

Water

Syllabus

Introduction - Impurities in water, hardness of water- units (no conversions), types and numerical problems, determination of hardness of water by EDTA method and numerical problems. Softening of water by Ion Exchange process and numerical problems, BOD, COD- definition, significance and Numerical problems. Water purification- membrane technology- Electrodialysis, Reverse osmosis, and Ultra filtration.

6.1 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, cannot be used directly for drinking, agricultural and industrial purpose.
- Hence, we are totally dependent on rain water and it is necessary to store water available from rains.
- The quality of water is of vital concern for humans, since it is directly linked with human health.
- Human body contains about 60% water.
- Water plays an important role in various life processes in the human body. In our daily life water is used for drinking, bathing, cooking and washing purposes.
- Water is also best solvent (also called as universal solvent) and it is used in many industries such as boiler industry for steam generation, textile, paper, pharmaceutical industry etc. for various solutions/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 cannot remain in the same state of purity when it falls on surface of earth. The water thus contaminated needs to be treated.

6.2 Sources of Water

The sources of water are broadly classified as :

1. Rain water

2. Surface water

- (i) River water (ii) Sea water
 (iii) Lake water (iv) Underground water

6.3 Impurities in Water

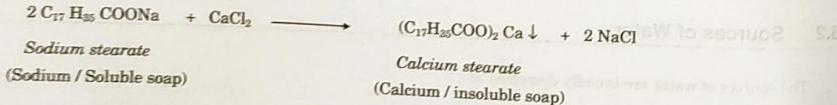
- Pure water shows a pH of 7 that means it is neither acidic nor basic. But when rain water falls on other surfaces, and gets accumulated in the form of water storages such as lakes, rivers etc. it comes in contact with several impurities : (i) minerals, (ii) oxides, (iii) sulphates, (iv) carbonates (v) bi-carbonates, and (vi) dissolved gases.
 - As a result it gets contaminated; and all these impurities change the characteristics of water.
 - 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.

6.4 Hard and Soft Water

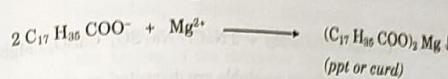
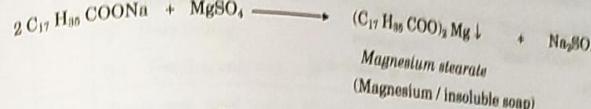
- Soft water is defined as, "water which does not prevent lathering with soap".
 - The contrary to this, hard water is defined as, "water which prevents lathering with soap". Thus this property or tendency of water is called as "hardness of water".

6.5 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.



OP



- 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.

6.6 Types of Hardness

There are two types of hardness, as :

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

6.6.1 Temporary or Carbonate or Alkaline Hardness

MU - Dec. 13, May 16, Dec. 16

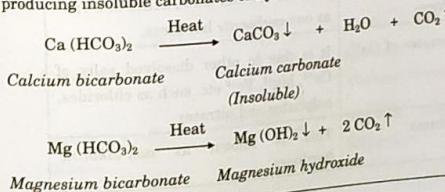
University Questions

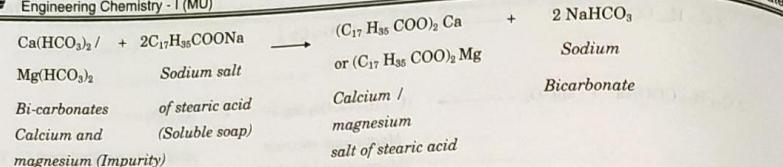
- Q.** What happens when temporary hard water is boiled ? Give equations to explain. (May 16, 3 Marks)

Q. Write two balanced equations to describe the changes that occur when hard water is boiled. (Dec. 16, 3 Marks)

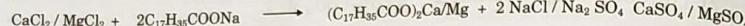
Q. Distinguish between alkaline and non alkaline hardness.

- It is defined as the hardness due to carbonates, hydroxides and other metals.
 - Temporary hardness is mostly removed by mere boiling of water, where bicarbonates are decomposed producing insoluble carbonates or hydroxides.





Or



- 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.

6.6.2 Permanent or Non-carbonate or Non-alkaline Hardness

MU - May 15, Dec. 16, May 17

University Questions

- Q. Differentiate between temporary and permanent hardness.
Q. Distinguish between alkaline and non alkaline hardness.

(May 15, May 17, 3 Marks)

(Dec. 16, 3 Marks)

- It is due to the presence of dissolved chlorides, sulphates and nitrates of calcium, magnesium, iron and other heavy metals.
- Permanent hardness is not destroyed on boiling.
- It requires special chemical treatment for removal of hardness causing salts, such as internal conditioning or external treatment (softening methods).
- The softening methods used on large scale in industries are Lime-Soda method, Zeolite-Permutit method and ion-exchange method.

Table 6.6.1

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.

Sr. No.	Temporary Hardness	Permanent Hardness
5.	Temporary hard water can be softened by (i) Only boiling. (ii) Treating only with lime.	Permanent hard water can be softened by treating with soda.
6.	Temporary hard water if used in steam production, deposits precipitates of carbonates of Ca^{+2} and hydroxides of Mg^{+2} at the bottom of the container (boiler) known as sludges. These deposits harden to form scales. The reactions taking place are : $\text{Ca}(\text{HCO}_3)_2 \xrightarrow{\Delta} \text{CaCO}_3 \downarrow + \text{H}_2\text{O} - \text{CO}_2 \uparrow$ $\text{Mg}(\text{HCO}_3)_2 \xrightarrow{\Delta} \text{Mg}(\text{OH})_2 \downarrow + 2\text{CO}_2 \uparrow$	Permanent hard water if used in steam production, forms scales.

6.7 Factors Influencing Hardness of Water (Causes of Hardness)

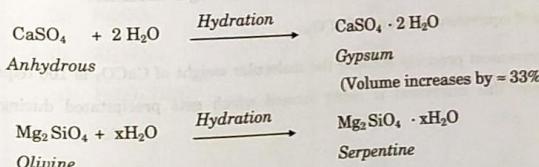
Causes of hardness

There are mainly three causes of hardness,

- Dissolved minerals
- Dissolved Oxygen
- Dissolved Carbon-dioxide

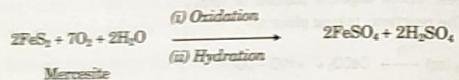
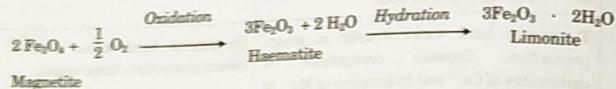
6.7.1 Dissolved Minerals

- 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,



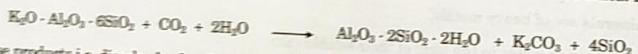
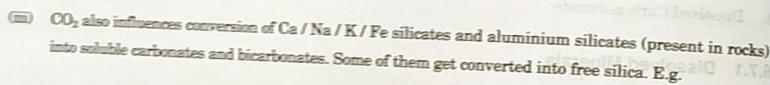
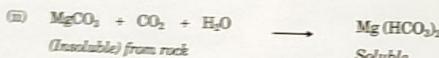
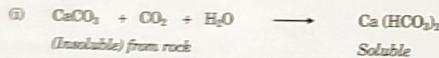
6.7.2 Dissolved Oxygen

- Dissolved oxygen is also one of the major factor to influence the hardness in water.
 - D_2O influences oxidation and hydration of metal oxides / sulphides as,



6.7.3 Dissolved CO₂

- 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.



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

6.8 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.

Calculation of Equivalents of CaCO_3

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

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

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

For example, 162 parts by mass of Ca(HCO₃)₂ (or 2 equivalents) would react with the same amount of soap as 100 parts by mass of CaCO₃ (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 of CaCO_3 .

Table 6.8.1 gives the multiplication factor for converting various substances into equivalents of calcium carbonates.

Table 6.8.1 : Calcium carbonate equivalents for soils

Dissolved salt	Molecular weights	Equivalent weight	Multiplication factor
(1) Salts of calcium :			
(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
(2) Salts of magnesium :			
(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
(3) Other salts/gases/acids :			
(a) NaAlO_2	82	82	100 / 164
(b) $\text{Al}_2(\text{SO}_4)_3$	342	57	100 / 114
(c) $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$	278	139	100 / 278
(d) HCl	36.5	36.5	100 / 73
(e) CO_2	44	22	100 / 44



Dissolved salt	Molecular weights	Equivalent weight	Multiplication factor
(4) Ions :			
(a) HCO_3^-	61	61	100 / 122
(b) CO_3^{2-}	60	30	100 / 60
(c) OH^-	17	17	100 / 34
(d) H^+	1	1	100 / 2

6.9 Units of Hardness

The following are the different 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 ($^{\circ}\text{Fr}$)

Most commonly ppm or mg/litre is used.

(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).

$$1 \text{ mg / litre} = 1 \text{ ppm}$$

Water classification on basis of hardness

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

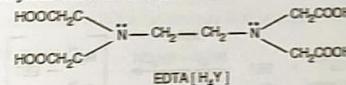
6.10 Determination of Hardness of Water

The hardness of water can be determined by following methods :

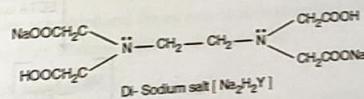
- (i) EDTA method – Used most widely
- (ii) O' Hehler's method – Not used commonly
- (iii) Soap titration method – Not used commonly

6.10.1 Determination of Hardness by EDTA Method

- EDTA is abbreviation of Ethylene diamine tetra acetic acid.



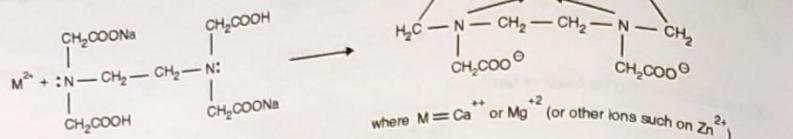
- This compound dissolves in water with great difficulty and in a very very small quantity.
- On the contrary its di-sodium salt dissolves in water quickly and completely. Hence for common experimental purpose, in place of EDTA, its di-sodium derivative is used.



- EDTA is a hexadentate ligand. It binds the metal ions in water i.e. Ca^{2+} or Mg^{2+} to give highly stable chelate complex. (These metal ions are bonded via oxygen or nitrogen from EDTA molecule).

Therefore, this method is called as complexometric titration.

The formation and structure of complex is as shown below :



6.10.2 Principle of EDTA Method

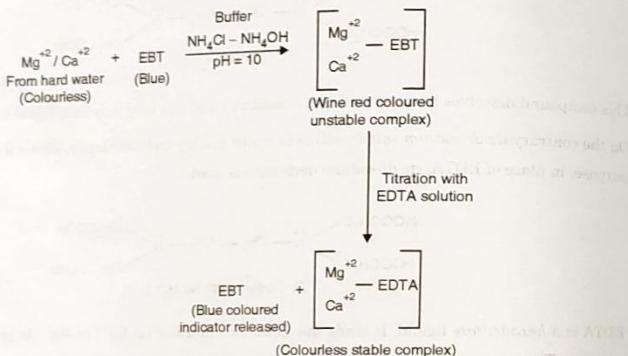
MU - May 14, Dec. 14, Dec. 18

University Questions

- Q. Give the principle of estimation of hardness of water using EDTA method (only equations). (May 14, 3 Marks)
Q. Explain the principle of EDTA method. (Dec. 14, Dec. 18, 3 Marks)

- The di-sodium salt of Ethylene Diamine Tetra Acetic Acid (EDTA) forms complexes with Ca^{2+} and Mg^{2+} , 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 Ca^{2+} and Mg^{2+} present in an aliquot of the sample with Na EDTA solution, using NH_4Cl - NH_4OH buffer solution of $pH = 10$ and Eriochrome Black T as the metal indicator.
- At pH 10, EBT indicator form wine red coloured unstable complex with Ca^{2+}/Mg^{2+} 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).

