MODULE- 6: WATER

Introduction: Water is nature's most wonderful, abundant and useful compound. Human beings can survive for a number of days without food, but cannot survive without water. Water is not only essential for the lives of animals and plants but it is also very important in industries. It is used in steam generation, as a coolant in power & chemical plants, production of steel, rayon, paper, atomic energy, textiles, chemicals, ice, for air-conditioning, drinking, bathing, sanitary, washing, irrigation, fire-fighting, etc.

Different sources: of water are rain water, river water, lake water, sea water, underground water, spring and well water.

Impurities in Water: There are mainly three types of impurities in water. They are (1) Physical impurities; (2) Chemical impurities; (3) Biological impurities.

(1) Physical Impurities: These include colour, turbidity, taste, odour, etc. Colour in water is due to metallic substances like salts of iron, manganese, algae, weeds, etc. Turbidity is due to colloidal matter. Different taste is due to the presence of metallic ions like iron, aluminium, manganese, etc. Odour in water is undesirable for domestic as well as industrial purposes. Disagreeable odour is due to the presence of living organisms, decaying vegetation including algae, bacteria, fungi and weeds.

(2) Chemical Impurities: These include inorganic and organic chemicals released from dyes, paints and varnishes, drugs, insecticides, pesticides, detergents, textiles, etc. Acidity in water is harmful. Surface water and groundwater attain acidity from industrial wastes like acid, mine, drainage, pickling liquors, etc. Acidity is also caused by the presence of free CO_2. Polluted water acquires CO_2 from the biological oxidation of organic matter. Dissolved O_2 in industrial water is not desirable. It induces corrosion reactions. Dissolved O_2 in water is essential to the life of aquatic organisms such as fishes. Dissolved NH3 in water arises from the decomposition of nitrogenous organic matter.

(3) Biological Impurities: These are algae, pathogenic bacteria, fungi, viruses, parasites, etc. The source of these contaminations is discharge of domestic and sewage wastes, excreta, etc.

Hardness of Water: Hardness of water is that characteristic property which prevents the lathering of soap. This is due to the presence of certain salts of calcium, magnesium and other heavy metals dissolved in water. When a sample of hard water is treated with soap, it does not produce lather. It forms a white precipitate or scum. Soap is sodium or potassium salt of higher fatty acids like oleic, palmitic or stearic acid. When this soap reacts with hard water, it forms insoluble salts of calcium and magnesium which precipitate out as white scum. For instance, when soap like sodium stearate comes in contact with hard water, calcium chloride present in hard water reacts with it to form a white precipitate of insoluble calcium stearate as shown below:

$$2C_{17}H_{35}COONa + CaCl_2 \rightarrow (C_{17}H_{35}C00)_2Ca + 2NaCl$$
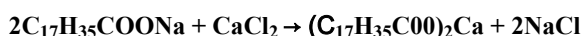
Sodium stearate (soap) Hardness Calcium stearate (Insoluble white precipitate) Hard water also contains magnesium salts. The reaction of soap with magnesium sulphate is as follows:

$$2C_{17}H_{35}COONa + MgSO_4 \rightarrow (C_{17}H_{35}C00)_2 Mg + + Na2SO_4$$
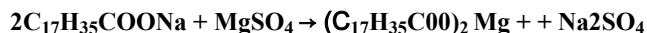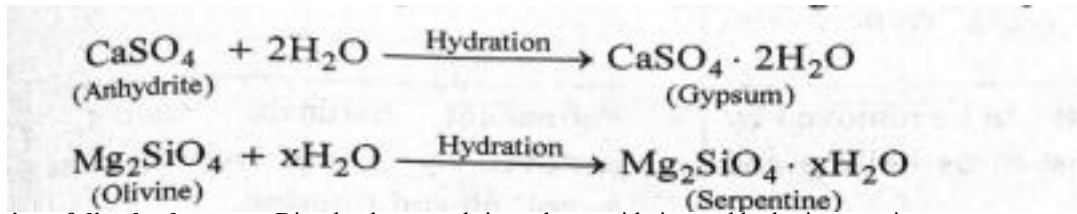
Sodium stearate (soap) Hardness Magnesium stearate (Insoluble white precipitate) Thus, water which does not produce lather with soap solution readily, but forms a white precipitate (scum or curd) is called hard water. Water which gives lathers easily with soap solution is called soft water. Such water does not contain dissolved calcium and magnesium salts in it.
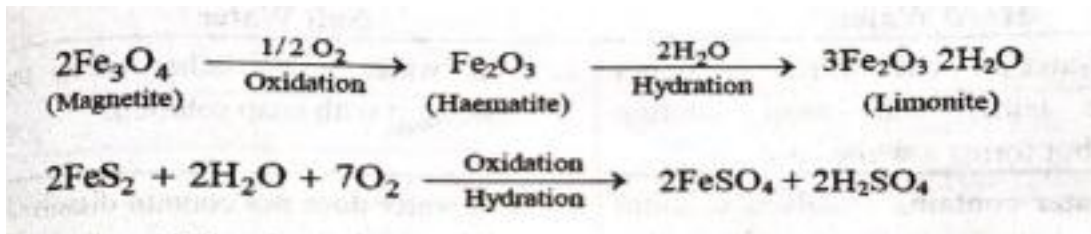
Causes of Hardness: When water flows over or percolates through the ground rocks or solids, there is some physical and chemical changes take place. Due to these changes, it gets contaminated with dissolved salts of calcium and magnesium. We call it the hardness of water.

