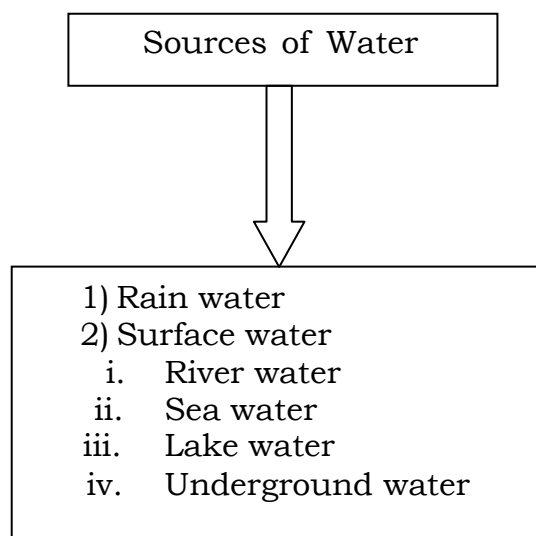# WATER

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

❖ Introduction:

- Water is found abundantly in nature. It is essential for the survival of plants, animals & human beings and is equally important for use in industries.
- Earth's 71% surfaces are covered by water and the remaining 29% by land. About 97% of the earth's water supply is in the ocean, which is unfit for human consumption and other uses because of its high salt content.
- Of the remaining 3%, 2% is locked in the polar ice caps and only 1% is available as fresh water in rivers, lakes, streams, reservoirs and ground water which is suitable for human consumption.
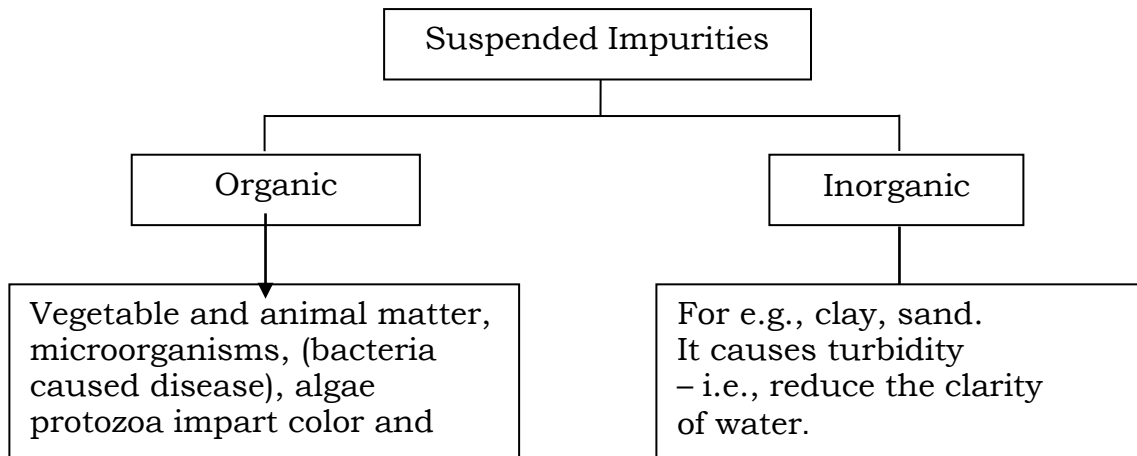