Reaction



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

6.10.3 Procedure for EDTA Titration

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

Step 1 : Preparation of reagents

Step 2 : Titrations

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 to 1 L. The hardness of this solution would be 1 mg of $CaCO_3$ equivalent per ml (1 mg $CaCO_3$ / ml).

(b) 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.

(c) Indicator :

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

(d) Buffer solution of pH 10 :

67.5 grams of NH_4Cl are added to 570 ml of concentrated ammonia solution. The mixture is then diluted to 1 litre with distilled water.

Step 2 : Titration

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

(a) Standardization of EDTA solution :

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

(b) Estimation of total, hardness :

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

(c) Estimation of permanent hardness :

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

Using the data of V_1 , V_2 and V_3 ; total and permanent hardness is calculated. The difference of these two values gives temporary hardness of water.



Method 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).

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

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

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

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

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

$$\text{Thus, permanent hardness of water in 50 ml sample} = \left[V_3 \times \frac{50}{V_1} \right] \text{ mgs of } \text{CaCO}_3 \text{ equivalent hardness.}$$

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

From above two equations we can calculate temporary hardness as

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

Advantages of EDTA method

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

6.11 Softening of Water

- **Softening :** "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.
- Under such circumstances softening methods are required to be used.
- The following methods are used for softening of water.

1. Lime soda process.
2. Zeolite process or permuto process.
3. Ion-exchange or deionization or demineralisation process

6.11.1 Hot and Cold Lime-Soda Process / Method

MU - May 12, May 13, Dec. 13, Dec. 15

University Questions

- Q. Why is the Hot lime Soda process preferred over the Cold lime soda process? (May 12, Dec. 15, 3 Marks)
- Q. With the help of chemical equations explain the principle of lime soda process. (May 13, 6 Marks)
- Q. Give well balanced equations of the reactions that take place in the Lime soda process. (Dec. 13, 5 Marks)

Principle

- In this method hard water is treated with calculated amounts of slaked lime, $[\text{Ca(OH)}_2]$ 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,

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

Soda required for softening,

$$S = \frac{106}{100} \left[\text{Permanent } (\text{Ca}^{+2} + \text{Mg}^{+2} + \text{Al}^{+3} + \text{Fe}^{+2}) + \text{H}^+ (\text{HCl or H}_2\text{SO}_4) + \text{AlCl}_3 - \text{HCO}_3^- - \text{NaHCO}_3 \right] \text{ all in terms of their } \text{CaCO}_3 \text{ equivalents.}$$

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

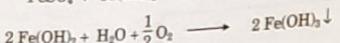
(i) Reactions with lime

Lime reacts in following ways, during softening of water.

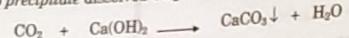
1. To neutralize any free acid present. For example
- $$\begin{array}{l} 2\text{HCl} + \text{Ca(OH)}_2 \longrightarrow \text{CaCl}_2 + 2\text{H}_2\text{O} \\ \text{H}_2\text{SO}_4 + \text{Ca(OH)}_2 \longrightarrow \text{CaSO}_4 + 2\text{H}_2\text{O} \end{array}$$



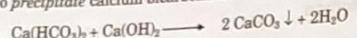
2. To precipitate iron and aluminium salts, if any, as hydroxides.



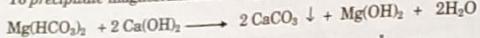
3. To precipitate dissolved CO_2 as CaCO_3



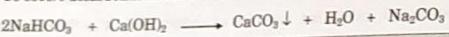
4. To precipitate calcium bicarbonate as CaCO_3



5. To precipitate magnesium salts as hydroxides.



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



Note : CaCl_2 and CaSO_4 produced are to be treated as permanent hardness. Hence in formula for Lime and soda calculations, Mg^{+2} , Al^{+3} , Fe^{+2} are considered.

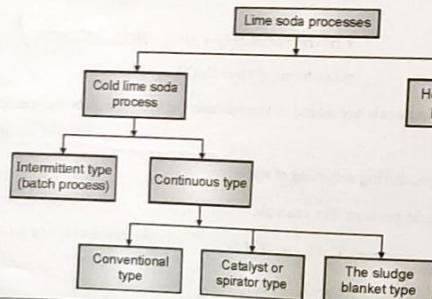
(ii) Reactions with soda

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



1. Cold lime soda process

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

Disadvantages

- 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.
- $\text{NaAlO}_2 + 2 \text{H}_2\text{O} \longrightarrow \text{NaOH} + \text{Al}(\text{OH})_3 \downarrow$ (Sodium aluminate)
- 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

(i) Intermittent type (batch process)

- In this Process, there is a set of two tanks which are used for softening water. Each tank has inlets for raw water and chemicals, and outlets for softened water and sludge.
- The tanks are equipped with mechanical stirrer.
- A calculated quantity of chemicals and raw water slowly enter the tank simultaneously and are allowed to mix thoroughly by mechanical stirring and contents of the tank are kept undisturbed for about two hours, during which precipitates settle down completely.
- The clear softened water is collected through a float pipe and sent to the filtering unit.
- The sludge formed at the bottom of the tank is removed through *sludge outlet* and washed with water.
- The continuous supply of soft water is maintained by employing a set of tanks for alternate cycles of reaction and settling.

(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.

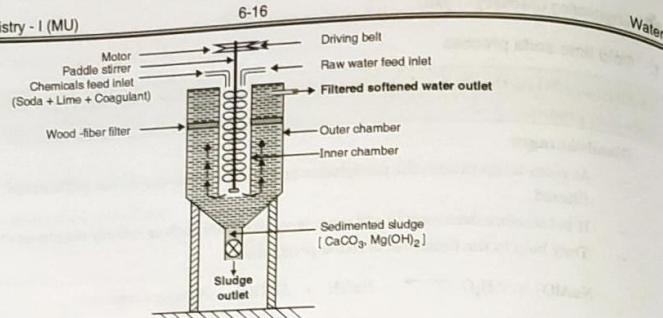


Fig. 6.11.1 : Continuous cold lime soda softener

2. Hot lime soda process

- **Definition :** 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 over cold one because, at higher temperature (i) The reactions are fast (ii) Precipitation is more complete (iii) Settling rate and filtration rates are increased.
- As a result, the *precipitate and sludge formed settle rapidly* and coagulants, and also chemicals needed are in *smaller quantities* than that of cold process.
- Dissolved gases are eliminated from water to a certain extent. The softened water recovered has hardness of about 15 to 30 ppm.

Construction :

Hot lime soda plant essentially consists of three parts.

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.

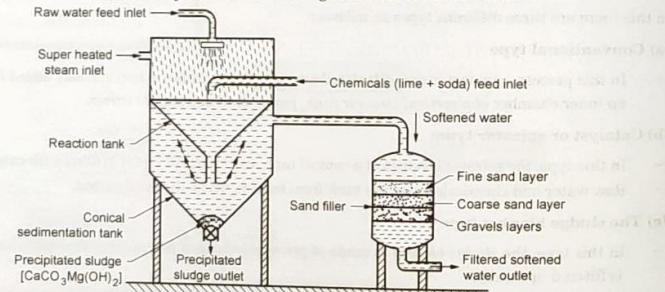


Fig. 6.11.2 : Continuous hot lime soda process

Advantages of lime soda process

1. It is a very economical process.
2. This process increases pH value of the treated water; thereby corrosion of pipes is reduced.
3. To a certain extent, iron and manganese are also reduced.
4. Certain quantity of minerals is 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

1. The hardness of softened water is about $50\text{-}60 \text{ ppm}$ by cold lime soda process which is not good for use in high pressure boilers, and about $15\text{-}30 \text{ ppm}$ 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.

6.11.2 Zeolite or Permutit Process

MU - May 12, Dec. 12, Dec. 14, May 15, Dec. 15, May 18, May 19

University Questions

- Q. Explain with a neat diagram, the Zeolite process of water softening including the following points :
 (i) Principle
 (ii) Process
 (iii) Softening and regeneration reactions
 (iv) Advantages and limitations (May 12, Dec. 14, Dec. 15, 6 Marks)
- Q. Discuss zeolite process with the help of diagram, chemical reactions and advantages. (Dec. 12, 5 Marks)
- Q. Describe Zeolite method with a labelled diagram. (May 15, 6 Marks)
- Q. Explain the zeolite method for softening of water giving suitable diagram and reactions. What are the limitations of this method ? (May 18, 6 Marks)
- Q. Draw a neat labeled diagram and explain zeolite process of softening of hard water. Discuss its merits and demerits. (May 19, 6 Marks)

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

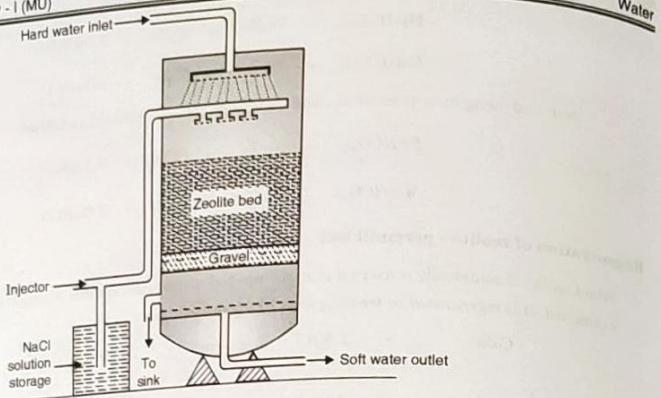


Fig. 6.11.3 : Zeolite Softner

Limitations of zeolite process

1. Turbid water (containing suspended impurities) cannot 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^{3+} , 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.

6.11.3 Ion Exchange Process / Demineralization Process

MU - May 13, May 14, May 16, Dec. 16, May 17, Dec. 18

University Questions

- Q. Explain demineralization of water by ion exchange method. (May 13, 5 Marks)
- Q. With a neat diagram explain the principle of Ion- Exchange method of softening of water and also give the softening and regeneration reactions. (May 14, 5 Marks)
- Q. Discuss the softening and regeneration reactions in the Ion-exchange process. (May 16, 6 Marks)
- Q. What are the advantages of Ion exchange process ? (Dec. 16, 3 Marks)
- Q. What are cation and anion exchangers ? (May 17, 3 Marks)
- Q. Explain Ion-Exchange process for softening of hard water. What are its advantages and disadvantages. (May 17, 6 Marks)
- Q. Draw the diagram for demineralization process and write suitable reactions involved in the process. What are the advantages and disadvantages of the method? (Dec. 18, 6 Marks)

In this process, a reversible exchange of ions occurs 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
- (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 represented as RH_2 or RH^+ .
- These resins are capable of exchanging rapidly cations like Ca^{2+} and Mg^{2+} by hydrogen ions. For example, Divinyl benzene copolymer, formaldehyde resins, Amberlite IR – 120, Zeocarb, Dowex-50, Duolite, Sulphonated or carboxylated styrene etc. are some of the commercially available cation exchange resins.
- Their exchange reactions with cations (Ca^{2+} and Mg^{2+}) are as follows :



2. Anion exchange resins ($R'(OH)^-$)

- The resin containing basic functional groups (e.g. $-NH_2$, $=NH$, etc. as hydrochloride) exchange their anions with other anions, which come in their contact are called as anion exchange resins.
- These resins are capable of exchanging rapidly anions (Cl^- , SO_4^{2-}) by OH^- ions. They are represented as $R+$ and OH^- where $R+$ represents the insoluble matrix. For example amino-formaldehyde resins, copolymer of styrene and divinyl benzene. Amberlite 400, Zeolite -FF, etc. Their exchange reactions with anions (SO_4^{2-} , CO_3^{2-} etc.) are as follows :