The various changes causing hardness of water are as follows:
  - ☐ **Dissolution:** Mineral constituents of rocks like sodium chloride, gypsum ($CaSO_4.2H_20$) etc. dissolved in it.
  - ☐ **Hydration:** Some minerals like anhydrite ($CaSO_4$), Olivine (Mg_2SiO_4) etc undergo hydration leading to the formation of products of increased volume, due to which the disintegration of mineral bearing rocks take place.
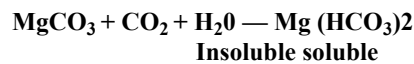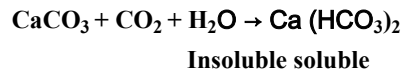
$$CaSO_4 + 2H_2O \xrightarrow{\text{Hydration}} CaSO_4 \cdot 2H_2O$$
$$\text{(Anhydrite)} \qquad\qquad\qquad \text{(Gypsum)}$$

$$Mg_2SiO_4 + xH_2O \xrightarrow{\text{Hydration}} Mg_2SiO_4 \cdot xH_2O$$
$$\text{(Olivine)} \qquad\qquad\qquad \text{(Serpentine)}$$

☐ **Action of dissolved oxygen:** Dissolved oxygen brings about oxidation and hydration reactions.

$$2Fe_3O_4 \xrightarrow[\text{Oxidation}]{1/2\ O_2} Fe_2O_3 \xrightarrow[\text{Hydration}]{2H_2O} 3Fe_2O_3\ 2H_2O$$
$$\text{(Magnetite)} \qquad \text{(Haematite)} \qquad\qquad \text{(Limonite)}$$

$$2FeS_2 + 2H_2O + 7O_2 \xrightarrow[\text{Hydration}]{\text{Oxidation}} 2FeSO_4 + 2H_2SO_4$$

☐ **Action of dissolved carbon dioxide:**

(a) It converts insoluble carbonates of calcium, magnesium and iron into soluble bicarbonates. For

example,

$$CaCO_3 + CO_2 + H_2O \rightarrow Ca\ (HCO_3)_2$$
$$\text{Insoluble} \qquad\qquad \text{soluble}$$

$$MgCO_3 + CO_2 + H_2 0 — Mg\ (HCO_3)2$$
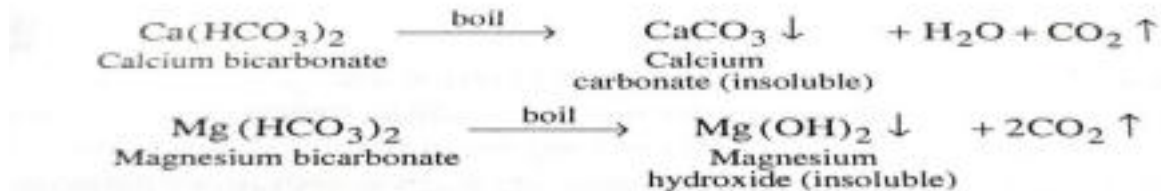$$\text{Insoluble} \qquad\qquad \text{soluble}$$

 (b) It converts rock forming silicates and aluminosilicates of sodium, potassium, calcium and iron into soluble carbonates, bicarbonates and silica.

For example, $K_2O.Al_2O_3.6SiO_2 + CO_2 + 2\ H_2 0 {-}{\rightarrow} Al_2O_3.2SiO_2.2H_2 0 + K_2CO_3 + 4SiO_2$

(c) Rocks containing feldspar disintegrate and charge nearby river water with dissolved salts, fine clay and silica in suspension.

Types of Hardness: There are two types of hardness, as follows:

(1) Temporary or Carbonate or Alkaline Hardness: This type of hardness is caused by the presence of dissolved bicarbonates of calcium, magnesium and other heavy metals and the carbonate of iron. Temporary hardness can be destroyed by boiling water. When hard water containing bicarbonates is boiled, the bicarbonates are decomposed forming insoluble carbonates or hydroxides which are deposited as a crust at the bottom of the vessel. For instance, when hard water containing calcium or magnesium bicarbonate is boiled, the following reactions take place:

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

$$Mg\ (HCO_3)_2 \xrightarrow{\text{boil}} Mg(OH)_2 \downarrow \quad + 2CO_2 \uparrow$$
$$\text{Magnesium bicarbonate} \qquad\qquad \text{Magnesium}$$
$$\text{hydroxide (insoluble)}$$

2. Permanent or Non-carbonate or Non-alkaline Hardness: This type of hardness is caused by the presence of chlorides, nitrates and sulphates of calcium, magnesium, iron and other heavy metals. Permanent hardness cannot be destroyed by the boiling of water.

Comparisons:

Temporary Hardness	Permanent Hardness
1. It is due to bicarbonates and carbonates of Ca^{2+}, Fe^{2+}, Mg^{2+} etc.	It is due to chlorides, sulphates, nitrates of Ca^{2+}, Fe^{2+}, Mg^{2+} etc. other than carbonates and bicarbonates.
2. It is known as carbonate or alkaline hardness.	2. It is known as non-carbonate or non-alkaline hardness.
3. Temporary hardness leads to formation of loose deposits of carbonates and hydroxides of Ca^{2+}, Mg^{2+} respectively, if used in boilers.	3. Permanent hardness leads to formation of adherent scales.
4. Temporary hardness can be removed by simple techniques such as boiling and filtering.	4. Permanent hardness cannot be removed by simple techniques such as boiling and filtering.

Hard Water	Soft Water
1. Hard water is one which does not produce lather with soap solution readily but forms a white curd.	1. Soft water gives lather easily by shaking it with soap solution.
2. Hard water contains dissolved calcium and magnesium salts in it.	2. Soft water does not contain dissolved calcium and magnesium salts.
3. Cleansing quality of soap is depressed and a lot of soap is wasted during washing and bathing.	3. Cleansing quality of soap is not depressed and soap is not wasted during washing and bathing.
4. Due to the presence of dissolved hardness producing salt, boiling point of water is elevated. Consequently more fuel and time are required for cooking.	4. Less fuel and time are required for cooking in the soft water.

Disadvantages of Hard Water: As hard water does not lather with soap solution, it has the following disadvantages:

(1) In domestic use:
(a) Washing: Does not lather freely with soap.
(b) Bathing: Does not lather freely with soap.
(c) Cooking: Boiling point of water is elevated. Therefore, more fuel and time are required. (d) Drinking: Causes bad effect on digestive system.