❖ Source of water:

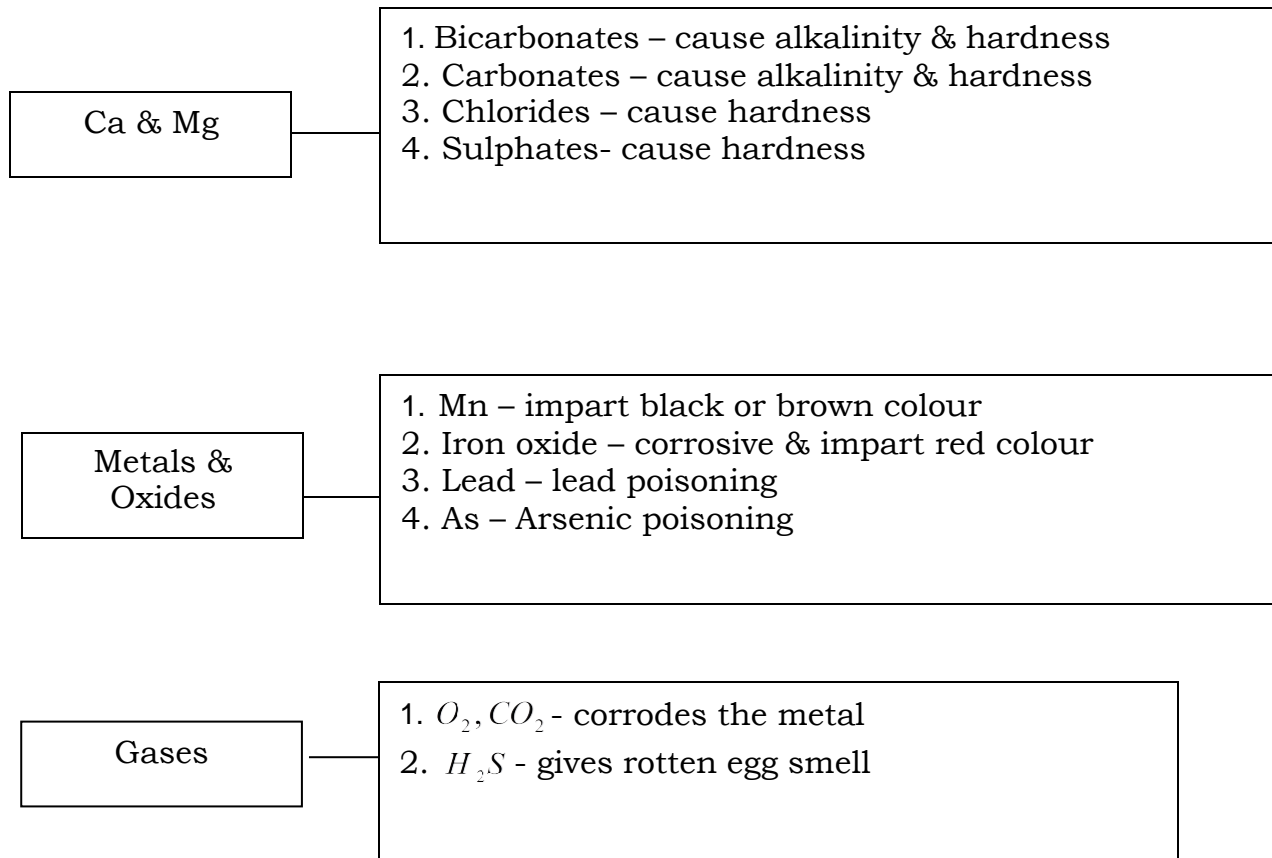The sources of water are broadly classified as:

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┌─────────────────────────┐
│     Sources of Water    │
└─────────────────────────┘
             │
             ▼
┌─────────────────────────┐
│ 1) Rain water           │
│ 2) Surface water        │
│    i.   River water     │
│    ii.  Sea water       │
│    iii. Lake water      │
│    iv.  Underground water│
└─────────────────────────┘
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❖ Impurities in water:

➢ Suspended impurities:

Suspended impurities are dispersion of solid particles that are large enough to be removed by filtration or on settling.