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

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

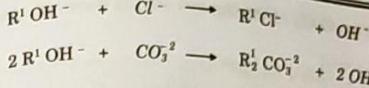
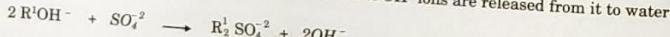
Principle of ion exchange process

- 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 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,

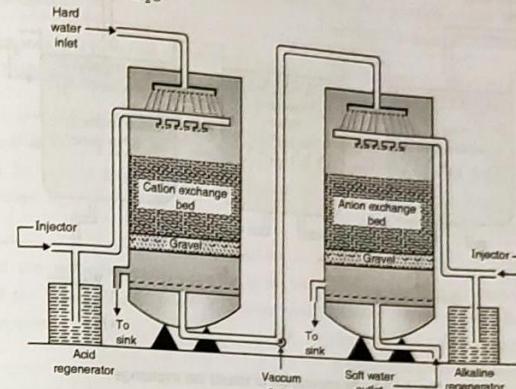
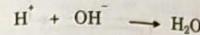


Fig. 6.11.4 : Demineralization of water

Process of ion-exchange/demineralisation

- The hard water is first passed through cation exchange column and then through anion exchange column (Fig. 6.11.4).
- Thus, the water coming out from anion exchange bed becomes *free of cations as well as from anions*.
- The resulting ion-free water is *deionised water* or *demineralised water*.
- The water is finally freed from dissolved gases by passing it through a degasifier, which is a tower heated from both sides and is connected to a *vacuum pump*.
- High temperature and low pressure reduces the quantity of dissolved gases.
- Water obtained by this process is very near to distilled water, which is the requirement of boiler feed water. *This process is very good for high pressure boilers.*

Regeneration of exhausted resins

- The capability of these ion-exchange resins to exchange ions from hard water is based on their ion-exchange capacities.
- When their ion-exchange capacities are lost, they are said to be *exhausted*.
- When the resins are exhausted, the supply of water is stopped.
- The exhausted cation exchanger is *regenerated* by passing dilute HCl or H_2SO_4 solution.

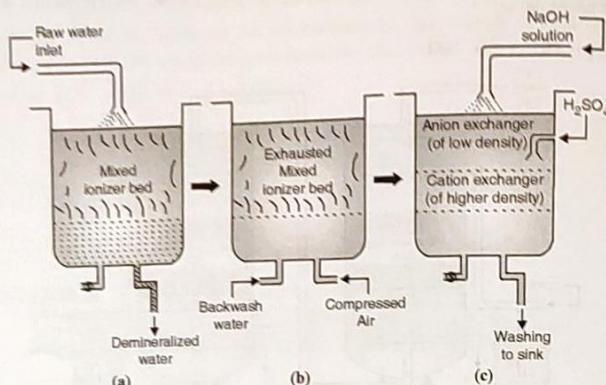
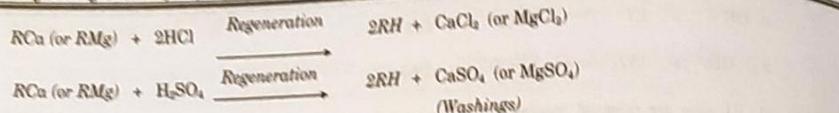
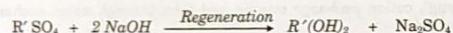
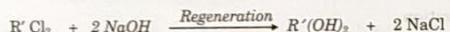


Fig. 6.11.5 : Regeneration of mixed ion exchange

- 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 Na_2SO_4) 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.

Comparison between Zeolite Process and Lime Soda Process

Table 6.11.1

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.
4.	The size of the softening plant depends upon the hardness of the water. Hence, plant is compact and occupies less space.	The size of softening plant depends upon quantity of hard water to be softened. Hence, size is not compact, but increases with quantity of water and thus occupies more space.
5.	This process cannot be used for hot water, acidic water, turbid water and water with suspended impurities.	This process does not have any such restrictions.
6.	The process is simple and efficiency is high.	The process is not simple, as it involves settling, coagulation and filtration, and hence efficiency is low.
7.	Process is disadvantageous because temporary hardness forms bicarbonates of sodium.	Process is advantageous, because temporary hardness gets completely removed as precipitates of CaCO_3 and Mg(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 caustic embrittlement.	The soft water obtained does not create problems of caustic embrittlement in boilers because the resultant products such as CaCO_3 and Mg(OH)_2 are removed by filtration.

Comparison between Ion-Exchange Process and Zeolite Process

Table 6.11.2

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.

Sr. No.	Ion-Exchange Process	Zeolite Process
2.	The resultant water is <i>suitable</i> for all types of boilers, especially <i>high pressure</i> boilers.	The resultant water is <i>not suitable</i> for use in <i>high pressure</i> boilers. Water can be <i>used only in low or medium pressure</i> boilers.
3.	The cation and anion exchange beds used are <i>more expensive</i> . Hence, capital cost is high.	Zeolite softener is comparatively <i>cheap</i> , hence capital cost is lower.
4.	The softening plant is <i>not compact</i> , hence occupies more space.	The softening plant is <i>compact</i> . Hence occupies less space.
5.	The process effectively <i>removes all the hardness</i> causing substances. 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.
7.	Soft water obtained <i>does not cause caustic embrittlement</i> in boilers and is suitable for boilers as it is free from Na^+ ions.	Soft water obtained is <i>not suitable for boilers</i> , due to the presence of NaHCO_3 , which subsequently forms NaOH , <i>causing thereby caustic embrittlement</i> in boilers.

6.12 BOD and COD

6.12.1 Biochemical Oxygen Demand (BOD)

MU - May 14, May 19

University Questions

- Q. Define and explain the significance of BOD.
Q. Define and briefly explain Biological Oxygen Demand (BOD)

(May 14, 2 Marks)

(May 19, 2 Marks)

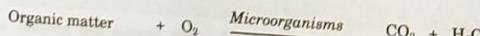
Waste water contains two types of organic matter :

- (i) Biologically active or biologically degradable organic matter which can be oxidized by bacteria.
- (ii) 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 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 :

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

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

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

Where $(\text{DO})_1$ = Dissolved oxygen of diluted water sample immediately after its preparation. $(\text{DO})_2$ = Dissolved oxygen of diluted water sample after incubation for 5 days at 20°C, mg/L

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

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

Significance of BOD :

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

Therefore, BOD

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

6.12.2 Chemical Oxygen Demand (COD)

MU - May 14, May 19

University Questions

- Q. Define and explain the significance of COD.
Q. Define and briefly explain Chemical Oxygen Demand (COD).

(May 14, 2 Marks)

(May 19, 2 Marks)

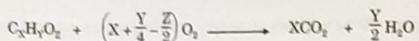
"The amount of oxygen required by organic matter in sample water for its oxidation by strong oxidizing agent is known as Chemical Oxygen Demand or COD of the sample".

Principle of determination of COD :

- A known volume of sample is refluxed with a known excess of $\text{K}_2\text{Cr}_2\text{O}_7$ solution in 50% H_2SO_4 , in the presence of Ag_2SO_4 (Catalyst), and HgSO_4 .
- $\text{K}_2\text{Cr}_2\text{O}_7$ is strong oxidizing agent, in acidic medium. It oxidizes the organic matter into CO_2 and H_2O .

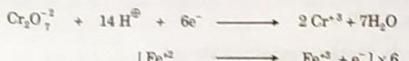
Note : Organic matter of both types i.e. (i) Biologically oxidisable and (ii) Biologically inert

Reaction :



The unreacted dichromate solution is then titrated against std. FAS solution

$(FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O)$ 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.

6.12.3 Difference between BOD and COD

University Question		MU - Dec. 12, May 13, Dec. 17, May 18
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.	$BOD = \frac{(DO)_1 - (DO)_2}{x} ppm$ Where, $(DO)_1$ = DO in blank titration $(DO)_2$ = DO of the sample after x = Volume of sample Total volume to which it was diluted	$COD = \frac{(V_2 - V_1) \times N \times 8 \times 1000}{V} ppm$ Where, V_1 = Volume of FAS for sample titration V_2 = Volume of FAS for blank titration V = Volume of sample taken for the test N = Normality of FAS solution

Sr. No.	BOD	COD
5.	BOD is normally less than COD.	COD is more than BOD as it is the measure of oxygen required for the oxidation of biologically oxidisable and biologically inert organic matter.

6.13 Water Purification (Membrane Technology)

6.13.1 Electrodialysis (ED)

MU - Dec. 13

Q. Write short notes on : Electrodialysis.

(Dec. 13, 2 Marks)

- 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 H_2S 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.

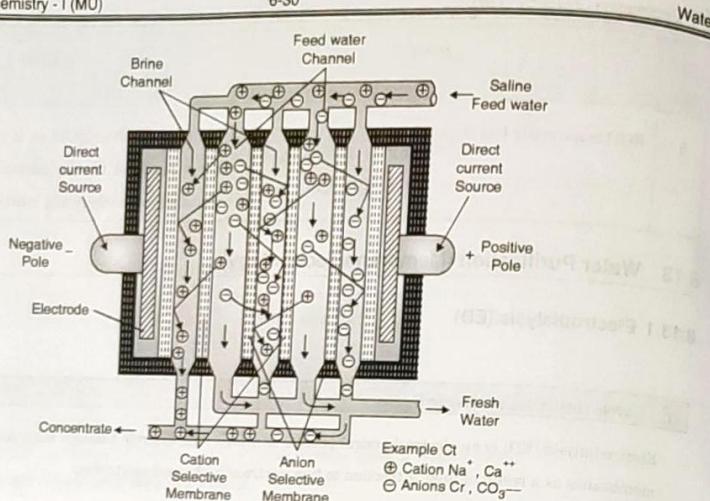


Fig. 6.13.1 : Shows movement of ions in ED

- 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 (Fig. 6.13.1).
- 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.

6.13.2 Reverse Osmosis (RO)

MU - May 12, Dec. 13, May 14, May 15, May 16, Dec. 17, May 18, Dec. 18, May 19

University Questions

- Write a short note on Reverse Osmosis. (May 12, Dec. 13, May 15, Dec. 17, Dec. 18, May 19, 3 Marks)
- Discuss the Reverse Osmosis method of purification of water. (May 14, May 16, May 18, 3 Marks)

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. 6.13.2, where the solvent flows from low concentration solution to higher concentration solution, through the semipermeable membrane, until difference in water levels creates a sufficient pressure to counteract the original flow. The difference in levels represents osmotic pressure of the solution.
- In the reverse osmosis, we apply external pressure on the higher concentration solution slightly higher than its osmotic pressure.
- The flow of solvent takes place in reverse direction i.e. from higher concentration solution to lower concentration solution, through the SPM. Thus in RO, we separate water from its contaminants rather than contaminants from water.

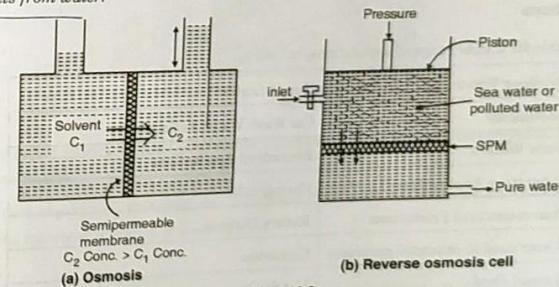


Fig. 6.13.2

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 uses 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

6.13.3 Ultrafiltration

MU - Dec. 13, May 15, Dec 16, May 17

University Questions

- Q. Write short note on Ultrafiltration.
Q. What are the industrial applications of ultrafiltration ?