(2) In industrial use:
(a) Textile industry: Causes much of the soap to go as waste.
(b) Sugar industry: Causes difficulty in crystallization of sugar.
(c) Dyeing industry: Yields impure shades and give spots on the fabric.
(d) Paper industry: React with chemicals and affect the colour.
e) Laundry: Causes much of the soap to go as waste.
(f) Concrete making: Affects the hydration of cement and strength.
(g) Pharmaceutical industry: May produce certain undesired products.
(3) In steam generation in boilers:
(a) Scale and sludge formation
(b) Corrosion
(c) Priming and foaming
(d) Caustic embrittlement

Measurement of Hardness of Water: The extent of hardness is measured in terms of concentration of ions contributing to hardness. This is expressed in terms of equivalent amount of $CaCO_3$. This method is convenient because it allows the multiplication and division of concentration when required. Also the molecular weight of $CaCO_3$ is 100 and equivalent weight is 50. $CaCO_3$ is the most insoluble salt which can be precipitated in water treatment. Therefore, $CaCO_3$ is chosen. The equivalents of $CaCO_3$ for a hardness producing substance can be calculated by using the following formula: The equivalent of $CaCO_3$,

$$= \frac{\left[\begin{array}{c}\text{Mass of hardness} \\ \text{producing substance}\end{array}\right] \times \left[\begin{array}{c}\text{Chemical equivalent} \\ \text{of } CaCO_3\end{array}\right]}{\text{Chemical equivalent of hardness producing substance}}$$

$$= \frac{\left[\begin{array}{c}\text{Mass of hardness} \\ \text{producing substance}\end{array}\right] \times 50}{\text{Chemical equivalent of hardness producing substance}}$$

For calculating the equivalents of $CaCO_3$ of different hardness producing substances the molecular weights and equivalent weights of those substances are considered. The weight of $CaCO_3$ is 100 and its equivalent weight is 50. The following table explains how to use the multiplication factor or conversion factor to get the equivalents of $CaCO_3$ table:

Dissolved salt/ion	Molar Mass	Chemical equivalent	Multiplication factor for converting into equivalents of $CaCO_3$
$Ca(HCO_3)_2$	162	81	100/162
$Mg(HCO_3)_2$	146	73	100/146
$CaSO_4$	136	68	100/136
$FeCl_2$	127	63.5	100/127
$CaCl_2$	111	55.5	100/111
$MgSO_4$	120	60	100/120
$MgCl_2$	95	47.5	100/95
$CaCO_3$	100	50	100/100
$MgCO_3$	84	42	100/84
CO_2	44	22	100/44
$Ca(NO_3)_2$	164	82	100/164
$Mg(NO_3)_2$	148	74	100/148
HCO^{3-}	61	61	100/122
OH	17	17	100/34
$CO3^{2-}$	60	30	100/60
$NaAlO_2$	82	82	100/164
$Al2(SO_4)_3$	342	57	100/114

FeSO$_4$.7H$_2$O	278	139	100/278
H$^+$	1	1	100/2
HCl	36.5	36.5	100/73

Table: Calculation of equivalents of CaCO$_3$

Units of Hardness: The most commonly used units of hardness are as follows:
(1) Parts Per Million (ppm): 1 ppm = 1 part of CaCO3 equivalent of hardness in 10^6 parts of water.

(2) Milligram Per Litre (mg/L): It is the number of milligrams of CaCO3 equivalent of hardness present per litre of water. Thus 1 L of water weighs 1 kg.

Weight of 1 L of water = 1 kg = 1000gm = 10^6 mg

.: 1 mg/L = 1 mg of CaCO3 equivalent of hardness per 10^6 mg of water

= 1 part of CaCO3 equivalent per 10^6 parts of water = 1ppm

.: 1 mg/L = 1ppm

(3)Degree Clark (^{0}Cl): also called grains per gallon. i.e. 1 part of CaCO3 equivalent per 70,000 parts of water. **(4)**

Degree French (^{0} Fr): 1 part of CaCO3 equivalent per 10^5 parts of water.

Relationship between units:
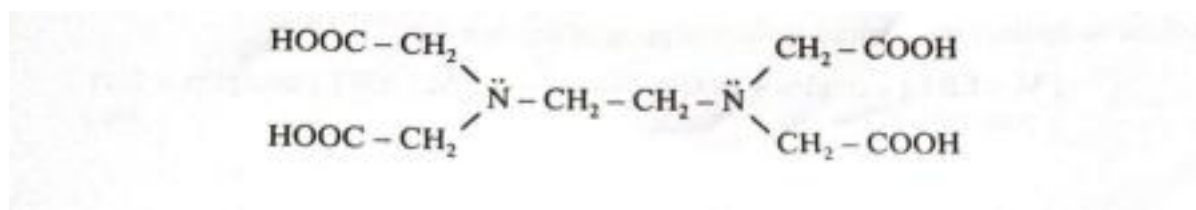
1 ppm = 1mg/l = 0.1^0 Fr = 0.07 ^{0}Cl
1 mg/l = 1ppm = 0.1 ^{0} Fr = 0.07 ^{0}Cl
1 ^{0}Cl = 1.43^0 Fr = 14.3 ppm = 14.3 mg/l
1 ^{0} Fr = 10 ppm = 10 mg/l = 0.7 ^{0}Cl
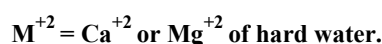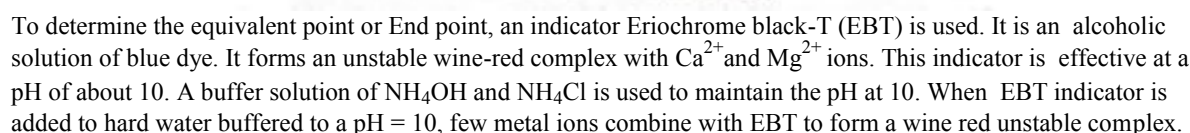**Degree of Hardness is Total Hardness of water.**

Determination of Hardness of Water by EDTA Method: Hardness of water can be accurately determined by EDTA method. EDTA is an abbreviated form of Ethylene Diamine Tetra-acetic acid. The structure is as follows:


Ethylene Diamine Tetra-acetic acid

In the form of its sodium salt, it yields an anion which forms complex ions with Ca^{2+} and Mg^{2+} ions. Thus, it is a complexometric method. EDTA is used as its di- sodium salt. Its molecular weight = 372.24.

The **Complex ion formed with Ca^{+2} or Mg^{+2} ions** has a following structure:

where M = Ca or Mg.

To determine the equivalent point or End point, an indicator Eriochrome black-T (EBT) is used. It is an alcoholic solution of blue dye. It forms an unstable wine-red complex with Ca^{2+} and Mg^{2+} ions. This indicator is effective at a pH of about 10. A buffer solution of NH_4OH and NH_4Cl is used to maintain the pH at 10. When EBT indicator is added to hard water buffered to a pH = 10, few metal ions combine with EBT to form a wine red unstable complex.

$$M^{+2} + EBT \rightarrow [M - EBT] \text{ complex, at pH = 10}$$

(Blue) (Wine red)

$$M^{+2} = Ca^{+2} \text{ or } Mg^{+2} \text{ of hard water.}$$

During the course of titration against EDTA solution, EDTA combines with free M^{+2} ions to form stable complex M-EDTA.

