatment
Sr.No	Salt	Reactions	Need
		$\text{Mg}(\text{NO}_3)_2 + \text{Ca}(\text{OH})_2 \rightarrow \text{Ca}(\text{NO}_3)_2^* + \text{Mg}(\text{OH})_2$ $\text{Ca}(\text{NO}_3)_2^* + \text{Na}_2\text{CO}_3 \rightarrow \text{CaCO}_3 \downarrow + 2\text{NaNO}_3$	L + S
4.	HCO_3^- (e.g. NaHCO_3)	$2\text{NaHCO}_3 + \text{Ca}(\text{OH})_2 \rightarrow \text{CaCO}_3 + \text{H}_2\text{O} + \text{Na}_2\text{CO}_3$	+ L - S
5.	Ca^{2+} (Perm. Ca From CaCl_2 or CaSO_4 or $\text{Ca}(\text{NO}_3)_2$)	$\text{Ca}^{2+} + \text{Na}_2\text{CO}_3 \rightarrow \text{CaCO}_3 \downarrow + 2\text{Na}^+$ $\text{CaCl}_2 + \text{Na}_2\text{CO}_3 \rightarrow \text{CaCO}_3 \downarrow + 2\text{NaCl}$ $\text{CaSO}_4 + \text{Na}_2\text{CO}_3 \rightarrow \text{CaCO}_3 \downarrow + \text{Na}_2\text{SO}_4$ $\text{Ca}(\text{NO}_3)_2 + \text{Na}_2\text{CO}_3 \rightarrow \text{CaCO}_3 \downarrow + 2\text{NaNO}_3$	S S S S
6.	CO_2	$\text{CO}_2 + \text{Ca}(\text{OH})_2 \rightarrow \text{CaCO}_3 \downarrow + \text{H}_2\text{O}$	L
7.	H^+ (free acids like HCl, H_2SO_4 , etc.)	$2\text{H}^+ + \text{Ca}(\text{OH})_2 \rightarrow \text{Ca}^{2+} + 2\text{H}_2\text{O}$ $\text{Ca}^{2+} + \text{Na}_2\text{CO}_3 \rightarrow \text{CaCO}_3 \downarrow + 2\text{Na}^+$ $2\text{HCl} + \text{Ca}(\text{OH})_2 \rightarrow \text{CaCl}_2^* + 2\text{H}_2\text{O}$ $\text{H}_2\text{SO}_4 + \text{Ca}(\text{OH})_2 \rightarrow \text{CaSO}_4^* + 2\text{H}_2\text{O}$ $\text{CaCl}_2^* + \text{Na}_2\text{CO}_3 \rightarrow \text{CaCO}_3 \downarrow + 2\text{NaCl}$ $\text{CaSO}_4^* + \text{Na}_2\text{CO}_3 \rightarrow \text{CaCO}_3 \downarrow + \text{Na}_2\text{SO}_4$	(L + S) L S

9.	$\text{Al}_2(\text{SO}_4)_3$	$2\text{AlCl}_3 + 3\text{Ca}(\text{OH})_2 \rightarrow 2\text{Al}(\text{OH})_3 + 3\text{CaCl}_2^*$	$\left. \begin{array}{l} 3\text{CaCl}_2^* + 3\text{Na}_2\text{CO}_3 \rightarrow 6\text{NaCl} + 3\text{CaCO}_3 \downarrow \\ \text{Al}_2(\text{SO}_4)_3 + 3\text{Ca}(\text{OH})_2 \rightarrow 2\text{Al}(\text{OH})_3 \downarrow + 3\text{CaSO}_4^* \end{array} \right\}$	(L + S)
10	NaAlO_2	$3\text{CaSO}_4^* + 3\text{Na}_2\text{CO}_3 \rightarrow 3\text{Na}_2\text{SO}_4 + 3\text{CaCO}_3 \downarrow$		(L + S) - 1L
		$\text{NaAlO}_2 + 2\text{H}_2\text{O} \rightarrow \text{Al}(\text{OH})_3 \downarrow + \text{NaOH}$		

Problem 1.17.18: Water sample was found to contain following salts.

$$\text{CaCl}_2 = 55.5 \text{ mgs}; \quad \text{SiO}_2 = 20 \text{ ppm}.$$

$$\text{NaHCO}_3 = 12.6 \text{ mgs}; \quad \text{KCl} = 250 \text{ mgs};$$

$$\text{MgSO}_4 = 48 \text{ mgs}; \quad \text{CO}_2 = 2.2 \text{ ppm};$$

$$\text{Fe}^{++} = 2 \text{ ppm}; \quad \text{AlCl}_3 = 10 \text{ ppm};$$



Calculate the quantity of lime (85 % pure) and soda (95 % pure) for softening 50,000 litres of water.

Solution:

- Calculation of CaCO_3 equivalents for impurities

Salt	Qty mgs/lit	Multiplication factor	CaCO_3 equivalent ppm	Requirement of Lime (L) and / or Soda (S)
CaCl_2	55.5	1	55.5	L
SiO_2	20	$55.5 \times \frac{100}{111}$	50	S
NaHCO_3	12.6	$12.6 \times \frac{100}{(84 \times 2)}$	7.5	Add in L Subtract in S.
KCl	250	Does not react	-	-
MgSO_4	48	$48 \times \frac{100}{120}$	40	L + S
CO_2	2.2	$2.2 \times \frac{100}{44}$	5	L

Salt	Qty mgs/lit	Multiplication factor	CaCO_3 equivalent ppm	Requirement of Lime (L) and / or Soda (S)
$\text{Mg}(\text{HCO}_3)_2$	43.8	$43.8 \times \frac{100}{146}$	30	2L
Fe^{++}	2	$2 \times \frac{100}{55.8}$	3.58	L + S
AlCl_3	10	$10 \times \frac{100}{133.5}$	7.5	L + S

➤ Calculation of quantity of lime, required for softening of water

$$L = \frac{T_4}{100} \left[\text{Temporary } \text{Ca}^{+2} + 2 \times \text{Temporary } \text{Mg}^{+2} + \text{Permanent } (\text{Mg}^{+2} + \text{Fe}^{+2} + \text{Al}^{+3} + \text{H}^+ \text{ (HCl or H}_2\text{SO}_4)) + \text{CO}_2 + \text{HCO}_3^- - \text{NaAlO}_2 \right] \times \frac{\text{Vol. of Water}}{10^6}$$

$$\times \frac{100}{\% \text{ of purity}} \text{ kg}$$

all in terms of their CaCO_3 equivalents.

$$= \frac{74}{100} \left[\frac{\text{CaCO}_3 \text{ equivalents of } (\text{MgSO}_4) + 2 [\text{Mg}(\text{HCO}_3)_2] + \text{NaHCO}_3 + \text{CO}_2}{+\text{AlCl}_3 + \text{Fe}^{++}} \right] \times \frac{\text{Litres of water}}{10^6}$$

$$\times \frac{100}{\% \text{ purity of lime}} \text{ kg}$$

$$= \frac{74}{100} [40 + (30 \times 2) + 7.5 + 5 + 7.5 + 3.58] \times \frac{50000 \times 100}{10^6 \times 85} \text{ kg}$$

$$= \frac{74}{100} [40 + 60 + 7.5 + 5 + 7.5 + 3.58] \times \frac{5}{85} \text{ kg} = 5.379 \text{ kgs of lime}$$

- Calculation of quantity of soda required for softening and its cost

Soda requirements

$$S = \frac{106}{100} \left[\text{Permanent } (Ca^{+2} + Mg^{+2} + Al^{+3} + Fe^{+2} + H^+ (HCl \text{ or } H_2SO_4)) - HCO_3^- \right] \times \frac{\text{Vol. of Water}}{10^6} \times \frac{100}{\% \text{ of purity}} \text{ kg}$$

all in term of their $CaCO_3$ equivalents.

$$= \frac{106}{100} [CaCO_3 \text{ equivalents of } CaCl_2 + MgSO_4] \times \frac{\text{Litres of water}}{10^6}$$

$$\times \frac{100}{\% \text{ purity of soda}} \text{ kg}$$

$$= \frac{106}{100} [50 + 40 + 3.58 + 7.5 - 7.5] \times \frac{50000 \times 100}{10^6 \times 95} \text{ kg}$$

$$= \frac{106}{100} [93.58] \times \frac{5}{95} = 5.2207 \text{ kgs}$$

Ans.: Lime required = 5.379 kgs

Soda required = 5.2207 kgs

Problem 1.17.19: Calculate the quantities of lime and soda (90 % pure each) required for softening 25000 litres of hard water containing following ions/chemicals.

$$\begin{aligned} HCO_3^- &= 12.2 \text{ ppm}, & CO_2 &= 4.4 \text{ ppm}; \\ Ca^{+2} &= 30 \text{ ppm}, & Mg^{+2} &= 21.6 \text{ ppm}; \\ Fe_2O_3 &= 15.4 \text{ ppm}, & H_2SO_4 &= 4.9 \text{ ppm} \end{aligned}$$

Solution:

- Calculation of $CaCO_3$ equivalents for impurities

Salt/Impurity	Qty in mgs/lit	Multiplication factor	$CaCO_3$ equivalent ppm	Requirement of Lime (L) and / or Soda (S)
Ca^{+2}	30 ppm	$30 \times \frac{100}{40}$	75	S
Mg^{+2}	21.6 ppm	$21.6 \times \frac{100}{24}$	90	L + S
H_2SO_4	4.9 ppm	$4.9 \times \frac{100}{98}$	5	
CO_2	4.4 ppm	$4.4 \times \frac{100}{44}$	10	L
HCO_3^-	12.2 ppm	$12.2 \times \frac{100}{122}$	10	Add in L and subtract in S
Fe_2O_3	15.4 ppm	Does not contribute		$Fe_2O_3 \text{ does not contribute}$

Note : Ca^{+2} and Mg^{+2} are to be considered from permanent hardness causing salts.

- Calculation of quantity of lime, required for softening of water

Quantity of lime

$$L = \frac{74}{100} \left[\text{Temporary } Ca^{+2} + 2 \times \text{Temporary } Mg^{+2} + \text{Permanent } (Mg^{+2} + Fe^{+2} + Al^{+3} + H^+ (HCl \text{ or } H_2SO_4)) + CO_2 + HCO_3^- - NaAlO_2 \right] \times \frac{\text{Vol. of Water}}{10^6}$$

$$\times \frac{100}{\% \text{ of purity}} \text{ kg}$$

all in terms of their $CaCO_3$ equivalents.

$$= \frac{74}{100} [90 + 5 + 10 + 10] \times \frac{25000}{10^6} \times \frac{100}{90} \text{ kg}$$

$$\text{Applied Chemistry - I (MU)} \\ = 2.3638 \text{ kg}$$

Calculation of quantity of soda required for softening water.

Quantity of soda

$$S = \frac{10^6}{100} \left[\text{Permanent} (Ca^{+2} + Mg^{+2} + Al^{+3} + Fe^{+2} + H^+ (\text{HCl or } H_2SO_4)) - HCO_3^- \right] \times \frac{\text{Vol. of Water}}{10^6} \times \frac{100}{\% \text{ of purity}} \text{ kg}$$

all in terms of their $CaCO_3$ equivalents.

$$= \frac{10^6}{100} [\text{Perm of } Ca^{+2} + \text{Perm of } Mg^{+2} + H_2SO_4 - HCO_3^-] \times \frac{25000}{10^6} \times \frac{100}{90} \text{ kg}$$

$$\approx \frac{10^6}{100} [75 + 90 + 5 - 10] \times \frac{25}{100}$$

$$= 4.7111 \text{ kg}$$

Ans.: Quantity of lime required = 2.3638 kg

Quantity of soda required = 4.7111 kg

Problem 1.17.20: Calculate quantity of lime (90% pure) and soda ash (90% pure) required to soften 1,00,000 litres of water containing :

- D X $Mg(HCO_3)_2 = 73 \text{ mg/lit}$
 ✓ $MgCl_2 = 95 \text{ mg/lit}$
 $Ca(HCO_3)_2 = 162 \text{ mg/lit}$
 $CaCl_2 = 111 \text{ mg/lit}$
 ✓ $Na_2SO_4 = 15 \text{ mg/lit}$
 ✓ $SiO_2 = 10 \text{ mg/lit}$

$$\text{Applied Chemistry - I (MU)} \\ = 2.3638 \text{ kg}$$

Calculation of $CaCO_3$ equivalents for impurities

Salt	Qty (mg/lit)	Multiplication factor	$CaCO_3$ equivalent ppm	Requirement of Lime (L) and / or Soda (S)
$Mg(HCO_3)_2$	73	$73 \times \frac{100}{146}$	50	2L
$Ca(HCO_3)_2$	162	$162 \times \frac{100}{162}$	100	L
Na_2SO_4		Does not contribute		
$MgCl_2$	95	$95 \times \frac{100}{95}$	100	L + S
$CaCl_2$	111	$111 \times \frac{100}{111}$	100	S
SiO_2		Does not contribute		

Calculation of quantity of lime required for softening of water

Quantity of lime

$$L = \frac{74}{100} \left[\text{Temporary } Ca^{+2} + 2 \times \text{Temporary } Mg^{+2} + \text{Permanent } (Mg^{+2} + Fe^{+2} + Al^{+3} + H^+ (\text{HCl or } H_2SO_4)) + CO_2 + HCO_3^- - NaAlO_2 \right] \times \frac{\text{Vol. of Water}}{10^6} \times \frac{100}{\% \text{ of purity}} \text{ kg}$$

all in terms of their $CaCO_3$ equivalents.

$$L = \frac{74}{100} [100 + 2 \times 50 + 100 + 100] \frac{10^5}{10^6} \times \frac{100}{90} \text{ kg}$$

$$= \frac{74}{100} \times (400) \times \frac{1}{9} \text{ kg}$$

$$= 32.8 \text{ kg of lime}$$

► Calculation of quantity of soda 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.

$$S = \frac{106}{100} [100 + 100] \frac{10^5}{10^6} \times \frac{100}{90} \text{ kg}$$

$$= \frac{106}{100} \times (200) \times \frac{1}{9} \text{ kg}$$

$$= 23.55 \text{ kg of Soda.}$$

Ans. :

$$\text{Lime required} = 32.8 \text{ kg}$$

$$\text{Soda required} = 23.55 \text{ kg}$$

Problem 1.17.21: Calculate the quantity of lime and soda required for softening

of 1,00,000 litres of water containing following impurities in

ppm. The purity of lime is 70% and soda 85%.

$$\frac{Ca}{Mg} Cl_2 = 8.78, CaSO_4 = 35.0, MgSO_4 = 6.7, Na_2 SO_4 = 17.9$$

(Dec. 2008, 8 Marks)

Solution:

Conversion in $CaCO_3$ eq.

Salt/Impurity	Quantity ppm	Multiplication factor	$CaCO_3$ eq. ppm	Requirement Lime/Soda /Both
Ca (HCO_3) ₂	30.2	100/162	18.64	Lime
Mg (HCO_3) ₂	20.8	100/146	14.25	2 Lime
CaCl ₂	28.1	100/111	25.31	Soda
Mg Cl ₂	8.7	100/95	9.16	Lime + Soda

Salt/Impurity	Quantity ppm	Multiplication factor	$CaCO_3$ eq. ppm	Requirement Lime/Soda /Both
CaSO ₄	35.0	100/136	25.73	Soda
MgSO ₄	6.7	100/120	5.58	Lime + Soda
Na ₂ SO ₄	17.9	—	—	Does not consume L or Soda

$Na_2 SO_4$ has to be ignored as it does not consume lime or soda.

$$L = \frac{74}{100} \left[\text{Temporary } Ca^{+2} + 2 \times \text{Temporary } Mg^{+2} + \text{Permanent } (Mg^{+2} + Fe^{+2} + Al^{+3} + H^+ (HCl \text{ or } H_2SO_4)) + CO_2 + HCO^-_3 - NaAlO_2 \right] \times \frac{\text{Vol. of Water}}{10^6} \times \frac{100}{\% \text{ of purity}} \text{ kg}$$

all in terms of their $CaCO_3$ equivalents.

$$= \frac{74}{100} [18.64 + 2 \times 14.25 + 9.16 + 5.58] \times \frac{1,00,000}{10^6} \times \frac{100}{70} \text{ kg}$$

$$\text{Lime} = 6.5416 \text{ kg}$$

$$S = \frac{106}{100} \left[\text{Permanent } (Ca^{+2} + Mg^{+2} + Al^{+3} + Fe^{+2} + H^+ (HCl \text{ or } H_2SO_4)) - HCO^-_3 \right] \times \frac{\text{Vol. of Water}}{10^6} \times \frac{100}{\% \text{ of purity}} \text{ kg}$$

all in terms of their $CaCO_3$ equivalents.

$$= \frac{106}{100} [25.31 + 9.16 + 25.73 + 5.58] \times \frac{10^5}{10^6} \times \frac{100}{85} \text{ kg}$$

$$= \frac{106}{100} [65.78] \times \frac{10^5}{10^6} \times \frac{100}{85} \text{ kg}$$

$$\text{Soda} = 8.203 \text{ kg}$$

$$\text{Lime required} = 6.5416 \text{ kg}$$

$$\text{Soda required} = 8.203 \text{ kg}$$

Ans. :

Problem 1.17.22: Calculate the amount of Lime (80 % pure) and Soda (85 % pure) required for softening 10^6 litres of water containing the following constituents :

$$\text{NaCl} = 58.5 \text{ ppm}, \quad \text{MgCl}_2 = 9.5 \text{ ppm}$$

$$\text{HCl} = 36.5 \text{ ppm}, \quad \text{CaCO}_3 = 111 \text{ ppm}, \quad \text{MgSO}_4 = 60 \text{ ppm}.$$

(At wt. : Ca = 40, Mg = 24, S = 32, O = 16, Cl = 35.5, C = 12, H = 1, Si = 28)

Solution:

Conversion in CaCO_3 equivalents

Salt/Impurity	Quantity ppm	Multiplication factor	CaCO_3 equivalent ppm	Requirement Lime/Soda
Ca (HCO_3) ₂	162	100/162	100	Lime
Mg (HCO_3) ₂	7.3	100/146	05	2 Lime
MgCl ₂	9.5	100/95	10	L + S
HCl	36.5	100/2 × 36.5	50	No L or S
CO ₂	44	100/44	100	L
CaCl ₂	111	100/111	100	Soda
MgSO ₄	60	100/120	50	L + S

Now, $L = \frac{74}{100} [Temporary \text{Ca}^{+2} + 2 \times Temporary \text{Mg}^{+2} + Permanent (\text{Mg}^{+2} +$

$$Fe^{+2} + Al^{+3} + H^+ (\text{HCl or } \text{H}_2\text{SO}_4)) + CO_2 + HCO_3^- - NaAlO_2]$$

$$\times \frac{\text{Vol. of Water}}{10^6} \times \frac{100}{\% \text{ of purity}} \text{ kg}$$

all in terms of their CaCO_3 equivalents.

$$= \frac{74}{100} [100 + (2 \times 0.05) + 10 + 50 + 100 + 50] \times \frac{10^6}{10^6} \times \frac{100}{80}$$

$$= \frac{74}{100} [320] \times \frac{10^6}{10^6} \times \frac{100}{80} = 296 \text{ kgs}$$

Now

$$S = \frac{10^6}{100} [Permanent (\text{Ca}^{+2} + \text{Mg}^{+2} + Al^{+3} + Fe^{+2} + H^+ (\text{HCl} \\ \text{or } \text{H}_2\text{SO}_4)) - HCO_3^-] \times \frac{\text{Vol. of Water}}{10^6} \times \frac{100}{\% \text{ of purity}} \text{ kg}$$

all in terms of their CaCO_3 equivalents.

$$= \frac{10^6}{100} [10 + 50 + 100 + 50] \times \frac{10^6}{10^6} \times \frac{100}{85} \text{ kgs}$$

$$= \frac{10^6}{100} [210] \times \frac{10^6}{10^6} \times \frac{100}{85} \text{ kgs}$$

$$= 261.9 \text{ kgs}$$

$$\text{Lime required} = 296 \text{ kg}$$

$$\text{Soda required} = 261.9 \text{ kg}$$

Problem 1.17.23: 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,

(Dec. 2007, 5 Marks)

Solution:

Calculation of CaCO_3 equivalent :

Salt	Qty (mg/lit)	Multiplication factors	CaCO_3 equivalent ppm	Requirement of Lime (L) and / or Soda (S)
$\text{Ca}(\text{HCO}_3)_2$	81	$81 \times \frac{100}{162}$	50	L
MgCO_3	42	$42 \times \frac{100}{84}$	50	L
NaAlO_2	4.1	$4.1 \times \frac{100}{82}$	5	-L
HCl	3.65	$3.65 \times \frac{100}{36.5 \times 2}$	5	L + S
$\text{Ca}(\text{NO}_3)_2$	82	$82 \times \frac{100}{164}$	50	S
NaCl	4.5	—	—	—

Given :

Purity of lime = 90 %

Purity of soda = 95 %

Volume of raw water = 20000 liter

Calculation of lime,

$$L = \frac{74}{100} \left[\text{Temporary } \text{Ca}^{+2} + 2 \times \text{Temporary } \text{Mg}^{+2} + \text{Permanent } (\text{Mg}^{+2} + \text{Fe}^{+2} + \text{Al}^{+3} + \text{H}^+ (\text{HCl or } \text{H}_2\text{SO}_4)) + \text{CO}_2 + \text{HCO}_3^- - \text{NaAlO}_2 \right] \times \frac{\text{Vol. of Water}}{10^6}$$

$$\begin{aligned} &= \frac{74}{100} [50 + (2 \times 50) + 5 - 5] \times 20000 \times \frac{100}{90} \times \frac{1}{10^6} \text{ kg} \\ &= \frac{74}{100} [150] \times 20000 \times \frac{100}{90} \times \frac{1}{10^6} \text{ kg lime} \\ &= 2.467 \text{ kg} \end{aligned}$$

Calculation of soda,

$$\begin{aligned} S &= \frac{106}{100} \left[\text{Permanent } (\text{Ca}^{+2} + \text{Mg}^{+2} + \text{Al}^{+3} + \text{Fe}^{+2} + \text{H}^+ (\text{HCl or } \text{H}_2\text{SO}_4)) - \text{HCO}_3^- \right] \times \frac{\text{Vol. of Water}}{10^6} \times \frac{100}{\% \text{ of purity}} \text{ kg} \\ &\quad \text{all in terms of their } \text{CaCO}_3 \text{ equivalents.} \\ &= \frac{106}{100} [50 + 5] \times 20000 \times \frac{100}{95} \times \frac{1}{10^6} \\ &= \frac{106}{100} [55] \times 20000 \times \frac{100}{95} \times \frac{1}{10^6} \\ &= \frac{106}{100} [55] \times \frac{2}{95} \text{ kg} = 1.227 \text{ kg} \end{aligned}$$

Ans.

Lime Required = 2.549 kg

Soda Required = 1.227 kg

Problem 1.17.24: Calculate the amount of lime and soda needed to soften 50,000 litres of water containing the following impurities per litre of water : ✓

$\text{CaCl}_2 \approx 222 \text{ mg}$, $\text{Mg}(\text{NO}_3)_2 = 296 \text{ mg}$,
 $\text{Ca}(\text{HCO}_3)_2 = 324 \text{ mg}$, $\text{H}_2\text{SO}_4 = 196 \text{ mg}$ and organic matter
= 130 mg.

(Dec. 2009, 7 Marks)

Solution :

Calculation of CaCO_3 equivalents for impurities

$$\times \frac{100}{\% \text{ of purity}} \text{ kg}$$

all in terms of their CaCO_3 equivalents.

Salt/Impurity	Quantity in mg/L	Multiplication Factor	CaCO_3 equivalent	Requirement of Lime (L) and / or Soda (S)
CaCl_2	222	$222 \times \frac{100}{111}$	200	S
$\text{Mg}(\text{NO}_3)_2$	296	$296 \times \frac{100}{148}$	200	L + S

Salt/Impurity	Quantity in mg/L	Multiplication Factor	CaCO ₃ equivalent	Requirement of Lime (L) and/or Soda (S)
Ca (HCO ₃) ₂	324	$324 \times \frac{100}{162}$	200	L
H ₂ SO ₄	196	$196 \times \frac{100}{98}$	200	L + S
Organic matter	130		Does not consume Lime or Soda.	

Calculation of quantity of Lime required for softening 50000 litres of water.

Quantity of Lime :

$$L = \frac{74}{100} [Temporary Ca^{+2} + 2 \times Temporary Mg^{+2} + Permanent (Mg^{+2} +$$

$$Fe^{+2} + Al^{+3} + H^+ (HCl \text{ or } H_2SO_4) + CO_2 + HCO^-_3 - NaAlO_2]$$

$$\times \frac{Vol. of Water}{10^6} \times \frac{100}{% of purity} \text{ kg}$$

all in terms of their CaCO₃ equivalents.

$$\therefore L = \frac{74}{100} [200 + 200 + 200] \times \frac{50000}{10^6} \times \frac{100}{100} \text{ kg.}$$

$$= \frac{74}{100} [600] \times \frac{5}{100} \text{ kg}$$

$$= 22.2 \text{ kg}$$

Quantity of Soda :

$$S = \frac{106}{100} [Permanent (Ca^{+2} + Mg^{+2} + Al^{+3} + Fe^{+2} + H^+ (HCl \text{ or } H_2SO_4))$$

$$- HCO^-_3] \times \frac{Vol. of Water}{10^6} \times \frac{100}{% of purity} \text{ kg}$$

all in terms of their CaCO₃ equivalents.

$$S = \frac{106}{100} [200 + 200 + 200] \times \frac{50000}{10^6} \times \frac{100}{100} \text{ kg}$$

$$\therefore S = \frac{106}{100} [600] \times \frac{50000}{10^6} \times \frac{100}{100} \text{ kg.}$$

$$\therefore S = 31.8 \text{ kg.}$$

Answer :

$$\text{Lime required} = 22.2 \text{ kg.}$$

$$\text{Soda required} = 31.8 \text{ kg.}$$

Problem 1.17.25 : Calculate the amount of lime (85 % pure) and soda (95% pure) required to soften one million litre of water which contains

✓ CaCO₃ = 12.5 ppm ✓ MgCO₃ = 8.4 ppm, CaCl₂ = 22.2 ppm
✓ MgCl₂ = 9.5 ppm, CO₂ = 33.0 ppm, HCl = 7.3 ppm,
✓ NaHCO₃ = 16.8 ppm. (May 2010, 5 Marks)

Solution :

Calculation of CaCO₃ equivalents for impurities.

Salt/Impurity	Quantity in ppm	Multiplication factor	CaCO ₃ equivalent ppm	Requirement of Lime (L) and / or Soda (S)
CaCO ₃	12.5	$12.5 \times \frac{100}{100}$	12.5	L
MgCO ₃	8.4	$8.4 \times \frac{100}{84}$	10	L
CaCl ₂	22.2	$22.2 \times \frac{100}{111}$	20	S
MgCl ₂	9.5	$9.5 \times \frac{100}{95}$	10	L + S
CO ₂	33	$33 \times \frac{100}{44}$	75	L

Salt/Impurity	Quantity in ppm	Multiplication factor	CaCO ₃ equivalent ppm	Requirement of Lime (L) and/or Soda (S)
HCl ✓	7.3	$7.3 \times \frac{100}{2 \times 36.5}$	10	L + S
NaHCO ₃ ✓	16.8	$16.8 \times \frac{100}{84 \times 2}$	10	Add in Lime Subtract from Soda

Calculation of Lime (85% pure) required for one million litres of water.

$$L = \frac{74}{100} \left[\text{Temporary } Ca^{+2} + 2 \times \text{Temporary } Mg^{+2} + \text{Permanent } (Mg^{+2} + Fe^{+2} + Al^{+3} + H^+ (HCl \text{ or } H_2SO_4)) + CO_2 + HCO^{-}_3 - NaAlO_2 \right] \times \frac{\text{Vol. of Water}}{10^6}$$

$$\times \frac{100}{\% \text{ of purity}} \text{ kg}$$

all in terms of their CaCO₃ equivalents.

$$= \frac{74}{100} [12.5 + 2 \times 10 + 10 + 75 + 10] \times \frac{10^6}{10^6} \times \frac{100}{85} \text{ kg}$$

$$\text{Lime} = 111 \text{ kg.}$$

Quantity of Soda (95%) required for one million litres of water.

$$S = \frac{106}{100} \left[\text{Permanent } (Ca^{+2} + Mg^{+2} + Al^{+3} + Fe^{+2} + H^+ (HCl \text{ or } H_2SO_4)) - HCO^{-}_3 \right] \times \frac{\text{Vol. of Water}}{10^6} \times \frac{100}{95} \text{ kg}$$

all in terms of their CaCO₃ equivalents.

$$S = \frac{106}{100} [20 + 10 + 10 - 10] \times \frac{10^6}{10^6} \times \frac{100}{95} \text{ kg.}$$

$$= \frac{106}{100} [30] \times \frac{10^6}{10^6} \times \frac{100}{95} \text{ kg.} = \left[\frac{106 \times 30}{95} \right] \text{ kg.}$$

$$= 33.474 \text{ kg.}$$

Answer :

Lime required = 111 kg.

Soda required = 33.474 kg.

Problem 1.17.26 : Calculate the quantity of lime and soda required for softening 50,000 liters of water containing the following salts per liter:

$$\checkmark Ca(HCO_3)_2 = 8.1 \text{ mg}, Mg(HCO_3)_2 = 7.5, CaSO_4 = 13.6 \text{ mg},$$

$$\checkmark MgSO_4 = 12 \text{ mg}, MgCl_2 = 2 \text{ mg}, NaCl = 4.7 \text{ mg.}$$

(Dec. 2010, 5 Marks)

Solution :
Calculation of CaCO₃ equivalents of impurities.

Salt	Quantity mgslit ppm	Multiplication factor	CaCO ₃ equivalent in ppm	Requirement of lime (L) and/or soda (S)
Ca(HCO ₃) ₂ ✓	8.1	$8.1 \times \frac{100}{162}$	5	L (Temporary)
Mg(HCO ₃) ₂ ✓	7.5	$7.5 \times \frac{100}{146}$	5.13	2L (Temporary Mg)
CaSO ₄ ✓	13.6	$13.6 \times \frac{100}{136}$	10	S (Permanent)
MgSO ₄ ✓	12	$12 \times \frac{100}{120}$	10	L + S (Permanent)
MgCl ₂ ✓	2	$2 \times \frac{100}{95}$	2.1	L + S (Permanent)
NaCl —	4.7	$4.7 \times \frac{100}{58.5}$	8.0	No L or S

Lime required for softening :

$$L = \frac{74}{100} \left[\text{Temporary } Ca^{+2} + 2 \times \text{Temporary } Mg^{+2} + \text{Permanent } (Mg^{+2} + Fe^{+2} + Al^{+3} + H^+ (HCl \text{ or } H_2SO_4)) + CO_2 + HCO^{-}_3 - NaAlO_2 \right] \times \frac{\text{Vol. of Water}}{10^6} \times \frac{100}{\% \text{ of purity}} \text{ kg}$$

all in terms of their CaCO₃ equivalents.

$$\begin{aligned}
 &= \frac{74}{100} [5 + (2 \times 5.13) + 2.1 + 10] \times \frac{50,000}{10^6} \times \frac{100}{100} \\
 &= 0.74 \times 27.36 \times 0.05 \\
 &= 1.012 \text{ kg}
 \end{aligned}$$

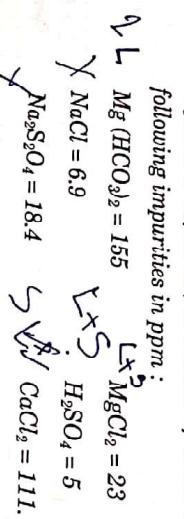
Soda required for softening :

$$S = \frac{106}{100} \int_{\text{X}} \text{Permanent} \left(\text{Ca}^{2+} + \text{Mg}^{2+} + \text{Al}^{3+} + \text{Fe}^{2+} + \text{H}^+ (\text{HCl or H}_2\text{SO}_4) \right) \\
 - \text{HCO}_3^- \int_{\text{X}} \frac{\text{Vol. of Water}}{10^6} \times \frac{100}{\% \text{ of purity}} \text{ kg}$$

all in terms of their CaCO_3 equivalents.

$$\begin{aligned}
 &= \frac{106}{100} [2.1 + 10 + 10] \times \frac{50,000}{10^6} \times \frac{100}{100} \\
 &= 1.06 \times 22.1 \times 0.05 \\
 &= 1.1713 \text{ kg}
 \end{aligned}$$

Problem 1.17.27: Calculate the amount of lime (90 % pure) and soda (95 % pure) required to soften 50,000 litres of same water containing the following impurities in ppm :



Solution: Calculation of CaCO_3 equivalents of impurities.