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                    ┌─────────────────────────┐
                    │  Suspended Impurities   │
                    └─────────────────────────┘
                      │                     │
          ┌───────────────────┐   ┌───────────────────┐
          │      Organic      │   │     Inorganic     │
          └───────────────────┘   └───────────────────┘
                    │                       │
   ┌──────────────────────────────┐  ┌──────────────────────────────┐
   │ Vegetable and animal matter, │  │ For e.g., clay, sand.        │
   │ microorganisms, (bacteria    │  │ It causes turbidity          │
   │ caused disease), algae       │  │ – i.e., reduce the clarity   │
   │ protozoa impart color and    │  │ of water.                    │
   └──────────────────────────────┘  └──────────────────────────────┘
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➢ Dissolved inorganic impurities:

```
┌──────────────┐   ┌──────────────────────────────────────────────┐
│              │   │ 1. Bicarbonates – cause alkalinity & hardness│
│   Ca & Mg    │───│ 2. Carbonates – cause alkalinity & hardness  │
│              │   │ 3. Chlorides – cause hardness                │
│              │   │ 4. Sulphates- cause hardness                 │
└──────────────┘   └──────────────────────────────────────────────┘
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┌──────────────┐   ┌──────────────────────────────────────────────┐
│              │   │ 1. Mn – impart black or brown colour         │
│  Metals &    │───│ 2. Iron oxide – corrosive & impart red colour│
│  Oxides      │   │ 3. Lead – lead poisoning                     │
│              │   │ 4. As – Arsenic poisoning                    │
└──────────────┘   └──────────────────────────────────────────────┘
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┌──────────────┐   ┌──────────────────────────────────────────────┐
│              │   │ 1. $O_2, CO_2$ - corrodes the metal          │
│    Gases     │───│ 2. $H_2S$ - gives rotten egg smell           │
│              │   │                                              │
└──────────────┘   └──────────────────────────────────────────────┘
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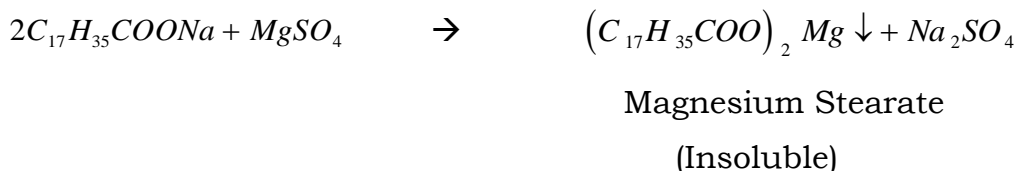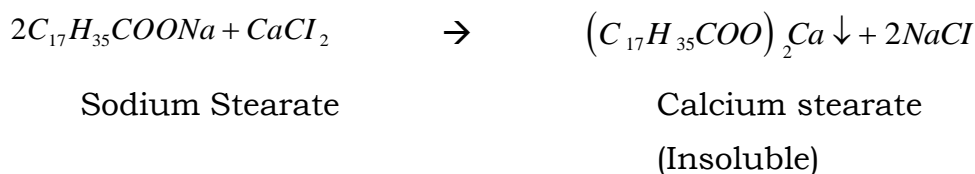
> **Organic impurities:**

It may be suspended or dissolved vegetable and animal matter which impart colour, taste, acidity and produce harmful disease-causing germs.

❖ **Hardness:**

> **Soft and hard water:**

- A sample of water which on shaking with soap solution produces lather instantly is called **Soft-water**. It does not contain any of the dissolved inorganic salts of Ca/Mg. The lathering action by soap is due to the reduction of surface tension of water by addition of soap.

- A sample of water which on shaking with soap solution does not give lather instantly but produces a white curd – like ppt. is called **Hard-water**. Such a sample contains dissolved bicarbonates sulphates, chlorides of Ca/Mg.

- Hardness in water is that characteristic which prevents the lathering of soap. Reaction of soap (Na / K salt of higher fatty acid like Oleic, Stearic) with $CaCI_2$ & $MgSO_4$ is as follows.

$$2C_{17}H_{35}COONa + CaCI_2 \quad \rightarrow \quad \left(C_{17}H_{35}COO\right)_2 Ca \downarrow + 2NaCI$$

Sodium Stearate   Calcium stearate
                                                                            (Insoluble)

$$2C_{17}H_{35}COONa + MgSO_4 \quad \rightarrow \quad \left(C_{17}H_{35}COO\right)_2 Mg \downarrow + Na_2SO_4$$

Magnesium Stearate
(Insoluble)

> **Classification:**

Hardness is of two types:

1) Temporary or Carbonate or Alkaline Hardness

2) Permanent or non-carbonate or non-alkaline Hardness

1) Temporary or Carbonate or Alkaline Hardness:

  a. Temporary hardness is caused by the presence of dissolved bicarbonates of calcium, magnesium and other heavy metals like Fe^{2+}, Al^{3+}. Hardness is destroyed by boiling of water, when bicarbonates are decomposed yielding insoluble carbonates or hydroxide.