(Dec. 13, May 15, May 17, 2 Marks)

(Dec. 16, 2 Marks)

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 :
 - (i) Characteristics of the membrane
 - (ii) Operating conditions
 - (iii) Quality of feed.

Process

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

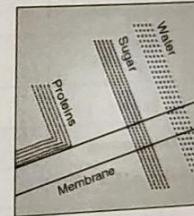


Fig. 6.13.3

- 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.



Water

- 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.

6.14 Solved Problems**6.14.1 Problems based on Carbonates and Non Carbonates Hardness (Total, Permanent, Temporary Hardness)**

Ex. 6.14.1 : A water sample contain :

- $\text{Ca}(\text{HCO}_3)_2 = 32.4 \text{ mg/l}$
- $\text{Mg}(\text{HCO}_3)_2 = 29.2 \text{ mg/l}$
- $\text{CaSO}_4 = 13.6 \text{ mg/l}$

Calculate temporary, permanent and total hardness

(At. wt. C = 40, Mg = 24, H = 1, Ca = 12, O = 16, S = 32)

Soln. :

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

$$\begin{aligned}\text{Thus, Temporary hardness} &= \text{Mg}(\text{HCO}_3)_2 + \text{Ca}(\text{HCO}_3)_2 \\ &= 20 + 20 = 40 \text{ ppm}\end{aligned}$$

$$\text{Permanent hardness} = \text{CaSO}_4 = 10 \text{ ppm}$$

$$\begin{aligned}\text{Total hardness} &= \text{Temporary} + \text{Permanent} = 40 + 10 = 50 \text{ ppm} \\ \text{Temporary Hardness} &= 40 \text{ ppm}\end{aligned}$$

$$\text{Permanent Hardness} = 10 \text{ ppm}$$

$$\text{Total Hardness} = 50 \text{ ppm}$$

...Ans.

...Ans.

...Ans.

Ex. 6.14.2 : A water sample contains :

- $\text{Mg}(\text{HCO}_3)_2 = 14.6 \text{ ppm}$
- $\text{Mg}(\text{NO}_3)_2 = 29.6 \text{ ppm}$
- $\text{Ca}(\text{HCO}_3)_2 = 8.1 \text{ ppm}$
- $\text{MgCl}_2 = 19 \text{ ppm}$
- $\text{MgSO}_4 = 24 \text{ ppm}$

Calculate the temporary and permanent hardness of water sample.

(At. wt. C = 40, Mg = 24, H = 1, Ca = 12, O = 16, S = 32)

MU - May 14, 3 Marks

Soln. :

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	$14.6 \times \frac{100}{146}$	10	Temporary
$\text{Mg}(\text{NO}_3)_2$	29.6	$29.6 \times \frac{100}{148}$	20	Permanent
$\text{Ca}(\text{HCO}_3)_2$	8.1	$8.1 \times 100/162$	05	Temporary
MgCl_2	19	$19 \times 100/95$	20	Permanent
MgSO_4	24	$24 \times 100/120$	20	Permanent

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

$$\begin{aligned}\therefore \text{Temporary hardness} &= 05 + 10 \\ &= 15 \text{ ppm}\end{aligned}$$

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

$$\begin{aligned}\therefore \text{Permanent hardness} &= 20 + 20 + 20 \\ &= 60 \text{ ppm}\end{aligned}$$

...Ans.

$$\begin{aligned}\text{Temporary hardness} &= 15 \text{ ppm} \\ \text{Permanent hardness} &= 60 \text{ ppm}\end{aligned}$$

...Ans.



Ex. 6.14.3 : Calculate temporary and total hardness of a water sample containing :

$$\text{Mg}(\text{HCO}_3)_2 = 7.3 \text{ mg/l}, \text{Ca}(\text{HCO}_3)_2 = 16.2 \text{ mg/l},$$

$$\text{MgCl}_2 = 9.5 \text{ mg/l}, \text{CaSO}_4 = 13.6 \text{ mg/l}.$$

MU - Dec. 12, 3 Marks

Soln.:

Conversion in CaCO_3 equivalents.

Salt	Quantity in ppm or mg/L	Multiplication Factor	CaCO_3 equivalent	Type of Hardness
$\text{Mg}(\text{HCO}_3)_2$	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

$$\text{Thus Temporary Hardness} = \text{Mg}(\text{HCO}_3)_2 + \text{Ca}(\text{HCO}_3)_2 \\ = 05 + 10 = 15 \text{ ppm}$$

$$\text{Permanent Hardness} = \text{MgCl}_2 + \text{CaSO}_4 = 10 + 10 = 20 \text{ ppm}$$

$$\begin{aligned}\text{Total Hardness} &= \text{Temporary Hardness} + \text{Permanent Hardness.} \\ &= \text{Mg}(\text{HCO}_3)_2 + \text{Ca}(\text{HCO}_3)_2 + \text{MgCl}_2 + \text{CaSO}_4 \\ &= 05 + 10 + 10 + 10 = 35 \text{ ppm}\end{aligned}$$

$$\text{Temporary Hardness} = 15 \text{ ppm}$$

$$\text{Total Hardness} = 35 \text{ ppm}$$

...Ans.

...Ans.

Ex. 6.14.4 : Classify the following salts into temporary and permanent hardness causing salts and also calculate their calcium carbonate equivalents.

- (i) $\text{Ca}(\text{HCO}_3)_2 - 16.2 \text{ mg/l}$
- (ii) $\text{MgSO}_4 - 1.2 \text{ mg/l}$
- (iii) $\text{FeCl}_2 - 12.7 \text{ mg/l}$
- (iv) $\text{NaCl} - 94 \text{ mg/l}$

MU - May 14, 3 Marks

Solution :

Salt	Type of Hardness	Multiplication factor for CaCO_3 equivalent	CaCO_3 equivalent mg/lit
$\text{Ca}(\text{HCO}_3)_2$	Temporary	$16.2 \times 100 / 162$	10
MgSO_4	Permanent	$1.2 \times 100 / 120$	01

Salt	Type of Hardness	Multiplication factor for CaCO_3 equivalent	CaCO_3 equivalent mg/lit
FeCl_2	Permanent	$12.7 \times 100 / 127$	10
NaCl	does not impart hardness	-	-

Ex. 6.14.5 : A water sample on analysis has been found to contain :

$$\text{MgCl}_2 = 19 \text{ mg/lit}, \text{CaCO}_3 = 5 \text{ mg/lit}$$

$$\text{Ca}(\text{HCO}_3)_2 = 29.5 \text{ mg/lit}, \text{CaSO}_4 = 13 \text{ mg/lit}.$$

Calculate temporary, permanent and total hardness.

Soln.:

Constituents	Amount present	Multiplication factor	CaCO_3 equivalents	Type of Hardness
MgCl_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

$$\therefore \text{Temporary Hardness} = 5 + 18.2 = 23.2 \text{ ppm}$$

$$\text{and } \text{Permanent Hardness} = 20 + 9.56 = 29.56 \text{ ppm}$$

$$\begin{aligned}\therefore \text{Total Hardness} &= \text{Temporary hardness} + \text{permanent hardness} \\ &= 23.2 + 29.56 = 52.76 \text{ ppm}\end{aligned}$$

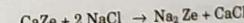
...Ans.

Ex. 6.14.6 : 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.

Soln.:

Using regeneration reaction,



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

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

Now,

Quantity of NaCl in regeneration,

$$= 30 \times 100 = 3000 \text{ gms NaCl}$$

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



$$\therefore 3000 \text{ gm NaCl} = \frac{3000 \times 100}{2 \times 58.5} = \frac{3000 \times 100}{117} = 2564.102 \text{ gms of CaCO}_3$$

$$= 2564102 \text{ mgs of CaCO}_3$$

Water

$$\therefore 4500 \text{ litres of hard water} = 2564102 \text{ mgs CaCO}_3$$

$$\therefore 1 \text{ litre of hard water} = \frac{2564102}{4500} \text{ mgs of CaCO}_3 = 56.98 \text{ mgs of CaCO}_3$$

$$= 56.98 \text{ ppm}$$

$$\therefore \text{Hardness of water sample} = 56.98 \text{ ppm}$$

...Ans.

Ex. 6.14.7 : 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?

Soln.:

Salts causing respective

Hardness are : Temperory : $\text{Ca}(\text{HCO}_3)_2$, $\text{Mg}(\text{HCO}_3)_2$
 Permanent : MgSO_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.

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

...Ans.

Ex. 6.14.8 : 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.

MU - Dec. 17, 4 Marks

Soln.:

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

Now, 1 litre of NaCl contains 30 g of $\text{NaCl} = 30000 \text{ mg NaCl}$

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

$58.5 \text{ mg of NaCl} = 50 \text{ mgs of CaCO}_3 \text{ equivalent hardness}$

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

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

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

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

$$\therefore 1 \text{ lt. of water} = \frac{3076923}{15000} \text{ mgs of CaCO}_3 = 205 \text{ mg/l of CaCO}_3$$

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

Water

$$\text{Hardness of water sample} = 205 \text{ ppm}$$

...Ans.

Ex. 6.14.9 : Two samples of water A and B were analysed for their salt content :

(i) Sample A was found to contain 168 mg MgCO_3 per litre.

(ii) Sample B was found to contain 820 mg $\text{Ca}(\text{NO}_3)_2$ per litre and 2 mg SiO_2 per litre. Calculate the total hardness of each sample and state which sample is more hard.

MU - Dec. 13, 3 Marks

Soln.:

Data Given : Sample A = $\text{MgCO}_3 = 168 \text{ mgs/litre}$

Sample B = (i) $\text{Ca}(\text{NO}_3)_2 = 820 \text{ mgs/litre}$

(ii) $\text{SiO}_2 = 2 \text{ mgs/lit.}$

To calculate Hardness of each sample.

(i) Hardness of each sample

(ii) Find the sample with higher hardness

$$\text{Sample A : CaCO}_3 \text{ equivalents of MgCO}_3 = 168 \times \frac{100}{84} = 200 \text{ mgs}$$

Thus Hardness of sample A is 200 ppm

$$\text{Sample B : CaCO}_3 \text{ equivalents of } \text{Ca}(\text{NO}_3)_2 = 820 \times \frac{100}{164} = 500 \text{ mgs/lit or ppm}$$

SiO_2 does not contribute to hardness.

Thus Hardness of sample B is 500 ppm.

Hardness sample A = 200 ppm

Sample B = 500 ppm i.e. sample B is of higher hardness.

...Ans.

...Ans.

Ex. 6.14.10 : An exhausted zeolite softener was regenerated by passing 150 litres of NaCl solution having a strength of 150 g/L of NaCl . If the hardness of the water is 600 ppm. Calculate the total volume of water that is softened by the softener.

MU - Dec. 13, Dec. 18, 4 Marks

Soln. :

Data given : Volume of NaCl solution = 150 litres

Weight of $\text{NaCl} = 150 \text{ gms / litre}$

Hardness of water sample = 600 ppm

To calculate volume of water softened

Quantity of NaCl consumed = $150 \times 150 = 22500 \text{ gms} = 22.5 \times 10^6 \text{ mgs}$

CaCO_3 equivalents of $\text{NaCl} = 22.5 \times 10^6 \times \frac{50}{58.5} \text{ mgs} = 19.23 \times 10^6 \text{ mgs}$

Now 600 mgs $\text{CaCO}_3 \equiv 1 \text{ Litre water}$



Hence, $19.23 \times 10^6 \text{ mgs CaCO}_3 \equiv 19.23 \times \frac{10^6}{600} \text{ litres} = 32050 \text{ litres water.}$

Volume of water softened = 32050 litres.

...Ans.