(May 2011, 5 Marks)

Salt	Quantity in ppm	Multiplication factor	CaCO_3 equivalents in ppm	Requirement of lime(L) and/or soda(S)
CaCl_2	111	$111 \times \frac{100}{111}$	100	S
MgCl_2	23	$23 \times \frac{100}{95}$	24.2	L + S
NaCl	6.9	$6.9 \times \frac{100}{58.5}$	Does not react	With lime and soda

Salt	Quantity in ppm	Multiplication factor	CaCO_3 equivalents in ppm	Requirement of lime(L) and/or soda(S)
$\text{Mg}(\text{HCO}_3)_2$	155	$155 \times \frac{100}{146}$	106.2	2L
Na_2SO_4	18.4	$18.4 \times \frac{100}{142}$	Does not react	With lime and soda
H_2SO_4	5	$5 \times \frac{100}{98}$	5.1	L + S

Quantity of lime :

$$\begin{aligned}
 L &= \frac{74}{100} \left[\text{Temp. } \text{Ca}^{2+} + 2 \times \text{Temp. } \text{Mg}^{2+} + \text{Perm. } (\text{Mg}^{2+} + \text{Fe}^{2+} + \text{Al}^{3+}) \right. \\
 &\quad \left. + \text{H}^+(\text{HCl or H}_2\text{SO}_4) \right] + \text{CO}_2 + \text{HCO}_3^- - \text{NaAlO}_2 \times \frac{\text{Vol. of Water}}{10^6} \\
 &\times \frac{100}{\% \text{ of purity}} \text{ kg all in terms of their } \text{CaCO}_3 \text{ equivalents.}
 \end{aligned}$$

$$\begin{aligned}
 \therefore L &= \frac{74}{100} \left[2 \times \text{Mg } (\text{HCO}_3)_2 + \text{MgCl}_2 + \text{H}_2\text{SO}_4 \text{ in terms of their } \text{CaCO}_3 \text{ equivalent} \right] \times \frac{50,000}{10^6} \times \frac{100}{90} \text{ kg} \\
 &= \frac{74}{100} [2(106.2) + 24.2 + 5.1] \times 0.05 \text{ kg} \\
 &= 8.9429 \text{ kg of lime}
 \end{aligned}$$

Quantity of soda :

$$\begin{aligned}
 S &= \frac{106}{100} [\text{Perm. } (\text{Ca}^{2+}, \text{Mg}^{2+}, + \text{Al}^{3+}, \text{etc.}) + \text{H}^+(\text{HCl, H}_2\text{SO}_4, \text{etc.}) - \text{NaHCO}_3] \\
 &\text{all in terms of their } \text{CaCO}_3 \text{ equivalents} \times \frac{\text{Vol. of water}}{10^6} \times \frac{100}{\% \text{ of Purity}} \text{ kg}
 \end{aligned}$$

$$\begin{aligned}
 \therefore S &= \frac{106}{100} \left[\text{CaCl}_2 + \text{MgCl}_2 + \text{H}_2\text{SO}_4 \text{ in terms of } \text{CaCO}_3 \text{ equivalent} \right] \times \frac{50,000}{10^6} \times \frac{100}{95} \text{ kg} \\
 &= \frac{106}{100} [100 + 24.2 + 5.1] \times 0.050 \text{ kg} \\
 &= \frac{106}{100} \times 129.3 \times 0.050 \text{ kg} \\
 &= 6.8529 \text{ Kg}
 \end{aligned}$$

Problem 1.17.28: Calculate the quantity of lime (90% pure) and soda (95% pure) required for softening 50,000 litres of water containing the following impurities.

$$\checkmark \text{Ca}(\text{HCO}_3)_2 = 81 \text{ mg/l}, \quad \text{MgCl}_2 = 95 \text{ mg/l},$$

$$\checkmark \text{CaSO}_4 = 68 \text{ mg/l}, \quad \text{SiO}_2 = 50 \text{ mg/l},$$

$$\checkmark \text{Mg}(\text{HCO}_3)_2 = 146 \text{ mg/l}, \quad \text{H}_2\text{SO}_4 = 49 \text{ mg/l}.$$

(Dec. 2011, 5 Marks)

Solution: Calculation of CaCO_3 equivalents of impurities.

Salts/ impurity	Quantity mg/l	Multiplication factor	CaCO_3 equivalents ppm	Requirement of Lime (L) and / or Soda (S)
$\text{Ca}(\text{HCO}_3)_2$	81	$\frac{100}{162}$	50	L
MgCl_2	95	$\frac{100}{95}$	100	L + S
CaSO_4	68	$\frac{100}{136}$	50	S
SiO_2 —	—	—	—	—
$\text{Mg}(\text{HCO}_3)_2$	146	$\frac{100}{146}$	100	2L
H_2SO_4	49	$\frac{100}{98}$	50	L + S

➤ Calculation of requirement of Lime in kg for 50000 litres of water:

Lime required

$$L = \frac{74}{100} \left[\text{Temporary } \text{Ca}^{+2} + 2 \times \text{Temporary } \text{Mg}^{+2} + \text{Permanent } (\text{Mg}^{+2} + \text{Fe}^{+2} + \text{Al}^{+3} + \text{H}^+ (\text{HCl or } \text{H}_2\text{SO}_4)) + \text{CO}_2 + \text{HCO}_3^- - \text{NaAlO}_2 \right]$$

$$\times \frac{\text{Vol. of Water}}{10^6} \times \frac{100}{\% \text{ of purity}} \text{ kg}$$

all in terms of their CaCO_3 equivalents.

$$= \frac{74}{100} [50 + 2(100) + 50 + 100] \times \frac{50000}{10^6} \times \frac{100}{90} \text{ kg}$$

$$= \frac{74}{100} [400] \times \frac{5}{90} \text{ kg} = 16.44 \text{ kg}$$

$$\therefore \text{Lime} = 16.44 \text{ kg}$$

Quantity of soda :

$$S = \frac{106}{100} \left[\text{Permanent } (\text{Ca}^{+2} + \text{Mg}^{+2} + \text{Al}^{+3} + \text{Fe}^{+2} + \text{H}^+ (\text{HCl or } \text{H}_2\text{SO}_4)) - \text{HCO}_3^- \right] \times \frac{\text{Vol. of Water}}{10^6} \times \frac{100}{\% \text{ of purity}} \text{ kg}$$

all in terms of their CaCO_3 equivalents.

$$= \frac{106}{100} [100 + 50 + 50] \times \frac{50000}{10^6} \times \frac{100}{95} \text{ kg}$$

$$= 11.15 \text{ kg}$$

$$\text{Ans.: Lime required} = 16.44 \text{ kg}$$

Soda required = 11.15 kg

Problem 1.17.29: Calculate lime (95% pure) and soda (90% pure) required for softening one million litres of water containing the following constituents:

$$\checkmark \text{Ca}(\text{HCO}_3)_2 = 81 \text{ mg/l}, \quad \checkmark \text{Mg}(\text{HCO}_3)_2 = 73 \text{ mg/l},$$

$$\checkmark \text{CaSO}_4 = 68 \text{ mg/l}, \quad \checkmark \text{MgCl}_2 = 95 \text{ mg/l},$$

$$\checkmark \text{Mg}(\text{NO}_3)_2 = 4.8 \text{ mg/l}, \quad \checkmark \text{H}_2\text{SO}_4 = 14.7 \text{ mg/l}.$$

(May 2012, 5 Marks)

Solution:

Calculation of CaCO_3 equivalents for impurities.

Salt/ impurity	Quantity	Multiplication factor	CaCO_3 equivalents ppm	Requirement of Lime (L) and / or Soda (S)
$\text{Ca}(\text{HCO}_3)_2$	81	$\frac{100}{162}$	50	L
$\text{Mg}(\text{HCO}_3)_2$	73	$\frac{100}{146}$	50	$2L$
CaSO_4	68	$\frac{100}{136}$	50	S
MgCl_2	95	$\frac{100}{95}$	100	$L + S$
$\text{Mg}(\text{NO}_3)_2$	14.8	$\frac{100}{148}$	10	$L + S$
H_2SO_4	14.7	$\frac{100}{98}$	15	$L + S$

Calculation of requirement of Lime in kg for 50000 litres of water.

Lime required

$$L = \frac{74}{100} \text{ Temporary } \text{Ca}^{+2} + 2 \times \text{Temporary } \text{Mg}^{+2} + \text{Permanent } (\text{Mg}^{+2} + \text{Fe}^{+2} + \text{Al}^{+3} + \text{H}^+ (\text{HCl or H}_2\text{SO}_4)) + \text{CO}_2 + \text{HCO}_3^- - \text{NaAlO}_2$$

$$\times \frac{\text{Vol. of Water}}{10^6} \times \frac{100}{\% \text{ of purity}} \text{ kg}$$

all in terms of their CaCO_3 equivalents.

$$= \frac{74}{100} [50 + 2(50) + 100 + 10 + 15] \times \frac{10^6}{10^6} \times \frac{100}{95} \text{ kg}$$

$$= \frac{74}{100} [275] \times \frac{100}{95} = 214.2 \text{ kg}$$

Quantity of soda :

$$S = \frac{10^6}{100} \left[\text{Permanent } (\text{Ca}^{+2} + \text{Mg}^{+2} + \text{Al}^{+3} + \text{Fe}^{+2} + \text{H}^+(\text{HCl or H}_2\text{SO}_4)) - \text{HCO}_3^- \right]$$

$$\times \frac{\text{Vol. of Water}}{10^6} \times \frac{100}{\% \text{ of purity}} \text{ kg all in terms of their } \text{CaCO}_3 \text{ equivalents.}$$

$$= \frac{10^6}{100} [50 + 100 + 10 + 15] \times \frac{10^6}{10^6} \times \frac{100}{90} \text{ kg}$$

$$= \frac{10^6}{100} [175] \times \frac{100}{90} \text{ kg}$$

$$= 206.1 \text{ kg}$$

Ans.: Lime required = 214.2 kg
Soda required = 206.1 kg

1.17.4 Problems based on Zeolite Process

Problem 1.17.30: 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 :

$$100 \text{ mL solution} \Rightarrow 15 \text{ gms NaCl}$$

$$\therefore 1 \text{ litre solution} \Rightarrow 150 \text{ gms NaCl}$$

$$\therefore 50 \text{ litres solution} \Rightarrow 7500 \text{ gms NaCl}$$

$$\Rightarrow \frac{7500 \times 50}{58.5} \text{ gms equivalents of } \text{CaCO}_3$$

$$\Rightarrow 6410.256 \text{ gms } \text{CaCO}_3 \text{ equivalent}$$

Thus zeolite bed removed 6410256 mgs equivalent of CaCO_3 hardness.

$\because 250 \text{ ppm hardness} \Rightarrow 1 \text{ litre of water}$

$$\therefore 6410256 \text{ ppm hardness} \Rightarrow \frac{6410256 \times 1}{250} \text{ litres of water}$$

$$\Rightarrow 25641.025 \text{ litres of water}$$

$$\approx 25641 \text{ litres of water}$$

Ans.: Thus 25641 litres of water softened by zeolite bed.

Problem 1.17.30(a) : Calculate amount of lime (90% pure) and soda (98% pure) for the treatment of 1 million litres of water containing

$\text{Ca}(\text{HCO}_3)_2 = 8.1 \text{ ppm}$, $\text{CaCl}_2 = 33.3 \text{ ppm}$, $\text{HCO}_3^- = 91.5 \text{ ppm}$, $\text{MgCl}_2 = 38 \text{ ppm}$, $\text{Mg}(\text{HCO}_3)_2 = 14.6 \text{ ppm}$. The coagulant $\text{Al}_2(\text{SO}_4)_3$ was added at the rate of 17.1 ppm.

(Dec. 2012, 6 Marks)

Solution:

$$\text{L} = \frac{74}{100} \left[\text{Temporary Ca}^{+2} + 2 \times \text{Temporary Mg}^{+2} + \text{Permanent } (\text{Mg}^{+2} + \text{Fe}^{+2} + \text{Al}^{+3}) + \text{H}^+(\text{HCl or H}_2\text{SO}_4) \right] + \text{CO}_2 + \text{HCO}_3^- - \text{NaAlO}_2$$

$$+ \text{H}^+(\text{HCl or H}_2\text{SO}_4) + \text{CO}_2 + \text{HCO}_3^- - \text{NaAlO}_2 \times \frac{\text{Vol. of Water}}{10^6} \times \frac{100}{\% \text{ of purity}} \text{ kg}$$

all in terms of their CaCO_3 equivalents

➤ Calculation of CaCO_3 equivalents for impurities.

Salt/ impurity	Quantity ppm	Multiplication factor	CaCO_3 equivalents ppm	Requirement of Lime (L) and / or Soda (S)
$\text{Ca}(\text{HCO}_3)_2$	8.1	$\frac{100}{162}$	5	L
CaCl_2	33.3	$\frac{100}{111}$	30	S
HCO_3^-	91.5	$\frac{100}{61 \times 2}$	75	Add in lime Subtract in soda + L - S
MgCl_2	38	$\frac{100}{95}$	40	L + S

Salt/ impurity	Quantity ppm	Multiplication factor	CaCO_3 equivalents ppm	Requirement of Lime (L) and / or Soda (S)
$\text{Mg}(\text{HCO}_3)_2$	14.6	$\frac{100}{146}$	10	2L
$\text{Al}_2(\text{SO}_4)_3$	17.1	$\frac{100}{114}$	15	+ L + S

➤ Calculation of quantity of Lime in kg required for softening water.

Quantity of lime,

$$\text{L} = \frac{74}{100} \left[\text{Temporary Ca}^{+2} + 2 \times \text{Temporary Mg}^{+2} + \text{Permanent } (\text{Mg}^{+2} + \text{Fe}^{+2} + \text{Al}^{+3}) + \text{H}^+(\text{HCl or H}_2\text{SO}_4) \right]$$

$$\times \frac{\text{Vol. of Water}}{10^6} \times \frac{100}{\% \text{ of purity}} \text{ kg} \quad \text{all in terms of their } \text{CaCO}_3 \text{ equivalents.}$$

$$= \frac{74}{100} [5 + 2 \times 10 + 40 + 30 + 15 + 75] \times \frac{10^6}{10^6} \times \frac{100}{90} \text{ kg}$$

$$= \frac{74}{100} [185] \times \frac{100}{90} \text{ kg}$$

$$= 152 \text{ kg}$$

➤ Calculation of Quantity of soda in kilogram required for softening water:

Quantity of soda :

$$\text{S} = \frac{106}{100} \left[\text{Permanent } (\text{Ca}^{+2} + \text{Mg}^{+2} + \text{Al}^{+3} + \text{Fe}^{+2}) + \text{H}^+(\text{HCl or H}_2\text{SO}_4) - \text{HCO}_3^- \right]$$

$$\times \frac{\text{Vol. of Water}}{10^6} \times \frac{100}{\% \text{ of purity}} \text{ kg} \quad \text{all in terms of their } \text{CaCO}_3 \text{ equivalents.}$$

$$= \frac{106}{100} [30 + 40 + 15 - 75] \times \frac{10^6}{10^6} \times \frac{100}{98} \text{ kg}$$

$$= \frac{106}{100} [10] \times \frac{100}{98} \text{ kg}$$

$$= 10.8 \text{ kg}$$

Ans. : Quantity lime = 152 kg

Quantity of soda = 10.8 kg

Problem 1.17.31: How many litres of 20 % 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 NaCl used in regeneration?

Solution:

Quantity of water softened = 20 litre

Hardness of water = 375 ppm

$$= 375 \text{ mgs CaCO}_3 \text{ equivalent per litre}$$

i.e. 20 litres water \Rightarrow 7,500 mgs CaCO₃ equivalent

Now NaCl used is 20 % solution.

i.e. 20 gms per 100 ml solution

Or 200 gms per 1000 ml solution.

Equivalents of CaCO₃ of this solution would be

$$= \frac{200 \times 50}{58.5} \times 1000$$

$$= \frac{10000}{58.5}$$

$$= 171 \text{ mgs}$$

\because 171 mgs CaCO₃ equivalents \Rightarrow 1 litre of NaCl solution

$\therefore 7.5 \times 10^3$ mgs equivalent of CaCO₃

$$\Rightarrow \frac{7.5 \times 10^3}{171} \text{ litres of NaCl solution}$$

$$\Rightarrow \frac{7500}{171} \text{ litres of NaCl solution}$$

Ans. : Hardness of water sample = 13.68 ppm

$\Rightarrow 43.85$ litres of NaCl solution

≈ 44 litres

Ans. : Volume of NaCl solution required = 44 litres

Problem 1.17.32: The hardness of 25000 litres of water was completely removed using zeolite softener. For regeneration of exhausted zeolite bed, 200 litres of NaCl solution containing 20 gms per litre NaCl was required. Calculate the hardness of water sample.

Solution:

Using regeneration reaction,



$$\text{i.e. } 2 \text{ NaCl} \equiv \text{CaCl}_2 \equiv \text{CaCO}_3$$

$$2(58.5) \text{ gms} \equiv 111 \text{ gm} \equiv 100 \text{ gm of CaCO}_3$$

Now, quantity of NaCl in regeneration

$$= 200 \times 20$$

$$= 4000 \text{ gms NaCl}$$

Thus (2×58.5) gms NaCl \Rightarrow 100 gms CaCO₃

$$\therefore 4000 \text{ gm NaCl} \Rightarrow \frac{4000 \times 100}{2 \times 58.5}$$

$$\Rightarrow \frac{4000 \times 100}{117}$$

$$\Rightarrow 3418.8 \text{ gms of CaCO}_3$$

$$\Rightarrow 341880 \text{ mgs of CaCO}_3$$

\because 25000 litres of hard water \Rightarrow 341880 mgs CaCO₃

$\therefore 1$ litre of hard water $\Rightarrow \frac{341880}{25000}$ mgs of CaCO₃

$$\Rightarrow 13.68 \text{ mgs of CaCO}_3$$

$$\Rightarrow 13.68 \text{ ppm}$$

Problem 1.17.33: 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 80×1000 mg

$$\begin{aligned} &= 80000 \text{ mgs of NaCl} \\ &= 80000 \times \frac{50}{58.5} \text{ mg of CaCO}_3 \text{ equivalents} \\ &\approx 68376.0 \text{ mg of CaCO}_3 \text{ equivalents} \end{aligned}$$

But the total quantity of water is 10^4 litres.

So the hardness present in the water sample

$$\begin{aligned} &= \frac{68376.0}{10^4} \text{ mg/lit} \\ &= 6.8376 \text{ mg/lit} \\ &= 6.84 \text{ mg/lit} \end{aligned}$$

Ans.: Hardness of water = 6.84 mg/lit

Problem 1.17.34: The hardness of 75,000 litres of a water sample was completely removed by a permumit. The exhausted permumit 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

$$\begin{aligned} 58.5 \text{ mg of NaCl} &\equiv 50 \text{ mgs of CaCO}_3 \text{ equivalent hardness} \\ &= 175500 \times \frac{50}{58.5} \\ &= 1,50,000 \text{ mgs of CaCO}_3 \text{ equivalents} \end{aligned}$$

hardness

But the total quantity of the water sample = 75,000 litre

$$\begin{aligned} \therefore 75000 \text{ lt. of water} &\equiv 1,50,000 \text{ mgs of CaCO}_3 \\ \therefore 1 \text{ lt. of water} &= \frac{150000}{75000} \text{ mgs of CaCO}_3 \\ &= 2 \text{ mg/l of CaCO}_3 \\ &= 2 \text{ ppm CaCO}_3 \end{aligned}$$

Ans.: Hardness of water sample = 2 ppm

Problem 1.17.35: 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

$$\begin{aligned} \text{Hardness} &= \text{concentration of NaCl} \times \text{litres of NaCl} \\ &= 75000 \times 300 \\ &= 225 \times 10^5 \text{ mg of NaCl} \\ &= 225 \times 10^5 \times \frac{50}{58.5} \text{ mg of CaCO}_3 \\ &= 19230769.23 \text{ mg} \end{aligned}$$

If 1 litre of water = 600 mgs of CaCO₃ equivalent hardness

x litres of water = 19230769.23 of CaCO₃ equivalent hardness

$$\therefore x = \frac{19250769.23}{600}$$

$$= 32051.28 \text{ litres of water}$$

Ans. : 32051.28 litres of water sample can be softened

Problem 1.17.36: 800 litres of raw water was soften by zeolite softener. After it got exhausted required 40 liters 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 :

$$= 110 \text{ gm/liter NaCl}$$

$$= 110 / 1000 \text{ ml.}$$

$$\text{Volume of Raw water} = 800 \text{ liter}$$

$$\text{Volume of NaCl for regeneration} = 40 \text{ liter}$$

To calculate hardness of water

\because 40 liter of NaCl consumed

$$= 40 \times 110 \text{ gm. NaCl}$$

\equiv 4400 gm of NaCl consumed for regeneration.

$$\equiv \frac{4400 \times 50}{58.5} \text{ gms equivalents of CaCO}_3$$

$\equiv 3760.7 \text{ gms equivalents of CaCO}_3$

Thus

$$800 \text{ litres of water} = 3760.7 \text{ gms CaCO}_3 \text{ equivalents}$$

$$\therefore 1 \text{ litre of water} = \frac{3760.7}{800} \text{ gms CaCO}_3 \text{ equivalents}$$

Ans. :

Hardness of water sample = 4700 ppm.

P

Problem 1.17.37: One litre of hard water containing 4.5 gm of CaCl₂ was passed through a permunti's softner. Calculate quantity of NaCl produced in soft water. (Dec. 2008, 5 Marks)

Solution :

$$\text{Volume of hard water} = 1 \text{ litre}$$

$$\text{Quantity of CaCl}_2 = 4.5 \text{ gm.}$$

To calculate = Quantity of NaCl produced in soft water



$$111 \quad 2 \times 58.5$$

Now since CaCl₂ quantity = 4.5 gm.

$$\text{NaCl produced} = \frac{4.5 \times 2 \times 58.5}{111}$$

$$= 4.74 \text{ gm}$$

Ans. : Quantity of NaCl in soft water = 4.74 gm.

Problem 1.17.38: A zeolite softener was completely exhausted and was regenerated by passing 100 litres of sodium chloride solution containing 120 gm per litre of NaCl. How many litres of sample of water of hardness 500 ppm can be softened by this softener? (May 2010, 5 Marks)

Given Data :

$$\text{Volume of NaCl solution} = 100 \text{ litres}$$

$$\text{Quantity of NaCl} = 120 \text{ gms/litre}$$

$$\text{Hardness of water} = 500 \text{ ppm}$$

To calculate = Volume of water softened.

$$= 4.7 \text{ gms CaCO}_3 \text{ equivalents}$$

$$= 4700 \text{ mgs CaCO}_3 \text{ equivalents}$$

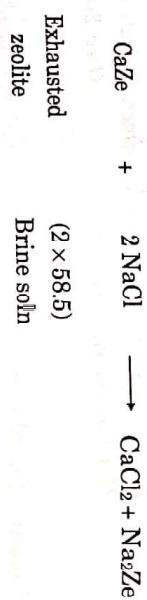
Thus hardness of water sample = 4700 ppm.

i.e. $2 \text{NaCl} \equiv \text{CaCl}_2 \equiv \text{CaCO}_3$

Solution :
 \therefore 100 litres of NaCl used, in regeneration and concentration of NaCl is 120 gm/litres.

$$\therefore \text{Quantity of NaCl consumed} = 100 \times 120 \\ = 12000 \text{ gms.}$$

Reaction :



$$\therefore \text{CaCO}_3 \text{ equivalents} = \left(12000 \times \frac{100}{2 \times 58.5} \right) \times 10^6 \text{ mgs}$$

$$= 10.26 \times 10^6 \text{ mgs CaCO}_3 \text{ eq.}$$

Now, Let V litres of 500 ppm (i.e. 500 mgs/litr) of water consumes 10.26×10^6 mgs CaCO₃ eq of NaCl.

$$\therefore V \times 500 = 10.26 \times 10^6$$

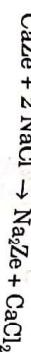
$$\therefore V = \left(\frac{10.26 \times 10^6}{500} \right) \text{ litres} \\ = (2.052 \times 10^4) \text{ litres} \\ = 20520 \text{ litres}$$

Ans.: 20520 litres of water was softened by Zeolite bed.

Problem 1.17.39: The hardness of 3500 litres of water was completely removed by zeolite softener. The zeolite had required 25 litres of 100 gm/lit of NaCl to regenerate. Calculate the hardness of the water.

Solution : (May 2011, 5 Marks)

Using regeneration reaction,



Now,
Quantity of NaCl in regeneration,

$$= 25 \times 100 \\ = 2500 \text{ gms NaCl}$$

Thus,

$$(2 \times 58.5) \text{ gms NaCl} \Rightarrow 100 \text{ gm CaCO}_3 \\ \therefore 2500 \text{ gm NaCl} \Rightarrow \frac{2500 \times 100}{2 \times 58.5} \\ = 2136.752 \text{ gms of CaCO}_3$$

$$= 2136752 \text{ mgs of CaCO}_3$$

$$\therefore 3500 \text{ litres of hard water} = 2136752 \text{ mgs CaCO}_3$$

$$\therefore 1 \text{ litre of hard water} = \frac{2136752}{3500} \text{ mgs of CaCO}_3$$

$$= 610.5 \text{ mgs of CaCO}_3$$

$$= 610.5 \text{ ppm}$$

∴ Hardness of water sample = 610.5 ppm

Problem 1.17.40: 15,000 litres of hard water was passed through a zeolite softener. The exhausted zeolite required 120 litres of NaCl having 30 g / litre of NaCl. Calculate the hardness of water. (Dec. 2011, 5 Marks)

Solution :

Let the hardness of the water sample be x mg/l

Now, 1 litre of NaCl contains 30 g of NaCl = 30000 mg NaCl

$\therefore 120 \text{ litres of NaCl contains } 120 \times 30000 = 3600000 \text{ mg of NaCl}$

58.5 mg of NaCl \equiv 50 mgs of CaCO₃ equivalent hardness

$$= 3600000 \times \frac{50}{58.5}$$

= **30,46,923 mgs of CaCO_3 equivalents hardness**

But the total quantity of the water sample = 75,000 litre

$$\therefore 15000 \text{ lt. of water} \equiv 30,46,923 \text{ mgs of } \text{CaCO}_3$$

$$\begin{aligned}\therefore 1 \text{ lt. of water} &= \frac{3046923}{15000} \text{ mgs of } \text{CaCO}_3 \\ &= 205 \text{ mg/l of } \text{CaCO}_3 \\ &= 205 \text{ ppm } \text{CaCO}_3\end{aligned}$$

Ans. : Hardness of water sample = 205 ppm

Problem 1.17.41: An exhausted Zeolite softener was regenerated by passing 300 litres of NaCl solution having a strength of 150 g per litre of NaCl . If the hardness of water sample was 480 ppm, calculate the total volume of water softened by this softener.

(May 2012, 5 Marks)

Solution:

Here, let the quantity of the water sample be x litre

Now, the hardness of the water sample is 480 ppm

$$\begin{aligned}\text{Hardness} &= \text{concentration of } \text{NaCl} \times \text{litres of } \text{NaCl} \\ &= 150000 \times 300 \\ &= 450 \times 10^5 \text{ mg of } \text{NaCl}\end{aligned}$$

$$\begin{aligned}&= 450 \times 10^5 \times \frac{50}{58.5} \text{ mg of } \text{CaCO}_3 \\ &= 384.6 \times 10^5 \text{ mg}\end{aligned}$$

If 1 litre of water \equiv 450 mgs CaCO_3 eq. H

Then x litre of water \equiv $6.410 \times 10^6 \text{ CaCO}_3$ eq. H

$$\begin{aligned}\therefore x &= \frac{6.410 \times 10^6}{450} \text{ litres} \\ &= 0.01424501 \times 10^6 \text{ litres} \\ &= 14245 \text{ litres.}\end{aligned}$$

Ans. : 14245 litre water sample can be softened.

1.17.5 Numericals on COD and BOD

Problem 1.17.41(b): A Zeolite softener was completely exhausted and was regenerated by passing 150 lit of NaCl solution, containing 50 g/litre of sodium chloride. How many litres of water

sample of hardness 450 ppm can be softened by this zeolite container. (May 2013, 4 Marks)

Solution:

Here let the quantity of water be x litres.

$$\begin{aligned}\text{Hardness} &= \text{Concentration of } \text{NaCl} \times \text{Litres of } \text{NaCl} \\ &= (150 \times 50 \times 1000) \\ &= 75,00,000 \text{ mgs of } \text{NaCl} \\ &= 75,00,000 \times \frac{50}{58.5} \text{ mgs } \text{CaCO}_3 \text{ eq.} \\ &\equiv 6.410 \times 10^6 \text{ mgs } \text{CaCO}_3 \text{ eq.}\end{aligned}$$

Ans. : Hardness of water sample = 205 ppm

Problem 1.17.41(b): Two BOD bottles contained each of 5 ml of sewage sample and water diluted with distilled water to 300 ml. One 100 ml portion of the blank consumed 6.4 ml of 0.05 N thiosulphate in the Winkler's method for the determination of dissolved oxygen while 100 ml of the second bottle incubated at 20 °C for the five days required 1.6 ml of the same thiosulphate solution. Calculate the BOD content of the sample.

Solution:

Difference in the volume of thiosulphate solution required for blank and the sample solution.

$$= 6.4 - 1.6 = 4.8 \text{ ml of } 0.05 \text{ N thiosulphate solution}$$

Since 1 litre of 1 N thiosulphate solution = 8 g oxygen

$$4.8 \text{ ml of } 0.05 \text{ thiosulphate solution n} = [(8 * 4.8 * 0.05) / 1000] * 100 / 300$$

$$= 3.4 \times 10^{-4} \text{ g oxygen for } 5 \text{ ml of sewage sample}$$

Oxygen required for 1000 ml of sewage sample = 0.128 g

BOD for sample = 1285 mg/lit

Problem 1.17.43: A 10 ml of sample of waste water was refluxed with 20 ml of potassium dichromate solution and after refluxing the excess unreacted dichromate required 26.2 ml of 0.1 M FAS solution.

A blank of 10 ml of distilled water on refluxing with 20 ml of dichromate solution required 36 ml of 0.1 M FAS solution.

Calculate the COD value of the wastewater.