$$Ca\left(HCO_3\right)_2 \xrightarrow{\text{On Heating}} CaCO_3 \downarrow H_2O + CO_2 \uparrow$$

(Insoluble)

$$Mg(HCO_3)_2 \xrightarrow{\text{On Heating}} Mg(OH)_2 \downarrow + 2CO_2 \uparrow$$

Or

$$MgCO_3 \downarrow + H_2O + CO_2 \uparrow$$
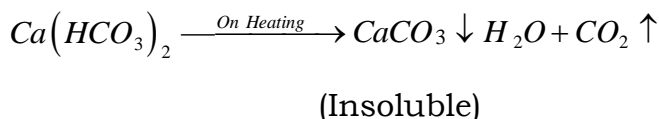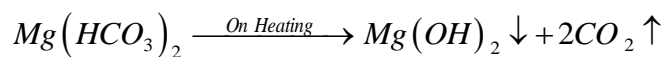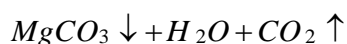
b. Ca/Mg carbonates or hydroxides thus formed being insoluble is deposited as a crust or scale at the bottom of the vessel while CO_2 escapes out. Precipitates are filtered off to get Soft-water.

2) Permanent or non-carbonate or non-alkaline Hardness:

a. Permanent hardness or non-carbonate hardness is due to the presence of chlorides, sulphates & nitrates of Ca, Mg, Fe and other heavy metals. This cannot be destroyed on boiling. Special softening methods are used.

❖ **Comparison:**

Sr. No.	Temporary Hardness	Permanent Hardness
1.	This type of hardness can be removed by easy means such as boiling of water. The name temporary indicates the property which is not difficult to be changed.	This type of hardness cannot be removed by simple techniques. Hence the term permanent is used to describe these characteristics. Special softening techniques are used.
2.	It is due to dissolved bicarbonates and Carbonates of Ca^{2+}, Mg^{2+}, Fe^2, etc.	It is due to dissolved chlorides, sulphates & nitrates of Ca^{2+}, Mg^{2+}, Fe^2 etc.
3.	It is caused due to carbonates hence known as carbonate hardness.	It is caused due to salts other than carbonates hence known as non-carbonates hardness.
4.	Temporary hard water if used in steam production deposits ppts of Carbonates & hydroxides of Ca^{2+}, Mg^{2+} at the bottom of the container. These deposits harden to form scales. The reaction taking place is $$Ca(HCO_3)_2 \rightarrow CaCO_3 + H_2O + CO_2 \uparrow$$ $$Mg(HCO_3)_2 \rightarrow Mg(OH)_2 + 2CO_2 \uparrow$$	Permanent hard water if used in steam production forms scales in boiler.

❖ **Measurements 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 reasons this compound is being formed which gets precipitated during water treatment.

➢ **Equivalents of Calcium Carbonate:**

- Concentrations of hardness as well as non-hardness constituting ions are expressed in terms of equivalent amount of $CaCO_3$. The choice of $CaCO_3$ is accepted because.
  1) Its M. wt. is 100 (Eq. Wt. = 50).
  2) It is the most insoluble salt that is precipitated in water treatment.
- Equivalent of $CaCO_3$ for a hardness producing substance is

$$= \frac{\text{Mass of hps} \times \text{Chemical equivalent of } CaCO_3}{\text{Chemical equivalent of hps.}}$$

$$\frac{\text{Chemical equivalent of } CaCO_3}{\text{Chemical equivalent of hps.}} \quad \text{Or} \quad \frac{\text{Molecular weight of } CaCO_3}{\text{Molecular weight of hps.}} = \text{Multiplication Factor}$$

*hps = Hardness producing substance

- If $Ca(HCO_3)_2$ is the hps – 162 parts by mass of $Ca(HCO_3)_2$ would react with the same amount of soap as 100 parts by mass of $CaCO_3$ Therefore the mass of $Ca(HCO_3)_2$ is multiplied by a factor 100/162 to give mass in terms of $CaCO_3$.

Salt	Molecular Mass	Chemical equivalent	Multiplication factor
$Ca(HCO_3)_2$	162	81	100/162
$Mg(HCO_3)_2$	146	73	100/146
$CaSO_4$	136	68	100/136
$CaCl_2$	111	55.5	100/111
$MgSO_4$	120	60	100/120
$MgCl_2$	95	47.5	100/95

$CaCO_3$	100	50	100/100
$MgCO_3$	84	42	100/84
CO_2	44	22	100/44
$Mg(NO_3)_2$	148	74	100/148

❖ **Units of Hardness:**

Hardness of water is expressed in terms of following units.

