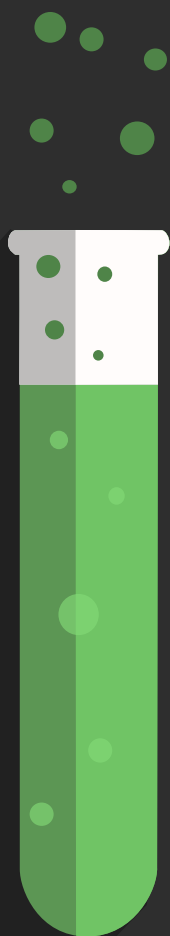Video
Solution
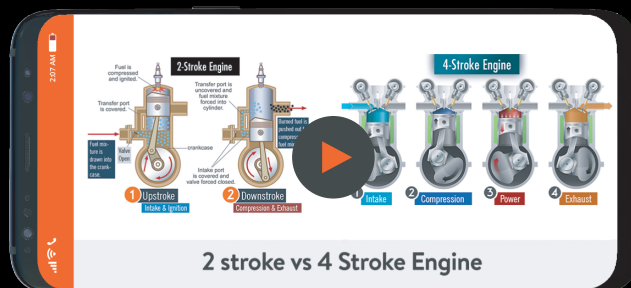
ENGINEERING CHEMISTRY

Swapnali Sarwade

Kamini Taware
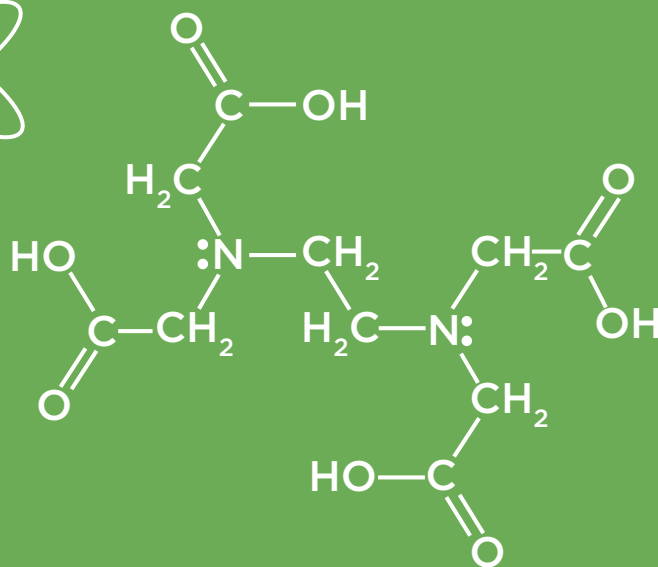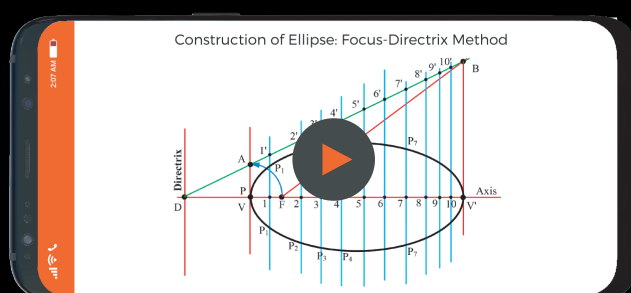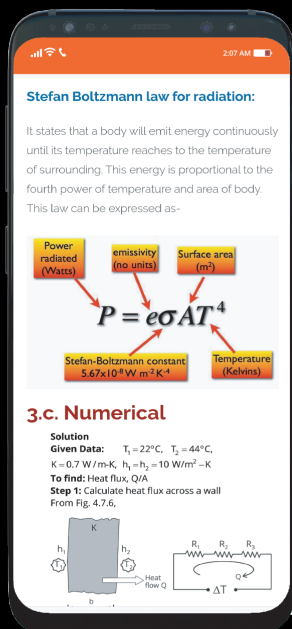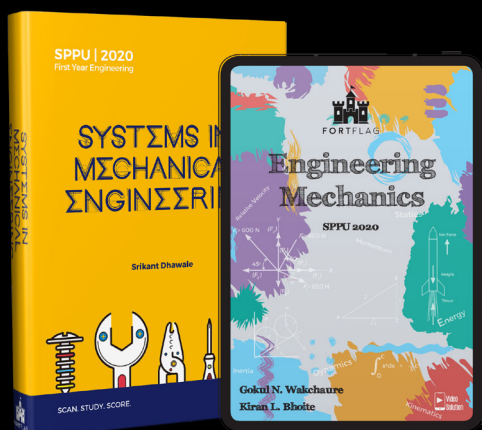
SCAN. STUDY. SCORE.

FORTFLAG

JOURNEY TO A SUCCESSFUL IN-SEM EXAM

Total Marks:30

UNIT-I — 15 Topics

1st MILESTONE

1. Introduction to water
2. Chemistry of water
3. Impurities in water
4. Types of water
5. Hardness of water and its causes
6. Classification of hardness of water

2nd MILESTONE

7. Calculation of hardness of water
8. Chemical analysis of water: Hardness determination
9. Determination of alkalinity in water
10. Effects of using hard water in boiler for steam generation

3rd MILESTONE

11. Purification of water
12. Zeolite Process (Permutit Process)
13. Ion exchange process/ Deminer alization process
14. Membrane Processes
15. Electrodialysis

UNIT-II — 19 Topics

1st MILESTONE

1. Introduction
2. Electrochemical cells
3. Reference electrode
4. Calomel electrode
5. Indicator electrode
6. Ion selective electrode
7. Glass electrode
8. Solid membrane ISE
9. Enzyme based membrane electrode
10. Gas sensing electrode

2nd MILESTONE

11. Introduction to Conductometry
12. Terms involved in conductometry
13. Conductivity meter
14. Fundamental of Conductometric titration
15. Conductometric Acid-Base titrations

3rd MILESTONE

16. Introduction pHmetry
17. pH meter
18. Standardization of pH meter
19. pH metric titration of strong acid with strong base

Water Technology

1. Introduction to Water

Water is a phenomenal substance. Its presence brings life and growth to all manner of organisms, and consequently its absence brings the opposite. Covering 70% of the Earth's surface, it is the only substance that occurs naturally on the planet in all three states; solid, liquid, and gas. Water is widely used for different applications such as agricultural, industrial, steam generation, domestic. To get water in pure form is important for its use. In this chapter focus is given on water analysis and its purification with various methods.

2. Chemistry of Water

❁ Water is a polar covalent compound with chemical formula H-O-H. Each molecule is bent shaped, with the partially negatively charged oxygen at the center and the pair of partially positive-charge hydrogen atoms on the other side of the molecule.

❁ Water has high dielectric constant of 80.10 at 20°C, this is because the water molecule has a dipole moment and so water can be polarized.

❁ Because of polar nature and high dielectric constant, it acts as a 'Universal solvent' as most of the chemical compounds dissolve in it.
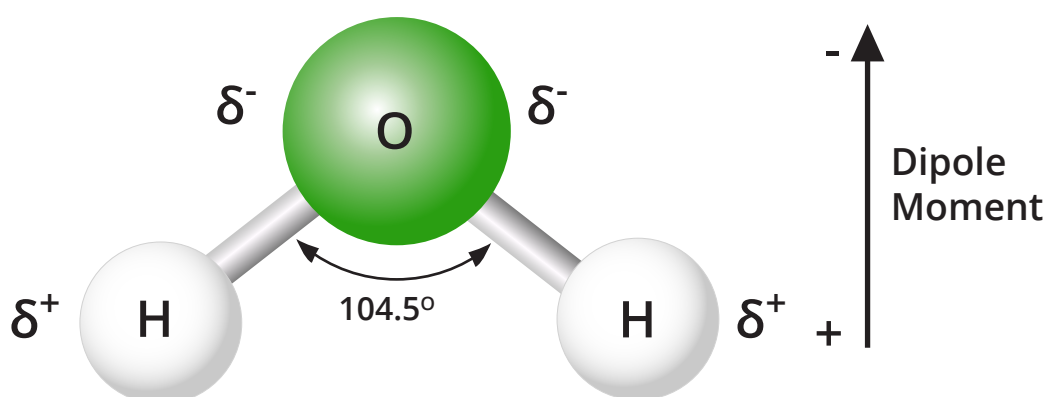
3. Impurities in Water

A) Suspended Impurities

❁ These are inorganic impurities like clay, mud, organic matter like vegetable, animal matter and industrial waste.

❁ They cause turbidity and give odor to water.

❁ These impurities are removed by sedimentation or filtration process.

B) Dissolved Impurities

❀ They are subdivided into two types:

i) Dissolved gases like CO_2, Cl_2, H_2S, SO_x, NO_x sometimes NH_3 and H_2S.

ii) Dissolved salts like bicarbonates, sulphates, chlorides, nitrates of Ca, Mg, Fe, Al, Na, K etc.

iii) Dissolved impurities are removed by special purification process.

C) Colloidal Impurities

❀ Colloidal particles of particle size less than 1000A.U. like fine clay, mud, organic matter etc. which make the water turbid.

❀ They cannot be removed by filtration but are usually removed by coagulation followed by filtration.

❀ Coagulating agents commonly used are potash alum, sodium aluminate, ferrous sulphate.
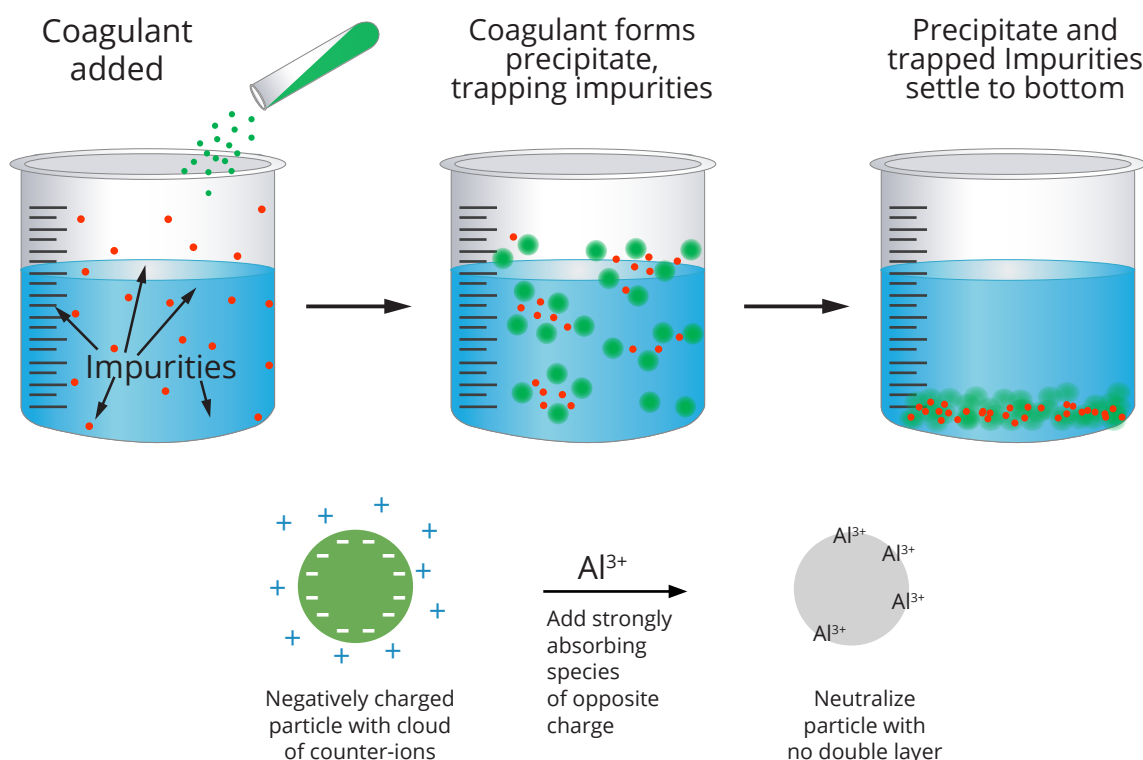
D) Biological Impurities

❀ These impurities include microorganisms like algae, fungi, bacteria etc.

❀ They can be removed by sterilization process.

❀ Sterilizing agents used are liquid chlorine, ozone and UV light.

It is found that presence of dissolved impurities in water is the main trouble for its domestic and industrial applications. Thus, dissolved impurities are discussed in detail with respect to their analysis and purification.

4. Types of Water

Based on sources from which water is obtained it is categorized in two types:

a) Hard water

b) Soft water

	Hard water	Soft water
Dissolved salts	It contains salts of Ca, Mg and other heavy metals.	It contains mineral salts of Na, K.
Test to distinguish	It does not produce lather with soap solution. It forms scum(white precipitate) with soap solution.	It produces lather with soap solution.
Chemical reaction with soap solution	$C_{17}H_{35}COONa$ + $CaCl_2$ (sodium stearate) (hardness) ↓ $(C_{17}H_{35}COO)_2Ca$↓ + $2NaCl$ (calcium stearate)	No reaction with soap solution.