Solution:

Difference in the volumes of the FAS required for the blank and sample solution = 36 - 26.2 = 9.8 ml

Since 1 litre of 1 M FAS = 8 g of oxygen

$$9.8 \text{ ml of } 0.1 \text{ M FAS} = 8 * 9.8 * 0.1 / 1000$$

$$= 7.84 * 10^{-3} \text{ of oxygen for } 10 \text{ ml of sample}$$

Oxygen required for 1000 ml of waste water = 0.784 g

COD for waste water sample = 784 mg/lit

Problem 1.17.43(a): The hardness of 100,000 litres of water completely removed by passing through zeolite softener, the softer than requires 400 litres of NaCl solution containing 100g/litre

Solution:

Let the hardness of the water sample be $x \text{ mg/l.}$

Now 1 litre of NaCl solution contains 100 g. NaCl.

∴ 400 litre of NaCl solution contains = 400×100

$$= 40000 \text{ gms NaCl}$$

$$= 40000 \times 10^3 \text{ mgs NaCl}$$

Now ∵ 58.5 mg NaCl ≡ 50 mgs CaCO₃ equivalents.

$$\therefore 40000 \times 10^3 \text{ mg NaCl} \equiv \left(40000 \times 10^3 \times \frac{50}{58.5} \right) \text{ mgs eq. CaCO}_3 \text{ hardness}$$

$$= 34188034.188 \text{ mgs eq. CaCO}_3 \text{ hardness}$$

But the total quantity of water sample = 100000 litres

$$\therefore 100000 \text{ litre of water} \equiv 34188034.188 \text{ mgs CaCO}_3$$

$$\therefore 1 \text{ litre of water} \equiv \frac{34188034.188}{100000} \text{ mgs CaCO}_3$$

$$= 341.88 \text{ mgs / litre CaCO}_3 \text{ eq. Hardness}$$

$$= 342 \text{ ppm.}$$

Ans.: Hardness of water sample = 342 ppm.

Problem 1.17.44: 10 ml of sewage water sample was taken in to two BOD bottles and then diluted with distilled water to 300 ml. One 100 ml portion of the first bottle incubated at 20°C for the five days required 2.0 ml of 0.05 N thiosulphate solution. While one 100 ml portion of the blank consumed 7.4 ml of 0.05 N thiosulphate in the Winkler's method for the determination of dissolved oxygen. Calculate the BOD content of the sample.

Solution:

Difference in the volume of thiosulphate solution required for blank and the sample solution = $7.4 - 2.0 = 5.4$ ml of 0.05 N thiosulphate solution

Since 1 litre of 1N thiosulphate solution = 8 g oxygen

$$\begin{aligned} 5.4 \text{ ml of } 0.05 \text{ thiosulphate solution} &= [(8 * 5.4 * 0.05) / 1000] * 100 / 300 \\ &= 7.2 * 10^{-4} \text{ g oxygen for } 10 \text{ ml of sewage sample} \end{aligned}$$

Oxygen required for 1000 ml of sewage sample = 0.072 g

BOD for sample = 72 mg/lit

Problem 1.17.45: A 5 ml sample of waste water was refluxed with 30 ml of potassium dichromate solution and after refluxing the excess unreacted dichromate required 23 ml of 0.1 M FAS solution. A blank of 5 ml of distilled water on refluxing with 30 ml of dichromate solution required 36 ml 0.1 M FAS solution. Calculate the COD value of the wastewater.

Solution:

Difference in the volumes of the FAS required for the blank and sample solution = $36 - 23 = 13$ ml

Since 1 litre of 1 M FAS = 8 g of oxygen

$$\begin{aligned} 13 \text{ ml of } 0.1 \text{ M FAS} &= 8 * 13 * 0.1 / 1000 \\ &= 10.4 * 10^{-3} \text{ g of oxygen for } 5 \text{ ml of sample} \end{aligned}$$

Oxygen required for 1000 ml of waste water = 2.08 g

COD for waste water sample = 2080 mg/lit

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.
- Q. 22 List the boiler problems and discuss any two major problems in detail.

Q. 23 What are scales ? How are they formed ? Mention the methods to prevent scale formation.

- Q. 24 Discuss the importance of the following substances in the treatment of the boiler feed water. (a) Sodium phosphate (b) Sodium aluminate (c) Hydrazine

- Q. 25 What are the different internal methods used for treating boiler water ? Discuss in brief.

1.18 Unsolved Problems

[Ans. : Lime = 8.085 kg., Soda not required.]

- Ex. 1 :** Calculate the quantity of lime and soda required for softening 5,00,000 litre of water containing following impurities.

$$\text{Ca}(\text{HCO}_3)_2 = 32.4 \text{ ppm};$$

$$\text{Mg}(\text{HCO}_3)_2 = 43.8 \text{ ppm};$$

$$\text{CaCl}_2 = 22.2 \text{ ppm};$$

$$\text{MgSO}_4 = 40.8 \text{ ppm};$$

$$\text{MgCl} = 5.7 \text{ ppm};$$

$$\text{MgCO}_3 = 3.6 \text{ ppm};$$

[Ans. : Lime 32.9 kg., Soda = 31.27 kg]

- Ex. 2 :** A sample of water has the following impurities per litre :

$$\text{Mg}(\text{HCO}_3)_2 = 58.4 \text{ mg};$$

$$\text{Ca}(\text{HCO}_3)_2 = 32.4 \text{ mg};$$

$$\text{Na}_2\text{SO}_4 = 435 \text{ mg}$$

Calculate the amount of soda required for treatment of 20,000 litres of water.

(Hint : SiO_2 and Na_2SO_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 :

$$\text{Mg}(\text{HCO}_3)_2 = 146 \text{ mg};$$

$$\text{CaCl}_2 = 111 \text{ mg};$$

$$\text{MgSO}_4 = 12 \text{ mg};$$

$$\text{Ca}(\text{NO}_3)_2 = 16.4 \text{ mg}$$

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 :
- | | |
|---|---|
| $\text{Ca}(\text{HCO}_3)_2 = 40.5 \text{ mg/lit.};$ | $\text{NaCl} = 58.0 \text{ mg/lit.};$ |
| $\text{SiO}_2 = 15 \text{ mg/lit.};$ | $\text{FeSO}_4 = 75.9 \text{ mg/lit.};$ |
| $\text{MgCl}_2 = 19 \text{ mg/lit.};$ | $\text{CaCl}_2 = 55.5 \text{ mg/lit.};$ |
| | $\text{MgCO}_3 = 84 \text{ mg/lit.}$ |

[Ans. : Lime = 2.72 kg; Cost = Rs. 4038.3., Soda = 2.35 kg; Cost = Rs. 68.15.]

- 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

$$\text{CaCO}_3 = 125 \text{ mg/lit.};$$

$$\text{O}_2 = 66 \text{ ppm};$$

$$\text{CaCl}_2 = 222 \text{ ppm};$$

$$\text{NaHCO}_3 = 33.6 \text{ ppm.}$$

[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.

$$\text{Ca}(\text{HCO}_3)_2 = 162 \text{ mg};$$

$$\text{CaSO}_4 = 136 \text{ mg};$$

$$\text{Mg}(\text{HCO}_3)_2 = 73 \text{ mg};$$

$$\text{MgCl}_2 = 95 \text{ mg};$$

$$\text{NaCl} = 585 \text{ mg}$$

[Ans. : Lime = 2.72 kg., Soda = 2.5 kg.]

- Ex. 7 :** A water sample was found to contain the following dissolved salts ;

$$\text{MgSO}_4 = 4.8 \text{ ppm};$$

$$\text{CaCl}_2 = 33.3 \text{ ppm};$$

$$\text{CaSO}_4 = 54.4 \text{ ppm.}$$

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.

- Q. 21 Write a brief note on caustic embrittlement.

- Q. 22 List the boiler problems and discuss any two major problems in detail.

Q. 23 What are scales ? How are they formed ? Mention the methods to prevent scale formation.

- Q. 24 Discuss the importance of the following substances in the treatment of the boiler feed water. (a) Sodium phosphate (b) Sodium aluminate (c) Hydrazine

- Q. 25 What are the different internal methods used for treating boiler water ? Discuss in brief.

Ex. 8 : Calculate the quantity of lime and soda for softening 70,000 litres of water containing the following dissolved salts.

$$\text{Ca}(\text{HCO}_3)_2 = 8.1 \text{ mg};$$

$$\text{NaCl} = 66 \text{ mg};$$

$$\text{CaSO}_4 = 13.6 \text{ mg};$$

$$\text{CaCl}_2 = 11.1 \text{ mg};$$

$$\text{MgSO}_4 = 18.0 \text{ mg};$$

$$\text{Mg}(\text{HCO}_3)_2 = 7.3 \text{ mg}.$$

[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 :

$$\text{Ca}(\text{HCO}_3)_2 = 16.2 \text{ mg};$$

$$\text{Mg}(\text{HCO}_3)_2 = 73 \text{ mg};$$

$$\text{NaCl} = 58.5 \text{ mg}$$

$$\text{MgCl}_2 = 9.5 \text{ ppm};$$

$$\text{CaSO}_4 = 136 \text{ mg};$$

[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 :

$$\text{CO}_2 = 300 \text{ ppm}; \quad \text{Mg}(\text{HCO}_3)_2 = 86.7 \text{ ppm};$$

$$\text{MgCl}_2 = 95 \text{ ppm}; \quad \text{Mg}(\text{NO}_3)_2 = 26.9 \text{ ppm};$$

$$\text{MgSO}_4 = 8.4 \text{ ppm}; \quad \text{H}_2\text{SO}_4 = 16.9 \text{ ppm}$$

[Ans. : Lime = 183.37 kg., Soda = 39.75 kg]

Ex. 11 : A sample of hard water was found to contain :

$$\text{CaCO}_3 = 120 \text{ mg/lit.}; \quad \text{MgCO}_3 = 8.4 \text{ mg/lit.};$$

$$\text{SiO}_2 = 50 \text{ mg/lit.}; \quad \text{CaSO}_4 = 8.6 \text{ mg/lit.};$$

$$\text{MgSO}_4 = 60 \text{ mg/lit.}; \quad \text{MgCl}_2 = 19 \text{ mg/lit.}$$

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.

$$\text{Free CO}_2 = 25 \text{ ppm};$$

$$\text{Mg}(\text{HCO}_3)_2 \text{ as MgCO}_3 = 16 \text{ ppm};$$

$$\text{CaSO}_4 \text{ as Ca}^{2+} = 15 \text{ ppm};$$

$$\text{Ca}(\text{HCO}_3)_2 \text{ as CaCO}_3 = 120 \text{ ppm}.$$

[Ans. : Lime = 530 kg., Soda = 198.76 kg.]

Ex. 13 : A sample of water contains the following salts expressed in gm/lit.

$$\text{Ca}(\text{HCO}_3)_2 = 0.343;$$

$$\text{CaSO}_4 = 0.235;$$

$$\text{MgCl}_2 = 0.147.$$

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.

$$\text{Ca}(\text{HCO}_3)_2 = 48.5 \text{ ppm};$$

$$\text{MgSO}_4 = 35 \text{ ppm};$$

$$\text{CaCl}_2 = 27.75 \text{ ppm};$$

$$\text{Mg}(\text{HCO}_3)_2 = 36.5 \text{ ppm};$$

$$\text{CaSO}_4 = 43 \text{ ppm};$$

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

[Ans. : Lime = 80.56 kg., Soda = 91.16 kg.]

Ex. 15 : A water sample on analysis gave the following compositions :

Calcium bicarbonate : 4.86 mg/lit.;

Magnesium chloride : 38 mg/lit.;

Calcium chloride : 333 mg/lit.;

Magnesium sulphate : 54.4 mg/lit.;

Calcium sulphate : 54.4 mg/lit.;

Magnesium bicarbonate : 29.2 mg/lit.

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 :

$$\begin{aligned} \text{CaCO}_3 &= 140 \text{ mg/lit.}; \\ \text{MgCO}_3 &= 8.4 \text{ mg/lit.}; \\ \text{SiO}_2 &= 20 \text{ mg/lit.}; \end{aligned}$$

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 : A water sample on analysis, gave the following data.

$$\begin{aligned} \text{MgCl}_2 &= 95 \text{ ppm}; \\ \text{H}_2\text{SO}_4 &= 49 \text{ ppm}; \\ \text{SiO}_2 &= 4 \text{ ppm}. \end{aligned}$$

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. 18 : A water sample containing following salts,

$$\begin{aligned} \text{MgCl}_2 &= 9.5 \text{ ppm}; \\ \text{CaSO}_4 &= 27.2 \text{ ppm}; \\ \text{SiO}_2 &= 0.4 \text{ ppm}. \end{aligned}$$

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. 19 : 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.

$$\begin{aligned} \text{Ca}(\text{HCO}_3)_2 &= 162 \text{ mg/lit.}; \\ \text{MgCl}_2 &= 10 \text{ mg/lit.}; \\ \text{NaCl} &= 117 \text{ mg/lit.}; \\ \text{Mg}(\text{HCO}_3)_2 &= 3 \text{ mg/lit.}; \end{aligned}$$

[Ans. : Lime = 32 kg., Soda = 37.45 kg]

Ex. 20 : A water sample on analysis gave the following data :

$$\begin{aligned} \text{Ca}^{2+} &= 40 \text{ ppm}; \\ \text{Mg}^{2+} &= 72 \text{ ppm}; \\ \text{CO}_2 &= 20 \text{ ppm}; \end{aligned}$$

Calculate the lime (88 % pure) and soda (89 % pure) required to soften 2 million litres of the water sample.

What is the carbonate and non-carbonate hardness of a sample of water which has the following impurities per litre ?

$$\begin{aligned} \text{Ca}(\text{HCO}_3)_2 &= 50.25 \text{ mg}; \\ \text{CaCl}_2 &= 22.2 \text{ mg}; \\ \text{MgCO}_3 &= 16.8 \text{ mg}; \\ \text{MgSO}_4 &= 6.0 \text{ mg}. \end{aligned}$$

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 ppm or 2.75 °Fr or 1.92 °Cl.]

Ex. 22 : Find carbonate and non-carbonate hardness of a sample of water which has the following impurities per lit.

$$\begin{aligned} \text{CaCO}_3 &= 12.5 \text{ mg/lit.}; \\ \text{MgCO}_3 &= 16.8 \text{ mg/lit.}; \\ \text{CaCl}_2 &= 11.1 \text{ mg/lit.}; \\ \text{NaHCO}_3 &= 13.6 \text{ mg/lit.} \end{aligned}$$

[Ans. : Carbonate hardness = 32.5 ppm., Non-carbonate hardness = 20 ppm.]

Ex. 23 : 50 ml of standard hard water containing 1 mg of pure 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. 24 : 0.25 gm of CaCO_3 is dissolved in dilute HCl and diluted to 250 ml. 25 ml of this solution required 24.0 ml of EDTA using Enochrome 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

Ex. 25 : What is carbonate and non-carbonate hardness of a sample of water which has the following impurities per litre

$$\text{Permanent Hardness} = 333 \text{ ppm}$$

$$\text{Temporary Hardness} = 135 \text{ ppm}$$

Ex. 25 : What is carbonate and non-carbonate hardness in the sample (permanent and temporary). [Ans. : Total Hardness = 468 ppm, Permanent Hardness = 333 ppm, temporary].

$$\text{Mg}(\text{HCO}_3)_2 = 146 \text{ mg/lit.}; \quad \text{MgCl}_2 = 95 \text{ mg/lit.};$$

$$\text{NaCl} = 50 \text{ mg/lit.}; \quad \text{Ca}(\text{HCO}_3)_2 = 81 \text{ mg/lit.};$$

$$\text{CaCl}_2 = 111 \text{ mg/lit.}; \quad \text{CaSO}_4 = 68 \text{ mg/lit.}$$

Express the results as ppm, °Cl and °Fr.

$$[\text{Ans.} : \text{Carbonate hardness} = 150 \text{ ppm} = 15 \text{ }^{\circ}\text{Fr} = 10.5 \text{ }^{\circ}\text{Cl.}]$$

$$\text{Non-carbonate hardness} = 250 \text{ ppm} = 25 \text{ }^{\circ}\text{Fr} = 17.5 \text{ }^{\circ}\text{Cl.}]$$

Ex. 26 : What is the carbonate and non-carbonate hardness of a sample of water which has the following impurities per litre ?

$$\text{Ca}(\text{HCO}_3)_2 = 81 \text{ mg/lit.}; \quad \text{MgCl}_2 = 95 \text{ mg/lit.};$$

$$\text{NaCl} = 38.5 \text{ mg/lit.}; \quad \text{CaCl}_2 = 22.2 \text{ mg/lit.};$$

$$\text{Mg}(\text{HCO}_3)_2 = 58.2 \text{ mg/lit.}; \quad \text{CO}_2 = 4.4 \text{ lit}$$

Express the results as ppm, Clarke's degree and french degree.

$$[\text{Ans.} : \text{Carbonate hardness} = 89.86 \text{ ppm} = 6.29 \text{ }^{\circ}\text{Cl} = 8.986 \text{ }^{\circ}\text{Fr.}]$$

$$\text{Non-carbonate hardness} = 120 \text{ ppm} = 8.4 \text{ }^{\circ}\text{Cl} = 12 \text{ }^{\circ}\text{Fr.}]$$

Ex. 27 : 0.1 g of 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.

Ex. 28 : A sample of water was found to contain the following salts in mgs litre;

$$\text{CaSO}_4 = 20.4; \text{MgCl}_2 = 9.5; \text{HCl} = 7.3$$

Calculate 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.

$$[\text{Ans.} : \text{Lime required} = 1.392 \text{ kgs; Soda required} = 3.71 \text{ kgs}]$$

$$\text{Cost of lime} = \text{Rs. } 12.53; \quad \text{Cost of soda} = \text{Rs. } 129.85]$$

Ex. 30 : 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 softner. [Ans. : 34.184.03 lit.]

Ex. 31 : 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.]

[Ans. : Temporary hardness = 125 ppm., Permanent hardness = 500 ppm., Total hardness = 625 ppm.]

Ex. 29 : The hardness of 30,000 litres of a water sample was completely removed by zeolite softener. 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. 32 : A water sample was found to contain the following salts in mgs litre;

$$\text{CaCO}_3 = 50 \text{ ppm.}; \quad \text{Fe}_2\text{O}_3 = 20 \text{ ppm.};$$

$$\text{MgCO}_3 = 14.4 \text{ ppm.}; \quad \text{Na}_2\text{SO}_4 = 20 \text{ ppm.};$$

$$\text{CaCl}_2 = 22.2 \text{ ppm.}; \quad \text{SiO}_2 = 5 \text{ ppm.};$$

$$\text{MgCl}_2 = 9.5 \text{ ppm.}; \quad \text{CO}_2 = 2.2 \text{ ppm.}$$

Calculate the amount of lime and soda required for softening 7500 litres of above water.

[Ans. : Soda required = 2.385 kg]

Lime required = 5.51004 kg

Ex. 34 : 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.

$$\begin{aligned} \text{Ca}^{++} &= 30 \text{ ppm}; \quad \text{HCO}_3^- = 12.2 \text{ ppm}; \\ \text{Mg}^{++} &= 21.6 \text{ ppm}; \quad \text{CO}_2 = 4.4 \text{ ppm}; \\ \text{H}_2\text{SO}_4 &= 4.9 \text{ ppm}. \end{aligned}$$

Calculate the cost of chemicals if lime is Rs. 7 per kg and soda is Rs. 35 per kg.

[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]

Problems for Practice

Ex. 1 A water sample contains the following impurities.

$$\begin{aligned} \text{CaSO}_4 &= 136 \text{ ppm}; \quad \text{MgCl}_2 = 95 \text{ ppm}; \\ \text{H}_2\text{SO}_4 &= 49 \text{ ppm}; \quad \text{MgSO}_4 = 60 \text{ ppm}; \\ \text{SiO}_2 &= 50 \text{ ppm}; \end{aligned}$$

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 :

$$\begin{aligned} \text{Mg}(\text{HCO}_3)_2 &= 14.6 \text{ mg/litre}; \quad \text{Ca}(\text{HCO}_3)_2 = 8.1 \text{ mg/litre}; \\ \text{Mg}(\text{NO}_3)_2 &= 29.6 \text{ mg/litre}; \quad \text{MgCl}_2 = 19.0 \text{ mg/litre}; \\ \text{MgSO}_4 &= 24.0 \text{ mg/litre}. \end{aligned}$$

Ex. 3 A sample of water was found to contain the following impurities :

$$\begin{array}{lll} \text{Mg}(\text{HCO}_3)_2 &= 156 \text{ mg/litre}; & \text{H}_2\text{SO}_4 = 4.9 \text{ mg/litre}; \\ \text{MgCl}_2 &= 23.75 \text{ mg/litre}; & \text{NaCl} = 5.6 \text{ mg/litre}; \\ \text{SiO}_2 &= 16.2 \text{ mg/litre}; & \end{array}$$

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 :

$$\begin{array}{lll} \text{Ca}(\text{HCO}_3)_2 &= 16.2 \text{ ppm}; & \text{MgSO}_4 = 6.0 \text{ ppm}; \\ \text{CaSO}_4 &= 6.8 \text{ ppm}; & \text{Mg}(\text{HCO}_3)_2 = 8.4 \text{ ppm}; \\ \text{CaCl}_2 &= 11.1 \text{ ppm}; & \text{SiO}_2 = 8.0 \text{ ppm}; \\ \text{NaCl} &= 14.0 \text{ ppm}. & \end{array}$$

Ex. 5 Calculate the temporary hardness and total hardness of a sample of water containing following salts :

$$\begin{array}{lll} \text{Mg}(\text{HCO}_3)_2 &= 7.3 \text{ mg/litre}; & \text{Ca}(\text{HCO}_3)_2 = 16.2 \text{ mg/litre}; \\ \text{MgCl}_2 &= 9.5 \text{ mg/litre}; & \text{CaSO}_4 = 13.6 \text{ mg/litre}; \end{array}$$

Ex. 6 A sample of water contains following impurities :

$$\begin{array}{lll} \text{Mg}(\text{HCO}_3)_2 &= 73 \text{ mg/litre}; & \text{CaCl}_2 = 222 \text{ mg/litre}; \\ \text{MgSO}_4 &= 120 \text{ mg/litre}; & \text{Ca}(\text{NO}_3)_2 = 164 \text{ mg/litre}; \end{array}$$

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 :

$$\begin{aligned}\text{MgCO}_3 &= 144 \text{ ppm}; \\ \text{MgCl}_2 &= 95 \text{ ppm}; \\ \text{Fe}_2\text{O}_3 &= 25 \text{ ppm}; \\ \text{Na}_2\text{SO}_4 &= 15 \text{ ppm};\end{aligned}$$

Ex. 8 Three water samples A, B and C were analysed for their salt content. Sample A was found to contain 168 mg of 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 :

$$\begin{aligned}\text{MgCO}_3 &= 8.4 \text{ mg/litre}; \\ \text{KNO}_3 &= 20.0 \text{ mg/litre}; \\ \text{CaCO}_3 &= 5.0 \text{ mg/litre}\end{aligned}$$

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 :

$$\begin{aligned}\text{Na}_2\text{SO}_4 &= 7 \text{ mg/lit.}; \\ \text{SiO}_2 &= 2 \text{ mg/lit.}; \\ \text{MgSO}_4 &= 12 \text{ mg/lit.}; \\ \text{CaCO}_3 &= 5 \text{ mg/lit.}; \\ \text{CaCl}_2 &= 22.2 \text{ mg/lit.};\end{aligned}$$

Ex. 14 The hardness of 50,000 litres of sample of water was completely removed by passing through a permuntit 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 :

$$\begin{aligned}\text{CaCO}_3 &= 10.0 \text{ ppm}; \\ \text{Mg}(\text{HCO}_3)_2 &= 36.5 \text{ ppm}; \\ \text{Al}_2(\text{SO}_4)_3 &= 17.1 \text{ ppm}; \\ \text{CaSO}_4 &= 20.4 \text{ ppm}; \\ \text{MgCl}_2 &= 19.0 \text{ ppm}; \\ \text{SiO}_2 &= 24.0 \text{ ppm.}\end{aligned}$$

Ex. 16 A sample of water contains 16.8 mg of MgCO_3 and 6.0 mg of 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 :

$$\begin{aligned}\text{MgCl}_2 &= 9.5 \text{ mg/lit.}; \\ \text{Ca}(\text{HCO}_3)_2 &= 81 \text{ mg/lit.}; \\ \text{FeSO}_4 &= 151.8 \text{ mg/lit.}; \\ \text{MgSO}_4 &= 120 \text{ mg/lit.};\end{aligned}$$

1.19 University Questions (Theory)

Dec. 2007

- Q. 1** What do you mean by hardness of water? Distinguish between alkaline and non-alkaline hardness of water. (Section 1.5 and 1.16.1) (2 Marks)
- Q. 2** Explain the theory of Lime-soda process with reference to the different functions of lime and soda. (Section 1.12.1) (5 Marks)

- Q. 3** Explain the terms :
- B.O.D.
 - C.O.D.

What is their significance? (Section 1.13.1)

May 2008

- Q. 4** Explain theory, procedure and limitations of Zeolite process with the help of a neat diagram. (Section 1.12.2) (6 Marks)

- Q. 5** What are carbonate and non-carbonate hardness? (Section 1.16.1) (3 Marks)

- Q. 6** Give brief account of reverse osmosis. (Section 1.15.6) (3 Marks)

- Q. 7** Write short note on : Activated sludge method to control water pollution (Section 1.14) (5 Marks)

Dec. 2008

- Q. 8** Explain the principle of EDTA method. (Section 1.10.2) (3 Marks)

- Q. 9** Define BOD and COD with it's significance. (Section 1.13.1) (5 Marks)

- Q. 10** Explain Reverse Osmosis and Ultrafiltration. (Section 1.15.6) (5 Marks)

- Q. 11** Write note on : Activated sludge process. (Section 1.14) (5 Marks)

May 2009

- Q. 12** How demineralization of water is carried out? (Section 1.12.3) (6 Marks)

- Q. 13** Give brief account of Ultrafiltration. (Section 1.15.7) (3 Marks)

Dec. 2009

- Q. 15** Explain the Ion-Exchange process of softening of hard water. What are its advantages and disadvantages? (Section 1.12.3) (7 Marks)

- Q. 16** Name the different (various) methods to control water pollution. Explain Activated sludge method in detail. (Section 1.14) (8 Marks)

- Q. 17** Write the Advantages and disadvantages of Lime-Soda process. (Section 1.12.1) (5 Marks)

May 2010

- Q. 18** Write a short note on Reverse osmosis membrane. (3 Marks)

- Q. 19** How is activated sludge process carried out for the treatment of waste water? Explain with flow sheet diagram. (Section 1.14) (5 Marks)

- Q. 20** Describe the demineralization process. State its advantages and disadvantages. (Section 1.12.3) (5 Marks)

Dec. 2010

- Q. 21** Explain the principle of EDTA method. (Section 1.10.2) (5 Marks)

- Q. 22** Explain the following terms with their significance : (Section 1.14.3)

- (i) Biological oxygen demand (ii) Chemical oxygen demand. (5 Marks)

- Q. 23** Write short notes on any two of the following : Reverse Osmosis. (6 Marks)

- Q. 24** What is activated sludge? Explain the method with a proper flow sheet diagram. What are its advantages? (Section 1.14) (5 Marks)

- Q. 25** Explain the hot lime soda method for softening of water with the help of a neat diagram. What are advantages and disadvantages of lime soda process? (Section 1.12.1) (5 Marks)

May 2011

May 2013

Q. 26 Explain the reverse osmosis and ultrafiltration. (Section 1.15.6 and 1.15.7) (5 Marks)

✓

Dec. 2011

Q. 38 Differentiate between BOD and COD. (Section 1.13.3) (3 Marks)

✓

Q. 39 Explain demineralization of water by ion exchange method. (Section 1.12.3) (3 Marks)

✓

Q. 27 Explain the principle of EDTA method. (Section 1.10.2) (3 Marks)

✓

Q. 28 Define COD and BOD. Give its significance. (Section 1.13.1) (5 Marks)

✓

Q. 29 What is reverse osmosis? Give its applications. (Section 1.15.6) (5 Marks)

✓

Q. 30 Outline the chemical reactions involved in the Lime-soda method of softening water. (Section 1.12.1(1)) (5 Marks)

✓

Q. 31 With a neat flow chart explain the waste water treatment. (Section 1.14)

May 2012

(5 Marks)

Q. 32 Why is the Hot lime Soda process preferred over the Cold lime soda process? (Section 1.12.1) (3 Marks)

Q. 33 Explain with a neat diagram, the Zeolite process of water softening including the following points : (3 Marks)

- principle
- process
- softening and regeneration reactions
- advantages & limitations (Section 1.12.2)

(6 Marks)

Q. 34 Write a short note on any one of the following : Reverse Osmosis (Section 1.15.6) (3 Marks)

Dec. 2012

May 2008

Q. 35 Distinguish between BOD and COD. (Section 1.13.3) (3 Marks)

Q. 36 Discuss zeolite process with the help of diagram, chemical reactions and advantages. (Section 1.12.2) (5 Marks)

✓

Q. 37 Explain activated sludge process with the help of flow sheet diagram. (Section 1.14.1) (6 Marks)

Q. 1 800 liters of raw water was soften by zeolite softener. After it got exhausted required 40 liters of NaCl solution containing 110 gm per liter of NaCl for its regeneration. Calculate the hardness of water. (Please refer Problem 1.17.36) (4 Marks)

Q. 2 Calculate lime (90%) pure and soda (95%) pure required for softening of 20000 liters of water containing following impurities :

- Ca (HCO_3)₂ = 81 mg per liter
- MgCO₃ = 42 mg per liter
- NaIO₂ = 4.1 mg per liter
- HCl = 3.65 mg per liter
- Ca (NO₃)₂ = 82 mg per liter
- NaCl = 4.5 mg per liter

(At wt. Ca = 40, H = 1, C = 12, O = 16, Mg = 24, Na = 23, Al = 27, Cl = 35.5, N = 14) (Please refer Problem 1.17.23) (5 Marks)

Dec. 2007

Q. 38 Differentiate between BOD and COD. (Section 1.13.3) (3 Marks)

✓

Q. 39 Explain demineralization of water by ion exchange method. (Section 1.12.3) (3 Marks)

Q. 27 Explain the principle of EDTA method. (Section 1.10.2) (3 Marks)

✓

Q. 28 Define COD and BOD. Give its significance. (Section 1.13.1) (5 Marks)

✓

Q. 29 What is reverse osmosis? Give its applications. (Section 1.15.6) (5 Marks)

✓

Q. 30 Outline the chemical reactions involved in the Lime-soda method of softening water. (Section 1.12.1(1)) (5 Marks)

Q. 3 A water sample contain :
 (i) Ca (HCO_3)₂ = 32.4 mg/l
 (ii) Mg (HCO_3)₂ = 29.2 mg/l
 (iii) CaSO₄ = 13.5 mg/l
 Calculate temporary, permanent and total hardness
 (At. wt. C = 40, Mg = 24, H = 1, C = 12, O = 16, S = 32)
 (Please refer Problem 1.17.3)

(2 Marks)

Q. 4 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 :

- Ca $(\text{HCO}_3)_2 \rightarrow 16.2 \text{ ppm}$, $\text{CaSO}_4 \rightarrow 6.8 \text{ ppm}$.
- $\text{CaCl}_2 \rightarrow 11.1 \text{ ppm}$.
- $\text{MgSO}_4 \rightarrow 6.00 \text{ ppm}$.
- Mg $(\text{HCO}_3)_2 \rightarrow 8.4 \text{ ppm}$.
- $\text{SiO}_2 \rightarrow 8.00 \text{ ppm}$.
(At. wt. Ca = 40 Mg = 24, S = 32, O = 16, Cl = 35.5, H = 1, Si = 28)
- $\text{NaCl} = 58.5 \text{ ppm}$, Mg $(\text{HCO}_3)_2 = 7.3 \text{ ppm}$, $\text{HCl} = 36.5 \text{ ppm}$, $\text{CaCl}_2 = 111 \text{ ppm}$, $\text{MgSO}_4 = 60 \text{ ppm}$.
(At wt. : Ga = 40, Mg = 24, S = 32, O = 16, Cl = 35.5, C = 12, H = 1, Si = 28) (Please refer Problem 1.17.22)

Dec. 2008

Q. 6 Calculate the quantity of lime and soda required for softening of 1,00,000 litres of water containing following impurities in ppm. The purity of lime is 70% and soda 85%. Ca $(\text{HCO}_3)_2 = 30.2$, Mg $(\text{HCO}_3)_2 = 20.8$, $\text{CaCl}_2 = 28$; Mg $\text{Cl}_2 = 8.78$, $\text{CaSO}_4 = 35.0$, $\text{MgSO}_4 = 6.7$, $\text{Na}_2\text{SO}_4 = 17.9$.
(Please refer Problem 1.17.21)

(8 Marks)

Q. 7 One litre of hard water containing 4.5 gm of CaCl_2 was passed through a permittit's softner. Calculate quantity of NaCl produced in soft water.
(Please refer Problem 1.17.37)

(5 Marks)

May 2009

Q. 8 A water sample contains :

- Mg $(\text{HCO}_3)_2 = 14.6 \text{ ppm}$
- Mg $(\text{NO}_3)_2 = 29.6 \text{ ppm}$
- Ca $(\text{HCO}_3)_2 = 8.1 \text{ ppm}$
- Mg $\text{Cl}_2 = 19 \text{ ppm}$
- Mg $\text{SO}_4 = 24 \text{ ppm}$.