When nearly all free M^{+2} (Ca^{+2} or Mg^{+2}) ions have formed [M-EDTA] complex, , the next drop of EDTA added displaces the EBT indicator from [M-EBT) complex and the wine-red colour changes to blue colour due to EBT. Thus, the change of wine-red colour to distinct blue colour is the end point of titration.

[M – EBT] Unstable complex + EDTA → [M - EDTA] Stable complex + EBT
(Wine-red)   **(Colourless complex)**   **Blue**
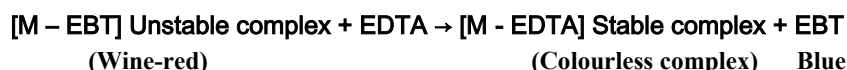
The following steps are involved:

(1) Preparation of standard hard water: Dissolve 10 g of pure dry $CaCO_3$ in minimum of dilute HCl and then evaporate the solution to dryness in a water bath. Dissolve the residue in distilled water to make a 1 L solution. Each ml of this solution contains 1 mg of $CaCO_3$ equivalent hardness.

(2) Preparation of EDTA solution: Dissolve 4 g of pure EDTA crystals + 0.1 g $MgCl_2$ in 1 L of distilled water.

(3) Preparation of indicator: Dissolve 0.5 g of Eriochrome black-T in 100 ml of alcohol.

(4) Preparation of buffer solution: Add 67.5 g of NH_4Cl to 570 ml of concentrated ammonia solution and then dilute with distilled water to 1 L.

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

(6) Titration of unknown hard water: Titrate 50 ml of water sample just as in step (5). Let volume used is V2 ml.

(7) Titration of permanent hardness: Take 250 ml of the water sample in a large beaker. Boil it, till the volume is reduced to about 50 ml [when all the bicarbonates are decomposed to insoluble $CaCO_3$ + Mg $(OH)_2$]. Filter, wash the precipitate with distilled water, and collect the filtrate and washings in a 250 ml measuring flask. Finally make up the volume to 250 ml with distilled water. Then, titrate 50 ml of boiled water sample just as in step (5). Let volume used by V3 ml.

Advantages of EDTA Method: This method is definitely preferable to the other methods, because of (1) greater accuracy, (ii) convenience, and (iii) more rapid procedure.

Softening of Water by Ion-exchange Process or Demineralization process:

Resins available for water treatment include cation-exchange resins of the strongly and weakly acidic types, anion-exchange resins of the strongly and weakly basic types and highly porous modifications of strong acid cation exchangers and strong base anion exchangers. These resins are available in granular or bead-like form and may be obtained in an effective size and uniformity coefficient.

For effective water treatment, ion exchangers should possess the following properties:

1. They should be non-toxic.
2. They should not discolour the water being treated.
3. They should possess a high ion-exchange capacity. (It depends upon the total number of ion active groups per unit weight of the exchanger and is expressed as mill-equivalents per gram of the exchanger). 4. They should be physically durable.
5. They should be resistant to chemical attack.
6. They should be cheap and commonly available.
7. They must be capable of being regenerated and back-washed easily and economically. 8. They should have a large surface area since ion-exchange is a surface phenomenon. At the same time, their resistance to flow must be compatible with hydraulic requirements.

Ion-exchange resins are insoluble, cross-linked, long-chained organic polymers with a microporous structure. The functional groups attached to the chains are responsible for the ion-exchanging properties. Resins containing acidic functional groups like - COOH, – SO_3H, etc. are capable of exchanging their H+ ions with other cations, which come into their contact. Those containing basic functional groups like – NH_2, = NH as hydrochloride, etc. are capable of exchanging their anions with other anions which come into their contact. The ion-exchange resins are classified as follows:

1: Cation Exchange Resins (RH+): These are mainly styrene-divinylbenzene copolymers, which on sulphonation or carboxylation, become capable of exchanging their hydrogen ions with the cations in the water.
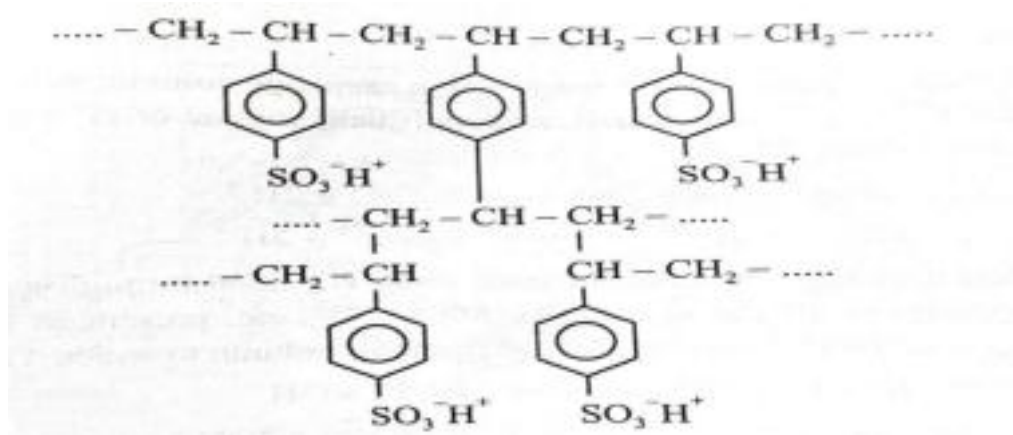
Fig: Acidic or cation exchange resin (sulphonate form)