5. Hardness of Water and it's Causes

✵ Due to dissolution of different atmospheric gases such as NO_x, SO_x, rain water becomes acidic in nature. When this acidic water flows over the rocks, various minerals from it slowly get dissolved in water as a result of following reactions.

a) Dissolution: Some minerals from rocks are readily soluble in water such as NaCl, $CaCl_2$ etc.

b) Hydration: Some rock minerals like anhydrites and silicates readily undergo hydration forming soluble salts.

Example: $CaSO_4 \xrightarrow{\text{hydration}} CaSO_4.2H_2O$

anhydrate Gypsum
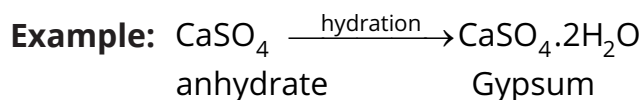
c) Oxidation: Dissolved oxygen present in water causes oxidation of some rock minerals which then undergo hydration and get forms water soluble salts.

$2Fe_2S + 7O_2 + 2H_2O \longrightarrow 2FeSO_4 + 2H_2SO_4$
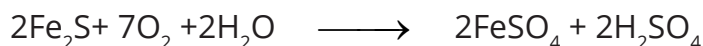
d) Action of dissolved carbon dioxide:

i) It converts insoluble carbonates of Ca, Mg,Fe into soluble bicarbonates.

$CO_2 + H_2O \longrightarrow H_2CO_3$

$$CaCO_3(s) + H_2CO_3 \longrightarrow Ca(HCO_3)_2$$

ii) Metal silicates and alumina silicates reacts with dissolved CO_2 and get converted into soluble carbonates, and bicarbonates and silica.

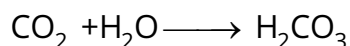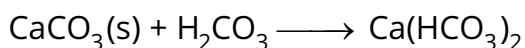❀ Thus, hard water mainly contains soluble salts such as bicarbonates, chlorides, sulphates and nitrates of Ca, Mg along with other metals like Fe, Al and Mn.

6. Classification of Hardness of Water

❀ Based on nature of dissolved salt present, hardness present in water is classified as

   a) Temporary Hardness

   b) Permanent Hardness

Temporary Hardness	Permanent Hardness
It is caused due to presence of bicarbonate salts of Ca, Mg, Fe, Al, Mn in water.	It is caused due to presence of soluble chloride, sulphate, nitrate saltsof Ca, Mg, Fe, Al, Mn in water.
It can be removed easily by mere boiling of water followed by filtration.	It cannot be removed easily from water for its removal special softening methods are used.
On boiling soluble bicarbonate salts are converted into insoluble carbonate or hydroxide form. $Ca(HCO_3)_2 \longrightarrow CaCO_3 \downarrow + H_2O + CO_2 \uparrow$ $Mg(HCO_3)_2 \longrightarrow Mg(OH)_2 \downarrow + 2CO_2$	These salts remain in dissolved state even after vigorous boiling.
Temporary hardness is also called as alkaline or carbonate hardness.	Permanent hardness is also called as nonalkaline or non-carbonate hardness.

Exercise - 1.1
Questions based on 1st Milestone

Scan using FORTFLAG app for detailed solution.

Q 1. What is hardness of water? How is it classified?

Q 2. What is hardness of water? Define temporary and permanent hardness.

Q 3. What happens when water contains $Mg(HCO_3)_2$ as an impurity is boiled merely? Write the chemical reaction involved.

Q 4. Explain any three causes of hardness in water.

Q 5. Why hardness of water is expressed in terms of $CaCO_3$ equivalent unit?

7. Calculation of Hardness of Water

❀ Hardness of water is the net amount of hardness causing impurities present in water in a known volume.

❀ The concentration of dissolved impurities is usually expressed in terms of calcium carbonate equivalent.

❀ The calcium carbonate equivalent unit is accepted as molecular weight of $CaCO_3$ is 100 (and equivalent weight is 50) and it is the most insoluble salt in water. Thus, amount of any salt can be easily expressed in terms of calcium carbonate equivalent unit.

❀ The calcium carbonate equivalent for any dissolved salt from water can be calculated, if its amount in mg per liter of solution in water is known as follows

$$CaCO_3 \text{ equivalent of salt} = \frac{\text{Equivalent weight of } CaCO_3 \times \text{Amount of salt given}}{\text{Equivalent weight of salt given}}$$

If the dissolved salt has **only bivalent cations,** then the above formula can be written as,

$$CaCO_3 \text{ equivalent of bivalent salt} = \frac{\text{Molecular weight of } CaCO_3 \times \text{Amount of salt given}}{\text{Molecular weight of salt given}}$$

Units used for expressing calcium carbonate equivalent hardness:

i) Milligrams per litre (mg / lit): 1 mg/lit hardness is 1 mg of calcium carbonate equivalent hardness present in 1 litre of water.

ii) Parts per million (ppm): 1 ppm hardness is 1 part of calcium carbonate equivalent hardness present in million parts of water i.e. 10^6 parts of water.

   1 ppm = 1 mg hardness in 10^6 mg of water

   Relation between mg / lit and ppm:

   1 mg / lit = 1 ppm

≡ STEPS & FORMULA | Numerical based on Hardness calculation

Note:

   ❀ Temporary hardness is caused due to presence of bicarbonate salts of Ca, Mg, Fe, Al, Mn in water.

   ❀ Permanent hardness is caused due to presence of soluble chloride, sulphate, nitrate salts of Ca, Mg, Fe, Al, Mn in water.

   ❀ Total hardness of water sample in ppm or mg/L = temporary hardness + permanent hardness.

Formula:

$$CaCO_3 \text{ equivalent of salt} = \frac{\text{Equivalent weight of } CaCO_3 \times \text{Amount of salt given}}{\text{Equivalent weight of salt given}}$$

If the dissolved salt has only bivalent cations, then following formula is used

$$CaCO_3 \text{ equivalent of bivalent salt} = \frac{\text{Molecular weight of } CaCO_3 \times \text{Amount of salt given}}{\text{Molecular weight of salt given}}$$

Step 1: Note the Amount of salt given in mg/L.

Step 2: Calculate Molecular weight/equivalent weight of each salt with following steps

   i) Molecular weight of salt= sum of atomic weight of all constituent atoms.

   ii) Equivalent weight of salt $= \dfrac{\text{Molecular weight of salt}}{\text{Valance factor}}$

   iii) Note that equivalent weight of $CaCO_3$ is 50

   [Molecular weight of $CaCO_3$= Atomic weight of Ca+ atomic weight of C + 3(atomic weight of O)]

   Molecular weight of $CaCO_3 = 40 + 12 + 3 \times 16 = 100$

   Equivalent weight of $CaCO_3 = \dfrac{\text{Molecular weight of salt}}{\text{Valance factor}} = \dfrac{100}{2} = 50$

Step 3: Calculate $CaCO_3$ equivalent weight of each salt with the formula

$$CaCO_3 \text{ equivalent of salt} = \frac{\text{Equivalent weight of } CaCO_3 \times \text{Amount of salt given}}{\text{Equivalent weight of salt given}}$$

Step 4: Calculate now temporary, permanent and total hardness of water sample

Exercise - 1.2
Questions based on Hardness calculation

Q 1. Calculate the temporary and permanent hardness of a water sample, having following analysis: $Mg(HCO_3)_2$ = 73 mg/L , $Ca(HCO_3)_2$ = 162 mg/L , $CaSO_4$ = 136 mg/L , $MgCl_2$ = 95 mg/L , $CaCl_2$= 111 mg/L , NaCl = 100 mg/L .

Q 2. Calculate carbonate and noncarbonate hardness of water sample containing following dissolved salts in mg/L: $Mg(HCO_3)_2$ = 58.5 , $Ca(HCO_3)_2$= 40.5, $MgSO_4$ = 3, $Ca(NO_3)_2$= 41, $CaCl_2$ = 33.3, SiO_2 = 10 $MgCl_2$ = 9.5

Q 3. Calculate total, temporary hardness of water sample containing following dissolved salts in mg/L: $Mg(HCO_3)_2$ = 29.2 , $Ca(HCO_3)_2$ = 32.4 , $MgSO_4$= 6, $MgCl_2$ = 9.5 mg/L , $Ca(NO_3)_2$= 32.8, $CaCl_2$ = 38.8 , $Al_2(SO_4)_2$ = 5.7

Q 4. Analytical report of raw water sample is as follows: $MgCO_3$ = 25 ppm , $MgCl_2$ = 9.5 ppm , $CaSO_4$ = 3.4 ppm , $Mg(HCO_3)_2$ = 7.3 ppm . Calculate total hardness of water sample.

Q 5. Calculate alkaline and non-alkaline hardness of water sample containing following dissolved salts in mg/L: $Mg(HCO_3)_2$ = 2.9, $Ca(HCO_3)_2$ = 32.4, $MgSO_4$ = 9, $MgCl_2$ = 9.5, $CaCl_2$ = 38.8, $Al_2(SO_4)_3$ = 34.5, $FeSO_4$ = 21

Q6. A sample of water is found to contains following dissolving salts in milligrams per litre $Mg(HCO_3)_2$ = 73, $CaCl_2$ = 111, $Ca(HCO_3)_2$ = 81, $MgSO_4$ = 40, $MgCl_2$ = 95. Calculate temporary and permanent hardness and total hardness.

8. Chemical Analysis of Water

i) Determination of hardness of water by EDTA method

❊ Hardness in water is mainly contributed by soluble salts such as such as bicarbonates, chlorides, sulphates and nitrates of Ca, Mg along with other metals like Fe, Al and Mn.

❊ To determine total and even temporary and permanent hardness of water EDTA method is used.

❊ It is **complexometric titration** method which involves soluble and stable coordinating complex formation between hardness causing metal cations and complexing agent (EDTA Ethylene diamine tetra acetic acid)
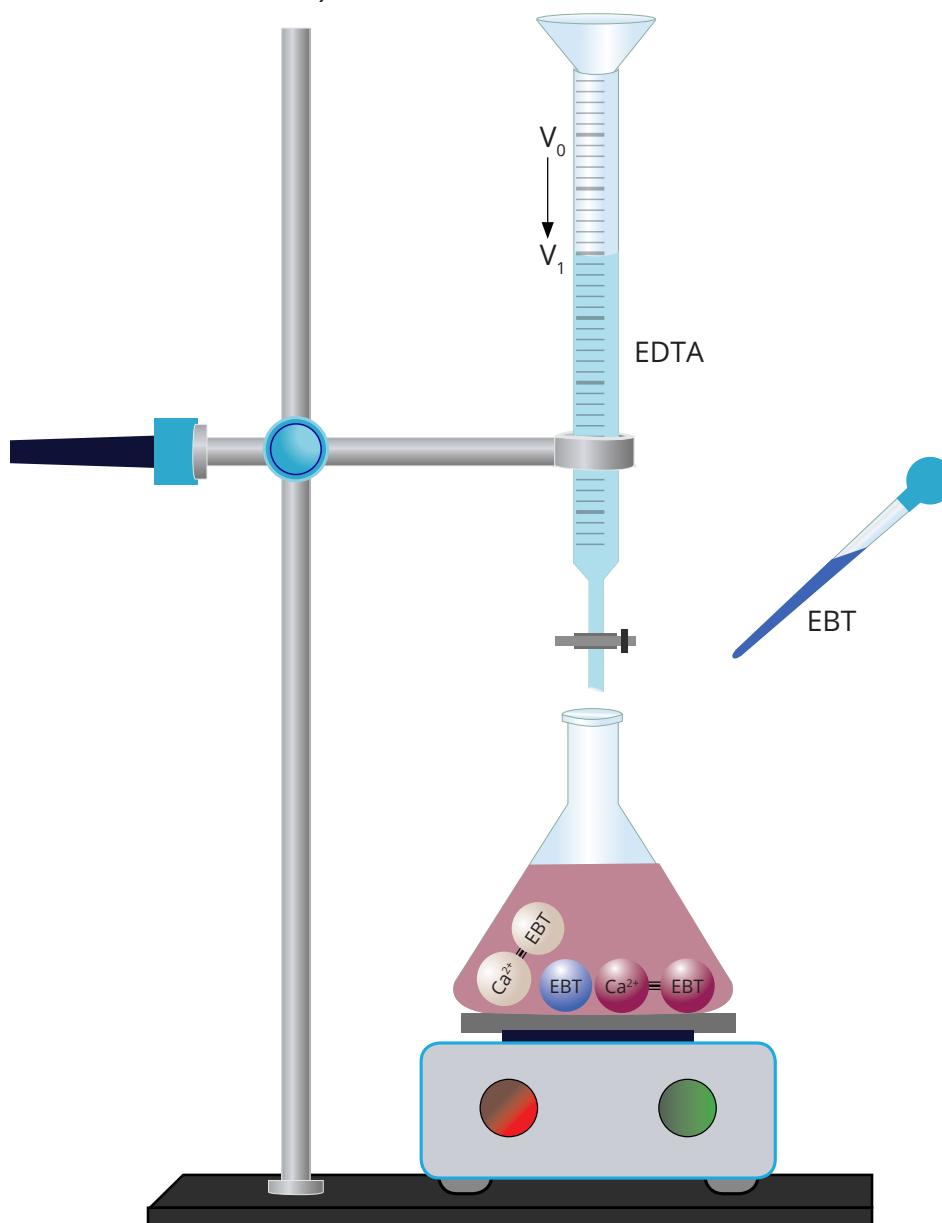
Principle

❊ EDTA method involves titration of water sample against disodium salt solution of EDTA (as EDTA is partially soluble in water to make aqueous solution disodium salt of EDTA is used.)