May 2010

Q. 13 Calculate the amount of lime (85 % pure) and soda (95% pure) required to soften one million litre of water which contains $\text{CaCO}_3 = 12.5 \text{ ppm}$, $\text{MgCO}_3 = 8.4 \text{ ppm}$, $\text{CaCl}_2 = 22.2 \text{ ppm}$, $\text{MgCl}_2 = 9.5 \text{ ppm}$, $\text{CO}_2 = 33.0 \text{ ppm}$, $\text{HCl} = 7.3 \text{ ppm}$, $\text{NaHCO}_3 = 16.8 \text{ ppm}$. (Please refer Problem 1.17.25)
(5 Marks)

Q. 9 Calculate the amount of Lime (80 % pure) and Soda (85 % pure) required for softening 10⁶ litres of water containing the following constituents :
(Please refer Problem 1.17.4)

- Ca $(\text{HCO}_3)_2 = 162 \text{ ppm}$, Mg $\text{Cl}_2 = 9.5 \text{ ppm}$
- NaCl = 58.5 ppm, Mg $(\text{HCO}_3)_2 = 7.3 \text{ ppm}$
- HCl = 36.5 ppm, CO₂ = 44.0 ppm
- CaCl₂ = 111 ppm, MgSO₄ = 60 ppm.

Q. 10 0.5 gm of CaCO_3 was dissolved in HCl and the solution made upto 500 ml with distilled water. 50 ml of the solution required 48 ml of EDTA solution for titration. 50 ml of hard water sample required 15 ml of EDTA and after boiling and filtering required 10 ml of EDTA solution. Calculate temporary hardness of water. (Please refer Problem 1.17.14)

(5 Marks)

(6 Marks)

Q. 11 Calculate temporary and total hardness of a water sample containing :
Mg $(\text{HCO}_3)_2 = 7.3 \text{ mg/l}$, Ca $(\text{HCO}_3)_2 = 16.2 \text{ mg/l}$, MgCl₂ = 9.5 mg/l, CaSO₄ = 13.6 mg/l. (Please refer Problem 1.17.5)

Q. 12 Calculate the amount of lime and soda needed to soften 50,000 litres of water containing the following impurities per litre of water :
 $\text{CaCl}_2 = 222 \text{ mg}$, $\text{Mg}(\text{NO}_3)_2 = 296 \text{ mg}$, Ca $(\text{HCO}_3)_2 = 324 \text{ mg}$, $\text{H}_2\text{SO}_4 = 196 \text{ mg}$ and organic matter = 130 mg.
(Please refer Problem 1.17.24)

(7 Marks)

- Q. 14** A zeolite softener was completely exhausted and was regenerated by passing 100 litres of sodium chloride solution containing 120 gm per litre of NaCl. How many litres of sample of water of hardness 500 ppm can be softened by this softener ? (Please refer Problem 1.17.38) (5 Marks)

Dec. 2010

- Q. 15** Hardness of 4,500 liters of water was removed completely by zeolite softener. This zeolite required 30 liters of 100 gm/lit of NaCl to regenerate. Calculate the hardness of water. (Please refer Problem 1.17.7) (4 Marks)

- Q.16** Calculate the quantity of lime and soda required for softening 50,000 liters of water containing the following salts per liter : (5 Marks)

$$\text{Ca}(\text{HCO}_3)_2 = 8.1 \text{ mg}, \text{Mg}(\text{HCO}_3)_2 = 7.5, \text{CaSO}_4 = 13.6 \text{ mg}, \\ \text{MgSO}_4 = 12 \text{ mg}, \text{MgCl}_2 = 2 \text{ mg}, \text{NaCl} = 4.7 \text{ mg}$$

(Please refer Problem 1.17.26)

(5 Marks)

- Q. 17** 1gm of CaCO_3 was dissolved in 1 liter of distilled water, 50ml of this solution required 45ml of EDTA solution for titration. 50ml of hard water required 25ml of EDTA for titration. The same sample of water after boiling consumed 15ml of EDTA for titration. Calculate the hardness of water. (Please refer Problem 1.17.15)

(5 Marks)

May 2011

- Q. 18** Calculate the amount of lime (90 % pure) and soda (95% pure) required to soften 50, 000 litres of same water containing the following impurities in ppm : (5 Marks)

$$\text{Mg} (\text{HCO}_3)_2 = 155 \quad \text{MgCl}_2 = 23 \\ \text{NaCl} = 6.9 \quad \text{H}_2\text{SO}_4 = 5 \\ \text{Na}_2\text{S}_2\text{O}_4 = 18.4 \quad \text{CaCl}_2 = 111. \\ (\text{Please refer Problem 1.17.27})$$

(5 Marks)

- Q. 19** A water sample on analysis has been found to contains : (5 Marks)

$$\text{MgCl}_2 = 19 \text{ mg/lit}, \quad \text{CaCO}_3 = 5 \text{ mg/lit} \\ \text{Ca} (\text{HCO}_3)_2 = 29.5 \text{ mg/lit}, \quad \text{CaSO}_4 = 13 \text{ mg/lit}. \\ \text{Calculate temporary, permanent and total hardness.} \\ (\text{Please refer Problem 1.17.6})$$

(5 Marks)

- Q. 20** 50 ml sample of water required 7.2 ml of N/20 disodium EDTA for titration. After boiling and filtration the same volume required 4 ml of EDTA. Calculated each type of hardness. (Please refer Problem 1.17.16) (5 Marks)

- Q. 21** The hardness of 3500 litres of water was completely removed by zeolite softener. The zeolite had required 25 litres of 100 gm/lit of NaCl to regenerate. Calculate the hardness of the water. (Please refer Problem 1.17.39) (5 Marks)

- Q. 22** Classify the following impurities into temporary, permanent and non-hardness causing impurities.

$\text{Ca}(\text{HCO}_3)_2, \text{MgSO}_4, \text{CaCl}_2, \text{CO}_2, \text{HCl}, \text{Mg} (\text{HCO}_3)_2, \text{CaSO}_4$ and NaCl .

- How many grams of CaCl_2 dissolved per litre gives 150 ppm of hardness ? (Please refer Problem 1.17.8) (5 Marks)

Dec. 2011

- Q. 23** 15,000 litres of hard water was passed through a zeolite softener. The exhausted zeolite required 120 litres of NaCl having 30 g / litre of NaCl. Calculate the hardness of water. (Please refer Problem 1.17.40) (5 Marks)

- Q. 24** 20 ml of standard hard water containing 1.2 g CaCO_3 per litre required 35 ml of EDTA. 50 ml of hard water sample required 30 ml of the same EDTA. Calculate the various hardnesses. (Please refer Problem 1.17.17) (5 Marks)

- Q. 25** Calculate the quantity of lime (90% pure) and soda (95% pure) required for softening 50,000 litres of water containing the following impurities.

$$\text{Ca}(\text{HCO}_3)_2 - 81 \text{ mg/l}, \text{MgCl}_2 - 95 \text{ mg/l}, \text{CaSO}_4 - 68 \text{ mg/l}, \text{SiO}_2 - 50 \text{ mg/l}, \\ \text{Mg} (\text{HCO}_3)_2 - 146 \text{ mg/l}, \text{H}_2\text{SO}_4 - 49 \text{ mg/l}. \\ (\text{Please refer Problem 1.17.28})$$

(5 Marks)

May 2012**May 2013**

Q. 26 Calculate lime (95% pure) and soda (90% pure) required for softening one million litres of water containing the following constituents:

$$\text{Ca}(\text{HCO}_3)_2 = 81 \text{ mg/l}, \text{Mg}(\text{HCO}_3)_2 = 73 \text{ mg/l}, \text{CaSO}_4 = 68 \text{ mg/l}, \text{MgCl}_2 = 95 \text{ mg/l}, \text{Mg}(\text{NO}_3)_2 = 14.8 \text{ mg/l}, \text{H}_2\text{SO}_4 = 14.7 \text{ mg/l}$$

(Please refer Problem 1.17.29)

Q. 27 An exhausted Zeolite softener was regenerated by passing 300 litres of NaCl solution having a strength of 150 g per litre of NaCl. If the hardness of water sample was 480 ppm, calculate the total volume of water softened by this softener. (Please refer Problem 1.17.41)

(5 Marks)

Dec. 2012

Q. 28 Calculate temporary, permanent and total hardness of water sample containing
 $\text{Mg}(\text{HCO}_3)_2 = 7.3 \text{ ppm}$, $\text{Ca}(\text{HCO}_3)_2 = 16.2 \text{ ppm}$.
 $\text{Mg Cl}_2 = 9.5 \text{ ppm}$, $\text{CaSO}_4 = 13.6 \text{ ppm}$.

(Please refer Problem 1.17.5)

(3 Marks)

Q. 29 Calculate amount of lime (90%) pure and soda (98% pure) for the treatment of 1 million litres of water containing $\text{Ca}(\text{HCO}_3)_2 = 8.1 \text{ ppm}$, $\text{CaCl}_2 = 33.3 \text{ ppm}$, $\text{HCO}_3^- = 91.5 \text{ ppm}$, $\text{MgCl}_2 = 38 \text{ ppm}$, $\text{Mg}(\text{HCO}_3)_2 = 14.6 \text{ ppm}$. The coagulant $\text{Al}_2(\text{SO}_4)_3$ was added at the rate of 17.1 ppm. (Please refer Problem 1.17.30(a))

(6 Marks)

Q. 30 The hardness of 100,000 litres of water completely removed by passing through zeolite softener, the softer than requires 400 litres of NaCl solution containing 100g/litre NaCl for regeneration. Calculate hardness of water sample. (Please refer Problem 1.17.43(a))

(4 Marks)

Q. 31 What is the total hardness of sample of water which has the following impurities in mg/l.

$$\text{Ca}(\text{HCO}_3)_2 = 162 \quad \text{CaCl}_2 = 22.2 \\ \text{Mg Cl}_2 = 95 \quad \text{NaCl} = 20$$

(Please refer Problem 1.17.17(a))

(3 Marks)

Q. 32 0.5 g of CaCO_3 was dissolved in dilute HCl and diluted to 500 ml, 50 ml of this solution required 45 ml of EDTA solution for titration. 50 ml of hard water sample required 15 ml of EDTA solution for titration. 50 ml of same water sample on boiling, filtering requires 10 ml EDTA solution. Calculate the temporary permanent and total hardness in ppm.

(Please refer Problem 1.17.14(a))

(6 Marks)

Q. 33 A Zeolite softner was completely exhausted and was regenerated by passing 150 lit of NaCl solution, containing 50 g/litre of sodium chloride. How many litres of water sample of hardness 450 ppm can be softened by this zeolite container. (Please refer Problem 1.17.41(a))

(4 Marks)

Note**CHAPTER
2**

Polymers and Rubbers

Syllabus

Polymers :

- Introduction to polymers, Thermoplastic and Thermosetting plastic.
- Ingredients of the plastic (Compounding of plastic.)
- Fabrication of plastic by Compression, Injection, Transfer, Extrusion molding. Preparation, properties and uses of Phenolformaldehyde, PMMA, Kevlar.
- Effect of heat on the polymers (Glass transition temperatures) Polymers in medicine and surgery.
- Conducting polymers, Industrial polymers.

Rubbers :

- Natural rubber (latex), Drawbacks of natural rubber, Compounding of rubber (vulcanization of rubber), Preparation, properties and uses of Buna-S, Silicone and Polyurethane rubber.

2.1 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.

Monomer and polymer:

- Thus the single repeating unit is called as *monomer*, and the resultant high molecular weight compound is called as *polymer*.

2.2 Classification of Polymers

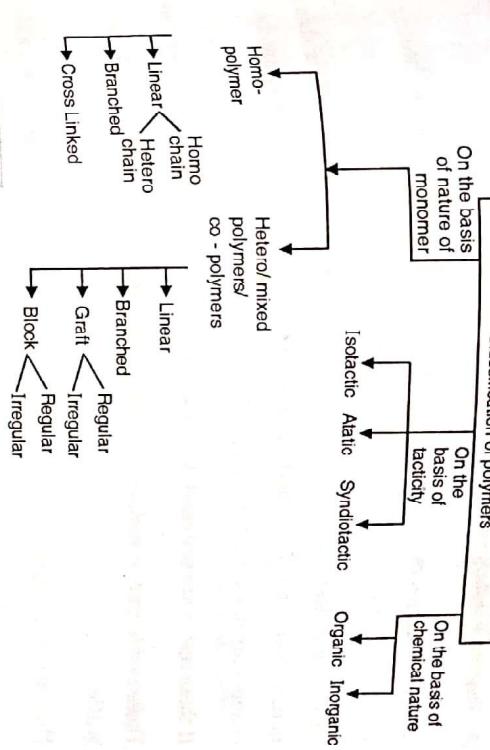
- On the basis of this physical property, the polymers with high degree of Polymerisation are known as *high polymers* while those having comparatively low degree of polymerisation are known as *oligopolymers*.

2.2 Classification of Polymers

The polymers are also classified on the basis of

- The nature of monomer
- Tacticity
- Chemical nature

2.3 Plastics



MU - May 2007

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

2.3.1 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 ;

- Thermo plastic
- Thermo setting

The characteristics of these two types is given below.

2.3.1.1 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.
- The method usually used to manufacture polymers is addition polymerisation.
- They are generally long chain linear polymers 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.

2.3.1.2 Thermo Setting Plastics

- These are the polymers, which on heating change irreversibly into hard and rigid materials.
- The melt of this 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.

2.3.2 Comparison of Plastics

MU - May 2008, Dec. 2009, Dec. 2011

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: $\begin{array}{c} & & & \\ -R-R-R-R-R-R-R-R- \\ & & & \\ -R-R-R-R-R-R-R-R- \\ & & & \\ -R-R-R-R-R-R-R-R- \end{array}$
4.	Monomer used in these is generally bifunctional.	In this, monomer used is Tri, Tetra or polyfunctional.

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, amine plastics, alkyl plastics, epoxy plastics, silicon plastics etc. are the best known examples of *thermosets*.

Sr. No.	Thermoplastics or thermosoftening Plastics	Thermosetting Plastics or Thermohardening Plastics
5.	They have low molecular weight	They have high molecular weight
6.	They are usually soft, weak and less brittle.	They are usually hard, strong and more brittle
7.	They are usually soluble in some organic solvents	Due to strong bonds and cross links, they are insoluble in almost all organic solvents
8.	They get softened on reheating readily because secondary forces between the individual chain can break easily by heat or pressure.	They do not soften on reheating because the cross links and bonds retain their strength on heating.
9.	They can be softened, reshaped and thus reused. (reclaimed from waste) (by reheating to a suitable temperature)	They retain their shape and structure even on heating. Hence, they cannot be reshaped and reused. (can not be reclaimed)
10.	Example : Polyethylene, polystyrene, PVC, PVA	Example : Phenolformaldehyde, ureaformaldehyde, Nylon 6 : 6.

2.4 Compounding of Plastics

MU - May 2009, Dec. 2010, May 2012, Dec. 2012, May 2013

- Plastics are manufactured synthetically using raw materials mostly from natural gas and petroleum, or from coal mines, forests, farms, paper and textile mills.
- 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.

Binders

- Binders hold 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.
- 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*.

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) | Plasticizers |
| (vi) | Lubricants |
| (vii) | Stabilizers. |

- They reduce shrinkage and brittleness.
- 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

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

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

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, benzoyl peroxide, metallic oxides etc.

Plasticizers

- These help to increase the plasticity of the plastics.

The adequate quantity of plasticizer also helps to soften the plastic at comparatively lower temperature.

Plasticizers 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 extent 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-isoo-decylphthalate 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.

Stabilizers

- 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.

2.5 Fabrication of Plastics or Moulding of Plastics

MU - Dec. 2007, May 2008, Dec. 2009, May 2010, Dec. 2011, May 2012, Dec. 2012

- 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.

principle of moulding (Fabrication)

The basic principle involved in this is partial melting (softening) of resinous mass by heating.

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.

Different methods of fabrication / moulding :

- (1) Compression moulding : suitable for thermosets
- (2) Injection moulding : suitable for thermoplasts
- (3) Transfer moulding : suitable for thermosets
- (4) Extrusion moulding : suitable for thermoplasts.

2.5.1 Compression Moulding MU - May 2010, Dec. 2011, May 2012, Dec. 2012

- 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. 2.5.1).
- 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.

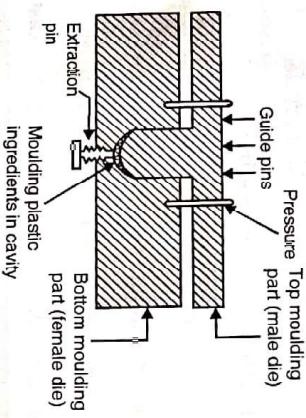


Fig. 2.5.1 : Compression moulding of plastics

2.5.2 Injection Moulding

MU - May 2009, Dec. 2009, May 2010, Dec. 2010, Dec. 2011, Dec. 2012, May 2013

2.5.3 Transfer Moulding

MU - Dec. 2007, May 2008, Dec. 2009, May 2010, Dec. 2011

- Automation of the entire cyclic operation is possible.

This method is the most widely used for moulding of thermoplastic because of high speed production, low mould cost, very low loss of material and low finishing cost.

However, there are limitations of design of articles to be moulded because a large number of cavities cannot be filled simultaneously.

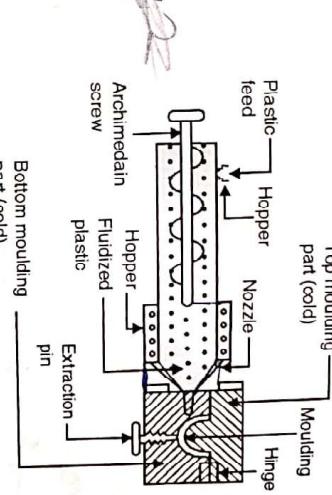


Fig. 2.5.2 : Injection moulding of plastic

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

- It is one of the most widely used processes for converting thermoplastic raw materials into finish product.
- 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. 2.5.2.
- Pressure upto 1758 kg/cm^2 is used for injections. The mould is kept cold to allow the hot plastic to cure and become rigid.
- When the material has been cured sufficiently, half of the mould is opened the finished article ejected without any deformation.

- 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

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

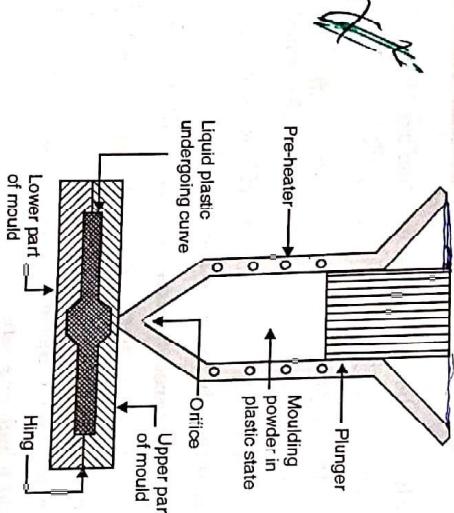


Fig. 2.5.3 : Transfer moulding of plastic

Extrusion Moulding

MU – May 2010, Dec. 2011

- It is mainly used for manufacturing continuous moulding articles of thermoplastic resins.

For example tubes, rods, strips, insulated electric cable etc.

In this method dry moulding powder or granular material is first fed through hopper into the rear of the heated chamber which has a revolving screw.

There are two types of moulding :

1. Vertical extruder moulding.
 2. Horizontal extruder moulding as shown in the following Fig. 2.5.4 and Fig. 2.5.5 respectively.
- When the screw is rotated the molten material is pushed forward through the small orifice of the die to form continuous uniform shaped articles.
- When the article leaves the orifice, it is allowed to pass through water for solidification of plastic material.

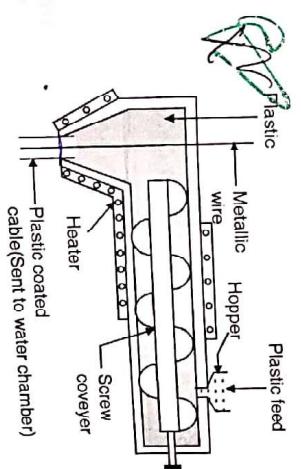


Fig. 2.5.4 . Moulding of insulated electric cable by vertical extrusion moulding

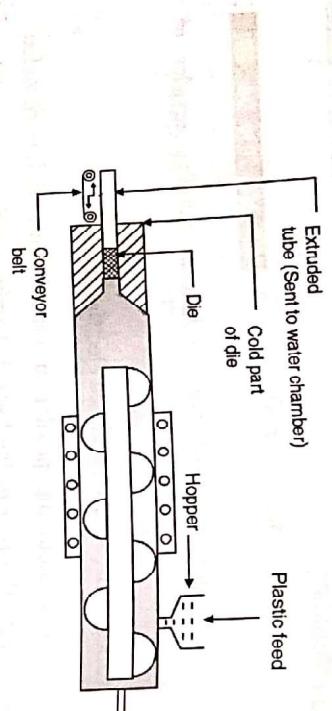


Fig. 2.5.5 : Moulding of tube by horizontal extrusion moulding

- The control of the temperature of heating chamber and speed of the extruder screw are the two most important factors of successful extruder operation.

2.6 Synthesis, Properties and Uses of Various Plastics

2.6.1 Phenol Formaldehyde Resins

MU - Dec. 2009, Dec. 2012

Synthesis

These are synthesised by condensation polymerisation.

Raw materials: Phenol or Resorcinol, Formaldehyde or Furfural

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

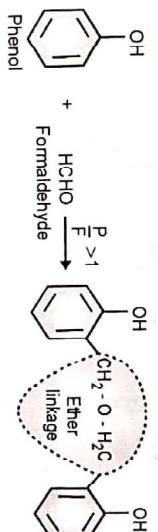
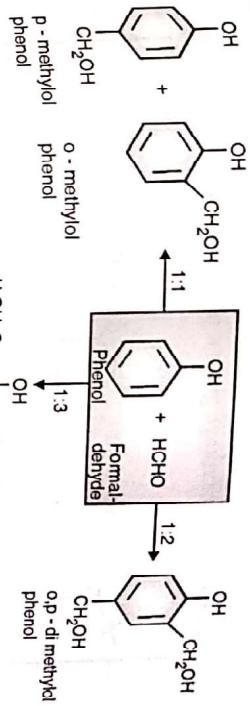
Step 1 : Preparation of O,O,P-tri methylol phenol resin

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,

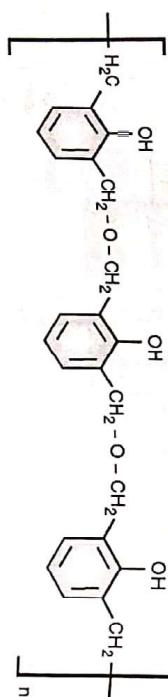


Step 2: Mono-methylol phenol (i.e. ortho or para) can undergo Polymerisation to give low molecular weight polymer known as Novolac.

Novolac

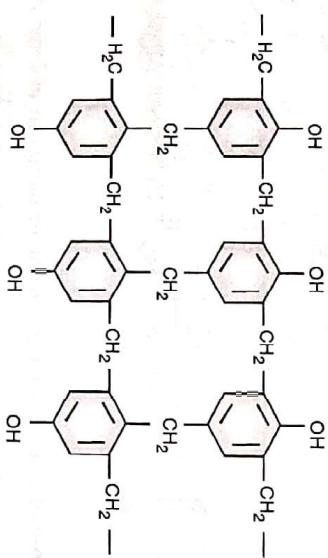
The linear polymer obtained as above is a thermoplastic, and dissolves in few aromatic solvents. Hence, is generally converted into a thermoset –bakelite.

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,



Properties of phenol Formaldehyde Resins

1. Phenolic resins or bakelite is a rigid, hard and infusible solid.
2. They are scratch resistant, water resistant and insoluble solids.
3. They are resistant to non-oxidising acids, salts and many organic solvents, but get attacked by alkalies, because of the presence of free hydroxyl group in their structures.
4. They possess excellent electrical insulating character.
5. PF Resins have Very low thermal conductivity. Does not melt when exposed to flame. Range of temperature – 180°C to + 120°C.

These properties make PF resins most suitable for their use as "Insulators"

Uses of PF Resins

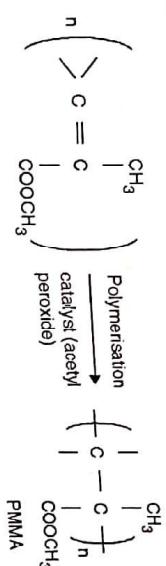
1. For making electric insulator parts like switches, plugs, switch boards, heater handles etc.
2. For making moulded articles like telephone parts, cabinet for radio and television etc.
3. For impregnating fabrics, wood and paper.
4. As a binder for grinding wheels.
5. It is used in paints and vanishes.
6. As a hydrogen-exchanger resin in water softening.
7. For making bearing, used in propeller shafts for paper industry and rolling mills.

2.6.2 PMMA (Polymethyl Methacrylate)

MU – Dec. 2008, May 2009, May 2010, May 2012

Synthesis

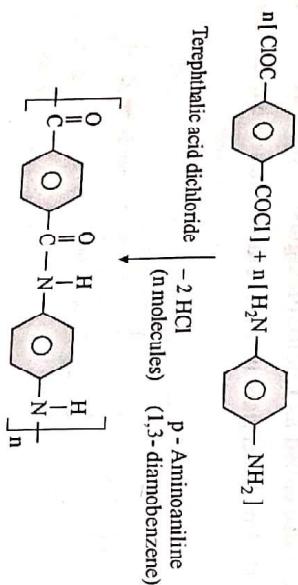
PMMA is (also called as Lucite/plexiglass). Synthesised by Polymerisation reaction of methyl methacrylate using a catalyst. Most commonly used catalyst is acetyl peroxide.



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 softens at about 130°C.
- Uses**
- Used 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.

MU - Dec. 2012, May 2013**Uses :**

Kevlar is used in

- 1. Aerospace and aircraft industries.
- 2. Making ropes, cables, protective clothings, bullet proof vests etc.
- 3. Helmets manufacturing.
- 4. Car parts e.g. brakes, tyres, clutch linings, etc.
- 5. Making many high performance materials.

2.7 Polymers in Medicines and Surgery**MU - May 2013**

Use of polymers as **biomaterial**, is increasing day by day. The biomaterials are the materials that can be implanted in body of living to provide special prosthetic function or used as diagnostic, surgical and therapeutic application.

Essential properties of biomaterial :

A polymer biomaterial when comes in contact of blood and tissues, should not cause any harm or destroy components of blood and tissues. Further it should not be toxic or allergic.

A biopolymer material should be easy to fabricate and should be easy to sterilize without alteration in properties. It should be, in short, biocompatible.

Applications of polymeric biomaterials

The polymeric biomaterials are used for,

(i) To construct artificial replacement for human organs :

Some man made polymers are used for complete replacement of organs e.g. artificial heart, heart-lung machines, artificial kidneys, legs, artificial faces, in plastic surgery etc.

(ii) To repair, sustain and augment function of organ :

Externally, plastics find applications from clothing, glasses for sight to fixtures. Internally, they are used for vascular prostheses, heart valves, pace makers, meshes and forms for reconstructive surgery, cannulae for haemodialysis etc.

Properties :

1. Kevlar possesses high stability against heat. It is highly flexible.
2. It is very strong (10 times stronger than aluminium, 5 times stronger than steel, if compared on a weight-for-weight basis).

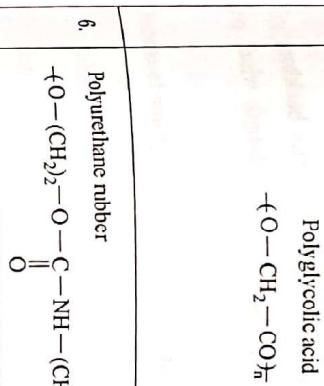
The plastics widely used in surgical implants are polytetrafluoroethylene, polysiloxanes, saturated aromatic polyesters, polypropylene, polyurethane, polyvinyl alcohol, etc.

(iii) To provide biochemical function :

Some polymers have definite and specific chemical interaction with the biochemistry of body. e.g. synthetic ion exchange resins for absorbing metabolites from blood, synthetic polyelectrolytes capable of absorbing specific viruses, polymers for production of interferon (antiviral agent), synthetic polypeptides, enzymes having higher biological activity.

Sr. No.	Structure of polymer biomaterial	Property/use
1.	$\begin{array}{c} \text{CH}_3 \\ \\ -\text{Si}-\text{O}-\text{n} \\ \\ \text{CH}_3 \end{array}$	Outstanding chemical inertness to body fluids, nontoxic, flexible for use in heart valves, blood filters, artificial heart, vascular tubing.
2.	Poly(methyl methacrylate) $\begin{array}{c} \text{CH}_3 \\ \\ -\text{H}_2\text{C}-\text{C}-\text{n} \\ \\ \text{COOCH}_3 \end{array}$	Transparent, easy to mould for use as contact lenses, dental restoratives.
3.	Polyvinyl chloride $\begin{array}{c} -\text{CH}_2-\text{CH}_n \\ \\ \text{Cl} \end{array}$	Strong, inert for syringes.
4.	Poly(lactic acid) $\begin{array}{c} \text{CH}_3 \\ \\ -(\text{O}-\text{C}-\text{CO})_n \\ \\ \text{H} \end{array}$	Biodegradable easily for use as surgical sutures, dialysis media, drug delivery, stents organs regeneration, controlled release, plastic surgery.

28 Conducting Polymers



MU - May 2008, Dec. 2009, May 2010, May 2013

Polymers, generally with high crystallinity, more commonly develop conductivity.

e.g. Cis-polyacetylene or poly para phenylene

There 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.

2.8.1 ICP

MU - May 2013

- These possess conjugated π electrons backbone.

- When such polymer faces electric field, these electrons get excited, and hence move through polymeric material.

- The orbitals of conjugated π 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 π electrons makes polymer to conduct electricity very efficiently.

e.g. Polyacetylenes

Polyquinoxoline

Poly-p-phenylene

Poly-m-phenylene sulphides etc.