6.14.2 Problems based on Calculation of Hardness by EDTA Method

Method of calculation

Titrations carried out in this method are :

- 50 ml Standard Hard Water (SHW) [containing 1 mg/ml CaCO_3 equivalent hardness] against EDTA solution = V_1 ml
- 50 ml unknown hard water (HW) against EDTA solution = V_2 ml.
- 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,

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

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

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.

$$\text{Thus, permanent hardness of water in 50 ml sample} \equiv \left[V_3 \times \frac{50}{V_1} \right] \text{ mgs of CaCO}_3 \text{ equivalent hardness.}$$

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

From above two equations we can calculate temporary hardness as

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

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

Ex. 6.14.11 : 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 Eriochrome Black T indicator.

Soln. :

Given data : Quantity of std. hard water = 50 ml
(1 mg/ml CaCO_3 equivalent)

Quantity of EDTA solution consumed by SHW = 20 ml

Quantity of water sample = 50 ml

Quantity of EDTA solution consumed by sample = 30 ml

Standardisation of EDTA

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

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

Calculation of total hardness

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

$$\therefore 1 \text{ ml HW} \equiv \frac{30}{50} \text{ ml EDTA solution} \equiv \frac{30}{50} \times \frac{50}{20} \text{ mgs. CaCO}_3 \text{ equivalent}$$

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

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

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

...Ans.

Ex. 6.14.12 : 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.

Soln. :

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

Concentration of standard hard water = 0.28 mg/ml

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

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

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

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

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

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

$$\frac{33 \times 1000}{100}$$

∴ 1000 ml of unknown hard water contains = $330 \text{ mgs of CaCO}_3 \text{ equivalent hardness}$

$$= 330 \text{ mgs of CaCO}_3 \text{ equivalent hardness}$$

$$\therefore \text{Total hardness i.e. H}_{\text{Total}} = 330 \text{ mg/l}$$

Now, 100 ml of boiled water required 10 ml EDTA

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

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

$$\therefore 1000 \text{ ml of boiled water contains} = \frac{1000 \times 10}{100}$$

$$= 100 \text{ mg of CaCO}_3 \text{ equivalent hardness}$$

$$\therefore \text{Permanent hardness i.e. H}_{\text{Permanent}} = 100 \text{ mg/L}$$

$$\text{Now, } H_{\text{Temporary}} = H_{\text{Total}} - H_{\text{Permanent}} = 330 - 100 = 230 \text{ mg/L}$$

$$\text{Total hardness of water} = 330 \text{ mg/l}$$

...Ans.

$$\text{Permanent hardness of water} = 100 \text{ mg/l}$$

...Ans.

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

...Ans.

Ex. 6.14.13 : 50 ml of standard hard water (1.2 g CaCO₃ / lit) requires 32 ml of EDTA solution. 100 ml of water sample consumes 14 ml EDTA solution. 100 ml of boiled and filtered water sample consumes 8.5 ml EDTA solution. Calculate temporary hardness of this sample from above experimental data.

Soln.:

Given data : Concentration of SHW = 1.2 g/lit

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

$$\text{Quantity of EDTA consumed by 50 ml S.H.W.} = 32 \text{ ml} = V_1$$

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

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

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

$$\text{Hardness} = ?$$

Standardization of EDTA

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

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

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

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

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

$$1 \text{ ml EDTA} = \frac{6.0}{32} = 0.15 \text{ mgs of CaCO}_3 \text{ equivalent H}$$

Calculation of total Hardness

$$100 \text{ ml H.W sample} = 14 \text{ ml EDTA} = 14 \times 0.15 \text{ mgs of CaCO}_3 \text{ per 100 ml of HW}$$

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

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

Calculation of permanent hardness

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

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

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

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

$$= 21 - 12.75 = 8.25 \text{ mgs of CaCO}_3$$

$$\therefore \text{Total hardness} = 21 \text{ ppm}$$

...Ans.

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

...Ans.

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

...Ans.

Ex. 6.14.14 : 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.

Soln.:

Given : Concentration of SHW = 15 g/lit = 15000 mg / 1000 ml

$$= 15 \text{ mg/ml}$$

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

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

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

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

$$\text{Volume of water sample (after boiling)} = 100 \text{ ml}$$

$$\text{Volume of EDTA for sample (after boiling)} = 12 \text{ ml} = V_3$$

$$\therefore 20 \text{ ml SHW} = 25 \text{ ml EDTA soln.} \equiv 300 \text{ mgs of CaCO}_3 \text{ Equivalent Hardness}$$

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

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

$$\text{Now, } 100 \text{ ml water sample} = 18 \text{ ml EDTA solution}$$

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

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

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

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

Now, 100 ml. water sample (after boiling) = 12 ml. EDTA solution

$$= [12 \times 12] \text{ mgs of } \text{CaCO}_3 \text{ Equation}$$

$$= 144 \text{ mgs of } \text{CaCO}_3 \text{ Equation}$$

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

$$\therefore \text{permanent Hardness} = 1440 \text{ ppm}$$

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

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

...Ans.

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

...Ans.

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

...Ans.

Ex. 6.14.15 : 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 solution after boiling and filtering required 10 ml of EDTA solution. Calculate temporary hardness of water.

Soln.:

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

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

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

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

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

$$\therefore 1 \text{ ml EDTA solution} = \left(\frac{50}{48} \right) \text{ mgs } \text{CaCO}_3 \text{ equivalent hardness}$$

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

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

sample

$$\therefore \text{Hardness per litre of sample} = \left[15 \times \frac{50}{48} \right] \times \frac{1000}{50} \text{ mgs/lit.} = \left[\frac{750}{48} \right] \times 20 \text{ mgs/lit.}$$

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

$$50 \text{ ml water sample after boiling} = 10 \text{ ml EDTA solution}$$

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

$$\therefore \text{Permanent hardness of one litre sample} = \left(10 \times \frac{50}{48} \right) \times \frac{1000}{50} \text{ mgs/lit.} = \left(\frac{500}{48} \right) \times 20 \text{ mgs/lit.}$$

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

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

$$= 312.50 - 208.33$$

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

$$\text{Total hardness} = 312.50 \text{ ppm}$$

...Ans.

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

...Ans.

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

...Ans.

Ex. 6.14.16 : 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.

MU - May 13, May 19, 6 Marks

Soln.:

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

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

$$\text{Now } 50 \text{ ml SHW required} = 45 \text{ ml EDTA} = 50 \text{ mgs } \text{CaCO}_3$$

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

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

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

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

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

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

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

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

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

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

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

$$= 333.33 - 222.22 = 111.11$$

$$\text{Total Hardness} = 333 \text{ ppm}$$

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

...Ans.

Ex. 6.14.17 : 1 gm of CaCO_3 was dissolved in 1 liter of distilled water, 50 ml of this solution required 45 ml of EDTA solution 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 hardness of water.

...Ans.

Soln.:

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

Quantity of SHW (1g/lit) = 50 ml

Quantity of EDTA consumed by 50 ml SHW = 45 ml

Quantity of hard water sample = 50 ml

Quantity of EDTA consumed = 25 ml

Quantity of EDTA consumed after boiling = 15 ml

Hardness = ?

Water

Standardization of EDTA :

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

$$= 1000 \text{ mgs / lit}$$

$$= \frac{1000}{1000} = 1 \text{ mg / ml CaCO}_3 \text{ equivalents hardness}$$

$$50 \text{ ml SHW} = 50 \times 1 \text{ mg CaCO}_3 = 50 \text{ mgs CaCO}_3$$

$$45 \text{ ml EDTA} = 50 \text{ ml SHW} = 50 \text{ mgs CaCO}_3$$

$$1 \text{ ml EDTA} = \frac{50}{45} = 1.11 \text{ mgs of CaCO}_3 \text{ equivalent hardness}$$

Calculation of total hardness :

$$\begin{aligned} 50 \text{ ml H.W. sample} &= 25 \text{ ml EDTA} = 25 \times 1.11 \text{ mgs of CaCO}_3 \text{ per 50 ml} \\ &= 27.75 \text{ mgs of CaCO}_3 \end{aligned}$$

$$\therefore \text{Total H per litre} = 555 \text{ mgs of CaCO}_3$$

Calculation of permanent hardness :

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

$$\text{Hence per litre} = 333 \text{ mgs of CaCO}_3$$

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

$$= 555 - 333 = 222 \text{ mgs of CaCO}_3$$

$$\therefore \text{Total hardness} = 555 \text{ ppm}$$

$$\therefore \text{Permanent hardness} = 333 \text{ ppm}$$

$$\therefore \text{Temporary hardness} = 222 \text{ ppm}$$

...Ans.

...Ans.

Ex. 6.14.18: 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. Calculate each type of hardness.

Soln.:

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

∴ 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

∴ 1 ml of $\frac{N}{20}$ CaCO_3 correspond to 0.0025 gm of 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 $\text{CaCO}_3 = 18$ mgs CaCO_3

∴ 1000 ml of hard water correspond to = (18×20) mgs CaCO_3 /lit = 360 ppm

Hardness of water = 360 ppm

Water

...Ans.

Ex. 6.14.19: 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.

Soln.:

Data given : Weight of $\text{CaCO}_3 = 1.2$ 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.

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

and Concentration of SHW = 1.2 g/lit = 1200 mg / 1000 ml.

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

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

$$= 24.0 \text{ mgs}$$

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

∴ 1 ml. EDTA = $\frac{24}{35}$ mgs equivalent CaCO_3 equivalent hardness

∴ Total hardness per 50 ml. = $\left(V_2 \times \frac{24}{35} \right)$ mgs of CaCO_3 equivalent hardness

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

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

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

$$\therefore \text{Permanent hardness per 100 ml} = \left(V_3 \times \frac{24}{35} \right) \text{ mgs of } \text{CaCO}_3 \text{ equivalent hardness}$$

$$\text{Water}$$

$$= \left(25 \times \frac{24}{35} \right) \text{ mgs of CaCO}_3 \text{ equivalent hardness} = 17.14 \text{ mgs}$$

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

Temporary Hardness = Total H. - Perm H. = 411.4 - 171.4
 = 240.0 ppm.

Total H. = 411.4 ppm. ...Ans.

Permanent H. = 171.4 ppm. ...Ans.

Temporary H. = 240.0 ppm. ...Ans.

Ex. 6.14.20 : What is the total hardness of sample of water which has the following impurities in mg/l.