2. Anion Exchange Resins (R'OH): These are styrene -divinyl benzene or amine-formaldehyde copolymers, which contain amino or quaternary ammonium or quaternary phosphonium or tertiary sulphonium groups as an integral part of the resin matrix. These, after treatment with dil. NaOH solution, become capable of exchanging their OH- anions with anions in water.
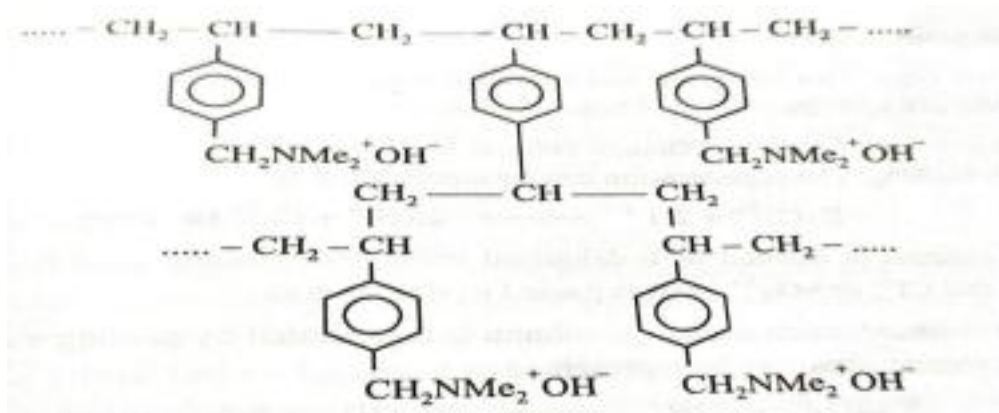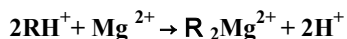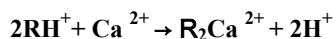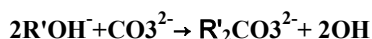
Fig: Basic or anion exchange resin (hydroxide form)
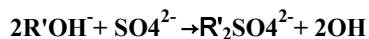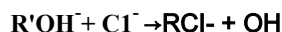
3: Process: The hard water is passed first through the cation exchange column, which removes all the cations like Ca^{2+}, Mg^{2+}, etc. from it, and an equivalent amount of H+ ions are released from this column to water. Thus **Reaction in Cation exchange column:**

$$2RH^+ + Ca^{2+} \rightarrow R_2Ca^{2+} + 2H^+$$

$$2RH^+ + Mg^{2+} \rightarrow R_2Mg^{2+} + 2H^+$$

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

$$R'OH^- + Cl^- \rightarrow RCl- + OH$$

$$2R'OH^- + SO_4^{2-} \rightarrow R'_2SO_4^{2-} + 2OH$$

$$2R'OH^- + CO_3^{2-} \rightarrow R'_2CO_3^{2-} + 2OH$$

H^+ and OH ions (released from cation exchange and anion exchange columns respectively) get combined to produce water molecules. $H+ OH^- \rightarrow H_2O$
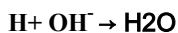
Thus, the water coming out from the exchanger is free from cations as well as anions. Ion-free water is known **as deionized or demineralised water**.
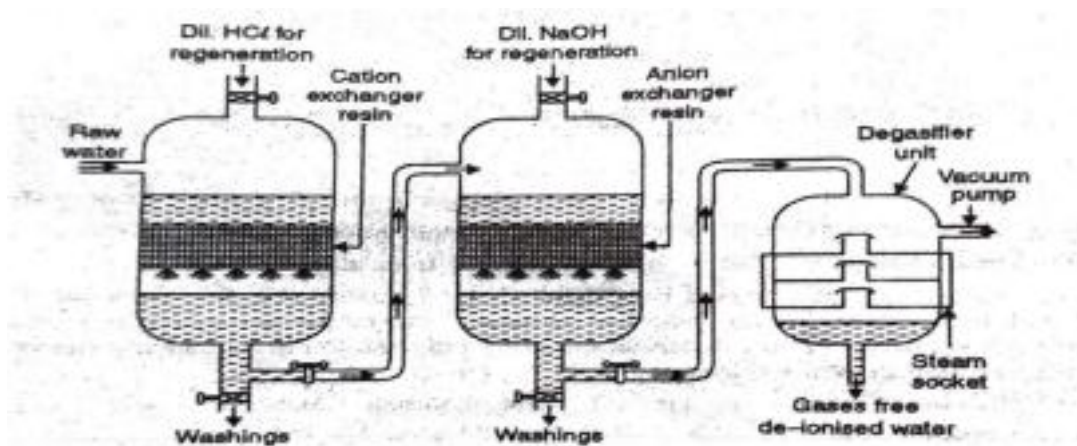

Fig: Demineralization of water

4: Regeneration: When capacities of cation and anion exchangers to exchange H^+ and OH ions respectively are lost,

they are said to be **exhausted.**

The **exhausted cation exchange column** is regenerated by passing a solution of dil. HCl or dil. H_2SO_4. The regeneration can be represented as:

$$R_2Ca^{2+} + 2H^+ \rightarrow 2RH^+ + Ca^{2+} \text{ (washing)}$$

The column is washed with deionised water and washing (which contains Ca^{2+}, Mg^{2+} etc. ions) is passed to sink or drain.

The **exhausted anion exchange column** is regenerated by passing a solution of dil. NaOH. The regeneration can be represented as:

$$R'_2SO_4^{2-} + 2OH^- \rightarrow 2R'OH^- + SO_4^{2-} \text{(washing)}$$

The column is washed with deionised water and washing (which contains SO_4^{2-} or Cl ions) is passed to sink or drain.

The regenerated ion exchange resins are then used again.

Advantages of Ion Exchange Process:

1. It produces water of very low hardness (2 ppm).
2. Treated water contains a negligible amount of total dissolved solids.
3. Water obtained can be used for high pressure boilers.
4. Highly acidic and alkaline water can be softened.

Disadvantages of Ion Exchange Process:

1. The equipment is costly.
2. More costly chemicals are needed.
3. The turbidity of water should be below 10 ppm as efficiency of the process gets affected.

Biological Oxygen Demand (BOD): BOD indicates the amount of decomposable organic matter in the sewage. It enables us to determine the degree of pollution in the sewage stream. Thus, it is very essential in sewage treatment, Biological oxygen demand (BOD) of sewage is defined as the amount of free oxygen required for the biological oxidation of the organic matter under aerobic conditions at 20°C for a period of 5 days. The unit of BOD is mg/L or ppm.

Determination of BOD:

A known volume of effluent sample is diluted with a known volume of diluted water. Water is diluted to ensure that sufficient oxygen is available for the complete aerobic oxidation of organic matter. The diluted sample is divided into two parts and kept in two stoppered bottles. The dissolved oxygen content of one of the bottles is determined which is the blank reading. This is denoted as DOb. Another bottle is incubated at 20° C for 5 days. Then the dissolved oxygen is determined. This is denoted as DOi. The difference between DOb and DOi; gives the BOD.