Aromatic: Polyaniline, polyanthrylene

Aromatic heterocyclic : polyphthalocyanine, polythiophene, polybutadienylenne.

2.8.2 DCP

MU - May 2013

- 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.

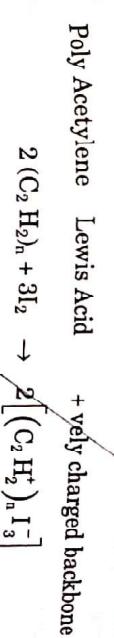
This technique is called as "doping". There are two types of doping :

- (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.

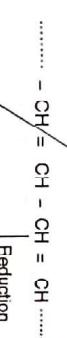
The lewis acids used are known as p-dopant.

e.g. I_2 , Br_2 , ASF_5 , PF_6 , Naphthylamine



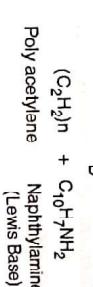
- N-doping : This technique involves reduction of ICP with Lewis base to form negative charge on backbone of ICP.

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

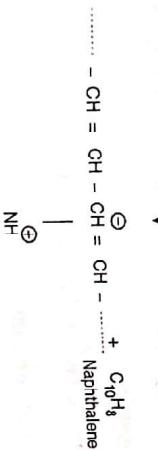


B^\ominus

Reduction



Reduction



NH^\oplus

MU - May 2013

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

1. Conducting element filled polymer [CEFP]

- 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 reasonably high.

Properties

(i) Cost is low.

(ii) They are light in weight.

(iii) Strong.

(iv) Can be easily moulded.

2. Blended conducting polymer [BCP]

- 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.

2.8.4 Co-ordination Conducting Polymers (Inorganic Polymers) MU - May 2013

- 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 (≤ 18).
- They are corrosion resistant.

2.8.5 Applications of Conducting Polymers

Conducting polymers are used,

- In rechargeable light weight batteries.
- Optically display devices

MU - Dec. 2008

3. In wiring in aircrafts and aerospace components.

4. In tele-communication systems.

5. In electromagnetic screening material.

6. Solar cells, photovoltaic devices, transistors, diodes, molecular wires and switches etc.

2.9 Industrial Polymers



Industrial polymers are the high performance polymer materials. Each of such polymers, possesses certain outstanding property.

They are in the form of the individual polymers or polymer blends or best in the form of polymer composites.

The polymers for the industrial purpose require to be possessing (i) high mechanical strength, (ii) high abrasion resistance, (iii) light in weight (iv) high tensile strength (v) high insulation property, sometimes high electrical conductivity (vi) high toughness.

The industrial or engineering plastics having such special features, find use as substitutes to metals, ceramics, natural fibers, ordinary glass.

Some industrial polymers with their characteristics properties and applications, are given below;

- (1) Polycarbonate : It is made from B is-phenol A and diphenyl carbonate. It is transparent, tough and has very high impact strength. It is used as bullet-proof transparent material and also for crash helmets, cooking utensil covers, bodies of camera, apparatus, for telephone booths, lenses, electrically insulating materials.
- (2) Teflon : It is obtained from tetrafluoro ethylene. Teflon has high softening temperature of more than 350°C . It has smooth surface, chemically very inert, very low coefficient of friction. It is useful for coating on non-stick

cookware, nonlubricated bearings, laboratory apparatus, tank linings, insulator in motors, cables.

- (3) **Bakelite** : Phenol and formaldehyde on reaction forms novolac resin, which on crosslinking in the moulds produces shaped Bakelite articles.

Bakelite is rigid, strong, high voltage insulator fire and heat resistant material. It is used for electrical goods, automobile parts, telephone parts, ion exchange resins. Novolac is used of varnishes as binder on abrasives or grinding wheels, plywood.

- (4) **Polyurathanes (Perlon v)** : Possess excellent industry flexibility, toughness, abrasion resistance. It is used in defence / oceanographic research, for coir foam, thermocole, as rubber.

- (5) **Silicones** : Silicone liquid, silicone solid, silicone rubber possess excellent chemical resistance, heat and fire resistance, electrical insulation silicone solid and rubbers have high abrasion resistance. They are used for aeroplane tyres, in chemical reactors, as sealants, for insulation for artificial heart, valves, tubes, high temperature insulating foams.

- (6) **Polyamides** : They possess very high tensile strength useful in making ropes, fibres, fabrics, nets, reinforcement of tyres. A ramid or Kevlar polyamide possesses tensile strength close to steel and is thermally stable, chemically resistant. Aramid fibres are used for reinforced fibres plastics, very high t.s. ropes, and as optical fibres for telephone cables, engine parts.

2.10 Elastomers or Rubber

- The organic polymers possessing elasticity to the extent of nearly 200 to 300 percent are known as Elastomers or Rubber.

- 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.

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.



Important properties of rubber are its

- Flexibility.
- Strength.
- Impermeability to water.
- High resistance to abrasion etc.

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

2.11 Types of Rubber

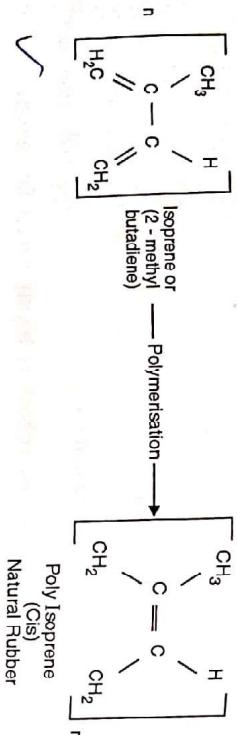
Rubber is of two types :

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

- 2.11.1 **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,



2.11.1.1 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_8), 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 pacha, balata etc.

2.11.2 Crepe Rubber

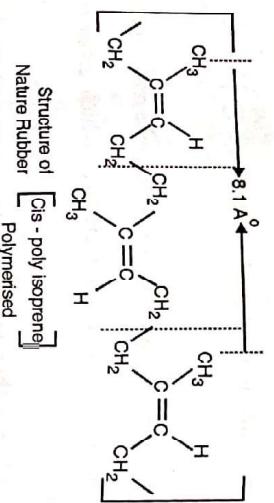
- The washed coagulum is allowed to stand so that the water gets drained out.
- The rubber coagulum is then made into sheets by passing through creping machines.
- The two rollers of creping machine are 0.5 m wide and 3 mm apart.
- These rollers have grooves on their surface. Which gives rubber sheets 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

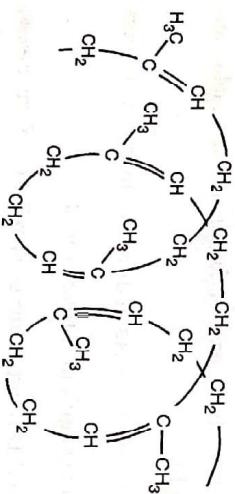
- To the coagulum, acetic acid or formic acid are added and the mixture is stirred thoroughly.
- This mixture is kept in tanks undisturbed for about 16 hours.
- A tough mass of coagulum is then formed.
- It is then passed through a series of rollers to form sheets, which are then hung for about 4 days 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.

2.11.1.3 Structure of Natural Rubber

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



- Being cis form, the polymer develops coiled structure, and hence possesses elasticity.
- When molecule is in linear / coiled form, the distance between methyl groups of the two monomeric units lying in same plane is $8.1\text{ }\text{\AA}^{\circ}$ (as shown in structure) and all $-\text{CH}_3$ groups are oriented outward.
- Coiled form can be represented as,



2.11.1.4 Properties and Drawbacks of Natural Rubber

MU - May 2012, May 2013

- The natural rubber has following properties, (drawbacks) :
 - 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 kg/cm^2).

4. Due to large percentage of unsaturation in its structure, it is easily attacked by various reagents such as HNO_3 , conc. H_2SO_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 difficult to store the rubber stocks.

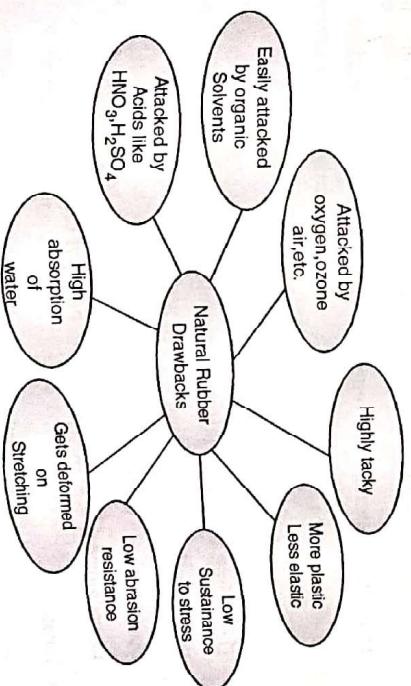
6. Durability and abrasion resistance of natural rubber is very low.

Thus the natural rubber does not have the desirable properties.

Hence to make its maximum use, it is essential to improve its properties.

The process by which the undesirable properties of natural rubber are improved upon is known as vulcanization.

Any catalyst used to improve the drawbacks of natural rubber is known as a vulcanizing agent.



2.12 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-mercaptop, benzothiazol and zinc alkylzanthate.

4. Antioxidants

- Natural rubber undergoes oxidation. For this antioxidant materials such as complex amines, polyphosphites are added.
- But, these materials get darken in the presence of light and therefore, a substance like β -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.

6. Reinforcing fillers

- These are added to give the strength and rigidity to the rubber products.
- Most common of all reinforcing fillers especially for the manufacture of motor car tyres is carbon black.

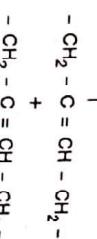
Other materials such as ZnO , $CaCO_3$, $MgCO_3$ are very widely used.

2.13 Vulcanization

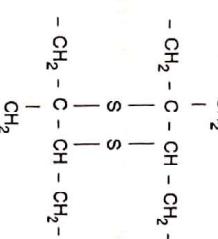
MU - Dec. 2007, May 2008, Dec. 2008, Dec. 2010, Dec. 2011

- To improve the properties of raw rubber, it is compounded with some chemicals like sulphur, H_2S , 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.

Straight Unsatuated Chains



Saturated Crosslinked Structure



Improvement

Undesirable properties	
Tacky	
Weak	Vulcanization →
Plastic	
Soluble	
Insoluble	Elastic

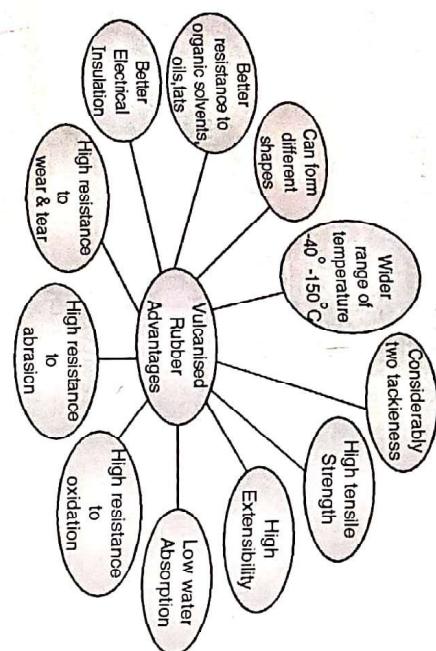
2.13.1 Vulcanizing Agents

- 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 :

2.13.2 Advantages Using Vulcanization

Vulcanized rubber possesses the following properties :

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



Comparison between Natural and Vulcanised Rubber OR Non-vulcanised and Vulcanised Rubber :

MU - Dec. 2007

Sr. No.	Natural/Non-vulcanised Rubber	Vulcanised Rubber
1.	Natural rubber is a hydrocarbon molecule with $-\text{CH}_3$ linkages either in cis or trans positions.	Vulcanised rubber is sulfurised hydrocarbon molecule, having cross-links of sulfur.
2.	Natural rubber is highly tacky, therefore can not be stacked for longer time.	Vulcanised rubber is non-tacky, hence easy to stack and store for longer time.
3.	It is weak and becomes brittle and gets deformed on stretching	It is strong and does not get deformed on stretching.
4.	It is more plastic in nature, less elastic.	It is more elastic in nature.
5.	It is soluble in organic solvents.	It is almost insoluble in organic solvents.

Sr. No.	Natural/ Non-vulcanised Rubber	Vulcanised Rubber
6.	It is attacked by acids like HNO_3 , H_2SO_4 , O_2 , and also O_3 .	It is almost resistant to attack of acids, and not attacked by O_2 , O_3 .
7.	It has low abrasion resistance, and high absorption of water.	It has no absorption of water and very good abrasion resistance.
8.	It has very low tensile strength, $\approx 20 \text{ kg/cm}^2$.	It has high tensile strength, and is related to % sulfur.
9.	If its useful range of temperature is very near to room temperature.	Its useful range of temperature is $40 - 150^\circ\text{C}$.
10.	It has almost no electrical insulation	It has high electrical insulation.

2.14 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.

2.14.3.1 Properties

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

2.14.3.2 Uses

For surface coatings and manufacture of foams and spandex fibre.

2.15 Applications of Rubber



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

- Tyres :** The manufacture of tyres is the leading application of rubber.
- 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.

Properties : (1) Buna-S is strong, highly resistant to oxidation

(2) It is high mechanical strength, and good load bearing capacity.

- 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.

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

- Mountings :** Mountings are sections of rubber sandwiched between two metal plants. Mountings reduce or isolate machine vibrations, prolong the life and improve the quietness of the equipment.
- Hoses :** All types of hoses are manufactured from rubber.
- 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.
- 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.
- Medicare :** Rubber is also used for making heart valves, transfusion tubing and padding for plastic surgery.
- Fuel :** Rubber like polysulphide rubber is used as a solid propellant fuel for rocket motors.

2.16 Glass Transition Temperature (T_g)

MU - Dec. 2007, May 2008, Dec. 2008, May 2010, Dec. 2011, May 2012

- When a plastic or rubber is cooled upto certain temperature, it becomes so hard and brittle that it breaks into pieces like glass, on application of stress.

- Definition : The temperature below which the polymer becomes hard, brittle and glassy and above which it is softer and flexible, is known as glass transition temperature.

2.16.1 Effect of Temperature on Polymer

- The hard and brittle state is the glassy state and soft flexible state is the viscoelastic state. If the viscoelastic state of polymer is heated further, the

MU - May 2013

- Below T_g the molecules in polymer do not move apart and do not have movements within the molecular chains.
- Therefore stress transfer property is lost and polymer below T_g is brittle.
- Above the T_g , the chain segments within the long molecules move locally like a person moving his hands, legs, leaning forward- backward but standing at one place, during exercise. Thus the polymers in the viscoelastic state have flexibility or stress transfer property.
- Above the temperature T_m ; the kinetic energy of the polymer molecules is high enough to cause movement within the chain segments as well to move from one position to another. Therefore this state has flow character like liquids.
- Some polymers have thermal degradation at and above T_m .

Polymer	T_g °C	T_m °C
Polyethylene	- 125	115
Polypropylene	- 18	175
Polystyrene	100°C	240°C
Polyvinyl chloride	80	212
Polyacrylonitrile	97	241

2.16.2 Factors Affecting T_g

- Crystallinity :** Higher the crystallinity of polymer, higher is its T_g value. Amorphous polymers have lower T_g .
- Molecular weight :** Higher the molecular weight of a polymer, greater is the T_g of the polymer. However, T_g value depends upon molecular weight upto 20,000, for vinylic polymers and after that there negligible effect.

(3) **Side groups on chain :** Presence of bulky side groups on the polymer chain, increases the T_g value. E.g. polyethylene has no side groups on chain and has T_g of - 125°C while polystyrene has - C_6H_5 groups on the chain and has much higher T_g of 100°C. Bigger sized side groups and greater polarity of the side groups have larger effect on T_g value.

(4) **Cross linking of polymer chains :** The T_g of a polymer increases with higher extent of crosslinking of polymer chains.

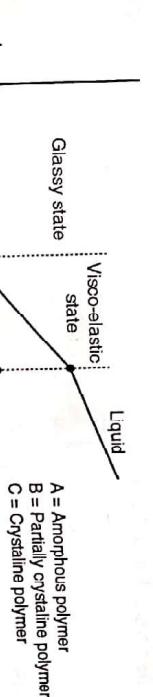
(5) **Plasticizer effect :** Addition a plasticizer of polymer decreases the T_g of polymer. Because, the polymer becomes amorphous and there is increase in chains mobility.

(6) **Coiled polymer chains :** The polymer having coiled or spring like chain structure, shows lower T_g . e. g. rubbers.

(7) **Force of attraction between chains :** The polymers having stronger force of intermolecular attraction, have greater T_g as the chains mobility is lesser in such cases.

- A polymer having higher T_m , is difficult for melt processing.

- T_g and T_m are approximately related as $3 T_g \approx 2 T_m$.



MU - May 2013

Fig. 2.16.1 : Effect of cooling on specific volume of polymer

2.16.3 Importance Significance of T_g

A polymer below its T_g is hard, stiff and brittle and therefore it is not preferred material for use at temperature below its T_g . In general, a polymer material should have much lower T_g than the operating temperature. e.g. polymers to be used for refrigerators, air conditioners or used in cold countries, should have lower T_g , so that they will not break during use.

2.17 University Questions and Answers

Dec. 2007

Q.1 Explain the term "glass transition temperature". What is its significance ?
(Section 2.16) (2 Marks)

Q. 2 Explain vulcanization giving examples. Distinguish between vulcanized and non-vulcanized rubber. (Section 2.13 and 2.13.3) (4 Marks)

Q.3 What is meant by fabrication of plastics ? Name different methods of fabrications. Explain transfer moulding with the help of a neat diagram. (Sections 2.5 and 2.5.3) (6 Marks)

May 2008

Q.4 Distinguish between thermoplastics and thermosetting resins.
(Section 2.3.2) (2 Marks)

Q. 5 What do you mean by fabrication of plastics ? Explain transfer moulding with the help of a neat diagram. (Sections 1.9) (6 Marks)

Q.6 Explain the following terms :

(i) Glass transition temperature (Section 2.16)

(ii) Explain the term 'vulcanization' with the help of a suitable example.
(Section 2.13) (3 Marks)

Q.6 Write short note on : Conducting polymers (Section 2.8) (5 Marks)

Dec. 2008

Q.9 State applications of conducting polymers. (Section 2.8.5) (3 Marks)

Q.10 Define vulcanisation of rubber. (Section 2.13) (3 Marks)

Q.11 Explain preparation methods and uses of
(i) PMMA (Section 2.6.2) (7 Marks)

Q.12 With reference to polymers explain :
(i) Glass transition temperature (Section 2.16) (7 Marks)

Q.13 Write note on : Preparation of Buna-S. (Section 2.14.1) (5 Marks)

May 2009

Q.14 Explain the preparation, properties and uses of PMMA.
(Section 2.6.2) (3 Marks)

Q.15 What are the main constituent of plastics ? Write the functions and examples of each constituent. (Section 2.4) (5 Marks)

Q.16 Write the preparation and uses of
(i) Buna-S Rubber (Section 2.14.1) (3 Marks)

Q.17 Write short note on : Injection Moulding Process. (Section 2.5.2) (5 Marks)

Dec. 2009

Q.18 Distinguish between thermoplastic and thermosetting polymers.
(Section 2.3.2) (3 Marks)

Q.19 Write note on synthesis, properties and uses of the following :
Phenol formaldehyde (Section 2.6.1) (8 Marks)

Q.20 Name the methods for Fabrication of Plastics. With the help of labelled diagram describe Transfer moulding and Injection moulding.
(Sections 2.5, 2.5.3 and 2.5.2) (7 Marks)

(5 Marks)

May 2010**May 2012****Q.22** Give synthesis properties and uses of - PMMA (Section 2.6.2) (2½ Marks)**Q.23** Define conducting polymer. Explain how polymers are made conductors with suitable examples. (Section 2.8)**Q.24** What is fabrication ? Explain any two methods of fabrication of plastics in detail. (Sections 2.5)**Dec. 2010****Dec. 2012****Q.25** Write the synthesis, properties and uses of the following :

(3 Marks)

Q.26 Buna-S (Section 2.14.1)

(4 Marks)

Q.27 Explain the following additives used for compounding of plastics :

(3 Marks)

Q.28 Explain in details the injection moulding method for fabrication of plastics.

(Section 2.5.2)

Dec. 2011**Dec. 2012****Q.29** Distinguish between thermoplastics and thermosettings.

(Section 2.3.2)

(5 Marks)

Q.30 What is glass transition temperature? What is its significance?

(Section 2.16)

(5 Marks)

Q.31 What is fabrication? What are the various types? With a neat diagram explain any one of them. (Sections 2.5, 2.5.1, 2.5.2, 2.5.3 and 2.5.4)

(6 Marks)

Q.32 What is vulcanization? How does it Improve the properties of rubber?

(Section 2.13)

(5 Marks)

Q.33 What is the repeat unit structure of natural rubber? State any two drawbacks of natural rubber. (Section 2.11.1-3 and 2.11.1-4) (3 Marks)**Q.34** What are the functions of the following constituents in the compounding of plastics

(i) Fillers (ii) Plasticizers (Section 2.4)

(4 Marks)

Q.35 Write preparation properties and uses of any two of the following

(i) Polymethyl methacrylate (PMMA) (Section 2.6.2)

(ii) Buna-S (Section 2.14.1)

(5 Marks)

Q.36 What is meant by fabrication of plastics? Explain Compression moulding with the help of a neat diagram. (Section 2.5 and 2.5.1) (6 Marks)**Q.37** Define glass transition temperature of polymer. What factors influence its value. (Section 2.16) (5 Marks)**Dec. 2012****Q.38** Write synthesis, properties and applications of Kevlar.

(Section 2.6.3)

(3 Marks)

Q.39 Write synthesis, properties and applications of Buna S.

(Section 2.14.1)

(3 Marks)

Q.40 Write synthesis, properties and applications of silicon rubber.

(Section 2.14.2)

(5 Marks)

Q.41 What is fabrication technology ? Mention various moulding techniques and explain injection moulding with the help of diagram. (6 Marks)

(Sections 2.5 and 2.5.2)

(5 Marks)

Q.42 Write chemical reactions for manufacturing of phenol formaldehyde resin. Explain its applications and properties also. (Section 2.6.1)

(5 Marks)

Q.43 Write a note on compounding of plastic. (Section 2.4)

(5 Marks)

May 2013

- Q. 44** What are nature rubbers ? What are their drawbacks ?
(Sections 2.11.1 and 2.11.1.4) (3 Marks)
- Q. 45** What are plasticizer and give its functions. (Section 2.4) (3 Marks)
- Q. 46** Explain fabrication of plastic with example of injection moulding.
(Section 2.5.2) (5 Marks)
- Q. 47** Write preparation properties and uses of following polymers :
Buna S (Section 2.14.1) (5 Marks)
- Kevlar (Section 2.6.3) (6 Marks)

- Q. 48** Explain effect of heat on polymers and factors affecting it.
(Section 2.16.1 and 2.16.2) (5 Marks)

CHAPTER 3 Lubricants

Syllabus

- Introduction :** Definition, Mechanism of Lubrication, Classification of lubricants, Solid lubricants (graphite & Molybdenum disulphide), Semisolid lubricants (greases Na base, Li base, Ca base, Axle greases), Liquid lubricants (blended oils).
- Important properties of lubricants, definition and significance, viscosity, viscosity index, flash and fire points, cloud and pour points, oiliness, Emulsification, Acid value and problems, Saponification value and problems.

3.1 Introduction

MU - 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.*) A¹.

- 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,

$$\text{Coefficient of friction} = \frac{\text{Frictional Resistance [Force of Friction]}}{\text{Applied force or load}}$$

- When the applied force is more than the resistance between two moving surfaces, the *wear* occurs.
- Here, if lubricating substances are applied on the moving surfaces, the *friction reduces*, and thereby *wear* also gets *minimized*. The different types of surfaces exhibit friction with varying extent.
- 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 every minute.

3.2 Lubricants and Lubrication

MU - Dec. 2007, May 2008, May 2009, Dec. 2009, May 2010, May 2011, Dec. 2012

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*.

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

MU - May 2008

- Lubricants *reduce friction, wear and tear of surfaces.*
- 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 of machines.
- (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 machine parts.
- (vii) Lubricants act 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.
- (viii) Lubricants help to *reduce maintenance cost* of machines, because a thin film of a lubricant reduces friction and thus controls *wear*.

Principle of Lubrication :

The basic principle of lubrication, is, lowering the co-efficient of friction, using lubricant. The effective results are achieved if an appropriate lubricant is applied on machine surfaces. This is to be done considering the working conditions of the machine, such as temperature, pressure, load, speed etc. At the same time nature of metal used for machine also plays vital role.

3.2.2 Mechanism of Lubrication

- The mechanism of lubrication is nothing but, "application of lubricant on sliding/moving surfaces and its action towards reducing frictional resistance".

MU - May 2009, Dec. 2009, May 2010

Lubricants
Friction depends upon following factors,

- The nature of the metal.
- The load on the metal.
- The temperature developed during operation/working.
- The pressure exerted during operation/working.

There are *three types of mechanisms* most widely used considering above factors,

- 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

MU - May 2007, May 2011 Dec. 2012

In this type of mechanisms, a *liquid lubricant with high viscosity* is applied in the form of thick film between two moving surfaces. The film is at least 1000 A° thick.

Such film helps to *avoid surface to surface contact* of moving surfaces. The hydrodynamic lubrication helps to reduce the coefficient of friction μ to about 0.001 to 0.03, which is *much lower* as compared to that for unlubricated surfaces (0.5 to 1.5).

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.

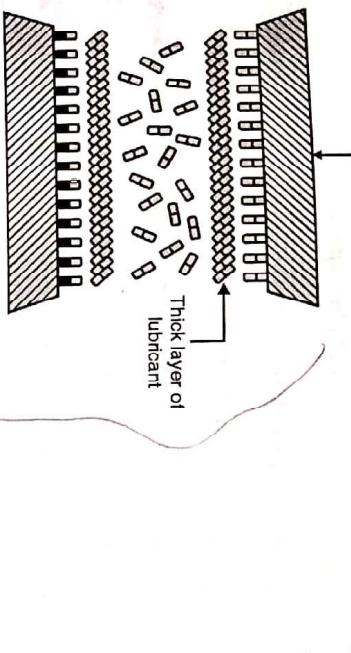
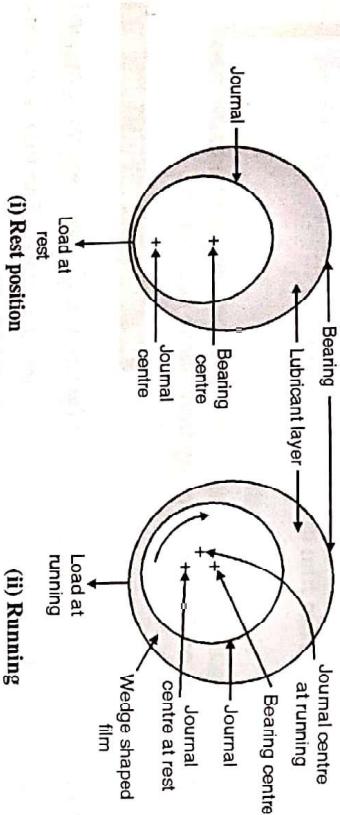


Fig. 3.2.1(a) : Hydrodynamic lubrication or fluid film lubrication

Fig. 3.2.1(b) : Fluid film lubrication
(i) Rest position
(ii) Running

- 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.

Essential characteristics of lubricants ideally required are,

- Adequate viscosity, oiliness and higher viscosity index.
- Lubricant should be resistant to seasonal impact.

But any single Veg. oil / Mineral oil may not satisfy these requirements. Therefore, in hydrodynamic lubrication generally following types of blends are used.

Blended oils : Veg. oils and/or Mineral oils blended with Anti oxidants / organo metallic compounds / long chain polymers.

Machines in which this mechanism of lubrication is used are :

- Sewing machines
- Clocks
- Watches
- Scientific instruments.

(Thus this mechanism is useful in machines where *load is low and speed is not very high*.)

3.2.2 Thin Film or Boundary Lubrication

MU – Dec. 2007, Dec. 2009, May 2010, Dec. 2010, May 2012

(This type of mechanism is useful under certain working conditions of machines, such as :

- If viscosity of liquid lubricant used for lubrication (oil) is low,
- The machine is to be operated at comparatively low speed
- During operation of machine, a shaft starts moving from rest at fixed intervals or
- The machine is operated under high load.)

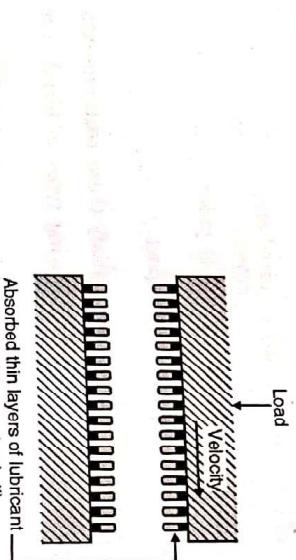


Fig. 3.2.2 : Boundary lubrication

- Under such working conditions a continuous thick film of lubricant cannot persist in between two sliding surfaces. To reduce friction in machines facing such working conditions, 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.
- Essential characteristics of lubricants most suitable for boundary lubrication are :

- high viscosity index,
- high resistance to oxidation
- stability at elevated temperature,
- adequate oiliness, and
- low pour-point.

e.g. Mineral oils blended with vegetable and/or animal oils, solid lubricants such as Graphite or Molybdenum di-sulphide, Soaps of vegetable or animal oils.

(The machines where boundary lubrication is commonly applied are, gears, rail axle boxes, tractors, rollers etc.)

3.2.3 Extreme Pressure Lubrication

MU – May 2007, Dec 2008, May 2009, Dec 2010

- 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*). Refer Table 3.3.1.
- The machines in which E.P.T. lubrication is applied are, *cutting tools, rock crushing machiches, wire drawing machines etc.*)

- Essential characteristics of lubricants most suitable for EPT lubrication, are :
 - should have tendency to adhere on metal surfaces,
 - should get aggregated by greater forces of attraction and form films which would stick on metal surface and is retained for longer time.
 - should be able to sustain high temperature and pressure.
- e.g.
 - Blended oils in which veg. oil mixed with chlorinated esters, (sulphurised oils, phosphates of org. compounds.

2. Solid lubricants [their colloidal suspension in oil or resin]

The metal reacts with additives, forming chloride / sulphate / phosphate, which remains on machine surface. These compounds are with high melting point, hence can sustain temperature fluctuation of machine, giving effective lubrication under extreme conditions.

Best results are obtained with iron, but with passive metals like silver, Al, Cu or Ti, the suitability is poor.

Comparision of fluid film and extreme :

Sr. No.	Fluid film lubrication or Thick film/Hydrodynamic lubrication	Extreme Pressure Lubrication
1.	This mechanism for lubrication is useful in machines where load is low and speed is not very high.	This mechanism for lubrication is useful in machines where load and speed both are high and also machine is under pressure and temperature.
2.	In this liquid lubricant with high viscosity is applied as thick film on machine surfaces in contact. Thickness of film is $\approx 1000\text{A}^\circ$	In this, mineral oils with special additives are used. Additives improve specific property of lubricant as per requirements of working condition of machines.
3.	The Co-efficient of friction is lowered to about 0.001 to 0.03 [unlubricated machine parts $\mu = 0.5$ to 1.5]	The blending can be done to have almost nil friction of machine parts, became on surface, metal forms temporary products with additives. e.g. chlorides, sulphates etc.
4.	Lubricant must have adequate viscosity and high viscosity index	In this, the lubricant with additives remains on surface of metal for long time as there is adherence due to chemical reaction.