❊ This titration is carried out using Eriochrome black-T indicator and at pH=10. To maintain pH=10 alkaline buffer solution (mixture of $NH_4Cl + NH_4OH$) is added. (Alkaline pH is required for neutralization of H^+ ions released during complex formation reaction between metal ions and EDTA. This causes complexation reaction to occur efficiently).

❊ When Eriochrome black-T indicator is added to water sample containing Ca^{2+}, Mg^{2+} ions at pH=10, it gives wine red colour to the solution due to formation of a weak, soluble complex of metal cations with indicator.
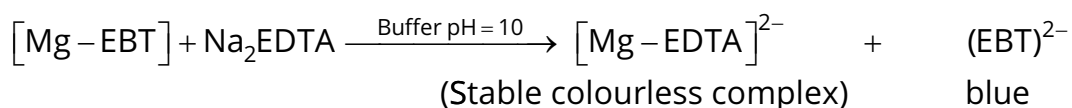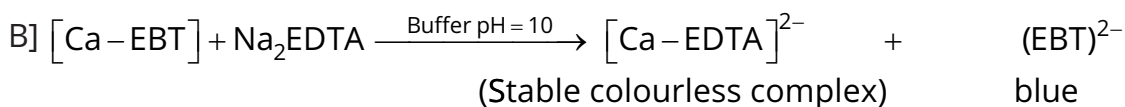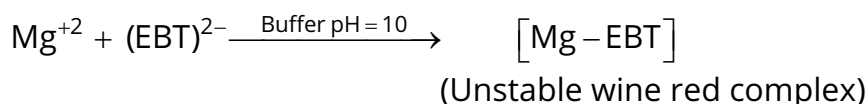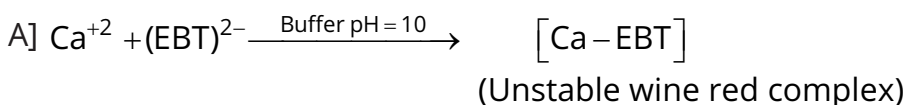
❊ When wine-red coloured solution is titrated with EDTA solution, unstable complexes of Eriochrome black-T are quickly converted into more stable complexes of EDTA. At this stage Eriochrome black-T is released from the metal - complexes, which gives or discharges blue colour to the solution.

❊ Thus in EDTA titration, using Eriochrome black T indicator, colour change is observed from wine red to blue.

Structure of Na$_2$EDTA
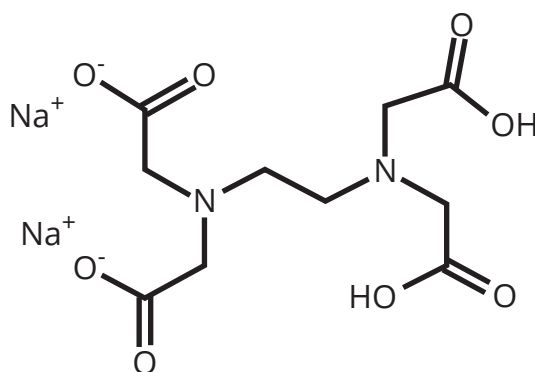
Chemical Reactions involved in the titration

A] $Ca^{+2} + (EBT)^{2-} \xrightarrow{\text{Buffer pH} = 10} \left[Ca - EBT \right]$
(Unstable wine red complex)

$Mg^{+2} + (EBT)^{2-} \xrightarrow{\text{Buffer pH} = 10} \left[Mg - EBT \right]$
(Unstable wine red complex)

B] $\left[Ca - EBT \right] + Na_2EDTA \xrightarrow{\text{Buffer pH} = 10} \left[Ca - EDTA \right]^{2-} + (EBT)^{2-}$
(Stable colourless complex)   blue

$\left[Mg - EBT \right] + Na_2EDTA \xrightarrow{\text{Buffer pH} = 10} \left[Mg - EDTA \right]^{2-} + (EBT)^{2-}$
(Stable colourless complex)   blue

Structure of [Ca-EDTA]$^{2-}$ complex
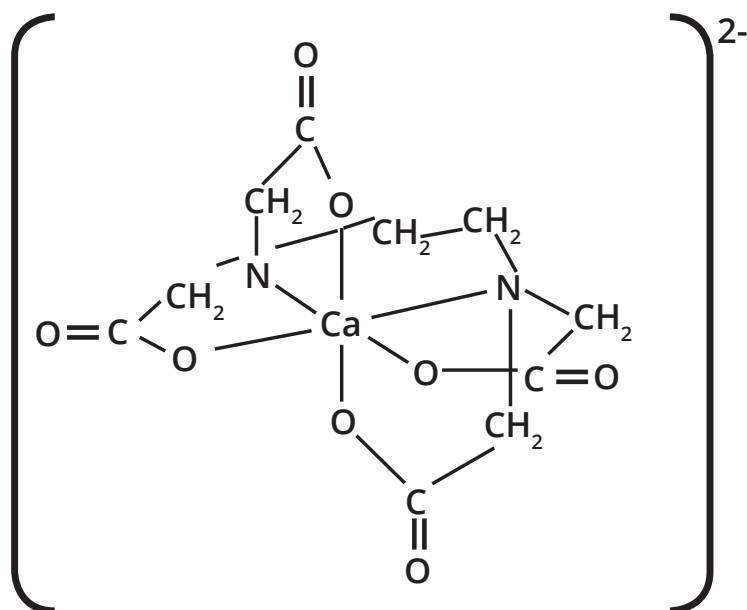
Chemicals required

i) Standard solution of Na_2EDTA (consider 1 M concentration)

ii) Hard water sample

iii) pH= 10 buffer solution (mixture NH_4Cl and NH_4OH in stochiometric proportion)

iv) Eriochrome black-T indicator (EBT)

Procedure

i) Determination of total hardness of the given water sample:

❀ Burette solution: Na_2EDTA solution.

❀ Conical flask: = 100 ml of sample water + 5 ml of pH= 10 buffer solution +2 drops of EBT indicator

❀ End point: colour change from wine red to blue.

100 ml of sample water + 5 ml pH= 10 buffer solution +2 drops of EBT indicator (in conical flask)

Wine red colour to solution

Titrate this solution with EDTA solution from burette

Note Burette reading as V_1 ml when solution colour changes to blue.
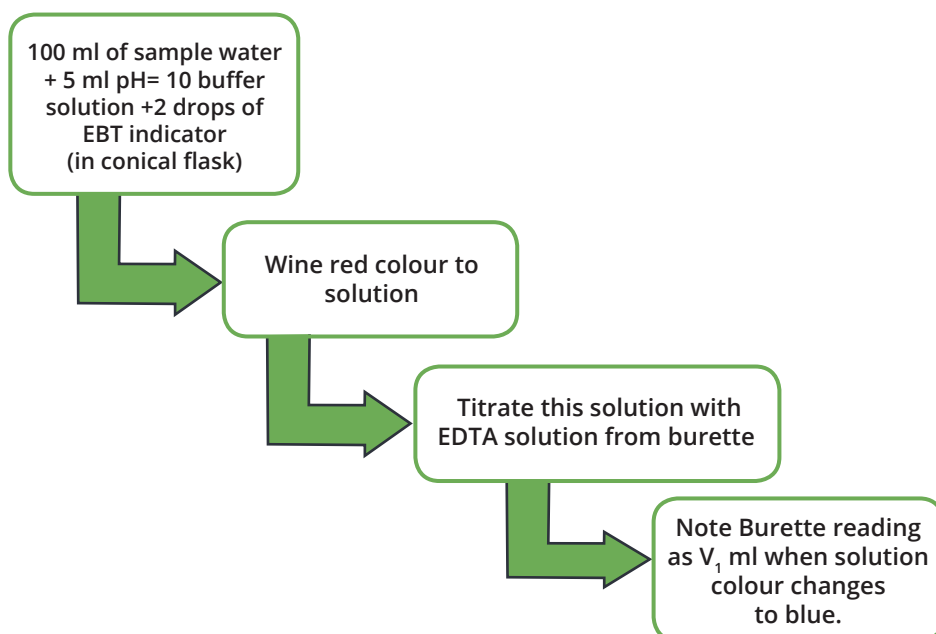
ii) Determination of permanent hardness of the given water sample:

✿ **Burette solution:** Na_2EDTA solution.

✿ **Conical flask:** 100 ml of boiled and filtered sample water (boiling process removes temporary hardness from water leaving only permanent hardness causing salts in water) + 5 ml of pH= 10 buffer solution +2 drops of EBT indicator

✿ **End point:** colour change from wine red to blue.
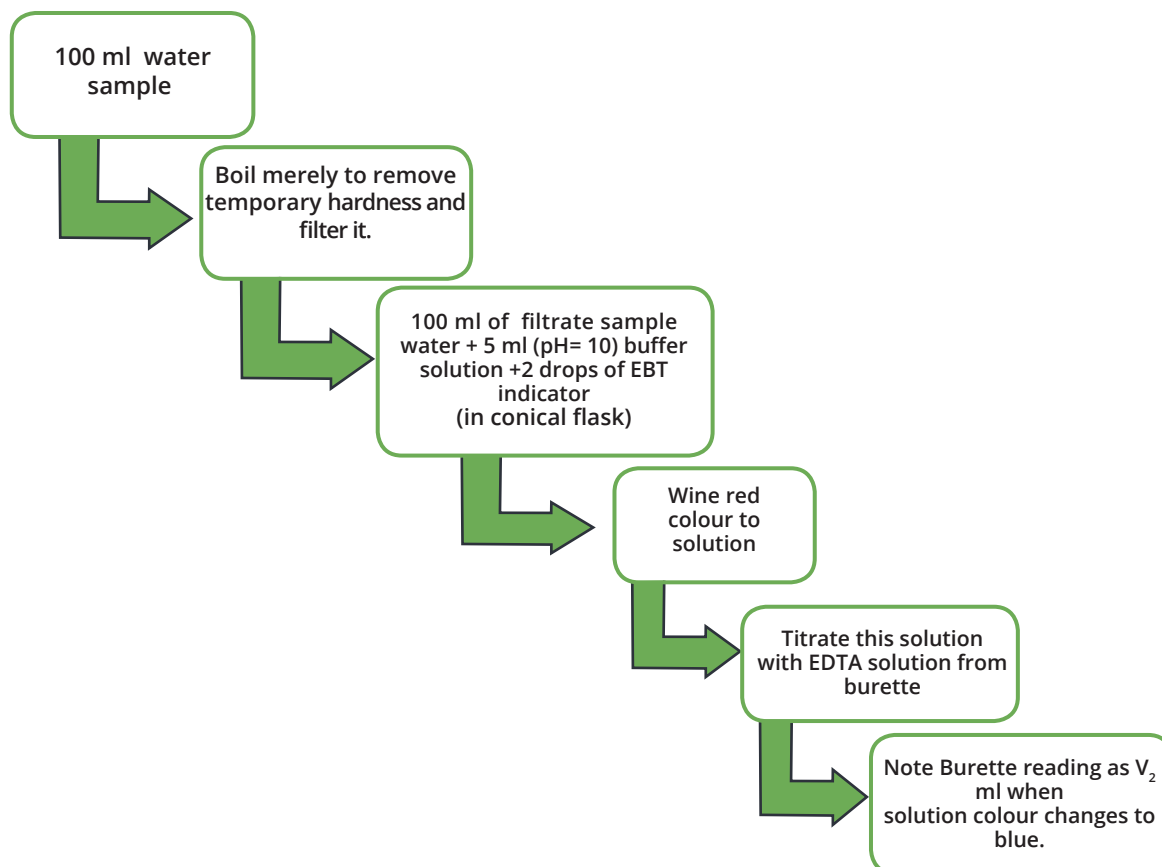
Calculations

It is known that,

1000 ml of 1M EDTA = 100 gm of $CaCO_3$ equivalent hardness

Thus,

> 1 ml of 1M EDTA 100 mg of $CaCO_3$ equivalent hardness

i) Determination of total hardness of the given water sample:
100 ml of hard water sample consumed V_1 ml of 1M EDTA

Since,

1 ml of 1M EDTA = 100 mg of $CaCO_3$ equivalent hardness

> V_1 ml of 1M EDTA = V_1 x 100 mg of $CaCO_3$ equivalent hardness

i.e. 100 ml hard water sample contains $V_1 \times$ 100 mg of $CaCO_3$ equivalent hardness

1000 ml of hard water sample = 1000 $\times V_1 \times$ 100 / 100 mg of $CaCO_3$ equivalent hardness

Total hardness of water sample= $1000 \times V_1$ mg/L or ppm

ii) Determination of permanent hardness of the given water sample:
100 ml of boiled hard water sample consumed V_2 ml of EDTA

Since,

1 ml of 1M EDTA 100 mg of $CaCO_3$ equivalent hardness

V_1 ml of 1 M EDTA = V_1 x 100 mg of $CaCO_3$ equivalent hardness

i.e. 100 ml boiled hard water sample contains $V_2 \times 100$mg of $CaCO_3$ equivalent hardness

1000 ml of boiled hard water sample = $1000 \times V_2 \times 100/100$ mg of $CaCO_3$ equivalent hardness

Permanent hardness of water sample= $1000 \times V_2$ mg/L or ppm

Temporary hardness of hard water sample= Total hardness – permanent hardness

☰ STEPS & FORMULA | Numerical based on EDTA method

A) Determination of Total hardness

Step 1: Note the following data:

i) Molarity of EDTA solution as 'M_1' molar.

ii) Volume of EDTA solution consumed as 'V_1' ml

iii) Volume of water sample taken for titration as 'V_2' ml

Step 2: Now, use following formula to find molarity of water sample 'M_2'

EDTA = Hard water

$M_1V_1 = M_2V_2$

Step 3: Total hardness of water is calculated with following formula and expressed in $CaCO_3$ equivalent in ppm unit.