.: BOD = (DOb - DOi) x (dilution factor) volume of solution after dilution /volume before dilution

BOD test is usually influenced by the type of microorganisms, presence of toxins, pH, some reduced mineral matters, etc.

Reaction: Organic matter + O_2 $\rightarrow$ CO_2 + H_2O

BOD is proportional to the amount of organic waste to be degraded. An average sewage has a BOD of 100-150 ppm. The higher the BOD of a sample, the higher will be the pollution caused by it. **Drinking water should have BOD**

preferably less than 1 ppm.

Significance of BOD: The BOD is important in sewage treatment as it indicates the amount of decomposable organic matter in sewage. The higher BOD of a sample indicates the presence of a higher amount of decomposable organic matter in the sample i.e. the sample is more polluted. From BOD values, the self purifying capacity of streams can be determined. Thus, it provides the degree of pollution at any time in the sewage stream.
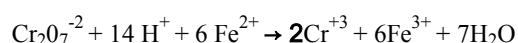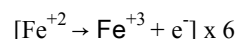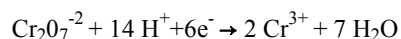
Chemical Oxygen Demand (COD): COD indicates the amount of oxygen consumed under specific conditions during the oxidation of organic and oxidisable inorganic matter. It is a measure of oxidisable impurities present in the sewage. **BOD measures only the oxygen consumed by living organisms while COD is a measure of both, biologically oxidisable as well as biologically inert organic matter. Therefore, COD values are higher than BOD values.**

Chemical oxygen demand (COD) may be defined as the amount of oxygen required for oxidation of chemically degradable organic matter in the hot conditions with the use of oxidant like acidified $K_2Cr_2O_7$ (potassium dichromate) in 90 minute to 3 hours. **The unit of COD is also mg/L or ppm.**

Determination of COD: A known volume (250 ml) of waste water sample is refluxed with a known excess of standard potassium dichromate ($K_2Cr_2O_7$) (1N) and dilute sulphuric acid (H_2SO_4) in presence of silver sulphate (Ag_2SO_4) for 19 hours. Silver sulphate is used as a catalyst to promote oxidation of straight chain aliphatic compounds, aromatic compounds and pyridine. The organic matter of the sample is oxidized to ammonia, carbon dioxide and water. The unreacted potassium dichromate ($K_2Cr_2O_7$) is titrated against Ferrous Ammonium Sulphate $FeSO_4.(NH_4)_2SO_4.6H_2O$ i.e., (FAS)Mohr's salt solution. This experimentally measured amount of potassium dichromate (consumed) is used to calculate the equivalent oxygen required by the waste water for degradation of the pollutants.

Reaction: $C_xH_yO_z$ (organic compound)+ (X+Y/4 – Z/2) $O_2 \rightarrow$ X CO_2 +Y/2 H_2O

The unreacted dichromate solution is titrated against $FeSO_4. (NH_4)_2SO_4.6H_2O$ i.e., (FAS) using ferroin as indicator. At the end point, blue colour changes to wine red.

$Cr_2O_7^{-2}$ + 14 H^+ +6e^- $\rightarrow$ 2 Cr^{3+} + 7 H_2O

[$Fe^{+2} \rightarrow Fe^{+3}$ + e^-] x 6

$Cr_2O_7^{-2}$ + 14 H^+ + 6 Fe^{2+} $\rightarrow$ **2**Cr^{+3} + 6Fe^{3+} + 7H_2O

The COD of the sample can be calculated as follows:

$$COD = \frac{(V1-V2)KOH * N \text{ of } KOH * 8000}{Vol. \text{ of sewage}} \text{ mg/l}$$

V1 and V2 are volumes of ferrous ammonium sulphate, in blank and test experiments respectively**. N** is the normality of Ferrous Ammonium Sulphate.

Significance of COD: The COD value is not affected by the presence of toxins and other unfavorable conditions for the growth of microorganisms. It measures the effect of pollutants on dissolved oxygen. It is taken as the basis for calculation of efficiency of treatment plants. It is important in proposing standards for discharging domestic and industrial effluents in various kinds of water. Due to its rapid determination over BOD, it has become important in the management and design of treatment plants.

Limitations of COD: COD is a poor measure of strength of organic matter as oxygen gets consumed in oxidation of some of the inorganic matter. Some organic matter like benzene does not get oxidized by the test. COD test fails to differentiate between bio-inert and bid-degradable materials.

Comparison:

| BOD	COD
BOD of water is a measure of the amount of oxygen required for biological oxidation of organic matter under aerobic condition at 20 °C for a period of 5 days.	COD of water is a measure of the amount of oxygen required by organic matter in a water sample for its oxidation by a strong oxidizing agent.
It measures the oxygen demand of biodegradable pollutants only.	It measures the oxygen demand of biodegradable pollutants along with non-biodegradable pollutants.
Less stable measurement method as it uses micro organisms which are susceptible to pH, temperature and other variables in the water.	More stable measurement method as it uses potassium dichromate which oxidises regardless of water conditions.
Slow process. It takes five days.	Fast process. It takes 2-3 hours.
BOD values are generally less than COD values.	COD values are generally greater than BOD values.

Water Purification: Water with high levels of dissolved salt is not suitable for domestic, industrial, irrigation uses. Sea water contains 3.5% dissolved salts. It can be desalinated into fresh water by the process of desalination. For the purpose of desalination, i.e., for the removal of dissolved salt from water, the membrane technology is employed. The following methods are used for desalination of water by using membrane technology.