Sr. No.	Fluid film lubrication or Thick film/Hydrodynamic lubrication	Extreme Pressure Lubrication
5.	It shows great impact of seasons, as temperature affects viscosity	Seasonal impact is almost eliminated.
6.	e.g. sewing machines, watches, clocks etc.	e.g. cutting tools, rock crushing machines, wire drawing machines etc.

Comparision of fluid film and boundary :

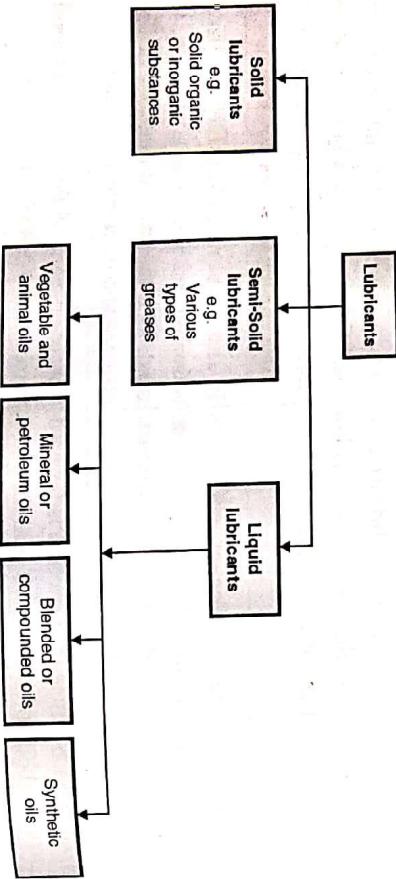
Sr. No.	Fluid film lubrication or Thick film/Hydrodynamic lubrication	Boundary Lubrication
1.	This mechanism for lubrication is useful in machines where load is low and speed is not very high.	This mechanism for lubrication is useful in machines where speed is low, load is high and a journal/shaft starts moving at a fixed interval.
2.	In this liquid lubricant with high viscosity is applied as thick film on machine surfaces in contact. Thickness of film is $\approx 1000\text{A}^\circ$	In this, a lubricant capable of getting adsorbed on lubricating surface is used; as a thin film introduced in the clearing spaces of moving surfaces.

Sr. No.	Fluid film lubrication or Thick film/Hydrodynamic lubrication	Boundary Lubrication
3.	The Co-efficient of friction is lowered to about 0.001 to 0.03 [unlubricated machine parts $\mu = 0.5$ to 1.5]	The co-efficient of friction is lowered to extent of 0.05 to 0.15.
4.	Lubricant must have adequate viscosity and high viscosity index	Lubricant must have tendency to develop adherence with the surface, high V. I., high resistance to oxidation, low pour point, adequate oiliness and high stability at elevated temperature.

Sr. No.	Fluid film lubrication or Thick film/Hydrodynamic lubrication	Boundary Lubrication
5.	It shows great impact of seasons, as temperature affects viscosity	Seasonal impact is minimised due to thin film and also adherence to the surfaces.
6.	e.g. sewing machines, watches, clocks etc.	e.g. Gears, rail axle, boxes, tractors, rollers etc.

3.3 Classification of Lubricants

On the basis of physical state, the lubricants are classified as follows :



3.3.1 Solid Lubricants

MU - May 2008, Dec. 2008, May 2011, May 2012, May 2013

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 because, due to high load and low speed, the film of liquid lubricant cannot remain in between sliding surfaces.

- When the machine parts are not easily accessible, i.e. if the design is intrinsic, then use of liquid or semisolid lubricant fails.
- When machine is at high working temperature and pressure, and hence under such conditions combustible lubricants (oils) are unsuitable.

The lubricating action of solid lubricants is due to their layered structure lattice.

The commonly and widely used lubricants are graphite (Fig. 3.3.1) and molybdenum-di-sulphide. (Fig. 3.3.2).

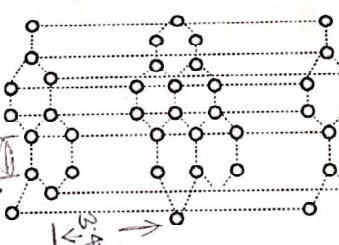


Fig. 3.3.1 : Layer structure of graphite

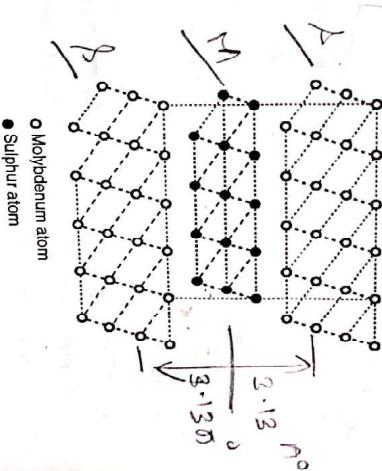


Fig. 3.3.2 : Layer structure of Molybdenum di-sulphide (Sandwich like)

Other examples are Mica, Teflon, 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.

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, soapy to touch, and not oxidized in the presence of air below 375°C temperature. It can be used upto 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.

Aquadag

- 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.
- The suspension of graphite in oil is known as 'oil-dag'. This is used particularly in I.C. engines.
- Graphite is also mixed with greases to form "graphite greases". These are used at still higher temperatures.

Teflon

- 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.

Molybdenum-di-sulphide

Molybdenum-di-sulphide possesses a sandwich like structure Fig. 3.32 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 co-efficient 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.

Oildag

- The suspension of graphite in oil is known as 'oil-dag'. This is used particularly in I.C. engines.
- Graphite is also mixed with greases to form "graphite greases". These are used at still higher temperatures.

3.3.2 Semisolid Lubricants (Greases)

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MU - May 2007, May 2009, May 2013

The most widely used semisolid lubricants are *greases and vaselines*. The semisolid lubricants are used under working conditions, such as,

- (i) *Low speed and high pressure, and high temperature* (upto 80°C)
- (ii) *Machineries used in textile mills, paper and food product manufacturing etc.* where spilling and spurting of lubricant is harmful to the product.
- (iii) *Machines where liquid lubricant cannot be maintained in position due to intermittent operations of machine parts such as shaft etc.*
- (iv) *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]

- Lubricants
- (ii) Sodium soap greases.
 - (iii) Lithium soap greases.
 - (iv) Barium soap greases.
 - (v) Aluminium soap greases.
 - (vi) Axle greases [sett greases].

Manufacture of greases

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The greases are manufactured by saponification of fatty oil with an alkali such as NaOH [sodal], Ca(OH)₂ [lime], Al(OH)₃ [aluminium] or LiOH [lithium].

Exception *Axle greases* are prepared by mixing lime or other heavy metal oxides with resin.

This mixture of oil and respective alkali, taken in appropriate proportion is allowed to stand for few hours. The stiff mass which is formed on the surfaces is separated. The stiff mass i.e. 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. To maintain consistency of the grease, *fillers like talc or mica are mixed, at last step*.

Reactions involved can be represented as,



The greases are named on the basis of the alkalis used in manufacture.

Properties of greases

- (1) 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.

- (2) Lithium soap greases :
 - (a) They have good oxidation stability.
 - (b) They have good stability at high temperatures and high mechanical stability.
 - (c) They can be used upto 150 °C maximum and - 55 °C minimum.
 - (d) They are costly and hence are used for special applications only. e.g. in aircrafts.

- (3) 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.

- (4) Axle greases :
 - (a) They are cheap.
 - (b) They are water insoluble.

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Properties of greases

- (1) 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.

3.3.3 Liquid Lubricants

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. |

3.3.3.1 Vegetable or Animal Oils

Vegetable or animal oils are extracted from plants/animals respectively. These oils are triglycerides of higher fatty acids.

Examples 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 it gets adhered to the machine surface and helps to reduce friction.

Drawbacks of vegetable or animal oils

- i) Vegetable/animal oils are very costly.
- ii) Also they tend to undergo oxidation, in the presence of oxygen or moisture, or emulsification with water at working temperature.

(iii) 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.

(iv) They also get *thickened or hardened* in the presence of air thereby increasing friction of machine parts.

(v) 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.

3.3.3.2 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.

3.3.3.3 Blended Oils

MU - May 2007, Dec. 2007, May 2010, Dec. 2010, May 2011, Dec. 2012

- Vegetable / animal / mineral oils, alone are not found suitable to meet requirements of machines. Hence, it is essential to prepare blended oils to suit the working conditions of machines.

Blending agents are used to improve properties such as viscosity index, oxidation stability, oiliness, pour point, flash point etc. Other additives such as corrosion/abrasion inhibitors, antifoaming agents, emulsifiers etc. are also mixed in appropriate proportion in blends. 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. [including EPT additives]

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.
Foam preventors.	Glycols or glycerols. Phenols or compounds of naphthalene. Pour point depressants.
Viscosity index improvers.	High molecular weight organic compounds e.g. haxanol.
Viscosity improvers.	Polystyrenes, polyesters etc. They act as thickeners.

Property	Substances/Compounds
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.
Antiewear additives	Substances like tricresylphosphate, Zn-dialkyl di thiophosphate.
Rust inhibitors	Fatty acids, Aminophosphates.

3.4 Important Properties of Lubricants

- Generally the lubricating 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 Property	Method Used
(1)	Acid value	Titrimetry
(2)	Saponification value	Titrimetry
(3)	Aniline point	Aniline point apparatus
(4)	Emulsification	Steam emulsion number (SEN)

Table 3.4.2

Sr. No.	Chemical Property	Method Used
3.	Cloud point and pour point determination.	Cloud and pour point apparatus.
4.	Volatile matter content.	Vaporimeter.
5.	Oxidation stability.	Slight's oxidation test.
6.	Carbon residue.	(a) Conradson's method (b) Ramsbottom method

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.

3. Lubricant should *reduce waste of energy*, thereby *increasing efficiency* of the machine.
4. 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,
1. Should have *high oiliness*.
 2. Viscosity should be *adequate* whereas the variation in the viscosity (viscosity index) should be to a lower extent i.e. VI should be as *high* as possible.
 3. *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.
 4. *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.
 5. Acid value of the lubricant should be *very low*.
 6. 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

3.6.1 Viscosity and Viscosity Index

MU - Dec. 2008, May 2009, Dec. 2012, May 2013

- 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.

3.6.1 Significance of Viscosity and Viscosity Index

MU - Dec. 2012

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

MU - Dec. 2007, Dec. 2008, May 2009, Dec. 2010

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.
- These constants are usually determined by using Pensky-Marten's flash point apparatus.

3.6.2.1 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

MU - 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.

3.6.3.1 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 Oiliness

MU - May 2008

It is a property by virtue of which an oil remains adhered to the lubricating surfaces.

It is directly related to specific gravity of oil. Lower the specific gravity, higher is oiliness. The oils are generally either saturated and unsaturated fatty acids (e.g. vegetable or animal oils) or hydrocarbon (mineral oils).

The vegetable/ animal oils are with high oiliness, as compared to mineral oils.

Oiliness is felt on touching, but it cannot be measured by any standard test.

Oiliness is an oil enhancement property provided through the use of chemical additives known as antiwear (AW) agents.

Most oils intended for use in heavier machine applications contain AW agents.

True lubricants differ from ordinary liquids of equal viscosity in as much as they possess the property of "oiliness." This is a property which enables them to maintain an unbroken film between surfaces when the loads are heavy.

- It is possessed most markedly by vegetables and animal oils and fats, and less markedly by mineral oils.

3.6.5 Emulsification

Emulsification is the property of an oil lubricant to get intimately mixed with water forming emulsion. In most of the cases of lubrication, such emulsion formation is not desirable as the emulsion has tendency to collect dirt, dust, grit, etc., causing more friction between the lubricated parts. Hence a good oil lubricant is the one which separates from water quickly.

Steam Emulsion Number (S.E.N) or Demulsification Number :

The emulsification property of oils is expressed in terms of steam emulsion number (S.E.N) which is determined by A.S.T.M. test.

Testing :

20 ml of the oil lubricant is taken in a tube and steam of 100°C is bubbled through it till the temperature of oil raises to 90°C. Then the tube is placed in a thermostat maintained at 90°C and the time in seconds is noted when the oil and water (condensed steam) separate out in distinct layers.

S.E.N. : It is the time in seconds required to separate water and oil at 90°C.

3.6.5.1 Significance

- (1) A good oil lubricant generally has a low steam emulsion number, so that even if water comes in contact with the oil in the lubricated parts, it will not form emulsion. The emulsion has tendency to collect dirt, dust, etc. Steam turbine oils are always associated with steam or water and it is essential that water should not emulsify the oil.
- (2) Petroleum oils have very low S.E.N. but vegetable oils have higher S.E.N. as the vegetable oil and water molecules have affection.

- (3) Whenever a stable oil in water or water in oil emulsion is required for lubrication (e.g. cutting, drilling operations, large I.C. engines, pneumatic compressors, etc.), then they are prepared by use of emulsifiers like soap, fatty acid, etc. In such specified use, the water and oil are not required to separate.

3.6.7 Saponification Value or Number

MU – May 2007, Dec. 2007, Dec. 2008, May 2009

Saponification value of an oil can be defined as, the number of milligrams of potassium hydroxide required to saponify one gram of oil.

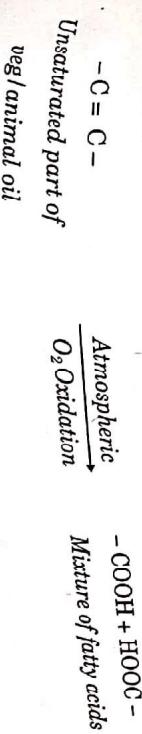
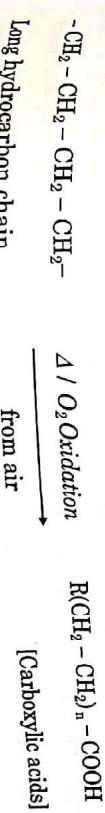
The saponification value is expressed as milligrams of KOH.

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.

3.6.7.1 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.



3.6.6 Acid Value

MU - May 2008

- Acid value is defined as the number of milligrams of KOH required to neutralize free fatty acids present in one gram of oil.
- Unit of acid value is mgs of KOH
- 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 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 O₂ 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.

3.6.6.1 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.

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

$$\text{Weight of oil} = 5 \text{ gms.}$$

$$\text{Blank titration reading} = 45 \text{ ml. } 0.5 \text{ N HCl.}$$

$$\text{Back titration reading} = 15 \text{ ml. } 0.5 \text{ N HCl}$$

Thus, volume of 0.5 N KOH required by the oil for saponification in terms of 0.5 N HCl = 45 - 15 = 30 ml.

$$\begin{aligned} \text{Saponification value} &= \frac{\text{Volume of KOH consumed} \times \text{Normality of KOH} \times 56}{\text{Weight of oil in gms.}} \\ &= \frac{30 \times 0.5 \times 56}{5} \\ &= 168 \text{ mg. KOH.} \end{aligned}$$

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.

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.

$$\text{Saponification value} = \frac{\text{Volume of alcoholic KOH} \times N_{\text{KOH}} \times 56}{\text{Weight of oil in gms.}}$$

$$180 = \frac{\text{Volume of alcoholic KOH} \times N_{\text{KOH}} \times 56}{\text{Weight of oil in gms.}}$$

$$180 = \frac{[\text{Blank} - \text{Back}] N_{\text{KOH}} \times 56}{\text{Weight of oil}}$$

$$180 = \frac{(50 - \chi) 0.4 \times 56}{1}$$

$$180 = (50 - \chi) 22.4$$

$$180 = 1120 - 22.4 \chi$$

$$22.4 \chi = 1120 - 180 = 940$$

$$\therefore \chi = \frac{940}{22.4}$$

$$= 41.96$$

$$\chi \approx 42 \text{ ml. of alcoholic KOH}$$

Ans. : Quantity of alcoholic KOH required per gm = 42 ml

Problem 3.7.3: 5 gms of an oil was saponified with 50 ml 0.5 N alcoholic KOH. After refluxing for 2 hours, the mixture was titrated by

15 ml of 0.5 N HCl. Find the saponification value of oil.

Solution :

Given Weight of oil = 5 gms

Quantity of 0.5 N alcoholic KOH = 50 ml.

Quantity of 0.5 N HCl required (Back titration) = 15 ml.

To find : Saponification value of oil.

Now,

$$\text{Saponification value} = \frac{\text{Volume of alcoholic KOH} \times N_{\text{KOH}} \times 56}{\text{Weight of oil in gms.}}$$

$$= [\text{Volume of KOH added to oil} - \text{Back titration reading}] \times \frac{N_{\text{KOH}} \times 56}{\text{Weight of oil}}$$

$$\therefore \text{S.V.} = \frac{(50 - 15) 0.5 \times 56}{5} = 196 \text{ mg KOH}$$

Ans. : Saponification value of oil = 196 mg KOH.

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

Weight of oil = 2.5 gms

Blank titration reading = 40 ml 0.5 N HCl

Back titration reading = 20 ml 0.5 N HCl

Normality of KOH = 0.25 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 ml 0.25 N KOH = 1 ml 0.5 N HCl.

Thus quantity of KOH added to oil (blank) = 80 ml.

and quantity of KOH unreacted (back) = 40 ml.

$$\text{Saponification value} = \frac{\text{Volume of alcoholic KOH} \times N_{\text{KOH}} \times 56}{\text{Weight of oil in gms}}$$

$$\therefore S.V. = \frac{[\text{Blank} - \text{Back}] \times N_{\text{KOH}} \times 56}{\text{Weight of oil}}$$

$$\therefore S.V. = \frac{(80 - 40) 0.25 \times 56}{2.5}$$

$$\therefore S.V. = \frac{40 \times 0.25 \times 56}{2.5} \text{ mg. KOH}$$

$$\therefore S.V. = 224 \text{ mg. KOH}$$

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

$$\text{Weight of oil} = 5 \text{ gms}$$

Strength of alcoholic KOH = 1.4 gm per 50 ml.

$$= 28 \text{ gms per 1000 ml.}$$

$$= 0.5 \text{ N}$$

$$\text{Normality of HCl} = 0.5 \text{ N.}$$

$$\text{Blank titration reading} = 40 \text{ ml. } 0.5 \text{ N HCl}$$

$$\text{Back titration reading} = 10 \text{ ml. } 0.5 \text{ N HCl}$$

To find : Saponification value,

$$S.V. = \frac{\text{Volume of alcoholic KOH} \times N_{\text{KOH}} \times 56}{\text{Weight of oil in gms.}}$$

$$\therefore S.V. = \frac{[\text{Blank} - \text{Back}] N_{\text{KOH}} \times 56}{\text{Weight of oil}}$$

$$\therefore S.V. = \frac{(40 - 10) 0.5 \times 56}{5} \text{ mgs KOH}$$

$$\therefore S.V. = 168 \text{ mgs KOH}$$

Ans. : Saponification value of oil = 168 mgs KOH.

Problem 3.7.6: 5 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.

Solution:

Given: Weight of oil = 5 gms

Volume of 0.5 N HCl, before saponification = 50 ml

Volume of 0.5 N HCl after saponification = 25 ml

: Volume of acid reacted with oil = $(50 - 25) = 25 \text{ ml}$

$$\text{Saponification value} = \frac{\text{Amount of KOH Consumed} \times \text{Normality of KOH} \times 56}{\text{Weight of oil in gms}}$$

$$= \frac{25 \times 0.5 \times 56}{5}$$

$$= 140 \text{ mg of KOH}$$

Ans. : Saponification value = 140 mg of KOH

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.

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

$$\because 50 \text{ ml KOH} = 45 \text{ ml } 0.5 \text{ N HCl}$$

$$\therefore N_1 V_1 = N_2 V_2$$

$$N_1 \times 50 = 0.5 \times 45$$

$$\therefore N_1 = \frac{0.5 \times 45}{50}$$

$$= 0.45 \text{ N}$$

$$\therefore \text{Normality of KOH} = 0.45 \text{ N}$$

$$\therefore \text{Weight of blended oil} = 16 \text{ gm}$$

$$\therefore \text{Weight of cottonseed oil} = 16 - x \text{ gm}$$

$$\text{Now, Saponification value} = \frac{(\text{Blank} - \text{Back}) \times N \times 56}{(16 - x)}$$

Blended oil contains castor oil and petroleum oil.

∴ petroleum oil has saponification value always zero.

∴ Let us calculate saponification value of the blended oil.

$$\text{Saponification-value} = \frac{\text{Volume of KOH} \times N_{\text{KOH}} \times 56}{\text{Weight of Blend}} \\ = \frac{13.5 \times 0.45 \times 56}{16}$$

Ans.: Saponification-value of blend = 21.26 mgs of KOH

$$\% \text{ castor oil} = \frac{\text{Saponification value of blend}}{\text{Saponification value of castor oil}} \times 100 \\ = \frac{21.26}{192} \times 100 \\ = 11.074 \%$$

Problem 3.7.10: 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)

Solution:

Given data:

$$\text{Wt. of lubricant} = 3 \text{ gm.}$$

$$\text{Blank titration reading} = 36 \text{ ml.}$$

$$\text{Back titration reading} = 12 \text{ ml.}$$

$$\text{Normality of HCl} = 0.5 \text{ N}$$

To calculate saponification value,

$$\text{Sap. Value} = \frac{\text{Vol. of KOH consumed} \times 28}{\text{Wt. of Oil}}$$

$$\frac{0.5 \times 16}{16} = 28$$

$$\begin{aligned} &= \frac{(36 - 12) \times 28}{3} \text{ mgs of KOH} \\ &= \frac{24 \times 28}{3} = (8 \times 28) \text{ mgs of KOH} \\ &= 224 \text{ mgs of KOH} \end{aligned}$$

Ans. Saponification Value = 224 mgs of KOH

Problem 3.7.11: 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 :

Weight of oil = 1.55 gms

Volume of KOH = 20 ml

Normality of KOH = $\frac{N}{2} = 0.5\text{N}$

Volume of HCl = 15 ml.

Normality of HCl = $\frac{N}{2} = 0.5\text{N}$

Saponification value = ?

$$\text{Saponification Value} = \frac{\text{Volume of KOH consumed} \times N_{\text{KOH}} \times 56}{\text{weight of oil}}$$

Problem 3.7.13: 2.5 g of a blended oil was saponified using express alcoholic KOH solution (0.5 N). After refluxing for two hours, the mixture was titrated against 0.5 N HCl solution. The burette reading was found to be 24 ml. The blank titration required 40 ml of the same HCl solution. Find the saponification value of the oil. If the oil used for blending has saponification value of 191, calculate percentage oil in the blend.

(May 2012, 4 Marks)

Solution:

Given Data :

Wt. Of Blended oil = 2.5 gms.

Normality of KOH (alcoholic) = 0.5 N

Ans. : Saponification value = 90.32 mgs of KOH

Problem 3.7.12: 1.25 gram of an oil was saponified with 50 ml 0.1 N potassium hydroxide solution. After refluxing, the mixture required 7.5 ml 0.1 N hydrochloric acid for neutralisation. Find saponification value of the oil. (Dec. 2009, 3 Marks)

Solution:

Weight of oil = 1.25 gm.

Volume of 0.1 N KOH = $V_1 = 50 \text{ ml}$.

Used for neutralisation

Volume of 0.1 N HCl = Excess = 7.5 ml = V_2

$$\therefore \text{Sap value} = \frac{\text{Volume of KOH used in saponification} \times N_{\text{KOH}} \times 56}{\text{Weight of oil}}$$

$$= \frac{(50 - 7.5) \times 0.1 \times 56}{1.25} = \frac{42.5 \times 0.1 \times 56}{1.25}$$

$$= 190.4$$

Answer: Saponification value = 190.4

Normality of HCl soln = 0.5 N
 Volume of HCl soln = 24 ml
 Blank Titration (B.R) = 40 ml

To find : Saponification value of oil

$$\text{Saponification value} = \frac{(\text{Blank} - \text{Back}) \times N_{\text{KOH}} \times 56}{\text{weight of oil}}$$

$$= \frac{(40 - 24) \times 0.5 \times 56}{2.5}$$

$$= 0.0224 \text{ mgs/gm.}$$

\therefore Saponification value = 179.2

Now for blending if oil with saponification value 191 is used,

$$\% \text{ blend} = \frac{\text{saponification value of sample 1} \times 100}{\text{saponification value of sample 2}}$$

$$= \frac{179.2}{191} \times 100$$

$$= 93.8\%$$

To find: Acid value,

Given

(Weight = Volume in ml \times Density)

$$\text{Weight of oil} \approx 5 \text{ ml} \times 0.89 = 4.45 \text{ gms.}$$

$$\text{Normality of KOH} = 0.01 \text{ N}$$

$$\text{Volume of KOH} = 2.5 \text{ ml.}$$

3.7.2 Problems based on Acid Value

Problem 3.7.14: 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:

$$\text{Weight of oil} = 10 \text{ gms}$$

$$\text{Normality of KOH} = 0.02 \text{ N.}$$

$$\text{Volume of KOH} = 0.2 \text{ ml.}$$

To find: Acid value,

$$\text{Acid value} = \frac{\text{Volume of KOH} \times N_{\text{KOH}} \times 56}{\text{Weight of oil in gms.}}$$

$$\text{Acid value} = \frac{0.2 \times 0.02 \times 56}{10}$$

Ans:

$$\text{Acid value of oil} = 0.0224 \text{ mgs. KOH}$$

Problem 3.7.15: An oil blend used was analysed for its acid value. 5 ml of oil required 2.5 ml $\frac{N}{100}$ 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)

$$\text{Weight of oil} \approx 5 \text{ ml} \times 0.89 = 4.45 \text{ gms.}$$

$$\text{Normality of KOH} = 0.01 \text{ N}$$

$$\text{Volume of KOH} = 2.5 \text{ ml.}$$

To find: Acid value,

$$\text{Acid value} = \frac{\text{Volume of KOH} \times N_{\text{KOH}} \times 56}{\text{Weight of oil in gms.}}$$

$$\text{Acid value} = \frac{2.5 \times 0.01 \times 56}{4.45}$$

$$= 0.315 \text{ mgs/gms.}$$

$$\text{Ans: Acid value} = 0.315 \text{ mgs KOH}$$

" This value is more than 0.1, the oil cannot be used for lubrication.

Problem 3.7.16: Find the acid value of a vegetable oil whose 5 ml required 2 ml of N/100 KOH during titration. (Density of oil = 0.92)

Solution:

Given

$$\text{Volume of oil} = 5 \text{ ml}, \quad \text{Volume of KOH} = 2 \text{ ml}$$

$$\text{Density of oil} = 0.92, \quad \text{Normality of KOH} = 0.01 \text{ N}$$

To find: Acid value

$$\therefore \text{Volume of oil} = 5 \text{ ml}$$

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.: Acid value = 0.243 mg of KOH.

Problem 3.7.17: 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 2009, 4 Marks)

Solution:

Given data :

$$\text{Volume of oil} = 9 \text{ ml}$$

$$\text{Density of oil} = 0.81 \text{ g/ml}$$

$$\text{Volume of KOH} = 1.5 \text{ ml}$$

$$\text{Normality of KOH} = 0.04 \text{ N}$$

$$\text{Now Acid value} = \frac{\text{Volume of KOH} \times \text{N}_{\text{KOH}} \times 56}{\text{wt. of oil}}$$

$$\text{Here wt. (mass) of oil} = \text{Volume} \times \text{density}$$

$$= 9 \times 0.81 = 7.29 \text{ gm}$$

$$\therefore \text{Acid value} = \frac{1.5 \times 0.04 \times 56}{7.29}$$

$$= 0.461 \text{ mgs of KOH}$$

Ans.: Acid value = 0.461 mgs of KOH

Problem 3.7.18: 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)

Solution:

Given :

$$\text{Volume of oil} = 20 \text{ ml}$$

$$\text{Density of oil} = 0.86 \text{ gm/ml}$$

$$\text{Normality of KOH} = 0.1 \text{ N}$$

$$\text{Amount of KOH} = 2.5 \text{ ml}$$

$$\text{Acid value} = ?$$

To find: Acid value

$$\text{Weight of oil} = \text{Volume} \times \text{density}$$

$$= 20 \times 0.86$$

$$\therefore \text{Weight of oil} = 17.20 \text{ gm}$$

$$\text{Acid value} = \frac{\text{Amount of KOH} \times \text{N}_{\text{KOH}} \times 56}{\text{Weight of oil}}$$

$$= \frac{2.5 \times 0.1 \times 56}{17.20}$$

\therefore Acid value = 0.814 mgs of KOH

Ans. : Acid value = 0.814 mgs of KOH

Problem 3.7.19: Find acid value of 3 gm of oil which required 0.2 ml of 0.025 N KOH to neutralise free acids present.

Solution:

Given:

$$\begin{aligned} \text{Weight of oil} &= 3 \text{ gm} \\ \text{Quantity of KOH} &= 0.2 \text{ ml} \\ \text{Normality of KOH} &= 0.025 \text{ N} \\ \text{Acid value} &=? \end{aligned}$$

To find: Acid value

$$\begin{aligned} \text{Acid value} &= \frac{\text{Volume of KOH consumed} \times N_{\text{KOH}} \times 56}{\text{Weight of oil}} \\ &= \frac{0.2 \times 0.025 \times 56}{3} \\ &= 0.0933 \text{ mgs of KOH} \end{aligned}$$

Ans. : Acid value = 0.0933 mgs of KOH

Problem 3.7.20: Find acid value of a vegetable oil whose 10 ml required 4.0 ml of 0.01 N KOH during titration.
(density of the oil = 0.92)
(Dec. 2008, 3 Marks)

Solution:

Given:

$$\begin{aligned} \text{Volume of oil} &= 10 \text{ ml} \\ \text{Volume of KOH} &= 4 \text{ ml} \\ \text{Normality of KOH} &= 0.01 \text{ N} \\ \text{Density of oil} &= 0.92 \end{aligned}$$

$$\begin{aligned} \text{To find} &= \text{Acid value} \\ \text{Now} \quad \text{Acid value} &= \frac{\text{Volume of KOH} \times N_{\text{KOH}} \times 56}{\text{wt. of oil in gm}} \\ \text{Here weight of oil} &= 0.92 \times 10 \\ &= 9.2 \text{ gm} \\ \therefore \text{Acid value} &= \frac{4 \times 0.01 \times 56}{9.2} \\ &= 0.243 \text{ mgs of KOH} \end{aligned}$$

Ans: Acid value = 0.243 mgs of KOH

Problem 3.7.21: Find acid value of given oil whose 20 ml required 2.8 ml of N KOH during titration. (density of oil = 0.86 gm/ml) state whether oil is proper for lubrication or not from acid value.

(May 2010, 3 Marks)

Solution:

Given data:

$$\begin{aligned} \text{Volume of oil} &= 20 \text{ ml.} \\ \text{Volume of KOH} &= 2.8 \text{ ml.} \\ \text{Normality of KOH} &= \frac{N}{10} \\ \text{Density of oil} &= 0.86 \text{ gm/ml.} \\ \text{Acid value} &= \text{Weight of oil} \end{aligned}$$

To find:

and whether oil is proper for lubrication?

$$\text{Acid value} = \frac{\text{Volume of KOH} \times N_{\text{KOH}} \times 56}{\text{Weight of oil}}$$

$$\begin{aligned} \therefore \text{Weight of oil} &= (\text{Volume} \times \text{density}) \text{ gms.} \\ &= 20 \times 0.86 = 17.2 \text{ gms.} \\ \therefore \text{Acid value} &= \frac{2.8 \times 0.1 \times 56}{17.2} = 0.911 \text{ mg of KOH.} \end{aligned}$$

Answer :

- (i) Acid value = 0.911 mgs of KOH.
- (ii) Since acid value exceeds 0.1, the oil is not proper for lubrication.

Problem 3.7.22: Find the acid value of a used oil sample whose 7ml required 3.8 ml N/50 KOH during titration. (density of oil = 0.88).