Total hardness of water = M_2 x 10^5 =......... ppm

B) Determination permanent hardness

Step 1: Note following data

i) Molarity of EDTA solution as 'M_1' molar.

ii) Volume of EDTA solution consumed during titration with boiled hard water as V_1 ml

iii) Volume of boiled water/ filtrate of boiled water sample taken for titration as 'V_3' ml

Step 2: Now, use following formula to find molarity of boiled water sample 'M_3'

EDTA = Boiled Hard water

$M_1V_1 = M_3V_3$

Step 3: Permanent hardness of water is calculated with following formula and expressed in $CaCO_3$ equivalent in ppm unit.

Total hardness of water = $M_3 \times 10^5$ =......... ppm

C) Determination of temporary hardness

Temporary hardness = Total hardness – Permanent hardness

Temporary hardness of water is expressed in $CaCO_3$ equivalent in ppm unit.

Exercise - 1.3
Questions Based on EDTA Method

Q 1. 100 ml of hard water consumed 15.6 ml of 0.01M EDTA. 100 ml of boiled water sample when titrated after boiling and filtration consumed 9.9 ml of same EDTA solution. Calculate the total, carbonate and non-carbonate hardness.

Q 2. 25 ml of hard water consumed 20 ml of 0.01M EDTA. 25 ml of boiled water sample consumed 15 ml of same EDTA solution. Calculate the total, permanent and temporary hardness.

Q 3. A 100 ml of water sample required 13.5 ml of 0.02M EDTA solution for titration using Eriochrome black- T as indicator. Another 100 ml of same water sample was boiled and filtrate required 6 ml of same EDTA solution. Calculate total, temporary and permanent hardness of water sample.

Q 4. 50 ml of hard water consumed 25 ml of 0.02M EDTA. 50 ml of boiled water sample consumed 15 ml of same EDTA solution. Calculate the total, alkaline and non-alkaline hardness of water sample.

Q 5. 50 ml water sample required 35 ml of 0.025 M EDTA solution for titration using Eriochrome black- T as indicator. 50 ml of boiled water sample required 19.2 ml of same EDTA for the end point. Calculate total and non-carbonate hardness of water sample.

Q 6. 50 ml of water sample required 18 ml of 0.05 M EDTA solution during titration. Whereas 50 ml of boiled water sample required 12.5 ml of same EDTA. Calculate total, permanent and temporary hardness of water sample.

9. Determination of Alkalinity Present in Water

❀ Alkalinity of water is a measure of its capacity to neutralize acid.

❀ Alkalinity of water is due of presence of soluble hydroxide, carbonate and bicarbonate salts like sodium or potassium hydroxide, sodium or potassium carbonates, sodium or potassium bicarbonates along with bicarbonates of calcium and magnesium.

❀ In municipal and industrial waste water there are many factors which contribute to alkalinity. Factors which contribute to alkalinity include different types of dissolved inorganic and organic compounds present in the water and mainly soluble bicarbonate, carbonate, hydroxide salts present in the water.

❀ Total alkalinity can be estimated by titrating water sample against standard acid and using phenolphthalein and methyl orange as indicators.

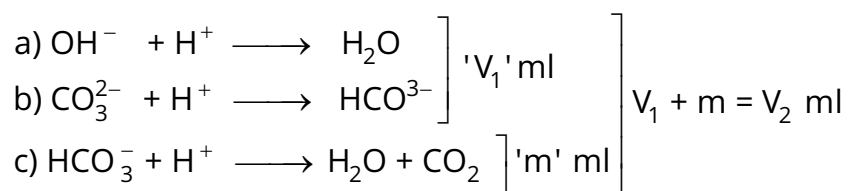❀ The possible combinations of alkaline salts present in water can be
    i) Only OH^-

   ii) only CO_3^{2-},

   iii) only HCO_3^- ,

   iv) OH^- & CO_3^{2-} together or

   iv) HCO_3^- & CO_3^{2-} together or

   vi) OH^- & HCO_3^- together or

   vii) OH^- & CO_3^{2-}, HCO_3^-

❀ Possibility of combination of OH^- and HCO_3^- ions together is ruled out because they combine as follows: $OH^- + HCO_3^- \longrightarrow H_2O + CO_3^{2-}$

❀ So from above combinations presence of OH^- & HCO_3^- together and OH^- & CO_3^{2-}, HCO_3 together is ruled out. [i.e. (vi) and (vii)]

❀ Thus, any given water sample may contain one of the above five combinations [i) to v)]

❀ The determination of total alkalinity is based on following reaction when water sample is titrated with standard acid solution.

$$
\left.
\begin{array}{l}
\text{a) } OH^- + H^+ \longrightarrow H_2O \\
\text{b) } CO_3^{2-} + H^+ \longrightarrow HCO^{3-}
\end{array}
\right] \text{'V}_1\text{'ml} \\
\text{c) } HCO_3^- + H^+ \longrightarrow H_2O + CO_2 \, \big] \text{'m' ml}
$$

$$V_1 + m = V_2 \text{ ml}$$

❀ The water sample when titrated against standard acid using phenolphthalein, end point obtained, marks the completion of reaction (a) and half of reaction (b) only.

❀ If reading of this titration is 'V_1' ml, then 'V_1' ml of acid used corresponds to complete neutralization of hydroxide ions and half neutralization of carbonate ions.

❀ When titration is further continued with methyl orange indicator, the end point obtained, marks the completion of half reaction i.e. (b) and (c). If reading of titration is 'V_2' ml, then 'V_2' ml is the volume of acid used, for complete neutralization of hydroxide, carbonate and bicarbonates (which are already present in water and those which are formed by half neutralization of carbonates).

❀ Thus, total amount of acid required during phenolphthalein and methyl orange titration i.e. ($V_1 + m$) ml represents the total alkalinity (V_2), where "m" is methyl orange reading.
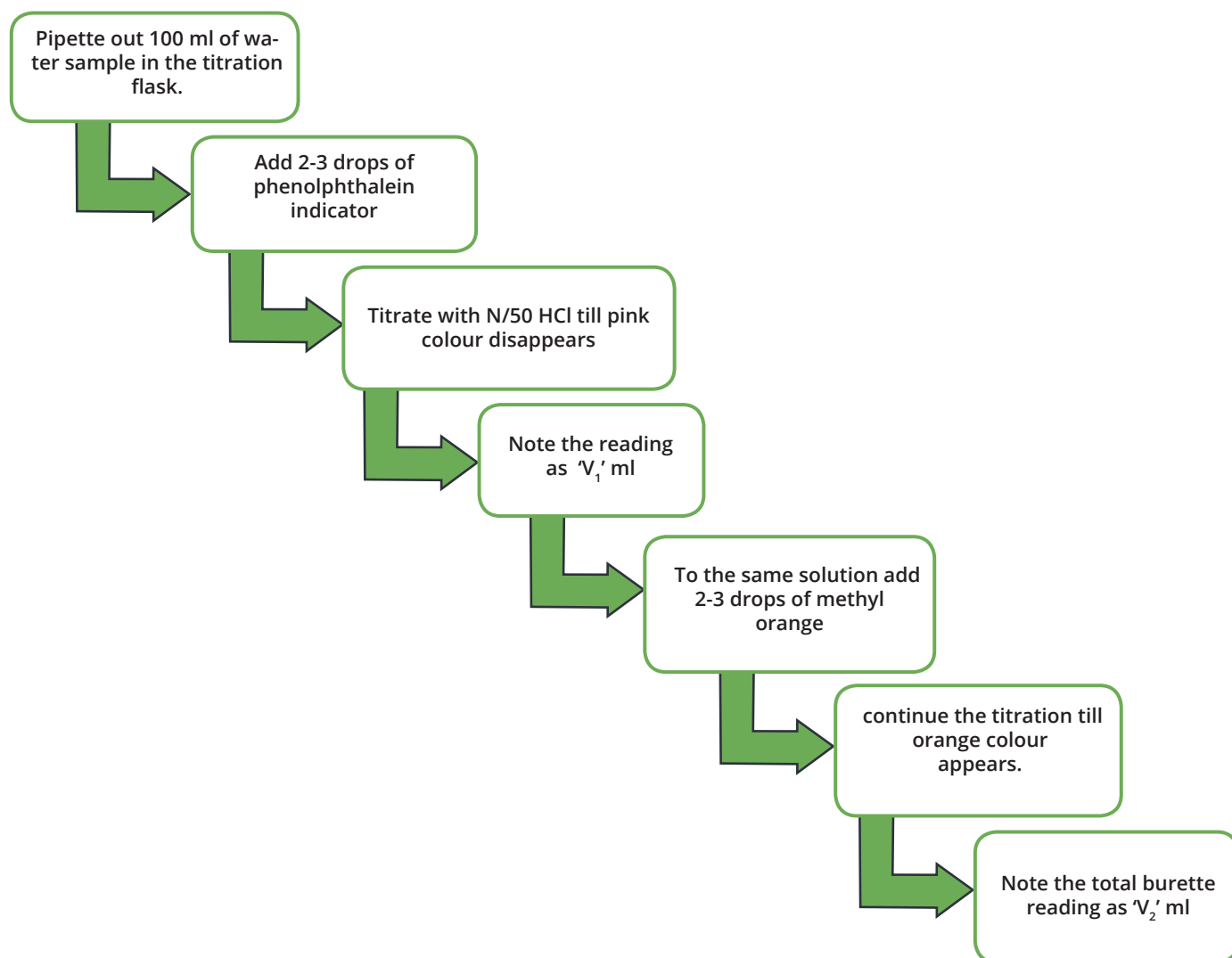
❀ With the titration readings obtained, phenolphthalein alkalinity (P) and total alkalinity (M) are calculated. Further using table of conditions for P and M, amounts of different types of alkalinities present in water can be determined.

Chemicals required

  i)   Water sample

  ii) N/50 HCl solution

  iii) Phenolphthalein indicator

  iv) Methyl orange indicator

Procedure

Pipette out 100 ml of water sample in the titration flask.

Add 2-3 drops of phenolphthalein indicator

Titrate with N/50 HCl till pink colour disappears

Note the reading as 'V$_1$' ml

To the same solution add 2-3 drops of methyl orange

continue the titration till orange colour appears.

Note the total burette reading as 'V$_2$' ml

Based on the titration reading, for different water samples, depending on alkalinity present we get different conditions. On that basis, we can identify and calculate amount of alkalinity present in water sample.

Conditions of P & M	Amount of OH^- Alkalinity	Amount of CO_3^{2-} Alkalinity	Amount of HCO_3^- alkalinity
P = 0	Absent	Absent	M
P = M	M	Absent	Absent

Conditions of P & M	Amount of OH^- Alkalinity	Amount of CO_3^{2-} Alkalinity	Amount of HCO_3^- alkalinity
P = 1/2 M	Absent	2P	Absent
P > 1/2M	2P-M	2[M-P]	Absent
P < 1/2M	Absent	2P	M-2P

Calculations

❀ Alkalinity is generally expressed as parts per million (ppm) in terms of $CaCO_3$.

❀ 1 litre of 1 N of any strong acid solution = 1 eq. wt. of any compound.
i.e. 1000ml of 1 N of any strong acid solution = 50 g of $CaCO_3$

Thus,

> 1 ml of 1 N of any strong acid solution = 50 mg of $CaCO_3$ equivalent

❀ Using this relation and volume of acid consumed by different alkalinity, amount of alkalinity can be calculated in terms of $CaCO_3$ equivalent expressed in ppm.

☰ STEPS & FORMULA | Numerical based on Alkalinity of water

Step 1: Note the following data given:

X= Volume of water sample titrated

N= Normality of acid used

V_1= Burette reading in presence of phenolphthalein

V_2 = total reading upto methyl orange end point

Step 2: Calculate P = phenolphthalein alkalinity in ppm unit with following formula

$$P = \text{Phenolphthalein alkalinity} = V_1 \times N \times 50 \times \frac{1000}{X}$$

Step 3: Calculate M = Total alkalinity in ppm unit with following formula

$$M = \text{Total alkalinity} = V_2 \times N \times 50 \times \frac{1000}{X}$$

Step 4: Now, use following table to know the amount of each alkalinity causing ions present in given water sample.