1: Electrodialysis: This is a method in which the ions of the salts present are pulled out of the salt water by passing direct current, using electrodes and thin rigid plastic membrane pairs natural or synthetic. When direct electric current is passed through saline water, the sodium ions (Na^+) start moving towards the negative pole (cathode); while the chloride ions (Cl^-) Start moving towards the positive pole (anode), through the membrane. As a result, the concentration of brine decreases in the central compartment; while it increases in two side compartments. Desalinated brine (or pure water) is removed from the central compartment from time to time; while concentrated brine in the side compartments) is replaced by fresh brine/sea water.
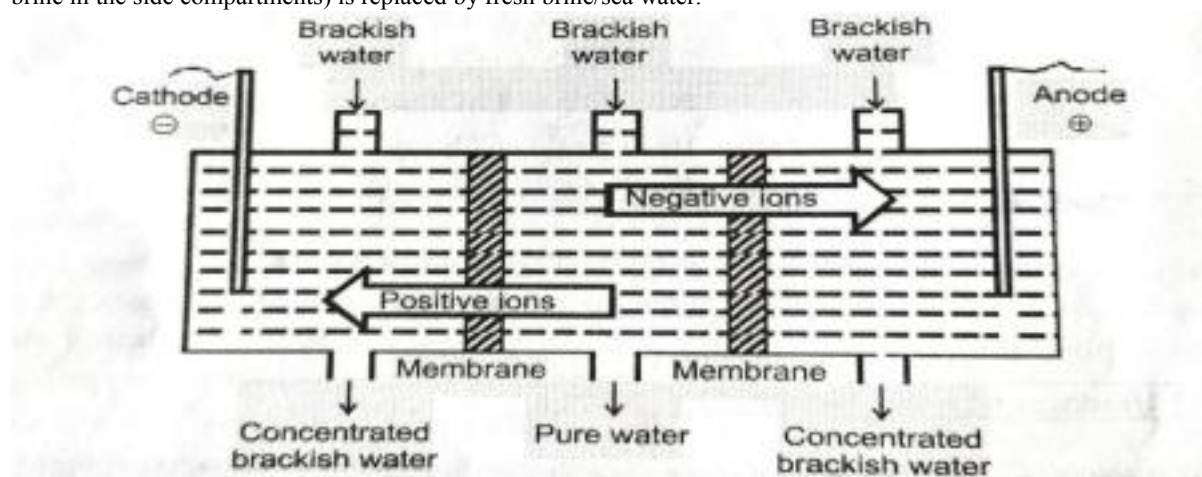
Fig: Electrodialysis of Saline water

For more efficient separation, usually, ions-selective membranes are employed. An ion-selective membrane has permeability for only one kind of ions with specific charge. For example, a cation-selective membrane is permeable to cations only, because of the presence of charged fixed (inside the membrane) functional groups (such as RSO_3^-, or $RCOO^-$). They reject anions having the same charge as that of fixed functional groups. Similarly, anion-selective membrane has positively charged fixed functional groups such as $R_4N^+Cl^-$.

Fig. 6.6 : Electrodialysis cell
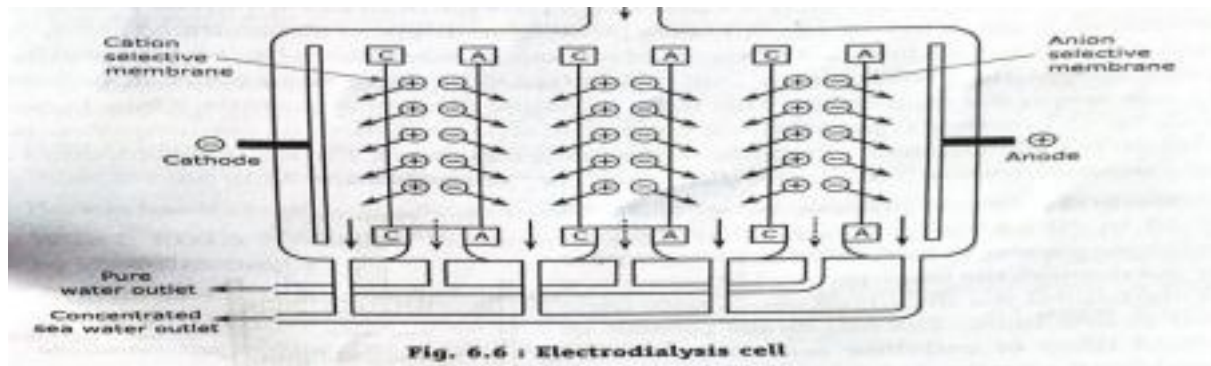
An Electrodialysis cell consists of a large number of paired sets of rigid plastic membranes. Saline water is passed under a pressure (of about 5-6 kg m^{-2}) between membrane pairs and an electric field is applied perpendicular to the direction of water flow. Just as magnets of like charges repel each other, the fixed positive charges inside the membrane repel positively charged ions (Na$^+$), yet permit negatively charged ions (Cl$^-$) to pass through. Similarly, the fixed negative charges inside the other type of membrane repel negatively charged ions (Cl$^-$), yet permit positively charged ions (Na$^+$) to pass through. Therefore water in one compartment of the cell is deprived of its salts: while the salt concentration in adjacent compartments is increased. Thus, we get alternate streams of pure water and concentrated brine. Fig:6.6

Advantages:

1. Easy operation and variability of ED equipment.
2. It is the most compact unit.
3. The cost of installation of the plant and its operation is economical.
4. If electricity is easily available, it is best suited.
5. Demineralization of biological solutions without affecting the quality.
6. Separation of salts and ions without changing phase and adding chemicals.
7. Higher feed recovery in many applications,

Disadvantages:
1. Sometimes pre-treatment is necessary before the Electrodialysis.
2. Suspended solids with a diameter that exceeds 10 μm need to be removed else they may plug the membrane pores.
3. Substances such as large organic anions, colloids, ion oxides and manganese-oxide can disturb the selective effect of the membrane.

2. Reverse Osmosis: There are various membrane techniques available for the separation of solutes on the basis of pore size which include reverse osmosis, ultra filtration etc.

Osmosis: When two solutions of unequal concentrations are separated by semipermeable membrane (which does not allow movement of solute particles) flow of solvent takes place from low concentration solution to high concentration solution side due to osmosis.
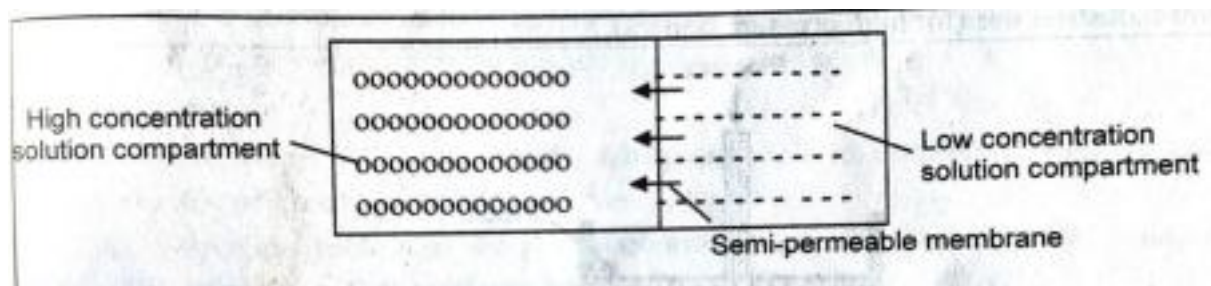
This passage of solvent from low concentration solution side compartment to high concentration solution side compartment is due to difference in vapour pressure of the two compartments. The flow continues till the concentration is equal on both sides. The driving force for osmosis is called osmotic pressure.