➢ **Parts per million (ppm)**

It is the number of parts of $CaCO_3$ equivalent in 10^6 parts of water.

➢ **Milligram per litre (mg/L)**

It is the number of milligram of $CaCO_3$ equivalent hardness present per litre of water.

- 1 litre of water weighs 1 Kg = 1000 gm = 10^6 mg

- 1 mg/L = 1 mg of $CaCO_3$ equivalent per 10^6 mg of water.

- 1 mg/L = 1 ppm.

➢ **Clarkes Degree $\left({}^0Cl \right)$**

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

➢ **Degree French $\left({}^0Fr \right)$**

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

$$1 \text{ ppm} = 1 \text{ mg / L} = 0.1 \ {}^0Fr = 0.07^0 \ Cl$$
$$1 \text{ mg/L} = 1 \text{ ppm} = 0.1 \ {}^0Fr = 0.07^0 Cl$$
$$1 \ {}^0Cl = 1.43 \ {}^0Fr = 14.3 \text{ ppm} = 14.3 \text{ mg/L}$$
$$1^0 Fr = 10 \ ppm = 10 \text{ mg/ L} = 0.7^0 Cl$$

❖ Determination of Hardness of water:

EDTA Titration method or Complex metric Titration Method:

➢ **Theory:**

1) The principle of this method is that hardness causing ions like Ca^{2+}, Mg^{2+} forms a weak unstable complex of wine red colour with indicator EB-T (Eriochrome Black – T).

2) When added in small amount to hard water buffered to a pH value of 10.0.

3) When such a complex is treated with EDTA, It extracts the metal ions from the metal ion dye complex to form a stable M-EDTA complex because of great affinity of EDTA to form stable complexes with metal ions releasing Eriochrome black – T free.

4) Thus, wine red colour changes to distinct blue marking the end point. End point indicates that there is complete extraction of metal ions by EDTA. This can be represented as

$$\begin{bmatrix} Ca^{2+} \\ Mg^{2+} \end{bmatrix} + \text{Eriochrome Black} - T \rightarrow \begin{bmatrix} Ca & EB - T \\ Mg \end{bmatrix} \text{complex}$$
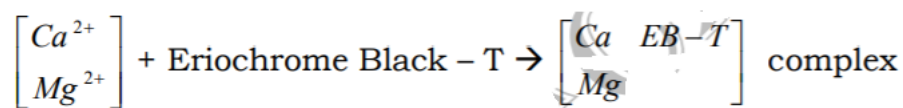
Unstable complex (wine red)

Unstable complex is replaced by

$$\begin{bmatrix} Ca \\ & \text{Eriochrome Black} - T \\ Mg \end{bmatrix} \text{Complex} + \text{EDTA}$$

$$\begin{bmatrix} Ca \\ & \text{EDTA complex} \\ Mg \end{bmatrix} + \text{Eriochrome Black-T}$$
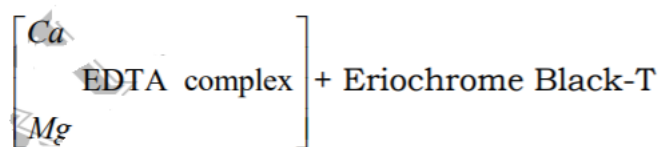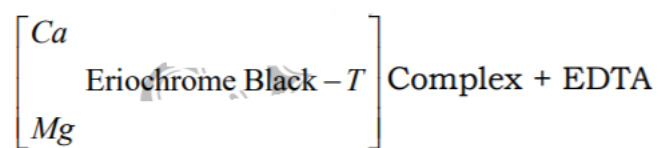
(Blue)

EDTA is Ethylene Di-amine tetra acetic acid.