State whether the oil is suitable for lubrication or not.

(Dec. 2010, May 2011, 3 Marks)

Solution :

Given data :

$$\text{Weight of oil} = (\text{Vol. in ml} \times \text{Density})$$

$$\begin{aligned} &= 7 \times 0.88 \\ &= 6.16 \text{ gms} \end{aligned}$$

$$\text{Normality of KOH} = N/50 = 0.20 \text{ N}$$

$$\text{Volume of KOH} = 3.8 \text{ ml}$$

We know that,

$$\text{Acid value} = \frac{\text{Volume of KOH} \times N_{\text{KOH}} \times 56}{\text{Weight of oil}}$$

$$\begin{aligned} &= \frac{0.8 \times 0.001 \times 56}{1.3} \\ &= 0.034 \text{ mgs of KOH} \end{aligned}$$

$$\text{Acid value} = 0.034 \text{ mgs of KOH}$$

∴ Oil is suitable for lubrication since its acid value is less than 0.1 mgs of KOH.

Problem 3.7.24: Find the acid value of a used lubricating oil sample whose 10 ml required 5 ml of N/50 KOH during titration. (Density of oil = 0.91 g/cc). State whether the oil is suitable for lubrication or not.

(May 2012, 3 Marks)

Solution :

Given Data :

$$\text{Volume of oil} = 10 \text{ ml}$$

$$\text{Density of oil} = 0.91 \text{ gm/cc}$$

$$\text{Volume of KOH solution} = 5 \text{ ml}$$

$$\text{Normality of KOH solution} = N/50$$

∴ This value is more than 0.1, the oil cannot be used for lubrication.

Problem 3.7.23: 1.3 g of a gear box oil is taken for acid value determination. It required 0.8 ml of 0.001 N KOH for neutralization. Calculate the acid value and mention whether the oil is suitable to be used further or not.

(Dec. 2011, 5 Marks)

Solution :

Given data :

$$\text{Weight of oil} = 1.3 \text{ gms}$$

$$\text{Normality of KOH} = 0.001 \text{ N}$$

$$\text{Volume of KOH} = 0.8 \text{ ml}$$

To find : (a) Acid value of oil

(b) Whether oil is suitable for lubrication ?

$$\text{Acid value} = \frac{\text{Volume of KOH} \times N_{\text{KOH}} \times 56}{\text{Weight of oil}}$$

$$\begin{aligned} &= \frac{0.8 \times 0.001 \times 56}{1.3} \\ &= 0.034 \text{ mgs of KOH} \end{aligned}$$

$$\text{Acid value} = 0.034 \text{ mgs of KOH}$$

∴ Oil is suitable for lubrication since its acid value is less than 0.1 mgs of KOH.

To find : (a) Acid value of oil

(b) Whether oil is suitable on lubricant?

Soln. :

$$\text{Weight (mass) of oil} = \text{volume} \times \text{Density}$$

$$= 10 \times 0.91 = 9.1 \text{ gms.}$$

$$\text{Acid value} = \frac{\text{Volume of KOH required} \times N_{\text{KOH}} \times 56}{\text{weight of oil}}$$

$$= \frac{5 \times 0.02 \times 56}{9.1}$$

$$= 0.615 \text{ mgs of KOH}$$

Ans. :

(a) Acid value of given oil sample is 0.615 mgs of KOH.

(b) Oil is not suitable for lubrication because its acid value is greater than 0.1 mgs of KOH.

Problem 3.7.25 : Find acid value of vegetable oil whose 5 ml requires 2 ml of $N/100$ KOH during lubrication (Density of oil is 0.92 g/ml).

Solution :

Given : Volume of oil = 5 ml

Density of oil = 0.92 g/ml

Volume of KOH solution = 2 ml

Normality of KOH solution = 0.01 N

To find Acid Value

$$\text{Acid value} = \frac{\text{Volume of KOH} \times N_{\text{KOH}} \times 56}{\text{weight of oil}}$$

$$= \frac{\text{Volume of KOH} \times N_{\text{KOH}} \times 56}{\text{volume of oil} \times \text{Density of oil}}$$

$$= \frac{2 \times 0.01 \times 56}{5 \times 0.92} \text{ mgs of KOH}$$

$$= \frac{112}{460} = 0.244 \text{ mgs of KOH}$$

Ans. : Acid value of oil sample = 2.44 mgs of KOH.

Problem 3.7.26 : 2.5 g of vegetable was mixed with 50 ml of KOH solution and heated for 1 hour. The mixture required 26.4 ml of 0.4 N HCl.

The blank titration reading was 49.0 ml. Find the saponification value of oil. (May 2013, 4 Marks)

Solution :

Given : Weight of oil = 2.5 gm,

Volume of KOH = 50 ml

Volume of HCl = 26.4 ml

$N_{\text{HCl}} = 0.4 \text{ N}$

Blank titration = 49 ml

To find : Saponification value

$$\text{Saponification value} = \frac{\text{Volume of KOH consumed} \times N_{\text{KOH}} \times 56}{\text{Weight of oil}}$$

$$\text{Normality of KOH solution} = \frac{N_1 V_1}{V_2}$$

$$\frac{\text{KOH}}{\text{HCl}}$$

$$N_1 \times 50 = 0.4 \times 49.0$$

$$\therefore N_1 = \frac{0.4 \times 49.0}{50} = 0.392 \text{ N}$$

$$\text{Saponification value} = \frac{(\text{Blank} - \text{Back}) \times N_{\text{KOH}} \times 56}{\text{Weight of oil}}$$

$$= \frac{(49.0 - 26.4) \times 0.392 \times 56}{2.5}$$

$$= \frac{22.6 \times 0.392 \times 56}{2.5}$$

$$= 198.45$$

Ans. : Saponification value = 198.45 mgs of KOH

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 Mention the essential qualities of a good lubricant.
- Q. 5 What is extreme pressure lubrication ? Discuss with suitable examples.
- Q. 6 What are the different mechanisms of lubrication ? Explain the boundary or thin film lubrication.
- Q. 7 Define and explain the importance of the following :
- Oiliness
 - Viscosity and Viscosity index
 - Cloud and pour point
 - Fire and flash point
 - Acid value and saponification value
 - Emulsification

3.8 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 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 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]

University Questions (Theory)**Dec. 2007**

Q. 1 What are blended oils ? How are they superior to vegetable and mineral oils ? (Section 3.3.3.1)

Q. 2 What are lubricants ? Explain the mechanism of thin film lubrication in detail. (Sections 3.2, 3.2.2.2)

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 3.6.7) (3 Marks)

Dec. 2008

Q. 4 Explain the following properties of lubricant with significance. (8 Marks)

(i) Viscosity and viscosity index (Section 3.6.1)

(ii) Flash point and fire point (Section 3.6.2)

(iii) Saponification value. (Section 3.6.7)

Q. 5 Write note on solid lubricants. (Section 3.3.1) (5 Marks)

Q. 6 Write note on : Extreme pressure lubrication (Section 3.2.2.3) (5 Marks)

May 2008

Q. 7 What are lubricants ? List different functions of lubricants. (3 Marks)

Q. 8 Explain any two of the following properties of lubricants :

(i) Oiliness (Section 3.6.4)

Applied Chemistry - I (MU)

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Lubricants

- (i) Acid value (Section 3.6.6)
(ii) Cloud point and pour point temperature (Section 3.6.3)
Q.9 Write short note on : Solid lubricant (Section 3.3.1)

May 2009

Q.10 What is Grease ? Under which situation it is used as a lubricant.
(Section 3.3.2)

(3 Marks)

Q.11 What are Lubricants ? (Section 3.2)

(4 Marks)

Explain the Extreme Pressure Lubrication. (Section 3.2.2.3)

(6 Marks)

Q.12 Write the definition and significance of the following terms :

(4 Marks)

(i) Flash Point and Fire Point (Section 3.6.2)

(ii) S. V. (Section 3.6.7)

(iii) Viscosity Index. (Section 3.6.1)

May 2011

Q.20 Define lubrication and explain the mechanism of hydrodynamic lubrication. (Section 3.2 and 3.2.2.1)

(5 Marks)

Q.21 Write a note on Solid Lubricants. (Section 3.3.1)

(5 Marks)

Q.22 Write a short note on : Blended oils. (Section 3.3.3)

(4 Marks)

May 2011

Q.23 List any five characteristics of a good lubricant with justification.

(5 Marks)

May 2012

Q.24 In what situations are solid lubricants used? Explain structure, properties and uses of any one solid lubricant. (Section 3.3.1)

(5 Marks)

Q.25 Explain Boundary lubrication. (Section 3.2.2.2)

(5 Marks)

Dec. 2012

Q.26 Define and write significance of Viscosity and Viscosity Index. (Section 3.6.1 and 3.6.1.1)

(3 Marks)

Q.27 What is lubrication ? Explain fluid film lubrication with the help of diagram. (Sections 3.2 and 3.2.2.1)

(6 Marks)

Q.28 Write a note on blended oil. (Section 3.3.3)

(4 Marks)

Applied Chemistry - I (MU)

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Lubricants

- Q.18** Write a note on Blended oils. (Section 3.3.3.3)
Q.19 Explain the following types of lubrication :
(i) Boundary lubrication (ii) Extreme pressure lubrication.
(Section 3.3.2.2 and 3.2.2.3)

May 2011

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- Q.17** Explain Flash point and Fire point with its significance.
(Section 3.6.2)

(3 Marks)

May 2013

Q. 29 Define grease. Under which situation it is used as a lubricant.
 (Section 3.3.2)

Q. 30 What are solid lubricants explain with two examples.
 (Section 3.3.1)

Q. 31 Explain the following properties and discuss its significance.
 Viscosity and Viscosity index. (Section 3.6.1)

Viscosity and Viscosity index. (Section 3.6.1)

(4 Marks)

Q. 4 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). (Please refer Problem 3.7.17)

(3 Marks)
 (6 Marks)

(4 Marks)

Q. 5 1.25 gram of an oil was saponified with 50 ml 0.1 N potassium hydroxide solution. After refluxing, the mixture required 7.5 ml 0.1 N hydrochloric acid for neutralisation. Find saponification value of the oil.
 (Please refer Problem 3.7.12)

(3 Marks)

3.10 University Questions (Problems)**Dec. 2007**

Q. 1 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.
 (Please refer Problem 3.7.10)

(4 Marks)

May 2008

Q. 2 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.
 (Please refer Problem 3.7.11)

(3 Marks)

Q. 7 Find the acid value of a used oil sample whose 7 ml required 3.8 ml of $\frac{N}{50}$ KOH during titration. (density of oil = 0.88). State whether the oil is suitable for lubrication or not. (Please refer Problem 3.7.23)

Dec. 2010

Q. 6 Find acid value of given oil whose 20 ml required 2.8 ml of $\frac{N}{10}$ KOH during titration (density of oil = 0.86 gm/ml) state whether oil is proper for lubrication or not from acid value. (Please refer Problem 3.7.21)

(3 Marks)

May 2010

Q. 8 Find the acid value of a used oil sample whose 7ml required 3.8 ml $\frac{N}{50}$ KOH during titration. (density of oil = 0.88). State whether the oil is suitable for lubrication or not. (Please refer Problem 3.7.22)

(3 Marks)

Q. 3

Find acid value of a vegetable oil whose 10ml required 4.0 ml of 0.01 N KOH during titration.
 (density of the oil = 0.92) (Please refer Problem 3.7.20)

(3 Marks)

Dec. 2011

Q. 9 1.3 g of a gear box oil is taken for acid value determination. It required 0.8 ml of 0.001 N KOH for neutralization. Calculate the acid value and mention whether the oil is suitable to be used further or not.
 (Please refer Problem 3.7.23)

(5 Marks)

May 2009

Q. 4 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). (Please refer Problem 3.7.17)

(4 Marks)

Dec. 2009

Q. 5 1.25 gram of an oil was saponified with 50 ml 0.1 N potassium hydroxide solution. After refluxing, the mixture required 7.5 ml 0.1 N hydrochloric acid for neutralisation. Find saponification value of the oil.

(3 Marks)

May 2012

- Q. 10** Find the acid value of a used lubricating oil sample whose 10 ml required 5 ml of N/50 KOH during titration. (Density of oil = 0.91 g/cc). State whether the oil is suitable for lubrication or not. (Please refer Problem 3.7.24)

(3 Marks)

- Q. 11** 2.5 g of a blended oil was saponified using express alcoholic KOH solution (0.5 N). After refluxing for two hours, the mixture was titrated against 0.5 N HCl solution. The burette reading was found to be 24 ml. The blank titration required 40 ml of the same HCl solution. Find the saponification value of the oil. If the oil used for blending has saponification value of 191, calculate percentage oil in the blend. (Please refer Problem 3.17.13)

(4 Marks)

Dec. 2012

- Q. 12** Find acid value of vegetable oil whose 5 ml requires 2 ml of N/100 KOH during lubrication (Density of oil is 0.92 g/ml).

(4 Marks)

(Please refer Problem 3.7.25)

May 2013

- Q. 13** 2.5 g of vegetable oil was mixed with 50 ml of KOH solution and heated for 1 hour. The mixture required 26.4 ml of 0.4 N HCl. The blank titration reading was 49.0 ml. Find the Saponification value of oil.

(4 Marks)

(Please refer Problem 3.7.26)

CHAPTER 4

Phase Rule

Syllabus

Gibb's Phase Rule, Explanation, One Component System (Water), Reduced Phase Rule, Two Component System (Pb-Ag), Limitations of Phase Rule.



4.1 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.

4.2 Gibb's Phase Rule

MU - Dec. 2007, Dec. 2008, May 2009, May 2010, Dec. 2012

Phase Rule Equation / Statement of Phase Rule

- Gibb's Phase rule may be stated as, "provided equilibrium between any number of phases is not influenced by gravitational, electric or magnetic forces or by surface action, but only by temperature, pressure and concentration, then the number of degrees of freedom (F) of the system is related to the number of components (C) and phases (P) by the phase rule equation."

$$F = C - P + 2$$

for any system at equilibrium at definite temperature and pressure." This rule does not have an exception, if applied properly by maintaining the variables at a fixed levels.

4.2.1 Explanation

MU - Dec. 2012

- 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, μ of a given component must be same in every phase.

Thus, if there is one component in three phases (say α , β and γ) and one of these (say α) is referred to as standard phases, then, this fact must be expressed in the form of the following two equations.

$$\mu_a = \mu_b$$

$$\mu_a = \mu_t$$

- 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,

$$F = \{P(C - 1) + 2\} - C(P - 1)$$

$$\therefore F = C - P + 2$$

4.2.2 Terms Involved in Gibb's Phase Rule

The following terms are involved in phase rule,

- | |
|-------------------------------------|
| (i) Phase |
| (ii) Components |
| (iii) Degrees of Freedom (variance) |

Let us discuss each term with examples.

4.2.2.1 Phase

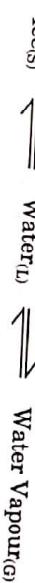
Definition :

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.

MU - Dec. 2012

Examples

- 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,



- All gases mix freely to form homogeneous mixtures. Therefore, any mixture of gases, say O_2 and N_2 and H_2 forms one phase only.
- Two completely miscible liquids yield an uniform solution. Thus, a solution of alcohol and water is a one phase system.

- A mixture of two non-miscible liquids on standing forms two separate layers.

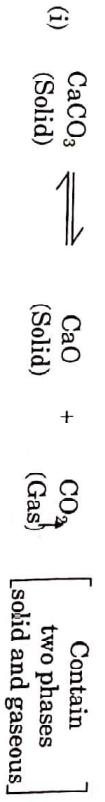
Thus, a mixture of an oil and water constitutes a two phases system.

- An aqueous solution of a solid substances like salt ($NaCl$) or sugar is uniform through out. Therefore, it is a one phase system.

- 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.

- Equilibrium given below,



(Two phases exist in equilibrium)

MU - May 2008, Dec. 2012, May 2013

4.2.2.2 Components

MU - May 2008, May 2010, Dec. 2012, May 2013

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".

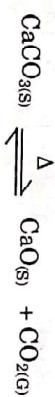
Examples

- 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. H₂O. Hence, system is regarded *one component system*.



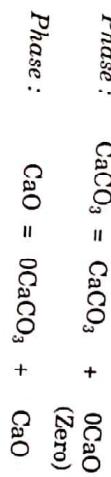
- In sulphur system, there are four phases, i.e. *rhombic* sulphur, *monoclinic* sulphur, *liquid* sulphur and sulphur *vapour*. The composition of all four phases can be expressed by one chemical individual sulphur (S). Hence, sulphur system is regarded as *one component system*.

- 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_{3(S)}, CaO_(S) and CO_{2(G)}. Thus, the decomposition of CaCO₃ gives CaO_(S) and CO_{2(G)}, 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 CaCO₃ and CaO are considered as components, then composition of each can be given as :

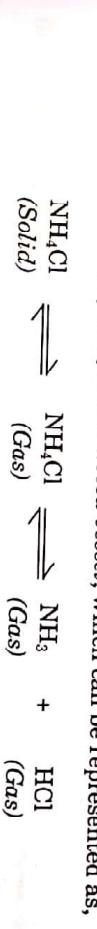


Thus it is a two component system.

- In the equilibrium, for reaction between iron metal and steam,



the composition of each phase can be expressed in terms of the components Fe, H₂O and H₂. Hence, it is a *three component system*.



In this case if proportions of NH₃ and HCl are equivalent, then the system is one component system; this is because the composition of both can be expressed in terms of NH₄Cl alone.

But if NH₃ or HCl is in excess, the system becomes a two component system.

- 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 H₂O. Hence, it is a *two component system*.

- Dissociation reaction, as,



[Two component system : CuSO₄ and H₂O].

4.2.2.3 Degree of Freedom (Variance)

MU - May 2008, May 2010, May 2012, Dec. 2012, May 2013

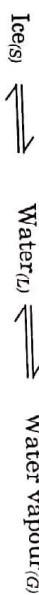
Definition

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*:

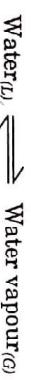
- (a) If all the three phases are in equilibrium, then no condition need to be specified because the three phases can be in equilibrium only at particular *temperature and pressure*,



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*.

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.

4.3 One Component System (Water)

MU - May 2009, May 2010, May 2011, Dec. 2011, May 2012

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*.

Applied Chemistry - I (MU)

- 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.

4.3.1 Water System

MU - Dec. 2007, May 2008, Dec. 2008, May 2009,
Dec. 2009, May 2010, Dec. 2012, May 2013

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
- $$F = C - P + 2$$
- 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. 4.3.1).

Hence when,

- | | | |
|----------|-----------------|------------------------|
| $P = 1,$ | then $F = 2 ..$ | System is Bivariant |
| $P = 2,$ | then $F = 1 ..$ | System is Monovariant |
| $P = 3,$ | then $F = 0 ..$ | System is Zero variant |

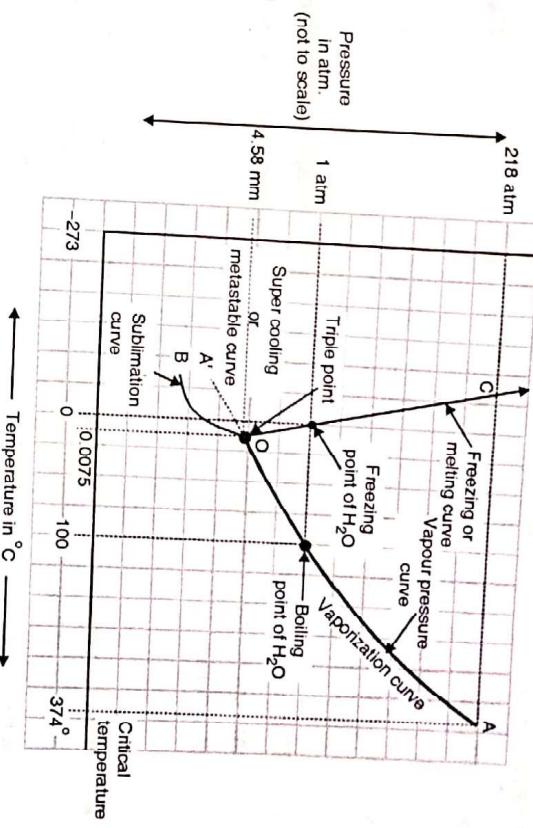


Fig. 4.3.1 : Phase diagram of water system

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.

- 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.

- Hence, each system has two degree of freedom, i.e. system is bivariant.
- 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,

$$F = C - P + 2$$

$$F = 1$$

- Hence, each two phases system has one degree of freedom, i.e. system is *univariant* or *monovariant*.

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
 - Area AOC represents conditions for solid phase, i.e. ice.
 - Area AOB represents conditions for liquid phase, i.e. water vapour.
 - Area BOC represents conditions for gaseous phase, i.e. water vapour.
- In all the three areas, there being '*one phase*' and '*one component*'. Therefore,

$$F = C - P + 2$$

$$F = 1 - 1 + 2$$

$$F = 2$$

3. Triple point

MU – May 2008, May 2009, Dec. 2009

- 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 0.075°C and 4.58 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.

4.3.2 Reduced or Condensed Phase Rule

MU – May 2008, Dec. 2008, May 2009, May 2011

- 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.*

4.4 Two Component Systems (Pb-Ag)

General characteristics of two-component systems

- 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).

- 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)

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

- The system will have *three variables* namely, *temperature, pressure and concentration*.
- The composition of all the individual phases of the system can be expressed by means of *not less than two components*.
- 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.
- Consequently, three variables – temperature, pressure and concentration of one of the two components must be specified in order to describe the system completely.

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

- 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.

4.5 Lead Silver System

MU – May 2009, May 2010, May 2011

- 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. 4.5.1) 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. 4.5.1.

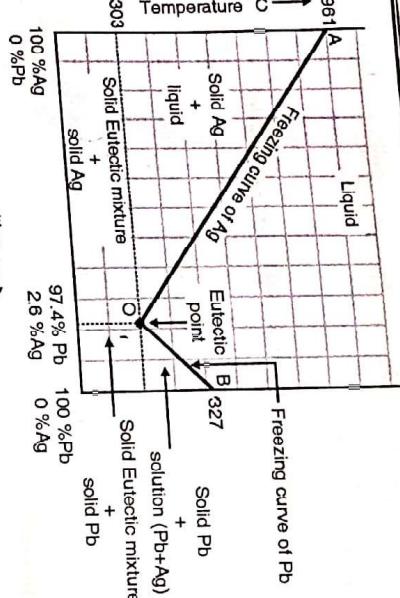


Fig. 4.5.1 : The phase diagram of Pb-Ag system

In the phase diagram shown in Fig. 4.5.1 of Pb-Ag system, following salient features are observed.

- The curve AO (Freezing curve of Ag)
- The curve BO (Freezing curve of Pb)
- The eutectic point 'O'
- The Area AOB

(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

(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 $\text{Ag} = 2.6\% : \text{Pb} = 97.4\%$ 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.

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 :

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

i.e. the system is univariant. The point O (303°C) corresponds to a fixed composition of $2.6\% \text{Ag}$ and $97.4\% \text{Pb}$ and is known as eutectic composition. On cooling the whole mass crystallizes out as such.

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 ($2.6\% \text{ Ag} : 97.4\% \text{ Pb}$).

4.5.1 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.

4.6 Applications of Phase Rule

MU – Dec. 2007, May 2009; Dec. 2010

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.

4.7 Limitations / Demerits of Phase Rule

MU - Dec. 2007, Dec. 2009, May 2011, Dec. 2012, May 2013

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

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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.

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 State Gibb's phase rule and explain the various terms involved in it with examples.
- Q. 7 What is phase rule? Explain the application of phase rule to "One Component" or "Water System".
- Q. 8 State limitations of phase rule.
- Q. 9 Explain shape memory effect and give its application.

4.8 University Questions (Theory)

- Dec. 2007**
- Q. 10 What is triple point? Explain it with reference to one component water system. (Section 4.3.1 (3)) (3 Marks)
 - Q. 11 What is condensed phase rule equation? Explain its application with the help of phase diagram to two Component Lead - Silver (Pb-Ag) system. (Section 4.3.2 and 4.5) (6 Marks)
 - Q. 12 State phase rule equation. Mention any three applications. (Section 4.2 and 4.6) (3 Marks)

- Q. 1** Give the demerits/limitations of phase rule. (Section 4.7.1) (2 Marks)
- Q. 2** State and explain phase rule. Discuss the application of phase rule to one component water system. (Section 4.2 and 4.6) (7 Marks)

- Q. 13** What is triple point? With reference to water-system explain it. (Section 4.3.1(3)) (3 Marks)

- Q. 3** What is triple point in phase diagram? Explain it with reference to one component water system phase diagram. (Section 4.3.1(3)) (2 Marks)
- Q. 4** Explain any two of the following terms:
 - (i) Phase (Section 4.2.1.1)
 - (ii) Components (Section 4.2.1.2)
 - (iii) Degrees of freedom (Section 4.2.1.3)
- Q. 5** State and explain condensed phase rule. (Section 4.3.2) (6 Marks)

Dec. 2008

- Q. 6** State and explain condensed phase rule. (Section 4.3.2) (3 Marks)
- Q. 7** Explain Heat resisting steels with suitable examples. (Section 4.10, Table 4.10.1) (3 Marks)
- Q. 8** Define Gibb's phase rule equation? (Section 4.2) Explain the application to one component system. (Section 4.3.1) (5 Marks)

May 2009

- Q. 9** What are stainless steels? Explain the specific effects of following elements on the properties of steels: (Section 4.9 and 4.10)
 - (i) Molybdenum
 - (ii) Silicon
 - (iii) Tungston
 - (iv) Cobalt

Dec. 2009

- Q. 13** What is triple point? With reference to water-system explain it. (Section 4.3.1(3)) (3 Marks)

Q. 14 State the limitations of Phase Rule. (Section 4.7) (3 Marks)

May 2010

Q. 15 Explain the terms : (3 Marks)

- (i) Degree of freedom (Section 4.2.2.3)
- (ii) Component. (Section 4.2.2.2)

Q. 16 What is phase rule ? Discuss in brief Lead-silver equilibrium with diagram. (Section 4.2 and 4.5) (5 Marks)

Q. 17 One component system-water. (Section 4.3) (5 Marks)

Dec. 2010

Q. 18 What are the Advantages/Applications/merits of phase rule ? (Section 4.6) (3 Marks)

May 2011

Q. 19 State the limitations of the phase rule. (Section 4.7) (3 Marks)

Q. 20 State condensed Phase Rule ? Explain the Lead-Silver System with phase diagram. (Section 4.3.2 and 4.5) (5 Marks)

Q. 21 Write short note on One Component System. (Section 4.3) (8 Marks)

Dec. 2011

Q. 22 Explain the application of phase rule to one component system.

(Section 4.3) (5 Marks)

May 2012

Q. 23 Using phase rule, find the number of degrees of freedom (F) in the following systems at equilibrium.

- (i) In the water system, when Ice (s) water (l) water vapour (g)
- (ii) A gaseous mixture of Nitrogen and Hydrogen. (Section 4.2.2.3) (5 Marks)

Q. 24 Explain application of Gibbs Phase Rule to one component system- water system. (Section 4.3) (5 Marks)

Q. 25 State the limitations of phase rule. (Section 4.7) (3 Marks)

Q. 26 Define phase rule and explain terms like phase, component and degree of freedom by giving appropriate examples. (Sections 4.2, 4.2.2.1, 4.2.2.2 and 4.2.2.3) (5 Marks)

Q. 27 Draw neat labelled phase diagram for water system. (Section 4.3.1) (5 Marks)

May 2013

Q. 28 Define phase, component and degree of freedom. (Sections 4.2.2.1, 4.2.2.2 and 4.2.2.3) (3 Marks)

Q. 29 Draw and explain the phase diagram of ice-water-water vapour system. (Section 4.3.1) (5 Marks)

Q. 30 Give limitations of phase rule. (Section 4.7) (4 Marks)

Dec. 2012

Note**CHAPTER****5**

Important Engineering Materials

Syllabus

- Cement :** Manufacture of Portland Cement, Chemical Composition and Constitution of Portland Cement , Setting and Hardening of Portland Cement, Concrete RCC and Decay. Refractories Preparation, properties and uses of Silica bricks, Dolomite bricks , Silicon Carbide (SiC).
- Nanomaterials, preparation (Laser and CVD method), properties and uses of CNFs

5.1 Cement

5.1.1 Introduction

Cement is a generic name for powdered materials which is initially have a plastic flow when mixed with water or other liquid, but form a solid structure in several hours with varying degree of strength and bonding properties which continue to improve with age. Specifically, portland cement is defined as finely ground calcium aluminate and silicates of varying composition which hydrate when mixed with water to form rigid continuous structure with a good compressive strength. The term cement designate a fine grey powder that is used for constructional purposes. Such cement has remarkable property, that is on addition of water it forms paste. Cement and water are mixed in a suitable proportion forming a paste, the paste adheres firmly to the aggregates such as sand, stone, gravel, bricks and other similar substances.

5.1.2 Classification of Cement

The cement can be classified mainly in to the following classes :

- Natural Cement.
- Portland Cement.
- Pozzolanic Cement.
- High Alumina Cement.
- Super Sulphate Cement.
- Special Cement :
 - Quick Setting Cement.
 - Expanding Cement.

5.1.3 Portland Cement

Of all above types, portland cement is most important. Chemically portland cement is defined as a mixture of complex silicates and aluminates of calcium containing less than 1.0% free lime and gypsum. Such cement when mixed with adequate quantity of water, forms a paste which possesses the setting and hardening and durable on standing.

5.1.4 Types of Portland Cement

There are five types of portland cement in which varying the percentage of constituents changes the rate of setting, heat evolution and strength characteristics.

Type I – Regular portland cement

Regular portland cement is also called as general portland cement, normally used for general concrete constructions. Other types of this cement are as white cement, quick setting cement, oil well cement and others for special uses. Average compound composition of this cement is : C₃S : 40-60%, C₂S : 10-30%, C₃A : 7-13%, C₄AF : 8%, CaSO₄ : 2.9%, CaO : 0.8% and MgO : 2.4%. It hardens to full strength in 28 days.

Type II – Moderate heat of hardening cement

This type of cement is also called as sulphate resisting portland cement, used in general concrete constructions, exposed to moderate sulphate action or where moderate heat of hydration is required. Average compound composition of this cement is : C₃S : 46%, C₂S : 29%, C₃A : 6%, C₄AF : 12%, CaSO₄ : 2.8%, CaO : 0.6%, MgO : 3.0%

Type III – High early strength cement

These are ground finer than type - I cement containing lime to silica ratio higher than that of regular cement. They contain a higher proportion of tricalcium silicate than regular portland cement. This cement is finely ground, quicker hardening and quicker heat evolution is observed , therefore can be used for road

construction than regular cement. Average percentage composition is $C_3S : 56\%$, $C_2S : 15\%$, $C_3A : 12\%$, $C_4AF : 8\%$, $CaSO_4 : 3.9\%$, $CaO : 1.3\%$, $MgO : 2.6\%$.

Type IV - Low heat portland cement

This type of cement contains lower percentage of tricalcium silicate and tricalcium aluminate. The percentage of tricalcium aluminoferrite is increased in addition to Fe_2O_3 to reduce the percentage of tricalcium aluminate. Low C_3S and C_3A which are largest contributors to heat of hydration. This type of cement is used when low heat of hydration is required. Average percentage composition is: $C_3S : 28\%$, $C_2S : 49\%$, $C_3A : 5\%$, $C_4AF : 18\%$, $CaSO_4 : 3.0\%$, $CaO : 0.3\%$, $MgO : 2.7\%$.