Reverse Osmosis: If a hydrostatic pressure in excess of osmotic pressure is applied on the higher concentration solution side, the solvent starts moving from higher concentration to lower concentration side compartment through semi-permeable membrane; this is the principle of reverse osmosis.

Thus, in the process of reverse osmosis pure solvent is separated from its contaminants, rather than removing contaminants from water. **This membrane filtration is also called 'super filtration' or 'hyper filtration'.**
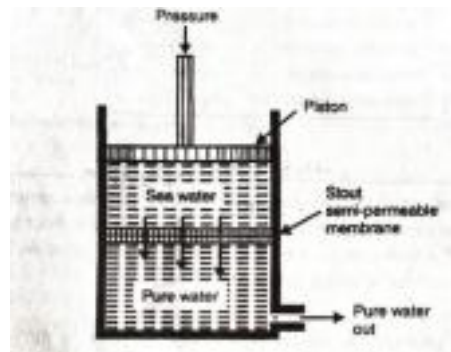
Fig: Reverse Osmosis Cell

Advantages:

1. Reverse osmosis can be used to remove ionic as well as non-ionic, colloidal and high molecular weight organic matter.
2. It removes colloidal silica which is not removed by demineralization.
3. The process is economical, simple, highly reliable and has low capital and operating cost. 4. The life of the semipermeable membrane is about two years and can be replaced within a few minutes there by nearly uninterrupted water supply.

Disadvantages:

1. RO units use a lot of water but have production efficiency close to 48% (for large scale industrial and municipal systems).
2. It is not practical for household systems to have low back pressure as it recovers only 5-15% of water that enters the system. This adds to the load on the household septic system.

Industrial Applications:

1. Due to low capital cost, simplicity, low operating cost and high reliability, reverse osmosis is used for desalination and purification of brackish and sea water for drinking and industrial use (for high pressure boilers). The process of removing common salt from sea water is known as **desalination**. The principle of reverse osmosis is applied to treat sea water. The membrane consists of thin films of cellulose acetate. Recently membranes made of polymethacrylate and polyamide polymers are used. In this process, pressure (15 to 40 kg cm2) is applied to sea water and water is forced through semi permeable membranes. (Ionic and non-ionic, dissolved salts are left behind].
2. Reverse osmosis can be used for a variety of specialized membrane application for chemical recovery and waste water reclamation. For example, Recovery of Nickel and Chromium solutions, purification of pickling acids, water from recycling in textile, electroplating, paper and pulp industries.

3. Ultrafiltration: Ultra filtration is a separation process using membranes with **pore sizes in the range [0.1 to 0.001 micron.** It is membrane filtration in which hydrostatic pressure forces a liquid against a semi-permeable membrane. Suspended solids and solute of high molecular weight are retained, while water and low molecular weight solutes pass through the membrane. Ultra filtration does this by pressuring the solution flow, which is tangential to the surface of the supported membrane. The solvent and other dissolved components that pass through the membrane are known as **permeate** and the components that do not pass through membrane are known as **retenate**. It is fundamentally not different from reverse osmosis. Generally low applied pressures are sufficient to achieve high flux rates from an ultrafiltration membrane. **Flux of a membrane is defined as the amount of permeate produced per unit area of membrane surface per unit time** which is expressed as gallons per square foot per day or as cubic meters per square meters per day.

Advantages:

1. It removes high molecular weight substances, colloidal materials, organic and inorganic polymeric molecules.
2. As only high molecular weight species are removed, the osmotic pressure differential across the membrane surface is negligible.
3. Low applied pressures are sufficient to achieve high flux rates from an ultrafiltration membrane.

Disadvantages: Low molecular weight organics and ions such as sodium, calcium, magnesium, chloride and sulphate are not removed.

Applications:

1. This separation is used in industry and research for purifying and concentrating macromolecular solutions, especially protein solutions.
2. It is used in industry to separate suspended solids from solution.
3. It is used in paint recovery in the automotive industry.
4. It is used in the fractionation of milk and whey.
5. It is used in removal of colloids.

Q.3) 1 gm of CaCO3 was dissolved in 1 lit. of distilled water. 50 ml of solution required 45 ml EDTA for titration. 50 ml of hard water required 25 ml of EDTA for titration. The same sample of water after boiling consumed 15 ml of EDTA for titration. Calculate the total, permanent and temporary hardness of water.

Q.4) A standard hard water sample was prepared by dissolving 2.5 g CaCO3 and making solution upto 1 lit. 50ml of above hard water required 45 ml of EDTA. 50ml of unknown hard water sample was titrated. It required 30ml of the same EDTA. The unknown hard water sample was boiled and filtered. 50 ml of this boiled sample required 20 ml of EDTA. calculate the hardness of all types of unknown sample.

Q.5) After treating 10,000 L of water by ion exchanger, the cationic rein required 200 L of 0.1 N HCl and anionic resin required 200 L of 0.1 N NaOH Solution. Find the hardness of the above sample of water.

Solution: 1N HCl ~ 1N CaCO3----(eq1)
Since 1N CaCO3= 50gm CaCO3/Lit.
.: 0.1N CaCO3= 5.0 gm CaCO3Lit.
1 lit. of 0.1N HCl= 5000 mg CaCO3
.: 200 L OF HCl = 200* 5000 mg of CaCO3
10,00,000 mg CaCO3
Since 10,000 Lit of hard water= 1000000 mg CaCO3
.: 1Lit. Hard water= 1000000/10000mg/lit
= 100mg/lit.
Hardness of sample=100 ppm.