$$HOOC\ H_2C \diagdown \atop HOOC\ H_2C \diagup N - CH_2 - CH_2 - N \diagup CH_2COOH \atop \diagdown CH_2COOH$$
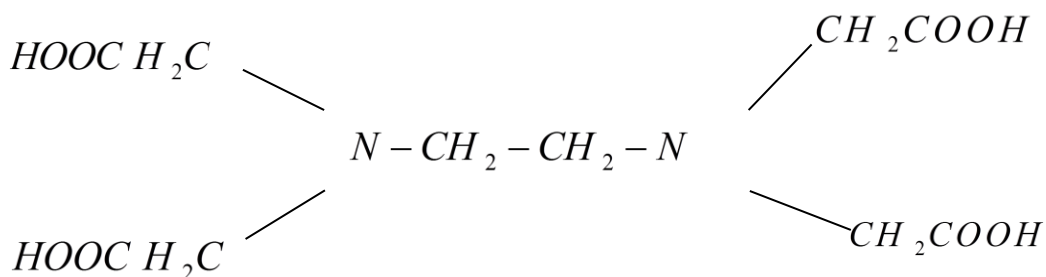
EDTA in the form of its di-sodium salt

$HOOC\,H_2C$

CH_2COONa

$$N - H2C - CH2 - N$$

$NaOOCH_2C$

CH_2COOH

$M = Ca^{2+}, Mg^{2+}$

O=C

C=O

O

O

H_2C

CH2

M

$HOOCH_2C$———N

N———CH_2COOH

H_2C

CH2

Structure of EDTA – M Complex

➤ **Procedure**

1) **Preparation of Hard water:**

   Dissolve 1 gm of pure dry $CaCO_3$ in minimum quantity of dilute HCl (1:1) and then evaporate the solution to dryness on a water bath. Dissolve the residue in distilled water to make 1 litre solution. Each ml of this solution thus contains 1 mg of $CaCO_3$ equivalent hardness.

2) **Preparation of EDTA solution:**

   Dissolve 4.0 gm of EDTA crystals + 0.1 gm $MgCl_2$ in 1 litre of distilled water.

3) **Preparation of Indicator:**

   Dissolve 0.5 gm of Eriochrome Black – T in 100 ml of alcohol.

4) **Buffer solution (pH=10):**

   Add 67.5 gm of NH_4Cl to 570 ml of conc. NH_3 soln. and dilute with distilled water to 1 litre.

➢ Titration Procedure:

1) Standardization of EDTA Soln.:

Rinse and fill the burette with EDTA soln. Pipette out 50 ml of standard hard water in a conical flask. Add 10-15 ml of buffer soln. & 4-5 drops of indicator. Titrate with EDTA soln. till wine red colour changes to blue. Let volume of EDTA consumed is V_1 ml.

2) Titration of unknown Hard water:

50 ml of unknown hard water mixed with buffer solution & indicator as in step1 & titrated against EDTA solution till wine red colour changes to blue. Let the volume of EDTA consumed be V_2 ml.

3) Titration of Boiled Hard water:

Take 250 ml of tap water in a beaker. Boil it till the volume is reduced to about 50 ml [when all bicarbonates are decomposed to insoluble $CaCO_3 / Mg(OH)_2$].

Filter & wash the ppt. with distilled water, collect filtrate & washings in a 250 ml measuring flask. Finally make up the volume to 250 ml with distilled water. Then titrate 50 ml of boiled water against EDTA solution. Let the volume consumed be V_3 ml.

➢ Calculations:

50 ml of standard hard water = V_1 ml of EDTA solution

50 ml of unknown hard water = V_2 ml of EDTA solution

50 ml of boiled hard water = V_3 ml of EDTA solution

1) 50 ml of SHW= 50 mg of $CaCO_3$ equivalent hardness.

   50 ml of SHW = V_1 ml of EDTA soln.

   V_1 ml of EDTA soln. = 50 mg of $CaCO_3$ equivalent hardness.

> **1 ml of EDTA soln. = 50/V_1 mg of $CaCO_3$ equivalent hardness.**

2) 50 ml of UHW= V_2 ml of EDTA soln.

   V_2 ml of EDTA soln. = $V_2 \times 50/V_1$ mg of $CaCO_3$ equivalent hardness

   50 ml of UHW = $V_2 \times 50/V_1$ mg of $CaCO_3$ equivalent hardness

   1000 ml of UHW = $1000 \times V_2/V_1$ mg of $CaCO_3$ equivalent hardness.