Step 5: With the conditions followed for P and M, calculate the amount of each alkalinity.

Conditions of P & M	Amount of OH- Alkalinity	Amount of CO_3^{2-} Alkalinity	Amount of HCO_3^- alkalinity
P = 0	Absent	Absent	M
P = M	M	Absent	Absent
P = 1/2 M	Absent	2P	Absent
P > 1/2M	2P-M	2[M-P]	Absent
P < 1/2M	Absent	2P	M-2P

Exercise - 1.4
Questions Based on Alkalinity of Water

Q 1. A water sample is not alkaline to phenolphthalein. However, 100 ml of the sample on titration with N/50 HCl required 17.5 ml to obtain end point using methyl orange as indicator. What is the type and amount of alkalinity present in the sample?

Q 2. A water sample is alkaline to phenolphthalein as well as methyl orange indicator. 100 ml of the sample on titration with N/50 HCl required 10.5 ml to obtain end point using phenolphthalein and further 10.5 ml using methyl orange as indicator. What is the type and amount of alkalinity present in the sample?

Q 3. 25 ml of water sample on titration with N/ 50 HCl required 27 ml for phenolphthalein end point. When methyl orange is added to the same, orange colour developed. Find the type and amount of alkalinity present in the water.

Q 4. 50 ml water sample requires 3.7 ml of 0.025 N H_2SO_4 upto phenolphthalein end point and further 4.8 ml upto methyl orange end point. Determine the type and amount of alkalinity present in water.

Q 5. 100 ml of water sample required 50 ml of 0.025N sulphuric acid for phenolphthalein end point and another 20 ml for methyl orange end point. Determine the type and amount of alkalinity present in water.

Q 6. A water sample is not alkaline to phenolphthalein. However, 50 ml of the water sample required 36.5 ml of 0.01N HCl for methyl orange end point. Determine the type and amount of alkalinity present in water.

Q 7. 50 ml water sample requires 7.4 ml of 0.025 N H_2SO_4 upto phenolphthalein end point and further 16 ml upto methyl orange end point. Determine the type and amount of alkalinity present in water.

Q 8. 25 ml of water sample on titration with N/ 50 HCl required 22 ml for phenolphthalein end point. When methyl orange is added to the same, orange colour developed. Find the type and amount of alkalinity present in the water.

Q 9. A water sample is alkaline to phenolphthalein as well as methyl orange indicator. 100 ml of the sample on titration with N/50 HCl required 15 ml to obtain end point using phenolphthalein and further 15 ml using methyl orange as indicator. What is the type and amount of alkalinity present in the sample?

Q 10. Water sample is not alkaline to phenolphthalein. However, 25 ml of this water sample on titration required 4.5 ml 0.02 N HCl for methyl orange end point. Determine the type and amount of alkalinity present in water.

Q 11. 100 ml of water sample requires 5.2 ml of 0.02 M HCl upto phenolphthalein end point and 15.8 ml for methyl orange end point. Find the type and amount of alkalinity present in water sample.

10. Effects of Using Hard Water in Boiler for Steam Generation

❋ The most important use of water in industry is for steam generation using boilers and as coolant.

❀ Water absorbs large amount of heat and it is converted into steam which is capable of carrying large amount of heat.

❀ This property make water to use as raw material for heating, steam engines and power generation.

❀ For generation of steam boiler is used. Boiler is a closed vessel made up of steel in which water under pressure is transformed into steam. This steam should be pure for its effective application and to avoid troubles in the boiler operation.

❀ Depending on the operating pressure of the boiler, the feed water should satisfy following requirements of hardness.

Type of boiler, steam pressure	Permitted hardness in feed water
Low pressure < 15 kg/cm^2	40 – 80 ppm
Medium pressure 15 – 30 kg/cm^2	4 – 40 ppm
High pressure > 30 kg/cm^2	0 – 3 ppm

❀ Feed water should have caustic alkalinity below 0.5 ppm, total alkalinity below 1ppm.

❀ If the boiler feed water is not upto the standard limit, it gives rise to number of problems in boiler like

i. Priming and Foaming

ii. Caustic embrittlement

iii. Boiler corrosion

iv. Scales and sludge formation

i. Priming and Foaming

Priming

❀ When a boiler produces steam rapidly some water droplets are carried along with steam that results into wet steam formation. i.e. steam contaminated with water droplets.

❀ The process of wet steam formation is called priming.

Foaming

❀ Production of persistent foam or bubbles on the surface of water in boilers.

Causes of Priming

i) Presence of large amount of dissolved salts and suspended impurity.

ii) High steam velocities and high water levels in boiler.

iii) Faulty boiler design

iv) Sudden increase in steaming rate.

Cause of foaming

❀ Presence of substances like oils, soaps. Substances which increases viscosity of the liquid and reduces their surface tension.

Disadvantages of Priming and Foaming

Priming and foaming occurs together and causes:

i) Wet steam produced during these processes carry dissolved salts which get deposited on parts of boiler, engine parts etc. These deposits reduce their efficiency.

ii) Dissolved salts from wet steam may enter the parts of other machinery like steam line, valves, blades, thereby decreasing the life of the machinery due to their corrosion.

iii) Actual height of the water in boiler cannot be judged properly, thereby the operation and maintenance of adequate quantity of water inside the boiler becomes difficult.

Prevention of Priming

i) Fitting mechanical steam purifiers.

ii) Avoiding rapid change in steaming rate.

iii) Maintaining low water levels in boilers.

iv) Efficient softening and filtration of boiler feed water.

Prevention of foaming

⚛ Adding antifoaming chemicals like castor oil. Antifoaming agents counteract on reduction of surface tension.

⚛ Removing oil impurities by adding coagulating agents like sodium aluminates.

ii. Caustic Embrittlement

⚛ During softening process by lime – soda, free soda (Na_2CO_3) is usually present in small portion in the softened water which is unused.

⚛ In high pressure boilers, soda undergoes hydrolysis to give sodium hydroxide and carbon dioxide.

$$Na_2CO_3 + H_2O \xrightarrow{\text{High Pressure}} 2NaOH + CO_2^-\uparrow$$
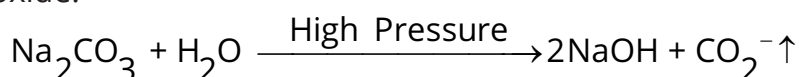
⚛ Formation of caustic soda makes the boiler water alkaline.

⚛ Caustic soda (NaOH) containing water flows into the minute cracks which are present in the inner walls of the boiler by capillary action.

⚛ Inside the cracks, water evaporates and the amount of sodium hydroxide increases progressively.

⚛ Caustic soda (NaOH) reacts with boiler metal i.e. iron, forming sodium ferrate and hydrogen as follows.

$$2\,Fe + 2NaOH + O_2 \longrightarrow 2\,NaFeO_2 + H_2^-\uparrow$$
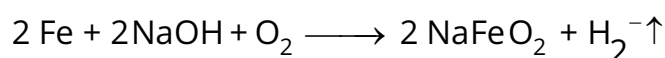
⚛ The products of the reaction, sodium ferrate and hydrogen also tend to penetrate along grain boundaries.

⚛ This causes brittlement of the boiler metal. thus, this trouble is known as caustic embrittlement.

Prevention Caustic embrittlement can be avoided by –

i) Using sodium phosphate as softening agent instead of sodium carbonate.

ii) By treating tannins and lignins to the water which seals the cracks and prevent direct contact of boiler wall with alkali.

iii. Boiler Corrosion

⚛ Boiler corrosion is the most serious problem caused by using unsuitable water.

⚛ Boiler corrosion can be defined as the destruction of boiler metal by a chemical or electrochemical attack by its environment.

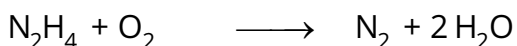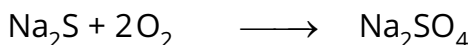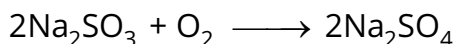⚛ Corrosion in boilers is due to the following reasons:

Dissolved Gases
a) Dissolved oxygen

⚛ Raw water generally has 8-9 ppm of dissolved oxygen.

⚛ Dissolved oxygen can attack the iron in the boiler to form rust.

$$4Fe + 4H_2O + O_2 \longrightarrow 4Fe(OH)_2$$

$$4\,Fe(OH)_2 + O_2 \longrightarrow 2\,[Fe_2O_3.2H_2O]$$
$$\text{rust}$$
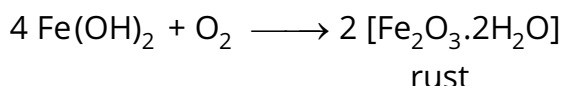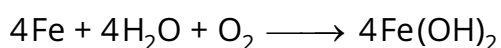
Prevention

⚛ Dissolved oxygen can be removed by adding calculated amount of sodium sulphite (Na_2SO_3) or sodium sulphide (Na_2S) or hydrazine (N_2H_4)

$$2Na_2SO_3 + O_2 \longrightarrow 2Na_2SO_4$$

$$Na_2S + 2O_2 \longrightarrow Na_2SO_4$$
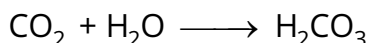
$$N_2H_4 + O_2 \longrightarrow N_2 + 2H_2O$$

Hydrazine reagent is preferred to remove dissolved oxygen as it does not release any salt in the water.
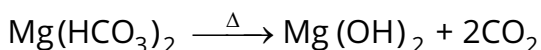
⚛ By mechanical de-aeration.

b)Dissolved carbon dioxide

⚛ Dissolved carbon dioxide (CO_2) in water forms carbonic acid.

$$CO_2 + H_2O \longrightarrow H_2CO_3$$

⚛ Carbonic acid is a weak acid, has a slow corrosive effect on boiler metal. Carbon dioxide is also released inside the boiler if water contains bicarbonates.

$$Mg(HCO_3)_2 \xrightarrow{\Delta} Mg(OH)_2 + 2CO_2$$

Prevention: Dissolved carbon dioxide may be removed by adding calculated amount of liquid ammonia (NH_4OH) or by mechanical de-aeration.

$$2\,NH_4OH + H_2CO_3 \longrightarrow (NH_4)_2CO_3 + 2H_2O$$

Acids from Dissolved Salt

⚛ When pH of boiler feed water is below 8.5, corrosion may occur due to acidic nature of water.

⚛ Water used in the boiler, if contains dissolved magnesium salts, they liberate acid on hydrolysis.

$$MgCl_2 + 2H_2O \longrightarrow Mg(OH)_2 + 2HCl$$
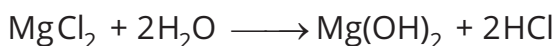
⚛ The liberated acid reacts with iron metal of the boiler in a chain reaction, producing HCl again and again as follows,

$$Fe + 2HCl \longrightarrow FeCl_2 + H_2$$

$$FeCl_2 + 2H_2O \longrightarrow Fe(OH)_2 + 2\,HCl$$
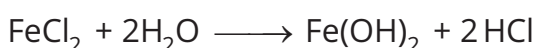
Hence, even small amount of Mg-salts can cause considerable corrosion of boiler metal.

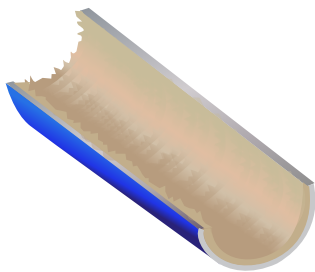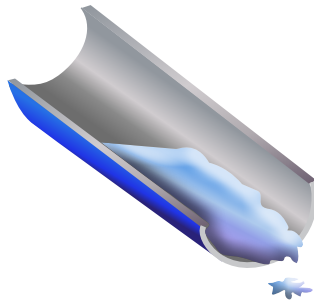## Prevention

⚛ Mg-salts can be removed by using zeolite or ion-exchange process (water softening processes).

iv. Scale and sludge formation

⚛ In boiler, water when heated at high temperature and pressure causes water to evaporate with high rate. Due to this, concentration of dissolved salts in water increases progressively.

⚛ When the concentration of dissolved salts reaches their saturation point, they get precipitate out either in the form of hard, adherent deposits termed as scale or loose, slimy precipitate termed as sludges.

	Scale	Sludge
Definition	These are hard, adherent deposits which stick to inner wall of boiler, when impurities precipitate out after their saturation point.	These are loose, slimy precipitates which floats in boiler water, when impurities precipitate out after their saturation point.
Causes	1. Decomposition of bicarbonates: bicarbonate salts on thermal decomposition forms precipitate as scale. $Ca(HCO_3)_2 \xrightarrow{\Delta} CaCO_3 \downarrow + CO_2 + H_2O$ $Mg(HCO_3)_2 \xrightarrow{\Delta} Mg(OH)_2 \downarrow + 2CO_2$	Sludge is formed by substances which have greater solubility in hot water than in cold water example $MgCO_3$, $MgCl_2$, $CaCl_2$, and $MgSO_4$.