Type V - Sulphate resisting portland cement

This type of cement is better than other four types, because it is good for sea water contact and it can withstand to the action of sulphate. Tricalcium aluminate is much lower than tricalcium aluminoferrite. Average percentage composition is: $C_3S : 38\%$, $C_2S : 45\%$, $C_3A : 4\%$, $C_4AF : 9\%$, $CaSO_4 : 2.7\%$, $CaO : 0.5\%$, $MgO : 1.9\%$.

5.1.5 Manufacture of Portland Cement

5.1.5.1 Raw Materials of Portland Cement

The raw material required for manufacturing of portland cement is discussed as follows :

1. Calcareous materials

The most important calcareous material is lime stone. It occurs in the form of chalk, metamorphic lime stone, sedimentary lime stones, carbonite lime stone, coral and secondary lime stones. Marl is calcareous sedimentary deposit is often used with small shells.

2. Argillaceous materials

The important argillaceous materials available for making portland cement are clay, slate, shale, ashes, blast furnace slag, cement rocks etc. Cement

rock itself is used as a raw material because of its richness in argillaceous materials and it may constitute the source of silica and alumina. Blast furnace slag produced from high grade ore may be used as a source of remaining 20% contains alumina and iron oxide. An addition to this, some plants use precipitated calcium carbonate, sand, waste bauxite and iron which are consumed in small amounts to adjust the composition of mixture.

3. Gypsum ($CaSO_4$)

Gypsum is added to regulate the setting of cement.

4. Pulverised coal

Pulverised coal is used as a fuel in the manufacturing process of portland cement.

5. Composition of raw material

Raw materials are mixed in calculated proportions, the average percentage composition is given as below

(Refer Table 5.1.1)

Table 5.1.1

Components	Formulae	Percentage
Lime	CaO	60 - 67
Silica	SiO ₂	17 - 25
Alumina	Al ₂ O ₃	3 - 8
Iron Oxide	Fe ₂ O ₃	2 - 4
Magnesium Oxide	MgO	1 - 5
Alkali Oxide	Na ₂ O/K ₂ O	0.3 - 1.5
Sulphur Trioxide	SO ₃	1 - 3

5.1.5.2 Functions of the Ingredients of Cement

1. Lime

Lime is the principal constituent of cement. It affects the strength of cement, if added in excess. Hence, properly calculated amount of lime is added in the manufacturing of portland cement. If it is excess in amount, it reduces strength of cement, because it makes the cement to expand and disintegrate.

On the other hand, lesser the amount of lime than required also reduces the strength and there will be the change in proportions of C_3S , C_2S , C_4A and C_4AH . This will alter the property like setting and hardening of cement and makes it quick-setting.

2. Silica

Lime undergoes reaction with silica to form dicalcium silicate (C_2S) and tricalcium silicate (C_3S). These C_2S and C_3S play important role in development of strength to cement.

3. Alumina

With reaction of alumina lime gives tricalcium aluminate which is responsible for setting of cement. If it is in excess quantity, then cement undergoes setting very fastly, because with the reaction of water, there is evolution of large amount of heat. Due to this, the application of cement paste for any structure becomes difficult. If it is in lesser quantity, then setting becomes slow. Therefore to get better quality of cement, correct quantity of tricalcium aluminate is required which will provide the ideal rate of setting.

4. Iron oxide

Iron oxide is responsible for the development of colour, strength and hardness to the cement.

5. Sulphur trioxide

Less proportion of sulphur trioxide is desirable because it impart soundness to cement. But if it is in excess then reduces the soundness of cement.

6. Alkalies

Alkalies causes the cement efflorescent.

5.1.5.3 Manufacturing Processes

Usually, there are two processes employed for the manufacturer of portland cement.

(1) Dry process

(2) Wet process

The selection of process for manufacture of cement is normally depend upon the nature of raw material. If the raw material is hard and dry then process is normally preferred. Where as if raw material is soft then wet process is preferred. Other than nature of raw material, the factors like consumption of fuel availability of raw material, the climate of the factory place are also consider for the selection of process for manufacture of cement. Normally in the both process the basic processes involved following major operations like :

1. Selection of raw materials
 2. Crushing and grinding
 3. Storage of slurry
 4. Burning the ground mix in a rotary kiln
 5. Cooling of hot clinkers
 6. Grinding of clinkers
 7. Storage and packing
-]]] Mixing of raw material

1. Dry process

In this process, the raw material are crushed in guratory crushers in to small pieces. Further these are ground in fine powder in ball mills and stored separately. Then mixed in proper proportions, pulverised in tube mills and homogenised in a mixing mill with the help of compressed air. This is called as dry raw mix, stored in storage bins also called as silos and kept ready to be fed in to a rotary kiln.

2. Wet process

In this process, the materials are finely ground and blended in the required proportion and stored in big storage tanks, known as silos. Argillaceous materials in thoroughly mixed with water for washing to remove organic matter, if any and then stored. Powdered calcareous (lime stone) and washed wet-clay are allowed to flow in proportioning tank. From this, the two raw materials led to grinding mills where they are mixed intimately to form paste called as slurry. This slurry is introduced into a rotary kiln.

5.1.5.4 Wet Process Manufacturing of Portland Cement

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This process involves the following major operations.

1. Mixing of raw material

Limestone's (calcareous material) are crushed in crusher and forwarded to tube mills to convert ground and fine powder, which is further stored in storage tank known as silos, fine clay or shale (argillaceous material) is mixed with water for washing to remove organic matter, if any and stored in. Powdered lime stone and washed wet clay are allowed to flow in a channel in the right proportions and led to grinding mills where they are mixed homogeneously to form paste called slurry. Then slurry is led to

connecting basin where the chemical composition is to adjusted if necessary. This slurry is finaly stored and fed to rotary kiln.

2. Burning of raw material

Burning of raw material is usually in a rotary kiln which is made up of steel tube, lined inside with refractory bricks and rotating at a speed of 0.5 to 2 rotations per minute. The kiln is slightly inclined so that material fed in at the upper end travels slowly to the lower and firing and discharging end. The kiln is supported by several tiers which run on rollers and the kiln is driven by an AC commulator motor.

The slurry of the raw materials enters from the upper end of the rotary kiln while the burning fuel like pulverised coal, oil or natural gas and air are induced from the lower end of the kiln. The slurry gradually descends in the kiln into different zones of increasing temperature. A typical rotary kiln with different temperature zones is illustrated in Fig. 5.1.1.

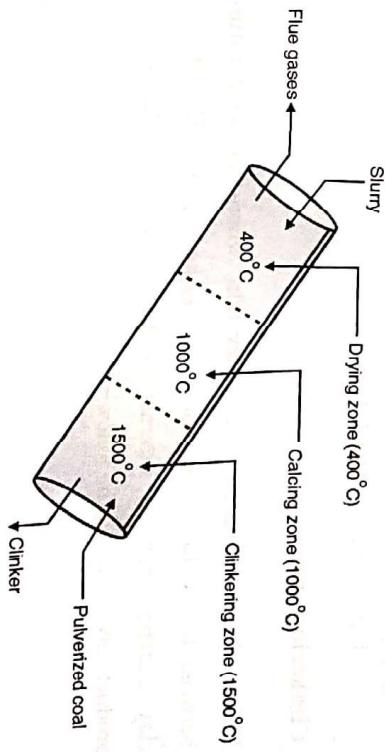


Fig. 5.1.1 : Schematic diagram of rotary kiln

(A) Chemical reactions in various zones of rotary kiln

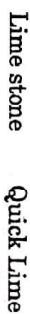
With reference to the temperature there are three zones in which various reaction takes place. The zones and reactions are discussed as below.

(a) Drying zone

The upper part of the kiln is known as Drying zone, where the temperature is about 400°C. In this zone most of the water is driven out of the slurry because of the hot gases.

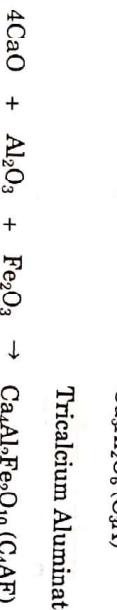
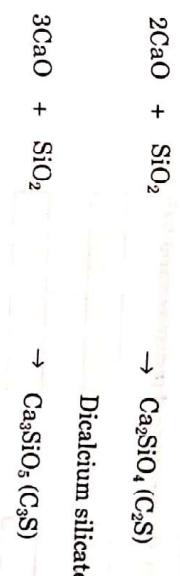
(b) Calcination zone

The central part of the kiln, where the temperature is about 1000°C, known as Calcination zone. In this zone lime stone of slurry undergo decomposition to form quick lime and carbon dioxide, which is latter escape out. The material forms small lumps called nodules. The following reaction takes place in this zone.



(c) Clinkering zone

This is the lower part of the rotary kiln, where the temperature is between 1500°C to 1700°C, known as Clinkering zone. Here lime and clay undergo chemical interaction that is fusion, yielding various products are shown in the following reactions.



The alumina and silicates of calcium then fuse together to form small, hard, greyish stones called clinkers.

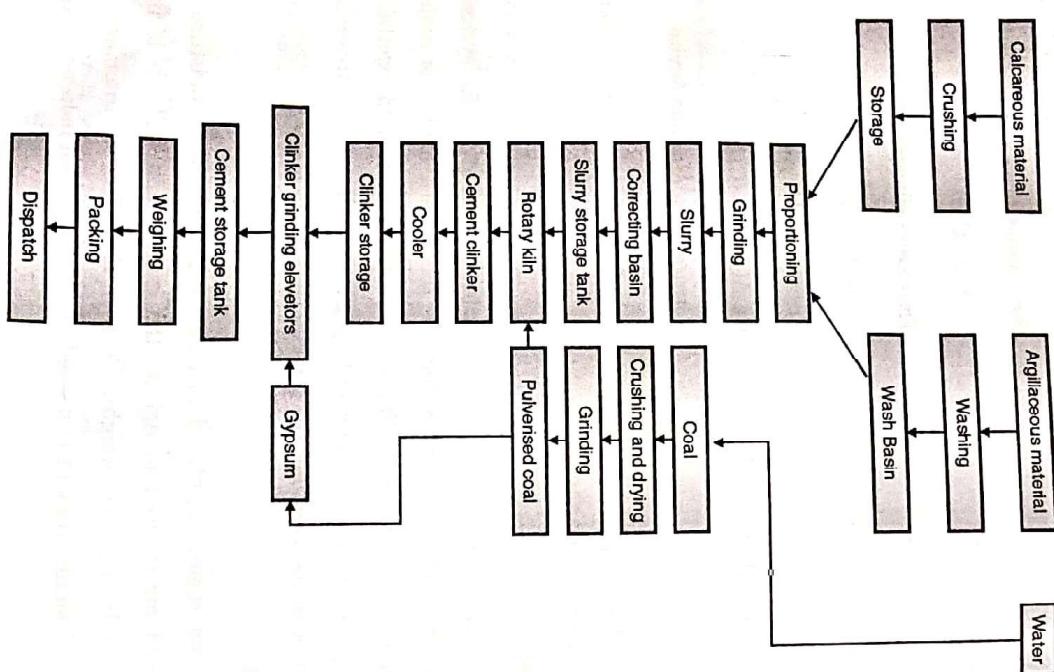
3. Grinding

The hot clinkers discharging from the kiln is cooled by various systems such as planetary coolers, rotary coolers. In the coolers, clinker is cooled with atmospheric air. The cooled clinker is then finely pulverised together with 2 to 6% gypsum (which acts as a setting time retarder of cement-water paste) in long tube mills. The finer the cement, the greater is the strength.

4. Packing

The ground cement is stored in concrete storage silos. Moisture free air compressed air is used to agitate the cement and to keep it free from compaction by its own weight. Further it is fed to automatic packing machines. Usually, cement is packed in jute bags each holding 50kg, nett of cement.

Flow chart for Manufacturing of P...



Average composition with respect to constitutional compounds of ordinary portland cement is given in the following Table 5.1.2.

Table 5.1.2

Sr.No.	Name	Abrivation/Formula	Percentage
1.	Dicalcium silicate	C_2S	27
2.	Tricalcium silicate	C_3S	48
3.	Tricalcium aluminate	C_3A	10
4.	Tetracalcium aluminoterite	C_4AH	08
5.	Free lime	CaO	0.9
6.	Magnesium oxide	MaO	2.5
7.	Gypsum	$CaSO_4$	2.8

3.1.1 Comparison of Wet and Dry Processes

Sr. No.	Dry process	Wet process
1.	It is adopted when the raw material are quite hard.	The wet process preferred when the raw materials are soft.
2.	The cost of grinding is more than that in wet process.	The cost of grinding is less than that in dry process.
3.	Size of kiln is shorter.	Size of kiln is longer.
4.	Fuel consumption is low.	Fuel consumption is higher.
5.	Process is slow.	Process is comparatively faster.
6.	More accurate control of composition may not be attained.	More accurate control of composition can be attained.
7.	Cement produced is of inferior quality.	Cement produced is of superior quality.
8.	Cost of production is less costly.	Cost of production is some what higher.
9.	On the whole, the process is costly.	On the whole, the process is cheaper.

5.1.8 Setting and Hardening

The setting and hardening of cement are mainly due to heat of hydration and hydrolysis reactions taking place when the different constitutional compounds in the cement, interact with water. It is agreed that, setting and hardening of cement are essentially due to the formation of interlocking crystals reinforced by the rigid gel formed by the hydration and hydrolysis of the constitutional compounds. When cement is mixed with adequate quantity of water plastic mass is formed, known as cement paste. Hydration reaction will take place with the formation of gel and crystalline products. The interlocking of crystals finally bind the inert particles of the aggregates. The process of solidification consist of:

1. Setting of cement
2. Hardening of cement

(1) Setting

Setting is defined as 'stiffening' of the original plastic mass, due to initial gel formation and hardening is development of strength of crystallisation. The strength developed by cement paste as any time depends upon the amount of gel formed and the extent crystallisation. Initial setting of cement paste is mainly due to tricalcium aluminate (C_3A), since its reaction is completed within a week. The following reaction takes place.



Tricalcium aluminate Hydrated tricalcium aluminate.

The gel of a aluminates begins to crystallise and at the same time dicalcium silicate (C_2S) begins to hydrate in 7 to 28 days. Thus, the initial set of cement is due to the formation by aluminate. The reaction is :

2[$2CaO \cdot SiO_2$] + 4 $H_2O \rightarrow 3CaO \cdot 2SiO_2 \cdot 6H_2O + Ca(OH)_2 + 250 \text{ kJ/kg.}$

Dicalcium silicate Tabermonite gel Crystallised calcium hydroxide.

(2) Final setting and hardening

Hardening is development of strength due to crystallisation. After setting, hardening starts, due to the gradual progress of crystallisation in the interior of the mass. The gel formed in this reactions, shrink with passage of time and leave some capillaries for the water to come in contact with C_2S and C_3S to undergo further hydration and hydrolysis reactions enabling the development of greater strength over a length of time.

5.1.9 ISI Specification of Portland Cement

As per Indian standards 269 : 1975, the ordinary portland cement should have following specification,

- (i) Lime saturation factor $\left[\frac{CaO - 0.7 SO_3}{2.8 SiO_2 + 1.2 Al_2O_3 + 0.65 Fe_2O_3} \right] = 0.66 \text{ to } 1.02.$
- (ii) The ratio $\frac{Al_2O_3}{Fe_2O_3}$ should not be less than 0.66.
- (iii) Insoluble residue should not exceed 2%.
- (iv) The weight of magnesia (MgO) should not exceed 6%.
- (v) Total sulphur content, calculated as sulphuric anhydride (SO_3) should not exceed 2.75%.
- (vi) Loss on ignition should not exceed 4%.
- (vii) Fineness should not exceed 10% after sieving residue (by weight) on BS 170 mesh test sieve.
- (viii) Setting time = Initial = 30 minutes

Final = 10 hrs.

(ix) Heat of hydration,

After seven days : $\leq 65 \text{ cal/gm.}$

After twenty eight days : $\leq 75 \text{ cal/gm.}$

(x) Compressive strength,

After three days : $\geq 1600 \text{ lb/sq. inch}$

After seven days : $\geq 2500 \text{ lb/sq. inch}$

(xi) Tensile strength,

After three days : $\geq 300 \text{ lb/sq. inch}$

After seven days : $\geq 375 \text{ lb/sq. inch}$

5.1.10 RCC and PCC

Cement cannot be used for construction activities directly because it is sensitive to moisture. The internal stresses developed in cement lead to cracking and reduction in its strength. Cement is generally mixed with sand and crushed stones, which are bound together by cement such mixture is called as "Concrete."

Concrete is a mixture of cement, sand and coarse materials, with water. (commonly used are crushed rock, natural gravel, crushed brick, cinders or blast furnace slag).

Reinforced cement concrete (RCC) is the ordinary concrete reinforced with steel rods or heavy wire mesh. The concrete on setting bonds very strongly with the reinforcements giving high compressive and tensile strengths.

Even if cracks develop in the concrete, considerable reinforcement i.e. strength is maintained.

Steel is used as reinforcement because its coefficient of thermal expansion is nearly the same as that of concrete. Further, steel has corrosion resistance in the cement environment, Glass, nylon or PE are also used.

5.2 Refractory Materials

5.2.1 Introduction

The substances or compounds which can withstand to high temperature without damage or spoilage are known as refractory material. Generally the materials having softening point 1580°C are termed as refractory material.

5.2.2 Classification of Refractory Material

There are three different methods of classification.

1. Classification on the basis of temperature
 - (a) Low refractory material having PCE less than 1580°C .
 - (b) High refractory material having PCE from 1600 to 1900°C .
 - (c) Super R.M. having PCE more than 2000°C .
2. Classification on the basis of chemical resistance
 - (a) Acid refractory material which has resistance towards acid. e.g. silica, aluminium silicates.
 - (b) Basis refractory material which has resistance towards basic compounds e.g. CaO , MgO , Al_2O_3 , dolomite, bauxite etc.
 - (c) Neutral refractory material which has resistance towards acids as well as bases.
e.g. chromite, graphite, zirconia refractory material.

3. Classification on the basis of chemical composition

This depends upon the actual chemical compound that are used while preparing refractory material, e.g. Raw material (main) for refractory,

- (a) Silica – SiO_2
- (b) Aluminium silicate – Al_2O_3 , SiO_2
- (c) Alumina – Al_2O_3
- (d) Magnesia – MgO
- (e) Dolomite – CaO , MgO
- (f) Lime – CaO
- (g) Zirconia – ZrO_2
- (h) Graphite – C

5.2.3 General Procedure of Manufacturing Refractory Material

Bricks :

The various steps involved in the preparation of different types of refractory material are identical with some change in the firing temperature. The steps involved in the preparation of refractory bricks are as follows.

1. Selection of raw material

The raw material is obtained from the mines which is analysed for its composition and the material which has required composition is taken for further process.

2. Crushing, grinding and powdering

If the raw material is in the form of stone, then it is converted into small pieces with the help of jaw crushers. Further, the small pieces are passed through grinders to obtain powder. The fine powder is produced by using ball mills in which the impact of the iron ball gives fine powder.

3. Sieving

The powder from the ball mill is passed over the sieve to have uniform size of the raw material. Generally, vibratory or tubular sieves are used. The grain size of raw material is important because compactness and porosity of the bricks depend upon the particle size of raw material.

4. Mixing and blending batches

The various raw materials are weighed according to batch size. Then, it is mixed in mixer after adding sufficient amount material of water (upto 20%) and binders. (Binders-gum, cellulose, molasses, clay etc.) Various types of mixers are available. The aim of mixing is to produce homogeneous body.

The proper mixing will give better results. The mixing time depends upon individual products. Different batches are again blend together and adjust the right composition of final bricks.

5. Fabrication and moulding

The aim of moulding refractory batches is to produce bricks , blocks, tiles or special shape which can be handled, place for firing and subsequently process to yield a permanent fully stable article. The above batches contain generally 4.22% of water. The material is moulded into required shape and

size using pressing or vibration moulding machines. Various machines are available for moulding purpose right from hand moulding to automatic moulding machines. The principal involved in the moulding is the pressing of fixed weight of refractory material in a fixed volume (mould) to acquire necessary shape.

6. Drying

The drying is carried out by exposing the moulded bricks into the sun or by using oven at 140°C. The drying is carried out to remove some moisture, so that the bricks can become hard.

7. Firing in the kiln

(a) The bricks are arranged in the kiln in such a way that they will get heated uniformly from all the sides. About 7000-8000 bricks are heated at a time in a kiln. Generally, vertical down draught kiln is used for firing.

(b) Heating in the kiln : The hot air or gases are passed through side tunnels which strikes to the dome and get deflected in downward direction. The bottom of the furnace is provided with suction pump, so the flow of hot gases can be controlled.

Initially, temperature is maintained at 140°C and 400°C to remove the moisture and chemically bonded water. Then, it is brought to 700-900°C to decompose any carbonates which are present into oxides. Further, it is slowly brought to the red hot temperature.

At this temperature, the raw material undergoes physical change to form refractory material (i.e. allotropic modification). This firing takes about 6-20 hours to form refractory material.

8. Cooling

Doors, windows and tunnel of the kiln are closed and hot refractory material, is allowed to cool under natural condition without using any cooling agent.

The cooling takes place within 7 days. Then, they are removed, inspected and stored in open space.

Table 5.2.1 : shows composition, properties and applications of Silica, Chrome Magnesite, Fire clay and Dolomite Refractories

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Sr. No.	Description	Silica refractory bricks	Dolomite Refractories	Silicon Carbide
1.	Composition of final product	$\text{SiO}_2 > 95\%$	$\text{CaO} + \text{MgO}$ = ≈ 50 % each	Sand = 60% Coke = 40%
2.	Raw material	Quartz sand, sandstone	CaCO_3 and MgCO_3	Sand + Coke, Saw Dust, Salt
3.	Binder	Lime, clay, silicates of Mg, Al	Silicates	Clay or Silicon Nitride or glue
4.	Drying Temp.	100 to 140°C	100 – 140°C	2000°C
5.	Firing temp. and duration	1500°C for 1.5 hrs or more	1500°C for 24 Hrs.	1500°C
6.	Cooling	6 - 7 day	One week	One week
7.	Colour	Yellowish to brown	Pale yellow	Black
8.	P. C.E	> 1750°C	–	–
9.	R. U. L	1680°C at 2.5 kg/cm²	< 1500°C at 3.5 kg/cm²	1750° under the load 3.5 kg/cm².
10.	Acidic/ Basic nature	Acidic in nature	Alkaline	Neutral

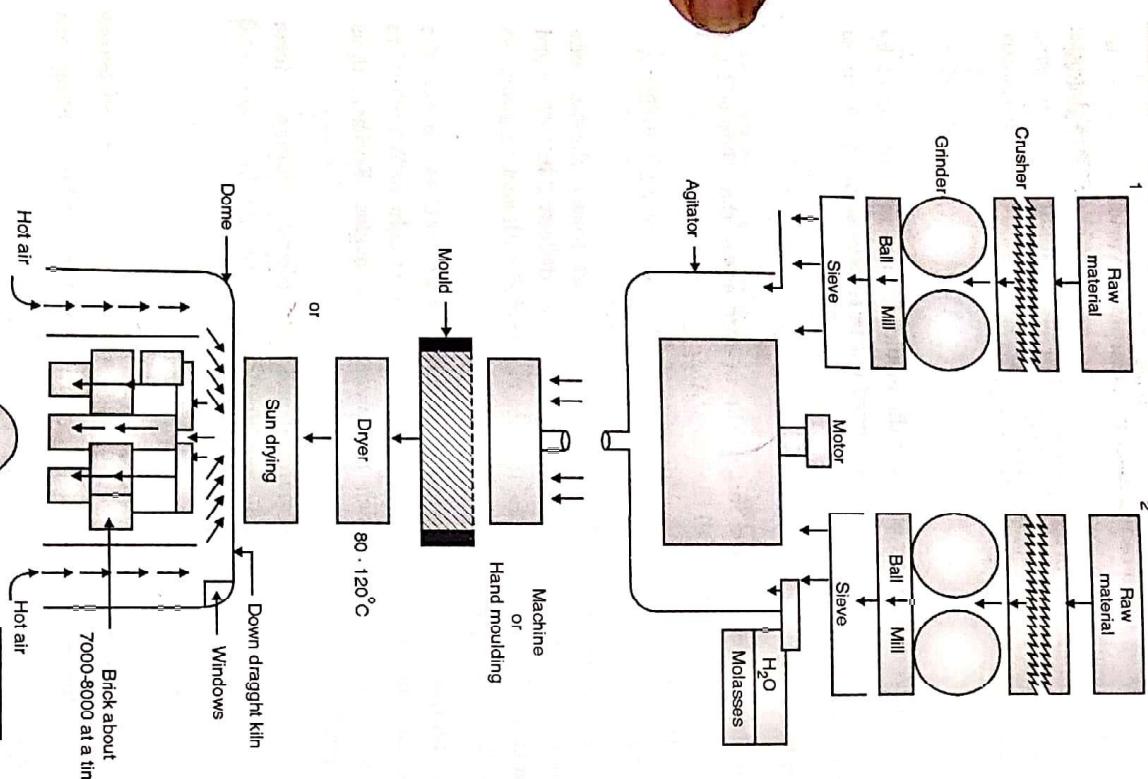


Fig. 5.2.1 : Flow sheet diagram for manufacturing of refractory material

Sr. No.	Description	Silica refractory bricks	Dolomite Refractories	Silicon Carbide
11.	Compression strength	> 250 kg/cm ²	Good	Good
12.	Thermal conductivity	High	High	High & low thermal expansion tends to get oxidised when heated in air at 900-1000 °C
13.	Uses	In steel making furnaces (Bessemer converters glass furnaces, electrical furnaces)	As repair material, basic electric furnace linings, ladle linings. As cheap substitute for magnesite bricks.	Partition walls in kilns, coke ovens, Heat treatment furnaces, Heating elements.

5.3 Introduction

MU - Dec. 2012

- The word nanotechnology was used for the first time in 1974 by Prof. Nan's of Tokyo Science University while explaining the silicon machined down to the small particle, smaller than one micron.
- Nanoscience can be defined as, the study of phenomena and manipulation of materials at atomic, molecular and macromolecular scales, where properties differ significantly from those at a larger scale.
- Nanotechnology can be defined as, "the design, characterisation, production and application of structures, devices and systems by controlling shape and size at the nanometre scale."

5.3.1 Nanomaterials

MU - May 2009. Dec. 2011. May 2012. Dec. 2012

- 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.
- Properties of Nanomaterials**
- 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.

Table 5.3.1 : The sizes of nanoscale objects

Object	Diameter
H-Hydrogen atom	0.1 nm
C ₆₀ -Buckminsterfullerene	0.7 nm
Carbon nanotube (single wall)	0.4 – 1.8 nm

Object	Diameter
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)	8000 nm
White blood cell	10000 nm

*Currently the semiconductor chips are being reduced to 20 nm by a technique *nanolithography*.

5.3.1.1 Manufacture/Preparation of Nanomaterials

Nano-materials can be manufactured either of the following methods (modes)

- (i) Top to bottom
- (ii) Bottom up

- *Top to bottom* method involves milling bulk material with normal size particles bulk to small particles (nanosize).
- *Bottom up* method involves forming objects from individual atoms or molecules and joining them. e.g. wood made up of cells of trees which are on the nanoscale.

The 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} .

5.3.1.2 Carbon Nanotubes (CNT's)

MU - Dec. 2007, May 2008, May 2010, Dec. 2011, Dec. 2012, May 2013

- 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*.
- Structural features**
- Each nanotube is made up of a *hexagonal network* of covalently bonded carbon atoms.
- a) Laser Method**
- The most commonly used methods are Laser method and CVD.

5.3.1.3 Methods of Preparation for CNTs

MU - Dec. 2012

There are five methods for preparation of CNTs, and Fullerenes.

1. Arc method
2. Laser method
3. Chemical Vapour Deposition [CVD]
4. Ball milling
5. Flame synthesis

MU - Dec. 2007, May 2010

- Carbon nanotubes are of two types :
 - (i) single-walled
 - (ii) multi-walled.
- A single-walled carbon nanotube (SWNT) consists of a *single graphene cylinder* whereas a multi-walled carbon nanotube (MWCNT) 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 CNFS depend on the diameter.

Table 5.3.2 : 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 ₂ /CH ₄	1000°C catalytic decomposition	Co/Ni/Fe on MgO	High yield of SWCNT
Acetylene	≈ 600°C	Cobalt	SWCNT MWCNT

- 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 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.

b) 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.

5.4 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.

- (3) CNTs can be either *metallic* or *semi-conducting* in their electrical behavior. Conductivity in MWNTs 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°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} 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 Tpa has been reported.
- (7) Young's modulus depends on the size and chirality of the single walled nanotubes, ranging from 1.22 Tpa to 1.26 Tpa.
- (8) They have calculated a value of 1.09 Tpa for a generic nanotube.

c) Thermal Conductivity and Expansion

- (1) CNTs exhibit *superconductivity below 20^\circ\text{K}* (approximate -253°C).
- (2) CNTs can adopt electrical properties and behave as semiconductors or even as metals.
- (3) They are exceptionally *strong* and *stiff* against axial strains.
- (4) CNTs possess high flexibility against non-axial strains.
- (5) CNTs are used in *nanoscale molecular electronics, sensing and actuating devices*, or as *reinforcing additive fibers* in functional composite materials.
- (6) CNTs show very high *thermal conductivity*.
- (7) Polymeric materials reinforced by CNTs also significantly improve the *thermal and thermomechanical properties of the composites*.

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' 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.

The most important application of carbon nanotubes are :

- As catalyst support
- In batteries Fuel Cells: H₂, 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

Review Questions

- Q. 1 Define nanomaterials.
- Q. 2 State the size of H atom, C₆₀, 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 Laser and CVD method for the preparation of carbon nanotubes with the advantages of and limitations of this method over the other methods.

5.6 University Questions (Theory)

Dec. 2012

Q. 1 What are (i) SWCNT and (ii) MWCNT ? Describe the production of SWCNT by LASER method. (Section 5.3.1.2 and 5.3.1.3(a))

May 2008

Q. 2 What are carbon-nanotubes ? Explain different types of carbon-nanotubes. (Section 5.3.1.2)

May 2009

Q. 3 What are Nano-materials ? Give two properties of Nano-materials which make them different and superior to Conventional materials.

(Section 5.3.1 and 5.3.1(a))

May 2010

Q. 4 Describe laser method for production of carbon nanotubes. Write applications of carbon nanotubes. (Section 5.3.1.3(a) and 5.5) (5 Marks)

Dec. 2011

Q. 5 Give the main physical changes that take place at the nano scale with its applications. (Section 5.3.1 and 5.5) (5 Marks)

Q. 6 What are CNTs? What are its types? Give their applications. (Section 5.3.1.2 and 5.5) (5 Marks)

May 2012

Q. 7 What are nano materials? Mention two reasons why properties of materials differ at the nano scale. (Section 5.3.1) (3 Marks)

Q. 8 What is nanomaterial ? Give two properties of nanomaterials which make them different and superior to conventional materials. (Sections 5.3 and 5.3.1)

(3 Marks)

Q. 9 Explain manufacturing process for the portland cement. (Section 5.1.5.4)

(4 Marks)

Q. 10 What is SWCNT and MWCNT ? Explain Laser method for the manufacturing of carbon nanotubes. (Sections 5.3.1.2 and 5.3.1.3)

(6 Marks)

May 2013

Q. 11 Write composition of Portland cement. (Section 5.1.6) (3 Marks)

Q. 12 Explain CVD method for preparation of carbonnanotubes. (Section 5.3.1.2) (4 Marks)

Q. 13 Write preparation properties and uses of : (6 Marks)

(i) Dolomite bricks

(ii) Silicon carbide (Table 5.2.1)

□□□