$\text{Ca}(\text{HCO}_3)_2 = 162$ $\text{CaCl}_2 = 22.2$

$\text{MgCl}_2 = 95$ $\text{NaCl} = 20$

MU - May 13, 3 Marks

Soln.:

Impurity	Quantity of mg/l	Multiplication factor	CaCO ₃ eq. ppm.	Type of Hardness
Ca(HCO ₃) ₂	162	$162 \times \frac{100}{162}$	100	Temporary
CaCl ₂	22.2	$22.2 \times \frac{100}{111}$	20	Permanent
MgCl ₂	95	$95 \times \frac{100}{95}$	100	Permanent
NaCl	Does not contributes to Hardness.			

$$\text{Total Hardness} = \text{Temporary H} + \text{Permanent H}$$

$$= \text{Ca}(\text{HCO}_3)_2 + \text{CaCl}_2 + \text{MgCl}_2 = 100 + 20 + 100 \text{ mg}$$

$$= 220 \text{ mgs/lit or ppm}$$

$$\text{Total Hardness of sample} = 220 \text{ ppm.} \quad \dots\text{Ans.}$$

Ex. 6.14.21 : Calculate all types of hardness of water sample containing :

$\text{Ca}(\text{HCO}_3)_2 = 81 \text{ ppm}$, $\text{MgSO}_4 = 60 \text{ ppm}$, $\text{MgCO}_3 = 42 \text{ ppm}$, $\text{Ca}(\text{NO}_3)_2 = 82 \text{ ppm}$. **MU - Dec. 14, 3 Marks**

Soln.:

Conversion of all the quantities of various chemicals in terms of CaCO₃ equivalents in ppm

	Impurity	Qty in mgs/lit	Mol. wt.	Type of hardness	CaCO ₃ equivalent ppm
1.	Ca(HCO ₃) ₂	81	162	Carbonate	$81 \times \frac{100}{162} = 50$

Impurity	Qty in mgs/lit	Mol. wt.	Type of hardness	CaCO ₃ equivalent ppm
2. MgSO ₄	60	120	Non-carbonate	$60 \times \frac{100}{120} = 50$
3. MgCO ₃	42	84	Carbonate	$42 \times \frac{100}{84} = 50$
4. Ca(NO ₃) ₂	82	100/164	Non-carbonate	$82 \times 100/164 = 50$

Calculation of carbonate (Temporary hardness)

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

$$= [50 + 50] = 100 \text{ ppm.}$$

Calculation of non-carbonate (permanent) hardness

$$= [\text{CaCO}_3 \text{ equivalent in ppm of } \text{Ca}(\text{NO}_3)_2 + \text{MgSO}_4]$$

$$= [50 + 50] = 100 \text{ ppm.}$$

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

$$= (100 + 100) \text{ ppm} = 200 \text{ ppm.}$$

$$\text{Carbonate (Temporary hardness)} = 100 \text{ ppm} \quad \dots\text{Ans.}$$

$$\text{Non-carbonate (Permanent) hardness} = 100 \text{ ppm} \quad \dots\text{Ans.}$$

$$\text{Total hardness} = 200 \text{ ppm} \quad \dots\text{Ans.}$$

Ex. 6.14.22 : 50 ml of standard hard water containing 1 mg of pure CaCO₃ per ml consumed 20 ml of EDTA. 50 ml of the water sample consumed 30 ml of same EDTA solution using Eriochrome Black T indicator. After boiling and filtering, 50 ml of the water sample required 10 ml of the same EDTA for titration. Calculate the total and permanent hardness of water sample. **MU - Dec. 13, 6 Marks**

Soln.:

Standard Hard Water concentration = 1mg/ml.

Data given : Standard Hard Water concentration = 1mg/ml.

Vol. of EDTA for 50 ml of SHW = 20 ml [V₁]

Vol. of EDTA for 50 ml sample = 30 ml [V₂]

Vol. of EDTA for 50 ml sample after boiling = 10 ml [V₃]

To calculate all types of Hardness in sample.

50 ml SHW ≡ 20 ml

Since

EDTA ≡ 50 mgs CaCO₃

1 ml EDTA ≡ 50/20 mgs

Hence

CaCO₃ = 2.50 mgs CaCO₃ eq. hardness

Now Total Hardness = $\left[V_2 \times 2.50 \times \frac{1000}{50} \text{ ppm} \right] = 1500 \text{ ppm}$

$$\text{Now Permanent Hardness} = \left[V_s \times 2.50 \times \frac{1000}{50} \text{ ppm} \right] = 500 \text{ ppm}$$

$$\begin{aligned}\text{Hence Temporary Hardness} &= H_{\text{Total}} - H_{\text{Permanent}} \\ &= 1500 - 500 = 1000 \text{ ppm}\end{aligned}$$

$$\text{Total Hardness} = 1500 \text{ ppm}$$

...Ans.

$$\text{Permanent Hardness} = 500 \text{ ppm}$$

...Ans.

$$\text{Temporary Hardness} = 1000 \text{ ppm}$$

...Ans.

Ex. 6.14.23 : Calculate the total hardness in ppm, in given water sample.

(i) 50 ml of standard hard water, containing 1 mg pure CaCO_3 per ml consumed 20 ml EDTA solution.

(ii) 50 ml of water sample consumed 30 ml EDTA solution using EBT Indicator. **MU - May 18, 4 Marks**

Soln. :

Given data

$$\text{Quantity of std. hard water} = 50 \text{ ml} \quad (1 \text{ mg/ml } \text{CaCO}_3 \text{ equivalent})$$

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

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

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

Standardisation of EDTA

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

$$\therefore 1 \text{ ml EDTA solution} = \frac{50}{20} \text{ ml SHW} = \frac{50}{20} \times 1 \text{ mg/mg } \text{CaCO}_3 \text{ equivalent}$$

Calculation of total hardness

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

$$\therefore 1 \text{ ml HW} = \frac{30}{50} \text{ ml EDTA solution} = \frac{30}{50} \times \frac{50}{20} \text{ mg/mg } \text{CaCO}_3 \text{ equivalent}$$

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

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

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

...Ans.

6.14.3 Numericals based on Ion Exchange Method

Ex. 6.14.24 : 10^3 L water was softened by I.E. method. For regeneration, 150 L of 0.1 N each of HCl and NaOH was needed by respective exhausted resins.

Calculate hardness of sample.

Soln. :

In I. E.,

Cations exchanged by cation exchanger and Anions exchanged by Anion exchanger.

Amount of acid or alkali used to regenerate the resin \equiv hardness of water sample.

$$\text{Hence, If } 10^3 \text{ L water} \equiv 150 \text{ L of } 0.1 \text{ N HCl}$$

$$\equiv 150 \text{ L of } 0.1 \text{ N NaOH}$$

$$\equiv 150 \times 0.1 \text{ L of } 1 \text{ N } \text{CaCO}_3 \equiv 15 \text{ L} \quad (\text{eq. Of } \text{CaCO}_3)$$

$$1 \text{ N } \text{CaCO}_3 \equiv 50 \text{ g}$$

$$10^3 \text{ L water} \equiv 15 \times 50 = 750 \text{ g. } \text{CaCO}_3 \text{ eq}$$

$$1 \text{ L water} \equiv \frac{750}{10^3} = 0.75 \text{ g } \text{CaCO}_3 \text{ eq.}$$

$$= (0.75 \times 1000) \text{ mg } \text{CaCO}_3 \text{ eq./lit}$$

$$\text{Hardness of water sample} = 75 \text{ mg/L or } 75 \text{ ppm.}$$

...Ans.

Ex. 6.14.25 : 100000 L of hard water was softened by I.E. method, and the exhausted resins were regenerated by 200 Litres of 0.1 N HCl and NaOH solutions each. Calculate hardness of water sample in ppm.

Soln. :

In I. E. method,

Cation exchange resin is regenerated by dil. HCl and Anion exchange resin is regenerated by dil. NaOH.

Amount of acid or alkali required for regeneration of respective resins \equiv Hardness of water sample.

If 100000 L of water softened and 200 L of 0.1 N HCl/NaOH is consumed for regeneration of resin.

$$\text{Then, } \text{Quantity of HCl} \equiv 200 \times 0.1 = 20 \text{ L eq. of } \text{CaCO}_3$$

$$\text{Now } 1 \text{ L } 1 \text{ N } \text{CaCO}_3 \equiv 50 \text{ gms of } \text{CaCO}_3$$

$$20 \text{ L } 1 \text{ N } \text{CaCO}_3 \equiv (50 \times 20) \text{ gm of } \text{CaCO}_3 \text{ eq}$$

$$\equiv 1000 \text{ gm of } \text{CaCO}_3 \text{ eq}$$

$$100000 \text{ L water} \equiv 1000 \text{ gm of } \text{CaCO}_3 \text{ eq}$$

$$1 \text{ L water} = \frac{1000}{100000} \text{ gm of } \text{CaCO}_3 \text{ eq}$$

$$\equiv 1 \times 10^{-2} \text{ gm of } \text{CaCO}_3 \text{ eq}$$

$$= (1 \times 10^{-2} \times 10^6) \text{ mg/g of } \text{CaCO}_3$$

...Ans.

$$\therefore \text{Hardness of water} = 10 \text{ ppm}$$

Ex. 6.14.26 : The exhausted ion exchange resins consumed 250 L. 0.1 N HCl and same of NaOH solutions for regeneration. The resins were used to soften 10^6 L water. Calculate total hardness of water sample in ppm.

Soln. :

Given data : Volume of Hard water : 10^6 L

Volume of HCl and NaOH solution : 250 L each

Normality of HCl and NaOH solution : 0.1 N each

To calculate : Hardness of water

In Ion exchange method, cation and anion exchanges are regenerated by HCl and NaOH solution.

$$\begin{aligned} \therefore \text{If } 10^3 \text{ L hard water} &\equiv 250 \text{ L } 0.1 \text{ N HCl} \\ &\equiv 250 \text{ L } 0.1 \text{ N NaOH [Equation of } \text{CaCO}_3] \\ &\equiv [250 \text{ L } \times 0.1 \text{ N}] 1 \text{ N CaCO}_3 \text{ eq.} \\ &\equiv 25 \text{ L eq CaCO}_3 (1 \text{ N}) \\ \therefore 1 \text{ N CaCO}_3 &\equiv 50 \text{ gm CaCO}_3 \\ \therefore 10^3 \text{ L water} &\equiv (25 \text{ L} \times 50) = 1250 \text{ g CaCO}_3 \text{ eq.} \\ \therefore 1 \text{ L water} &\equiv \left(\frac{1250}{10^3} \right) = 0.0125 \text{ g CaCO}_3 \text{ eq.} \\ &= (0.0125 \times 1000) \text{ mgs CaCO}_3 \text{ eq.} \\ \therefore \text{Hardness of water} &= 12.5 \text{ mg/l or ppm.} \end{aligned}$$

...Ans.

Ex. 6.14.27 : 25000 L Hard water was softened by Ion exchanger resins. For regeneration of exhausted resins, 150 L of 0.1 N HCl and 0.1 N NaOH solutions were consumed. Calculate Hardness of the water sample.

Soln.:

Data given : Volume of Hard water : 25000 L

Volume of HCl and NaOH solution : 150 L each

Normality of HCl and NaOH solution : 0.1 N each

To calculate : Hardness of water sample

Calculation : In Ion exchange method, the quantity of dil. Acid / dil. Alkali needed for regeneration is directly dependent on the total hardness of water sample i.e. the cations and anion exchanged.

$$\begin{aligned} \therefore \text{If } 25000 \text{ L hard water} &\equiv 150 \text{ L } 0.1 \text{ N HCl} \\ &\equiv 150 \text{ L } 0.1 \text{ N NaOH } \quad \text{[Equation of } \text{CaCO}_3] \\ &\equiv [150 \times 0.1] = 15 \text{ L } 1 \text{ N CaCO}_3 \text{ eq.} \end{aligned}$$

Now 1 N 1 L CaCO₃ ≡ 50 g CaCO₃

∴ 25000 L water ≡ (15 × 50) g CaCO₃ eq. ≡ 750 gms CaCO₃ eq.

$$\begin{aligned} \therefore 1 \text{ L water} &\equiv \left(\frac{750}{25000} \right) \text{ gms CaCO}_3 \text{ eq.} \\ &= \left(\frac{750}{25000} \times 1000 \right) \text{ mgs CaCO}_3 \text{ eq.} \equiv 30 \text{ mgs CaCO}_3 \text{ eq.} \end{aligned}$$

∴ Hardness of water sample = 30 mg/L or ppm.

...Ans.

Ex. 6.14.28 : The exhausted ion exchange resin, on softening 105 L water, was regenerated. The quantity of acid and alkali consumed was 300 L each of 0.1 N strength. Calculate the total hardness of water sample.

Soln.:

Data given : Volume of Hard water : 105 L

Volume of acid and alkali solution : 300 L each

Normality of acid and alkali solution : 0.1 N each

To calculate : Hardness of water sample

Calculation : Water softened = 105 L
and acid consumed for regeneration ≡ (300 × 0.1) L acid ≡ (300 × 0.1) L alkali
≡ eq. 1 N CaCO₃ ≡ (300 × 0.1)
≡ 30 L 1 N CaCO₃ eq.