	Scale	Sludge
	2. Decrease in the solubility of salt: Salts insoluble in superheated water. e.g. $CaSO_4$ and $CaCO_3$ deposit as scale in hot region of boiler.	
	3.Hydrolysis of magnesium salts: dissolved magnesium salts on hydrolysis forming magnesium hydroxide which turn as soft type of scale. $MgCl_2 + 2H_2O \longrightarrow Mg(OH)_2 + 2HCl$ $MgSO_4 + 2H_2O \longrightarrow Mg(OH)_2 + SO_4$	
	4. Presence of silica (SiO_2): silica present reacts with soluble salts of Ca and Mg, forming $CaSiO_3$ or $MgSiO_3$. These silicate deposits stick as hard scale.	
Effects on boiler	i) Wastage of fuel for uniform steam supply. ii) Decrease in efficiency – Sometimes scales may deposit in valves, condensers of the boiler and choke them partially. This leads to decrease in efficiency of the boiler. iii) Danger of explosion: scales are thermal insulators of heat thus deposited scale on boiler wall increases the heat required for uniform steam generation. due to overheating boiler metal becomes brittle and there is chance of explosion of boiler.	i) Sludge is poor conductors of heat, so they will waste a portion of heat generated. ii) If sludge is formed along with scales, then it get entrapped in scales and get deposited as scales. iii) Excessive formation of sludge decreases the efficiency of the boiler. Sludge settles down in the regions of poor water circulation such as pipe connection, plug opening etc. thereby causing choking of pipes.
Methods of removal	i) Soft scales can be removed with the help of scraper or piece of wood or wire brush. ii) By dissolving them, by adding some chemicals like EDTA solution, that leads to soluble complex formation. iii) Soft scales also can be removed along with sludge by blow down operation.	i) By frequent blow down operation (i.e. drawing off a portion of concentrated water and replacing it by fresh water). ii) Sludge can be scrapped off with mechanical means like wire brush, scrappers etc. iii) By using soft water.

Exercise - 1.5
## Questions Based on 2nd Milestone

Q 1. Give the principle involved in EDTA method for hardness determination.

Q 2. Write the chemical reactions involved in the EDTA method and also draw the structure of metal-EDTA complex.

Q 3. Explain the procedure for determination of total hardness of water sample by EDTA ethod.

Q 4. Explain the procedure for determination of permanent hardness of water sample by EDTA method.

Q 5. What is alkalinity of water? Which salts contribute to alkalinity to the water?

Q 6. Analyze why the alkalinity of water cannot be due to presence of OH^-, CO_3^{2-}, HCO_3^- together?

Q 7. Write the chemical reactions involved when water containing NaOH, K_2CO_3, is titrated with HCl solution.

Q 8. Explain the procedure for determination of alkalinity of water sample with the help of flow sheet.

Q 9. What is priming and foaming? Give any 3 disadvantages of priming and foaming.

Q 10. What is priming and foaming? State the prevention methods of priming and foaming.

Q 11. Explain causes, disadvantages and preventive measures for caustic embrittlement.

Q 12. Explain how dissolved oxygen in water causes boiler corrosion. Give the method of removal of dissolved oxygen from water.

Q 13. Addition of hydrazine is the preferred way to remove dissolved oxygen from water than sodium sulphide. Why?

Q 14. How dissolved magnesium salts causes boiler corrosion? How to minimize this type of boiler corrosion.

Q 15. Compare between scale and sludges.

Q 16. Define scales. Explain in brief four causes of deposit formation in boilers.

11. Purification of Water

The main purpose of water treatment is to remove hardness present in raw water.

Treatments of boiler feed water are of two types:
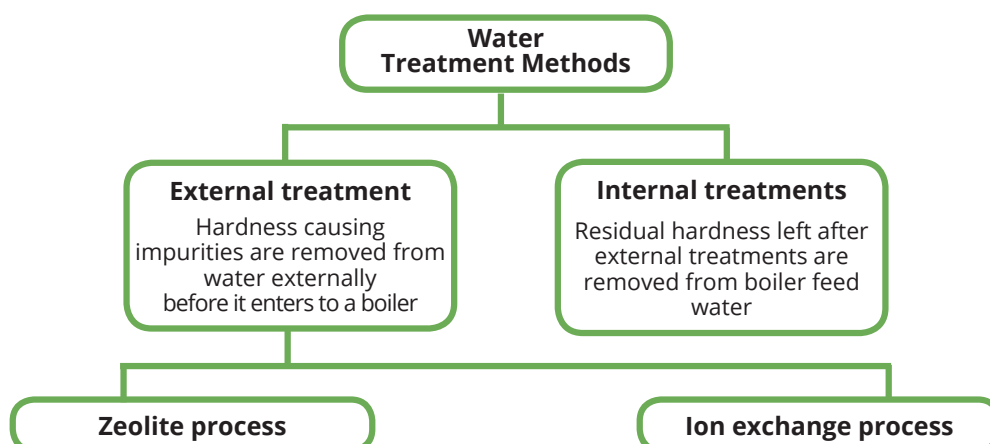
External treatments of water purification

The treatment in which scale forming and corrosive impurities are removed from water before it enters the boiler are known as external treatment.

External treatments are carried out by following two methods.

i) Zeolite process/ Permutit process

ii) Ion exchange process

12. Zeolite Treatment /Cation Exchange Process (Permutit Process)

❈ Zeolites are naturally occurring porous inorganic compounds,they contain fused sodium aluminates and silicates in three dimensional structure.

❈ The chemical structure of zeolite is represented as $Na_2O.Al_2O_3.x\ SiO_2.y\ H_2O$
(x= 2 to 10 & y= 2 to 6). They contain loosely bounded Na^+ ions on three-dimensional network structure.

❈ Zeolites are capable of exchanging their sodium ions with cations so, it is capable of exchanging hardness producing ions present in water.

❈ This process is also called as permutit process.

❈ Zeolite can be written as Na_2Z.The two Na+ ions are replaced by one Ca^{2+} or Mg^{2+} ion.
$$Na_2Z + Ca^{2+} \longrightarrow CaZ + 2Na^+$$
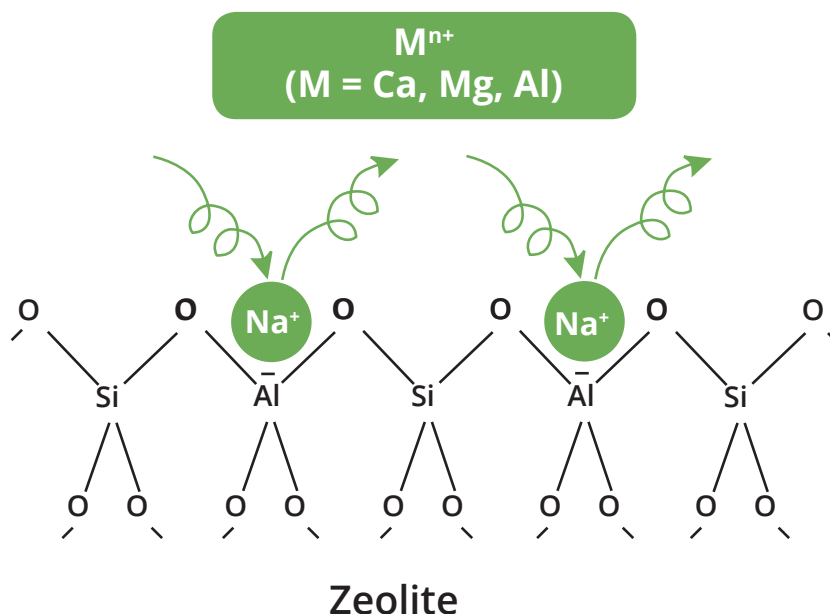
Zeolite

❈ Naturally occurring zeolite is Natolite- $Na_2O.Al_2O_3.SiO_2.2H_2O$.

❈ The synthetic zeolites are also prepared with the help of feldspar and China clay on heating.

❈ Two types of zeolites are commonly used in water softening

    a) Natural zeolite (Nonporous,green sand)

    b) Synthetic zeolite (Porous)

Principle

❈ Sodium zeolite has the property of capturing the heavy metal ions (Ca^{2+},Mg^{2+}) from the water and in exchange release equivalent amount of Na^+ in water. When hard water

is passed through zeolite bed, removal of heavy metal ions from water takes place by exchange process and the hard water is converted into soft water.

Process

i) The setup of zeolite process consists of cylindrical container in which a coarse powder of sodium zeolite is placed over a perforated plate.

ii) There is an inlet on the top for hard water and outlet at the bottom for collecting soft water.

iii) There is another inlet for adding 10% NaCl solution to regenerate the exhausted zeolite bed.

iv) When hard water percolates downwards through the zeolite bed, the hardness causing Ca^{2+}, Mg^{2+} etc. cations are retained in the bed and Na+ ions are released in the water in exchange.

v) At the end of process soft water is obtained, however, it contains equivalent quantity of sodium salt.

Reaction

$$Na_2Z + MgCl_2 \longrightarrow MgZ + 2NaCl$$

$$Na_2Z + Ca(HCO_3)_2 \longrightarrow CaZ + 2NaHCO_3$$

ZEOLITE PROCESS
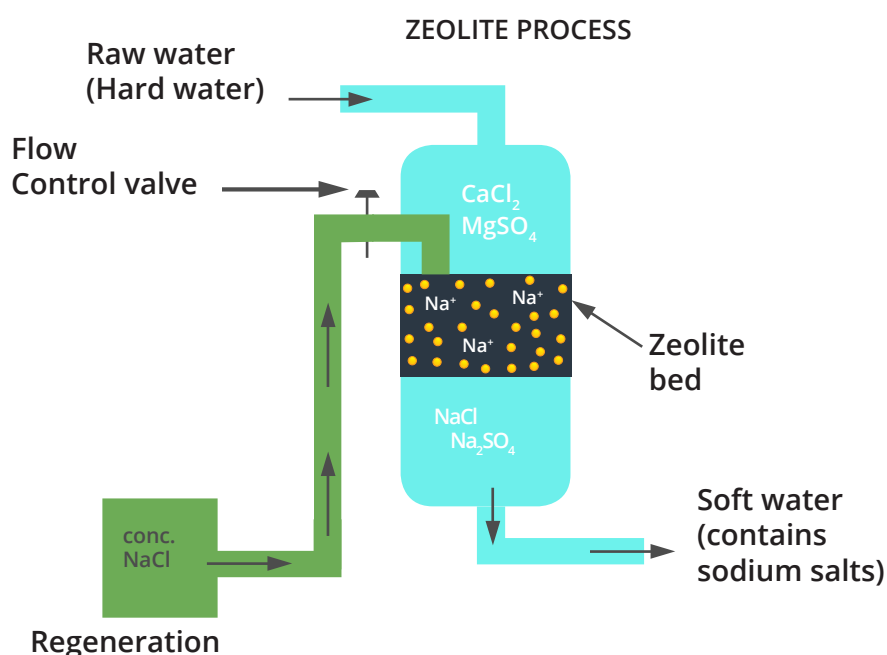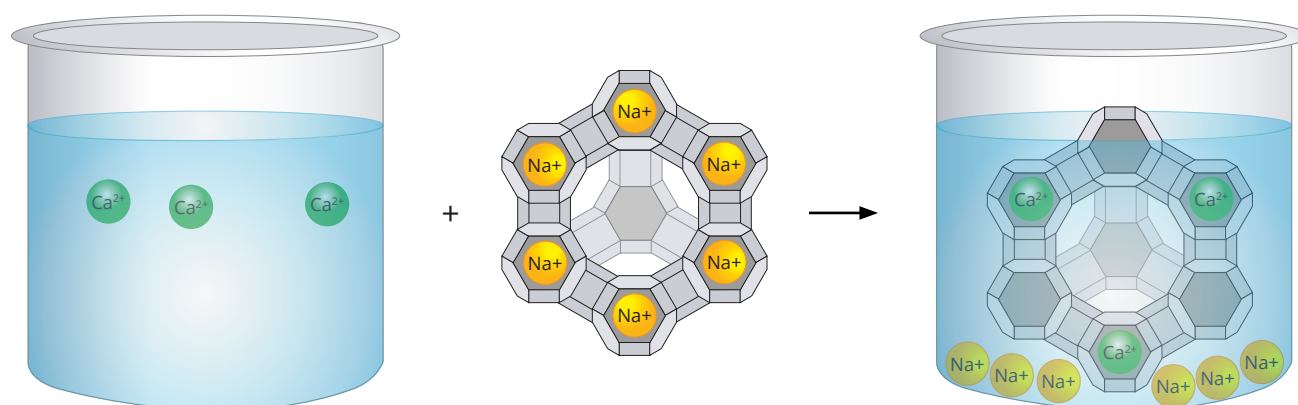
Regeneration Reaction

i) When large quantity of hard water is passed through the zeolite bed,the sodium zeolite bed completely gets changed to calcium and magnesium zeolite and there are no exchangeable Na^+ ions on it. Such a zeolite is said to be exhausted and need regeneration.

ii) The regeneration process is carried out passing 10% NaCl (brine) solution.

$$MgZ + 2NaCl \longrightarrow Na_2Z + MgCl_2$$

Exhausted zeolite Brine Regenerated zeolite Washing

Advantages

i) It is quite clean process and requires less time for softening.

ii) Soft water obtained has hardness between 5-10 ppm.

iii) Easy process to operate.

iv) Low cost of operating system.

v) The zeolite bed is whether active or exhausted can be easily tested with soap solution.