> **Total Hardness =** $1000 \times V_2/V_1 \, mg/L$

3) 50 ml of BHW= V_3 ml of EDTA soln.

V_3 ml of EDTA soln. = $V_3 \times 50 / V_1$ mg of $CaCO_3$ equivalent hardness

50 ml of BHW = $V_3 \times 50 / V_1$ mg of $CaCO_3$ equivalent hardness

1000 ml of BHW = $1000 \times V_3 / V_1 \; mg / L$

> **Permanent Hardness =**
>
> $1000 \times V_3 / V_1 \; mg / L$

Temporary hardness = Total hardness – Permanent hardness

$$= 1000 \times V_2 / V_1 - 1000 \times V_3 / V_1 \; mg / L$$

$$= 1000 / V_1 \left[V_2 - V_3 \right] mg / L$$

> **Temporary Hardness =**
>
> $1000 / V_1 \left[V_2 - V_3 \right] mg / L$

EDTA titration method is preferred because of greater accuracy, convenience and more rapid procedure.

❖ **Theory questions:**

1) Define temporary hardness and permanent hardness.
2) How is temporary hardness in water eliminated?
3) What is hardness? Name the substances that cause permanent hardness?
4) Differentiate between hard water & soft water.
5) Why is hard water unsuitable for boilers?
6) Write in brief "Disadvantages of hard water in different industries".
7) Differentiate between temporary hardness and permanent hardness.
8) What are the impurities associated with water? Give their effects if it is used in various industries.
9) What is hardness? Explain how you would determine hardness of water using EDTA method.

❖ **Problems on Carbonate & Non – Carbonate:**

➢ Note the following three points

▪ 1 ppm = 1 mg/l

▪ Multiplying factor = $\dfrac{\text{Mol. wt. } of\ CaCO_3\ (=100)}{\text{Mol. wt. of the impurity}}$

- $CaCO_3$ equivalent in ppm = impurity quantity in ppm × (M.F.)

  (M.F. → Multiplying Factor)

1) A water sample contains $Ca(HCO_3)_2 = 32.4\,mg/lit$, $Mg(HCO_3)_2 = 29.2\,mg/lit$ & $CaSO_4 = 13.5\,mg/lit$. Calculate all the three hardness.

   a. Calculations of $CaCO_3$ equivalents:

Impurity	Qty.(ppm)	Mol. wt.	M. F.	CaCO₃ Equivalent (ppm)
$Ca(HCO_3)_2$	32.4	162	100/162	$32.4 \times (100/162) = 20$
$Mg(HCO_3)_2$	29.2	146	100/146	$29.2 \times (100/146) = 20$
$CaSO_4$	13.5	136	100/136	$13.5 \times (100/136) = 10$

   b. Temporary hardness = $Mg(HCO_3)_2 + Ca(HCO_3)_2 = 20 + 20 = 40\,ppm$

   c. Permanent hardens = $CaSO_4$ = 10 ppm

   d. Total hardness = Tempo. + Perm. = 40 + 10 = 50 ppm.

2) Calculate the carbonate & non-carbonate hardness of a water sample containing $MgCl_2 = 9.5\,ppm$, $MgSO_4 = 48\,ppm$, $Ca(HCO_3)_2 = 16.2\,ppm$, $KCl = 12\,ppm$, $Mg(HCO_3)_2 = 14.6\,ppm$.