Now 1 N CaCO₃ ≡ 50 g/L

Thus 105 L water ≡ (30 × 50) g ≡ 1500 g. CaCO₃ eq.

$$\begin{aligned} \therefore 1 \text{ L water} &\equiv \left(\frac{1500}{105} \times 1000 \right) \text{ mgs CaCO}_3 \text{ eq.} \\ &= 15 \text{ mgs / L CaCO}_3 \text{ eq.} \end{aligned}$$

∴ Total hardness of water = 15 ppm.

...Ans.

6.14.4 Numericals on COD and BOD

Ex. 6.14.29 : A Zeolite softener was regenerated by passing 200 litre of NaCl solution, containing 50 g/litre of NaCl. How many litre of water of hardness 50 ppm can be softened by this softener

MU - May 15. 4 Marks

Soln.:

1 L. solution ≡ 50 gms NaCl

∴ 200 litre solution ≡ 10000 gms NaCl

≡ 10000 × 50 / 58 gms equivalents of CaCO₃

≡ 8620.690 gms CaCO₃ equivalent

≡ 8620690 mgs CaCO₃ equivalent

Thus zeolite bed removed 8620690 mgs equivalent of CaCO₃ hardness.

∴ 50 ppm hardness ≡ 1 litre of water

∴ 8620690 ppm hardness ≡ 8620690 × 1 / 50 litres of water

≡ 1724413.8 litres of water

≡ 1724413.8 litres of water

...Ans.

Ex. 6.14.30 : 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.

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

6.4 – 1.6 = 4.8 ml of 0.05 N thiosulphate solution

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

$$4.8 \text{ ml of } 0.05 \text{ thiosulphate solution} = [(8 * 4.8 * 0.05)/1000] * 100/300 \\ = 3.4 \times 10^{-4} \text{ g oxygen for } 5 \text{ ml of sewage sample}$$

Oxygen required for 1000 ml of sewage sample = 0.128 g

BOD for sample = 1285 mg/lit

...Ans.

Ex. 6.14.31 : The hardness of 50,000 litres of a sample of water was removed by passing it through a zeolite softener. The softener required 200 litres of NaCl solution containing 125g/L of NaCl for regeneration. Calculate the hardness of the sample of water.

MU - May 14, 4 Marks

Soln.:

Using regeneration reaction,



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

Now, Quantity of NaCl in regeneration,

$$= 125 * 200 = 25000 \text{ gms NaCl}$$

$$\text{Thus, } (2 * 58.5) \text{ gms NaCl} \Rightarrow 100 \text{ gm CaCO}_3$$

$$\therefore 25000 \text{ gm NaCl} \Rightarrow \frac{25000 * 100}{2 * 58.5} = 21367 \text{ gms of CaCO}_3$$

$$= 213600 \text{ mgs of CaCO}_3$$

$$\therefore 50000 \text{ litres of hard water} = 21367500 \text{ mgs CaCO}_3$$

$$\therefore 1 \text{ litres of hard water} = \frac{21365000}{50000} = 427.3 \text{ mgs of CaCO}_3 = 427.3 \text{ ppm}$$

$$\therefore \text{Hardness of water sample} = 427.3 \text{ ppm}$$

...Ans.

Ex. 6.14.32 : 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.

MU - May 17, Dec. 18, 3 Marks

Soln.:

COD calculation

Data given : Volume of sample : 10 ml

Volume of $\text{K}_2\text{Cr}_2\text{O}_7$: 20 ml

Volume of FAS : 36.2 ml

Strength of FAS : 0.1 M

Blank for 20 ml $\text{K}_2\text{Cr}_2\text{O}_7$: 46 ml same FAS

Difference in the volumes of the FAS required for the blank and sample solution = $36 - 26.2 = 9.8 \text{ ml}$

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

Water

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

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

$$\text{Oxygen required for } 1000 \text{ ml of waste water} = 0.784 \text{ g}$$

$$\text{COD for waste water sample} = 784 \text{ mg/lit}$$

Water

...Ans.

Ex. 6.14.33 : The hardness of 100,000 litres of water completely removed by passing through zeolite softener, the softener than requires 400 litres of NaCl solution containing 100g/litre NaCl for regeneration. Calculate hardness of water sample.

MU - Dec. 12, 4 Marks

Soln.:

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

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

$$\therefore 400 \text{ litre of NaCl solution contains} = 400 * 100$$

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

$$\text{Now } \because 58.5 \text{ mg NaCl} \equiv 50 \text{ mgs CaCO}_3 \text{ equivalents.}$$

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

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

But the total quantity of water sample = 100000 litres

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

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

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

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

$$\text{Hardness of water sample} = 342 \text{ ppm.}$$

...Ans.

Ex. 6.14.34 : 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.

Soln.:

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

$$5.4 \text{ ml of } 0.05 \text{ thiosulphate solution} = [(8 * 5.4 * 0.05)/1000] * 100/300$$

$$= 7.2 * 10^{-4} \text{ g oxygen for } 10 \text{ ml of sewage sample}$$

$$\text{Oxygen required for } 1000 \text{ ml of sewage sample} = 0.072 \text{ g}$$

$$\text{BOD for sample} = 72 \text{ mg/lit}$$

...Ans.

Ex. 6.14.35 : 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.

Soln.:

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

$$\text{Since 1 litre of 1 M FAS} = 8 \text{ g of oxygen}$$

$$13 \text{ ml fo } 0.1 \text{ M FAS} = 8 \times 13 \times 0.1/1000$$

$$= 10.4 \times 10^{-3} \text{ g of oxygen for 5 ml of sample}$$

Oxygen required for 1000 ml of waste water = 2.08 g

COD for waste water sample = 2080 mg/lit

...Ans.

Ex. 6.14.36 : 25 ml of sewage water is refluxed with 0.1 N $\text{K}_2\text{Cr}_2\text{O}_7$ solution in presence of H_2SO_4 and Ag_2SO_4 . The unreacted dichromate required 5.5 ml of 0.1N FAS solution. Blank titration consumed 15ml of 0.1N FAS solution. Calculate COD of the effluent in mg/lit.

MU - Dec. 14, 6 Marks

Soln.:

Difference in the volumes of the FAS required for the blank and sample solution = $15 - 5.5 = 9.5 \text{ ml}$

$$\text{Since 1 litre of 1 M FAS} = 8 \text{ g of oxygen}$$

$$9.5 \text{ ml fo } 0.1 \text{ M FAS} = 8 \times 9.5 \times 0.1/1000$$

$$= 7.96 \times 10^{-4} \text{ g of oxygen for 25 ml of sample}$$

Oxygen required for 1000 ml of waste water = $3.5 \times 10^{-2} \text{ g of oxygen per liter.}$

COD for waste water sample = 350 mg/lit

...Ans.

Ex. 6.14.37 : A 5 ml sample of waste water was refluxed with 30ml of potassium dichromate solution and after refluxing the excess unreacted dichromate required 23ml of 0.1M FAS solution. A blank of distilled water on refluxing with 30ml of dichromate solution required 36ml of 0.1M FAS solution. Calculate the COD value of the waste water.

MU - Dec. 15, 3 Marks

Soln.:

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

$$\text{Since 1 litre of 1 M FAS} = 8 \text{ g of oxygen}$$

$$13 \text{ ml fo } 0.1 \text{ M FAS} = 8 \times 13 \times 0.1/1000$$

$$= 10.4 \times 10^{-3} \text{ g of oxygen for 5 ml of sample}$$

Oxygen required for 1000 ml of waste water = 2.08 g

COD for waste water sample = 2080 mg/lit

...Ans.

Ex. 6.14.38 : Calculate the COD of an effluent sample if 25 c.c. of the effluent sample required 8.3 c.c. of 0.001 M $\text{K}_2\text{Cr}_2\text{O}_7$ for oxidation.

MU - May 16, 3 Marks

Soln.:

Data given : Volume of sample : 25 cc, Volume of $\text{K}_2\text{Cr}_2\text{O}_7$: 8.3 cc
Molarity of $\text{K}_2\text{Cr}_2\text{O}_7$: 0.001 M

$$\text{Since 1 mole FAS} = 1 \text{ mole } \text{K}_2\text{Cr}_2\text{O}_7 \equiv \frac{1}{2} \text{ mole of O}_2$$

$$\text{Hence, } 8.3 \text{ ml } \text{K}_2\text{Cr}_2\text{O}_7 \equiv \text{ same volume of FAS assuming same molarity}$$

$$\text{Hence if 1 litre of 1 M FAS} = 8 \text{ g of oxygen}$$

$$8.3 \text{ ml fo } 0.001 \text{ M FAS} = 8 \times 8.3 \times 0.001/1000$$

$$= 7.04 \times 10^{-5} \text{ g of oxygen for 25 ml of sample}$$

Oxygen required for 1000 ml of waste sample = $7.04 \times 10^{-5} \text{ g} \times 4 = 2816 \times 10^{-5} \text{ g/lit}$

COD for waste water sample = $2.816 \times 10^{-3} \text{ mg/lit}$

...Ans.

Ex. 6.14.39 : 6 ml of waste water was refluxed with 25 ml of $\text{K}_2\text{Cr}_2\text{O}_7$ solution and after refluxing the excess unreacted dichromate required 20 ml of 0.1 N FAS solution. A blank of distilled water on refluxing with 25 ml of $\text{K}_2\text{Cr}_2\text{O}_7$ solution required 35 ml of 0.1N FAS solution. Calculate the COD of waste water sample.

MU - Dec. 16, 3 Marks

Solution :

Data given : Volume of sample : 6mL

Volume of $\text{K}_2\text{Cr}_2\text{O}_7$: 25 mL

Volume of FAS : 20 mL

Strength of FAS : 0.1 N

Blank for 25 mL $\text{K}_2\text{Cr}_2\text{O}_7$: 35 mL same FAS

Difference in the volumes of the FAS required for the blank and sample solution = $35 - 20 = 15 \text{ mL}$

$$\text{Since 1 litre of 1 M FAS} = 8 \text{ g of oxygen}$$

$$15 \text{ ml fo } 0.1 \text{ M FAS} = 8 \times 15 \times 0.1/1000$$

$$= 12 \times 10^{-3} \text{ g of oxygen for 6 ml of sample}$$

Oxygen required for 1000 ml of waste water = 2 g

COD for waste water sample = 2000 mg/lit

...Ans.

Ex. 6.14.40 : A 10 ml of sample of water was refluxed with 20 ml potassium dichromate solution and after refluxing, the excess unreacted dichromate required 26.2 ml of 0.1 M FAS solution. A blank 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 of waste water.

MU - May 18, 3 Marks

Soln.:

COD calculation

Data given : Volume of sample : 10 ml

Volume of $K_2Cr_2O_7$: 20 ml

Volume of FAS : 36.2 ml

Strength of FAS : 0.1 M

Blank for 20 ml $K_2Cr_2O_7$: 46 ml same FASDifference 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

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

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

Oxygen required for 1000 ml of waste water = 0.784 g

COD for waste water sample = 784 mg/lit

...Ans.

Summary

- Impurities in water, hardness of water- units (no conversions), types and numerical problems, determination of hardness of water by EDTA method and numerical problems. Softening of water by Ion Exchange process and numerical problems, BOD, COD- definition, significance and Numerical problems. Water purification- membrane technology- Electrodialysis, Reverse osmosis, and Ultra filtration.
- Water is God's gift to all living creatures, from unicellular to multicellular and from plants to animals on earth.