Limitations

i) Water containing excess acidity or alkalinity may destroy zeolite crystals.

ii) Water having turbity in it, cannot be purified with this process as they block pores of zeolite.

iii) The coloured ions like Mn^{2+}, Fe^{2+} cannot be removed by this process.

iv) Warm water should not be softened as it may decompose sodium zeolite slowly.

v) This method is applicable only for small scale treatment.

vi) In Zeolite process $2Na^+$ ions are replaced by Ca^{2+}/Mg^{2+} ions. The soft water obtained by this process has excess of Na^+ ions.

☰ STEPS & FORMULA | Numerical based on Zeolite process

Note:

 1) Zeolite is cation exchanger containing Na^+ as a replaceable ion.

 2) Zeolite bed can be regenerated by passing NaCl solution.

Step 1: Calculate amount of NaCl required for regeneration in mg from its concentration.

 Formula: Amount of NaCl in mg = gm/lit x lit of NaCl x 1000

Step 2: Convert mg of NaCl into $CaCO_3$ equivalent as,

 1 equivalent of NaCl = 1 equivalent of $CaCO_3$.

Formula: Amount of NaCl in terms of $CaCO_3$ equivalent $= \dfrac{\text{Amount of NaCl in mg x 50}}{58.5}$

Step 3: Calculate hardness of water with following formula:

 Hardness of water in ppm $= \dfrac{CaCO_3 \text{ equivalent amount of NaCl}}{\text{Volume of water sample}}$

 Formula in step 3 can also be used to find volume of water softened.

Exercise - 1.6
Questions Based on Zeolite Process

Q 1. A zeolite bed exhausted by softening 4000 litres of water requires 10 litres of 15% NaCl solution for regeneration. Calculate the hardness of water sample.

Q 2. A Zeolite softener was completely exhausted and was regenerated by passing 100 litres of NaCl containing 120 gm/lit. of NaCl. How many liters of a water sample of hardness 500 ppm can be soften by this softener?

Q 3. A zeolite bed gets exhausted on softening 2400 lit. of water having hardness 200 ppm. How many litres of 8% NaCl will be required for regeneration of exhausted zeolite?

Q 4. An exhausted zeolite was completely regenerated by 120 litres of 10% NaCl. How many litres of hard water having hardness 750 ppm can be softened by this softener?

Q 5. A zeolite bed get exhausted by softening 2500 litres of a water sample and requires 10 litres of 10% for regeneration. Find the hardness of water sample

Q 6. How many litres of 10 % NaCl will be required to regenerate the exhausted zeolite after softening 15000 litres of water with harness 750 ppm?
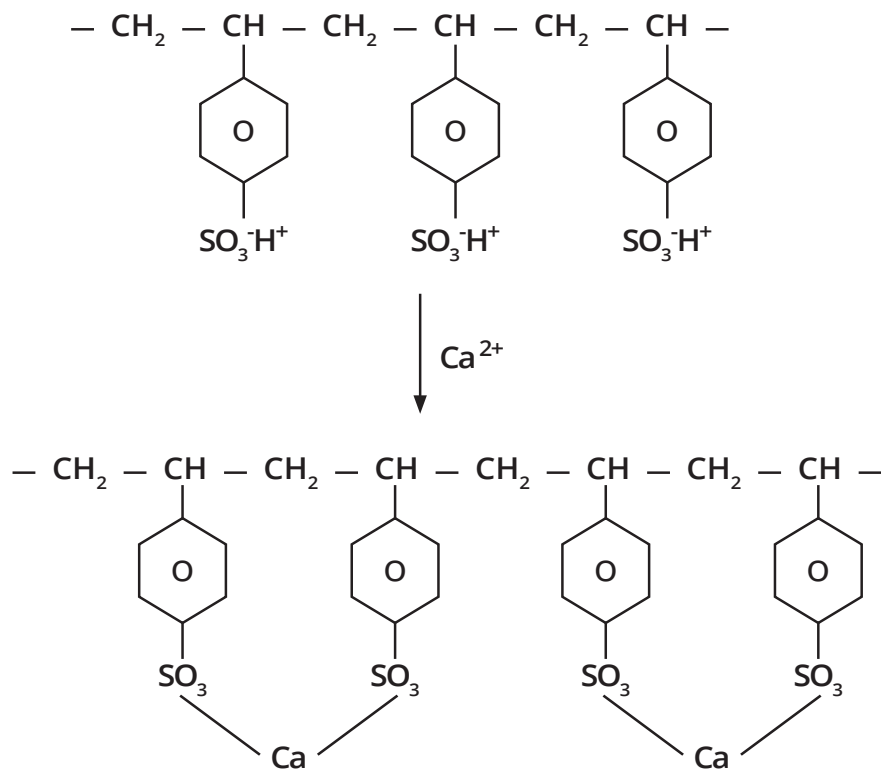
13. Ion exchange process/ Demineralization process

❖ The boiler feed water, as far as possible should be free from all types of impurities and if possible, it should be as pure as distilled water.

❖ Water of such quality can be obtained by demineralization or deionization process.

❖ The demineralized water is soft and it does not contain any dissolved salts. In this process, ion exchange resins are used as softener.

❖ Ion exchange resins are insoluble, cross linked, long chain organic polymers with microporous structure and the functional groups attached to the chain are responsible for the ion exchanging properties
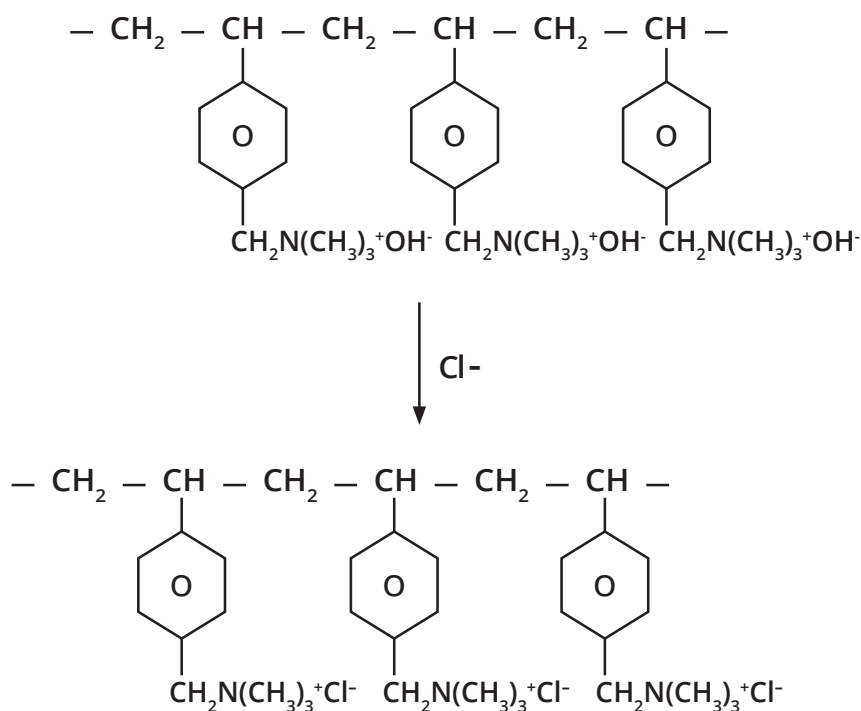
There are two synthetic resin are used

i) Cation exchanger resin

❖ This is a cross linked polymer having carboxylated/sulphonated aromatic ring attached to it.

❖ The resin containing acidic functional group such as –COOH,-SO$_3$H etc. are capable of exchanging their H$^+$ ion with other cations are cation exchange resin, represented as RH.

❖ Amberlite IR 120, Dowex 50, Nalcite-HCR are the commercially used resins of this type.

$$— CH_2 — CH — CH_2 — CH — CH_2 — CH —$$

Ring with $SO_3^-H^+$, $SO_3^-H^+$, $SO_3^-H^+$

$$\downarrow Ca^{2+}$$

$$— CH_2 — CH — CH_2 — CH — CH_2 — CH — CH_2 — CH —$$

Rings with SO_3 ... Ca ... SO_3 ... Ca

2) Anion exchanger resin

⚛ This is polymer having aromatic ring linked with the polymer chain and the rings are with quaternary ammonium group.

⚛ The OH⁻ ions are loosely held and are easily exchangeable with all the negative ions from water.

⚛ Amberlite 400, Dowex 3 are the commercially used resins of this type.

$$— CH_2 — CH — CH_2 — CH — CH_2 — CH —$$

$CH_2N(CH_3)_3^+OH^-$ $CH_2N(CH_3)_3^+OH^-$ $CH_2N(CH_3)_3^+OH^-$

$$\downarrow Cl^-$$

$$— CH_2 — CH — CH_2 — CH — CH_2 — CH —$$

$CH_2N(CH_3)_3^+Cl^-$ $CH_2N(CH_3)_3^+Cl^-$ $CH_2N(CH_3)_3^+Cl^-$

Principle

When hard water containing cationic and anionic impurities passed through the cations exchanger resin, it captures all cations (in exchange of H^+) and then through anion exchange resin captures all the anions (in exchange to OH^-) to give pure water free from all ionic impurities which is called as deionized or demineralized water.

Process

i) The hard water is passed through column containing porous cation exchanger resin cation exchanger; it removes all cations like Ca^{+2}, Na^+ etc. from hard water and equivalent amount of H^+ ions are released from this exchanger to water. Thus, water received from cation exchanger is acidic in nature.

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

$$RH + Na^+ \longrightarrow RNa + H^+$$

$$2RH + Mg^{2+} \longrightarrow R_2Mg + 2H^+$$
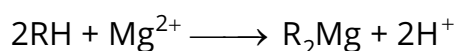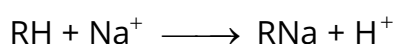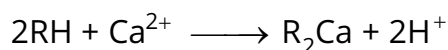
ii) Then the acidic output water from first column, then enters in another column containing porous anion exchange resin where all anions in water are captured and OH^- are released in exchange.

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

$$R'(OH) + Cl^- \longrightarrow R'Cl + OH^-$$
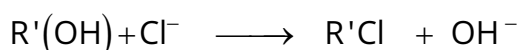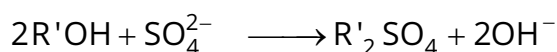
iii) The water flowing out from second exchanger resin contains equivalent amount of H^+ and OH^- ions which combine to form H_2O and there is no ionic impurity in the final water.

iv) Output of second column is then send to degasifier to remove dissolved gases from water. Thus, water obtained at the end of this process is free from all dissolved impurities. This method is also called as deionization or demineralization process.
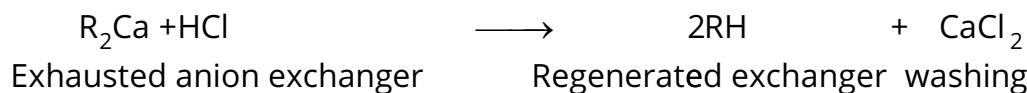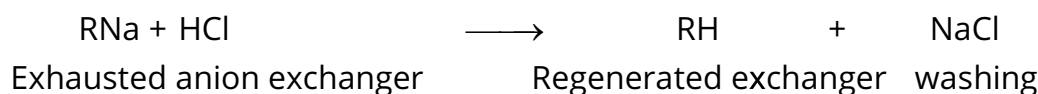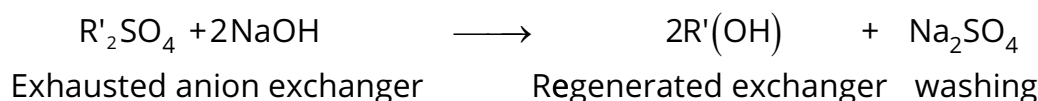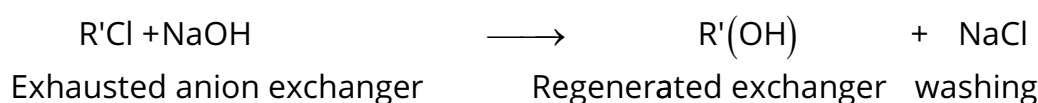
Ion exchange process
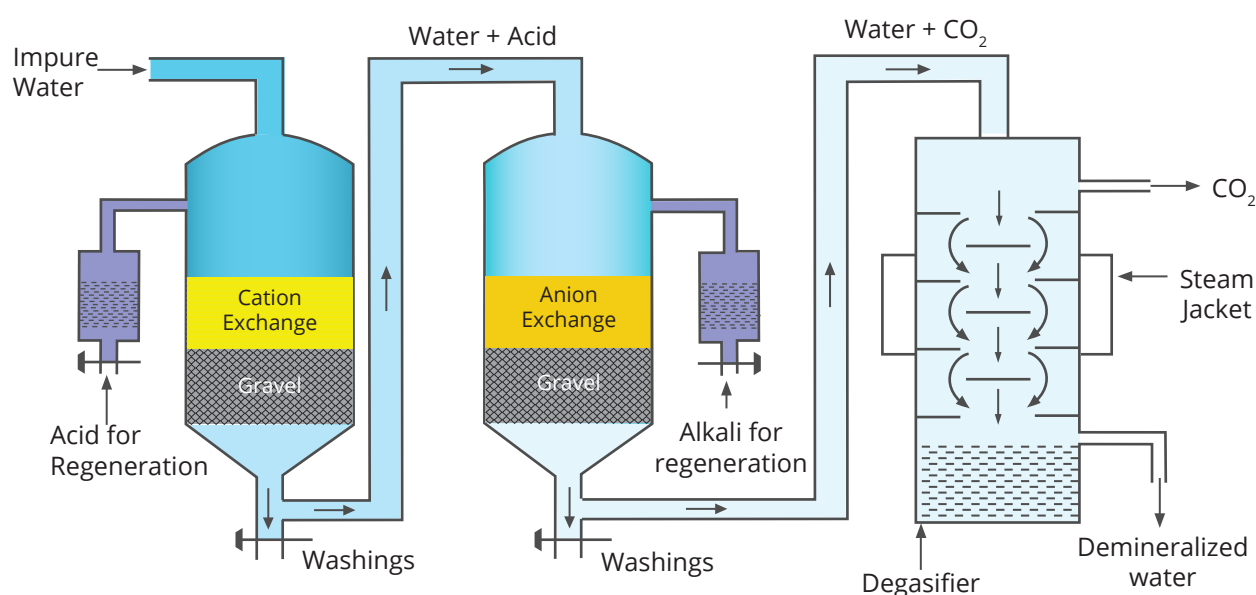
Regeneration