Sources of Water

The sources of water are broadly classified as :

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

Impurities in Water

- (i) Minerals, (ii) Oxides,
 - (iii) Sulphates, (iv) Carbonates
 - (v) bi-carbonates, and
 - (vi) Dissolved gases.
- 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

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".

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."

Types of Hardness

- There are two types of hardness, as :
 1. Temporary or carbonate or alkaline hardness.
 2. Permanent or non-carbonate or non-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.

Sr. No.	Temporary Hardness	Permanent Hardness
		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 <ol style="list-style-type: none"> (i) Only boiling. (ii) Treating only with lime. 	Permanent hard water can be softened by treating with soda.
6.	Temporary hard water if used in steam production, deposits precipitates of carbonates of Ca^{+2} and hydroxides of Mg^{+2} at the bottom of the container (boiler) known as sludges. These deposits harden to form scales. The reactions taking place are : $Ca(HCO_3)_2 \xrightarrow{\Delta} CaCO_3 \downarrow + H_2O - CO_2 \uparrow$ $Mg(HCO_3)_2 \xrightarrow{\Delta} Mg(OH)_2 \downarrow + 2 CO_2 \uparrow$	Permanent hard water if used in steam production, forms scales.

Factors Influencing Hardness of Water (Causes of Hardness)

Causes of hardness

There are mainly three causes of hardness

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

Measurement of Hardness

Calculation of Equivalents of CaCO_3

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

Equivalent of CaCO_3

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

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

Units of Hardness

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

Determination of Hardness of Water

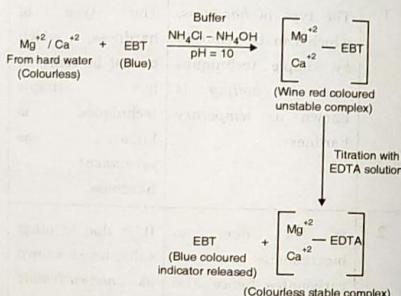
- The hardness of water can be determined by following methods :
 - EDTA method – Used most widely
 - O' Hehner's method – Not used commonly
 - Soap titration method – Not used commonly

Principle of EDTA Method

- The di-sodium salt of Ethylene Diamine Tetra Acetic Acid (EDTA) forms complexes with Ca^{2+} and Mg^{2+} , 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 Ca^{2+} and Mg^{2+} present in an aliquot of the sample with Na EDTA solution, using NH_4Cl . NH_4OH 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 $\text{Ca}^{2+}/\text{Mg}^{2+}$ 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).

Reaction



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

Procedure for EDTA Titration

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 to 1 L. The hardness of this solution would be 1 mg of CaCO_3 equivalent per ml (1 mg CaCO_3/ml).

(b) 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.

(c) Indicator

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

(d) Buffer solution of pH 10

67.5 grams of NH_4Cl are added to 570 ml of concentrated ammonia solution. The mixture is then diluted to 1 litre with distilled water.

Step 2 : Titration

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

(a) Standardization of EDTA solution

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

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

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

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

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

Using the data of V_1 , V_2 and V_3 ; total and permanent hardness is calculated. The difference of these two values gives temporary hardness of water.

Method of calculation

Titration carried out in this method are :

- 50 ml Standard Hard Water (SHW) [containing 1 mg/ml CaCO_3 equivalent hardness] against EDTA solution = V_1 ml
- 50 ml unknown hard water (HW) against EDTA solution = V_2 ml.
- 50 ml unknown hard water after boiling and dilution against EDTA solution = V_3 ml.

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

$$\therefore \text{permanent hardness of water per litre} = \left[\frac{V_2 \times 1000}{V_1} \right] \text{ mgs/lit}$$

Temporary hardness = Total hardness - Permanent hardness

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

Advantages of EDTA method

1. Highly accurate.
2. Highly convenient.

Softening of Water

The following methods are used for softening of water.

1. Lime soda process.
2. Zeolite process or permunt process.
3. Ion-exchange or deionization or demineralisation process

1. Cation exchange resins (RH₂) / (RH^{*})

Their exchange reactions with cations (Ca²⁺ and Mg²⁺) are as follows :

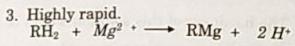


2. Anion exchange resins (R'(OH))



Principle of ion exchange process

When hard water is first passed through cation exchange bed which removes all cations like Ca²⁺, Mg²⁺, Na⁺ and releases hydrogen ions as,



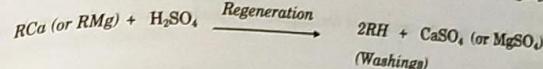
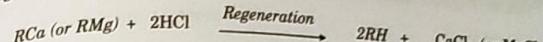
After this, the acidic hard water is passed through an anion exchange bed which removes all the anions like SO₄²⁻, Cl⁻ etc. present in the water, and equivalent amount of OH⁻ ions are released from it to water.



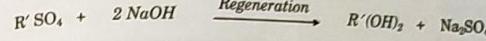
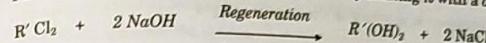
Process of ion-exchange/demineralisation

- The hard water is first passed through cation exchange column and then through anion exchange column
- Thus, the water coming out from anion exchange bed becomes free of cations as well as from anions.
- The resulting ion-free water is deionised water or demineralised water.

Regeneration of exhausted resins



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



Advantages of ion exchange process

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

Disadvantages of ion exchange process

1. The equipment is costly.
2. If water contains turbidity, then the output of process is reduced. Turbidity should be below 10 ppm.

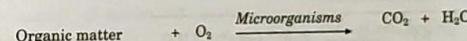
BOD and COD

Biochemical Oxygen Demand (BOD)

Waste water contains two types of organic matter :

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

Reaction



Principle of BOD

The principle involved in the determination of BOD is :

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

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

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

(DO)₂ = Dissolved oxygen of diluted water sample after incubation for 5 days at 20°C, mg/L

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

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

Significance of BOD :

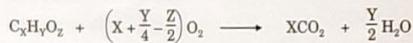
- The higher the BOD of a sample the higher the amount of decomposable organic matter in the sample and higher the pollution of the sample.
- Therefore, BOD
 - (1) Gives an idea about the extent of pollution at any time in the sewage sample
 - (2) Helps in pollution control.

Chemical Oxygen Demand (COD)

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

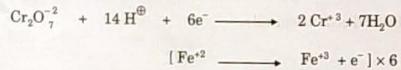
Principle of determination of COD :

- A known volume of sample is refluxed with a known excess of $\text{K}_2\text{Cr}_2\text{O}_7$ solution in 50% H_2SO_4 , in the presence of Ag_2SO_4 (Catalyst), and HgSO_4 .
- $\text{K}_2\text{Cr}_2\text{O}_7$ is strong oxidizing agent, in acidic medium. It oxidizes the organic matter into CO_2 and H_2O .

Reaction :

The unreacted dichromate solution is then titrated against std. FAS solution

$(\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6 \text{H}_2\text{O})$ using ferroin as indicator. At end point blue colour changes to wine red.

**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.
- Difference between BOD and COD

Water Purification (Membrane Technology)**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.

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.

Benefits

- ED can operate with minimal fouling or scaling, or chemical addition.

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.

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 Differentiate between hard water and soft water.
- Q. 6 Why is hard water unsuitable for boilers ?
- Q. 7 What is the principle involved in the determination of total hardness ?
- Q. 8 Write in brief "Disadvantages of hard water in different industries".
- Q. 9 Differentiate between temporary hardness and permanent hardness.
- Q. 10 What are the impurities associated with water ? Give their effects if it is used in various industries.
- Q. 11 Describe the demineralization (ion-exchange/de-ionisation) process for softening of hard water. Are there any drawbacks of this method ?
- Q. 12 Define BOD and COD- and give their significance.
- Q. 13 Describe the laboratory method to determine BOD and COD.
- Q. 14 What is the carbonate and non-carbonate hardness of a sample of water which has the following impurities per litre ?



$\text{Ca}(\text{HCO}_3)_2 = 50.25 \text{ mg}$; $\text{Ca}(\text{NO}_3)_2 = 8.2 \text{ mg}$;
 $\text{CaCl}_2 = 22.2 \text{ mg}$; $\text{KNO}_3 = 20.2 \text{ mg}$;
 $\text{MgCO}_3 = 16.8 \text{ mg}$; $\text{FeSO}_4 = 3.8 \text{ mg}$;
 $\text{MgSO}_4 = 6.0 \text{ mg}$.

Express the results as ppm, Clarke degree and French degree.

[Ans. : Carbonate hardness = 51 ppm or 5.1°Fr or 3.56°C , Non-carbonate hardness = 27.5 p.p.m or 2.75°Fr or 1.92°Cl .]

- Q. 15 Find carbonate and non-carbonate hardness of a sample of water which has the following impurities per lit.

$\text{CaCO}_3 = 12.5 \text{ mg/lit.}$; $\text{MgCl}_2 = 9.5 \text{ mg/lit.}$;
 $\text{MgCO}_3 = 16.8 \text{ mg/lit.}$; $\text{CO}_2 = 22 \text{ mg/lit.}$;
 $\text{CaCl}_2 = 11.1 \text{ mg/lit.}$; $\text{NaHCO}_3 = 13.6 \text{ mg/lit.}$

[Ans. : Carbonate hardness = 32.5 ppm.,
Non-carbonate hardness = 20 ppm.]

- Q. 16 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.]

- Q. 17 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 Erichrome Black-T indicator. 50 ml of a hard water sample required 22.5 ml of the same EDTA. 100 ml of the water after boiling and filtering required 120 ml of the said EDTA. Calculate the hardness in the sample (permanent and temporary).

[Ans. : Total Hardness = 468 ppm,
Permanent Hardness = 393 ppm,
Temporary Hardness = 135 ppm.]

- Q. 18 What is carbonate and non-carbonate hardness of a sample of water which has the following impurities per litre

$\text{Mg}(\text{HCO}_3)_2 = 146 \text{ mg/lit.}$; $\text{MgCl}_2 = 95 \text{ mg/lit.}$;
 $\text{NaCl} = 50 \text{ mg/lit.}$; $\text{Ca}(\text{HCO}_3)_2 = 81 \text{ mg/lit.}$;
 $\text{CaCl}_2 = 111 \text{ mg/lit.}$; $\text{CaSO}_4 = 68 \text{ mg/lit.}$

Express the results as ppm, $^\circ\text{Cl}$ and $^\circ\text{Fr}$.

[Ans. : Carbonate hardness = 150 ppm = $15^\circ\text{Fr} = 10.5^\circ\text{Cl}$. Non-carbonate hardness = 250 ppm = $25^\circ\text{Fr} = 17.5^\circ\text{Cl}$.]

- Q. 19 What is the carbonate and non-carbonate hardness of a sample of water which has the following impurities per litre ?

$\text{Ca}(\text{HCO}_3)_2 = 81 \text{ mg/lit.}$; $\text{MgCl}_2 = 95 \text{ mg/lit.}$;
 $\text{NaCl} = 38.5 \text{ mg/lit.}$; $\text{CaCl}_2 = 22.2 \text{ mg/lit.}$;
 $\text{Mg}(\text{HCO}_3)_2 = 58.2 \text{ mg/lit.}$; $\text{CO}_2 = 4.4 \text{ lit}$

Express the results as ppm. Clarke's degree and french degree.

[Ans. : Carbonate hardness = 89.88
ppm = $6.29^\circ\text{Cl} = 8.928^\circ\text{Fr}$.]

Non-carbonate hardness = 120 ppm = $8.4^\circ\text{Cl} = 12^\circ\text{Fr}$.]

- Q. 20 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.

[Ans. : Temporary hardness = 125 ppm.,
Permanent hardness = 500 ppm.
Total hardness = 625 ppm.]