When all H^+ and OH^- ions from resins are replaced by various cations like Ca^{2+}, Mg^{2+}ions and anions like Cl^-, SO_4^{-2} resin is said to be exhausted.

i) The exhausted cation exchange is regenerated by washing with dil.HCl solution.

$$RNa + HCl \longrightarrow RH + NaCl$$

Exhausted anion exchanger   Regenerated exchanger   washing

$$R_2Ca + HCl \longrightarrow 2RH + CaCl_2$$

Exhausted anion exchanger   Regenerated exchanger   washing

ii) The exhausted anion exchanger resin is regenerated by washing with dil. NaOH solution.

$$R'Cl + NaOH \longrightarrow R'(OH) + NaCl$$

Exhausted anion exchanger   Regenerated exchanger   washing

$$R'_2SO_4 + 2NaOH \longrightarrow 2R'(OH) + Na_2SO_4$$

Exhausted anion exchanger   Regenerated exchanger   washing

Advantages

i) The process can be used to soften acidic or alkaline water.

ii) This method gives water zero hardness and no ionic impurity.

iii) Equipment occupies small space.

iv) Process is easy to operate.

v) It produces water of very low hardness so treated water can be used in high pressure boilers.

Limitations

i) The equipment is costly and common expensive chemicals required.

ii) Process can be operated only for small scale purification of water.

iii) If water sample contain turbidity cannot be used for this process.

14. Membrane Processes

Desalination of brackish water

❋ A brackish water contains high concentration of salts and has peculiar salty taste. e.g. sea water (containing about 4 to 25 gm salt per liter),deep bore water from some areas.

❋ The sea water can be converted into fresh water or potable water,after removing dissolved salts.

Desalination

❋ The process of removing dissolved salts,common salt from sea water to make it potable or suitable for drinking and agriculture purpose is called desalination.

❋ There are many techniques which can be used for treatment of sea water.

✵ Desalination can be performed by two processes, membrane process and thermal process. Reverse osmosis(RO) and electrodialysis are two membrane processes and distillation is thermal process.
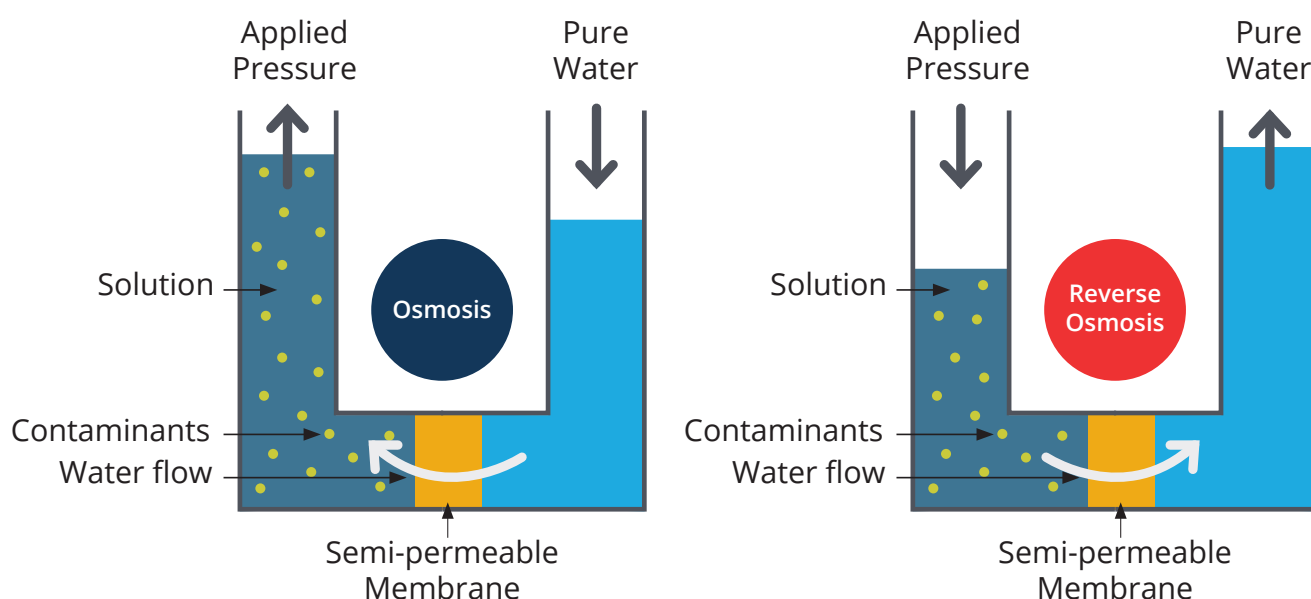
A) Osmosis

i) The movement of solvent between two solutions having different concentrations which are separated by semi-permeable membrane is known as osmosis.

ii) The solvent moves from the solution of lower concentration to higher concentration until both the solutions have the same concentration as shown in figure.

B) Reverse Osmosis

✵ Various membrane techniques are available,which selectively separate solute or contaminants on the basis of pore size.

✵ The type of membrane separation technologies includes reverse osmosis, hyper filtration, ultra-filtration etc. but reverse osmosis is commonly used.

Principle

✵ The reversal 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.

✵ In reverse osmosis process, salt rich impure water and pure water are separated by semi-permeable polymer membrane. This membrane is microporous that allows only tiny molecules like water to pass through.

✵ External pressure is applied on the higher concentration solution(impure water) slightly higher than its osmotic pressure.

✵ The flow of solvent takes place in reverse direction that is from higher concentration to lower concentration through semi-permeable membrane.

✵ In reverse osmosis we separate water from its contaminants rather than contaminants from water.

Semi-permeable Membrane

Method

i) Sea water or water polluted by ionic pollutants is filled in reverse osmosis cell.

ii) A pressure of 30 to 250 psi is applied on it to force the solvent to pass through semi-permeable membrane.

iii) Membrane consist of polymeric material film made up of proper porosity,from materials like acrylics, polyamides, aramids etc.

Advantages

i) RO is capable of removing/rejecting dissolved salts as well as organic substances along with bacteria and viruses present in water.

ii) It can convert sea water to drinking water at low cost and low capital.

iii) Pure water for high pressure boiler can be obtained.

iv) The process is simple and require few minutes.

v) It can also remove suspended colloidal particles.

vi) The life of membrane is nearly 2 years and it should be replaced after this period.

15. Electrodialysis

� The process of removing dissolved ionic impurities (salts,ionic dyes) from water by using membrane and electric field is known as electrodialysis.

Construction and Working

i) Electrodialysis cell consist of a large number of paired sets of plastic membranes.

ii) The membranes are ion selective that is cation selective membrane will allow only cation to pass through it, as this membrane consist of negatively charged fixed groups which repel anions and do not allow to go through.

iii) The anion selective membrane allows only anions to pass through and plastic membrane has cation repelling groups.

iv) When an electric field is applied perpendicular to the direction of flow of water the anions moves towards positively charged electrode through the anion selective membrane in the neighboring compartment but after that there is cation selective membrane and the movement is stopped.

v) Similarly cation move in the direction of negatively charged electrode and go in neighboring compartment. They cannot move further because next is anion selective membrane.

vi) The result will be alternate compartments with very high concentration of electrolyte and neighboring compartment to them with negligible concentration of ionic substance. Thus we get alternate streams of pure water from the Electrodialysis cell.

Cation permeable membrane   Anion permeable membrane
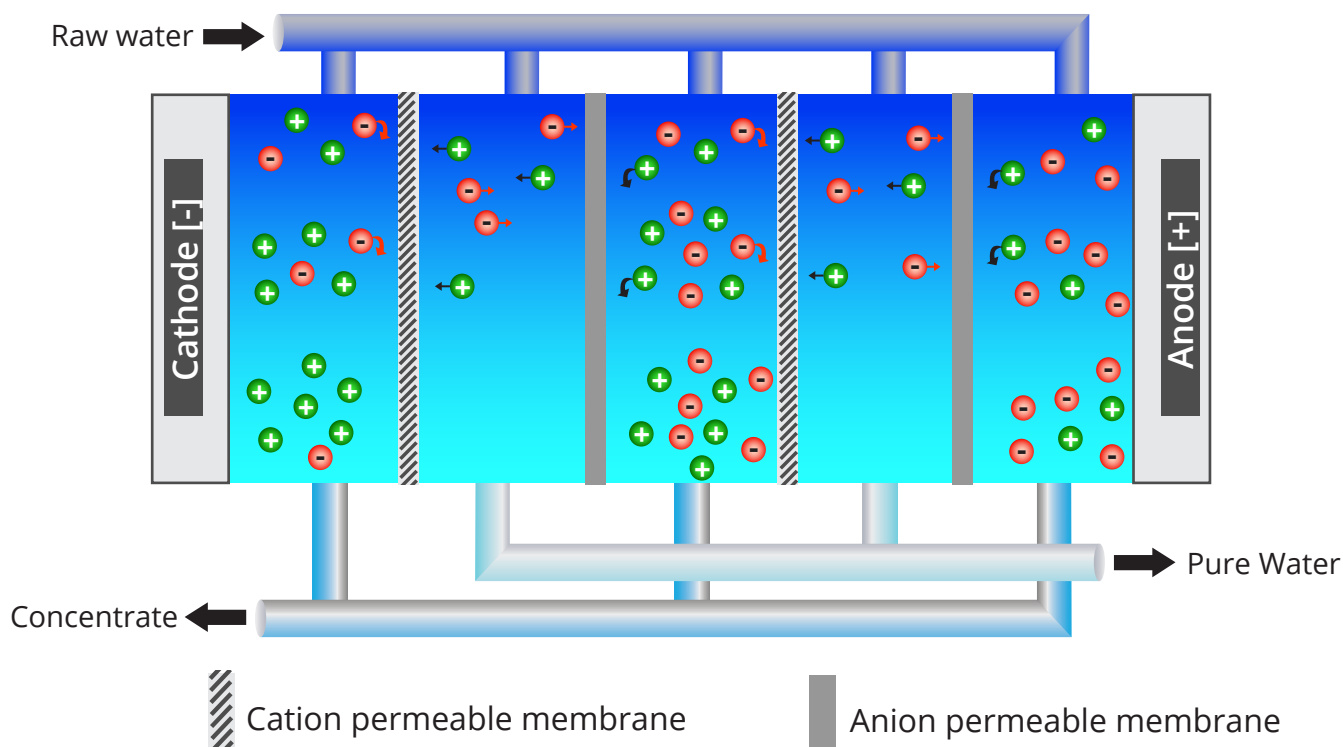
Applications

i) Removal of salts from sea water to get pure water.

ii) Removal of ionic pollutants (toxic salts, ionic dyes etc.) from treated industrial waste.

Limitations

i) Does not remove dissolved organic matter.

ii) Does not remove colloidal impurities.

iii) Membrane replacement required frequently, adds cost.

Exercise - 1.7
Questions Based on Water Softening Methods

Scan using FORTFLAG app for detailed solution.

Q 1. Give the principle of zeolite process of water softening. Write the chemical formula of zeolite.

Q 2. Give the exchange reaction of zeolite with following salts:
i) $Ca(HCO_3)_2$ ii) $MgCl_2$ iii) $CuSO_4$

Q 3. Describe the zeolite softening method with diagram, process, softening reactions for softening of hard water.

Q 4. Describe Deionisation method of water softening with ion-exchange and regeneration reactions.

Q 5. Describe deionization method for water softening with diagram, process, softening reactions for softening of hard water.

Q 6. What is reverse osmosis? Describe the process with labelled diagram.

Q 7. Describe reverse osmosis process for desalination of brackish water with labelled diagram. Give advantages and limitations of this process.

Q 8. Describe electrodialysis process for desalination of brackish water with labelled diagram. Give advantages and limitations of this process.

Q 9. Compare between reverse osmosis and electrodialysis method.

Q 10. Give comparison between zeolite process and ion exchange process.