   a. Calculations of $CaCO_3$ equivalents :

Impurity	Qty.(ppm)	Mol. wt.	M.F.	CaCO₃ Equivalent (ppm)
$MgCl_2$	9.5	95	100/95	$9.5 \times (100/95) = 10$
$MgSO_4$	48	120	100/120	$4.8 \times (100/120) = 40$
$Ca(HCO_3)_2$	16.2	162	100/162	$16.2 \times (100/162) = 10$
KCl	12	Does not cause hardness ∴no calculations		
$Mg(HCO_3)_2$	14.6	146	100/146	$14.6 \times (100/146) = 10$

   b. Carbonate hardness $= Ca(HCO_3)_2 + Mg(HCO_3)_2 = 10 + 10 = 20\,ppm$

   c. Non carbonate hardness $= MgCl_2 + MgSO_4 = 10 + 40 = 50\,ppm$

3) Calculate tempo, perm & total hardness of water sample containing

$Mg(HCO_3)_2 = 7.3\ ppm$, $Ca(HCO_3)_2 = 16.2\ ppm$, $MgCl_2 = 9.5\ ppm$, $CaSO_4 = 13.6\ ppm$,

a. Calculations of $CaCO_3$ equivalents:

Impurity	Qty.(ppm)	Mol. wt.	M.F.	CaCO$_3$ Equivalent (ppm)
$Mg(HCO_3)_2$	7.3	146	100/146	$7.3\times(100/146) = 5$
$Ca(HCO_3)_2$	16.2	162	100/162	$16.2\times(100/162) = 10$
$MgCl_2$	9.5	95	100/95	$9.5\times(100/95) = 10$
$CaSO_4$	13.6	136	100/136	$13.6\times(100/136) = 10$

b. Tempo. hardness due to $Mg(HCO_3)_2 + Ca(HCO_3)_2 = 5+10 = 15\ ppm$

c. Perm. Hardness due to $MgCl_2 + CaSO_4 = 10+10 = 20\ ppm$

d. Total hardness = Tempo + Perm. = 15+20 = 35 ppm

4) Calculate tempo. & perm. hardness of water sample containing

$Mg(HCO_3)_2 = 16.8\ mg/l$, $MgCl_2 = 19\ mg/l$, $MgSO_4 = 24\ mg/l$,

$Mg(NO_3)_2 = 29.6\ mg/l$, $CaCO_3 = 4\ mg/L$, $MgCO_3 = 10\ mg/l$.

a. Calculations of $CaCO_3$ equivalents:

Impurity	Qty. (ppm)	Mol. wt.	M.F.	CaCO$_3$ Equivalent (ppm)
$Mg(HCO_3)_2$	16.8	146	100/146	$16.8\times(100/146) = 11.5$
$Mgcl_2$	19	95	100/95	$19\times(100/95) = 20$
$MgSO_4$	24	120	100/120	$24\times(100/120) = 20$
$Mg(NO_3)_2$	29.6	148	100/148	$29.6\times(100/148) = 20$
$CaCO_3$	4	100	100/100	$4\times(100/100) = 4$
$MgCO_3$	10	84	100/84	$10\times(100/84) = 11.9$

b. Tempo. hardness due to $Mg(HCO_3)_2 + CaCO_3 + MgCO_3 = 11.5+4+11.9 = 27.4\ ppm$

c. Perm. Hardness due to $Mgcl_2 + MgSO_4 + Mg(NO_3)_2 = 20+20+20 = 60\ ppm$

5) A water sample contains $MgCl_2 = 19\ ppm$, $CaCO_3 = 5\ ppm$, $Ca(HCO_3)_2 = 29.5\ ppm$, $CaSO_4 = 13$. Find all the three harnesses.

a. $CaCO_3$ equivalents

Impurity	Qty. (ppm)	Mol. wt.	M.F.	CaCO₃ Equivalent (ppm)
$MgCl_2$	19	95	100/95	$19 \times (100/95) = 20$
$CaCO_3$	5	100	100/100	$5 \times (100/100) = 5$
$Ca(HCO_3)_2$	29.5	162	100/162	$29.5 \times (100/162) = 18.21$
$CaSO_4$	13	136	100/136	$13 \times (100/136) = 9.56$

b. Tempo. hardness due to $CaCO_3 + Ca(HCO_3)_2 = 5 + 18.21 = 23.21\ ppm$

c. Perm. Hardness due to $MgCl_2 + CaSO_4 = 20 + 9.56 = 29.56\ ppm$

d. Total hardness = Tempo. + Perm. = 23.21 + 29.56=52.77 ppm

6) What is the total hardness of a water sample having the following impurities in mg/l? $Ca(HCO_3)_2 = 162$, $CaCl_2 = 22.2$, $MgCl_2 = 95$, $NaCl = 20$

a. $CaCO_3$ equivalents:

Impurity	Qty.(ppm)	Mol. wt.	M.F.	CaCO₃ Equivalent (ppm)
$Ca(HCO_3)_2$	162	162	100/162	$162 \times (100/162) = 100$
$CaCl_2$	22.2	111	100/111	$22.2 \times (100/111) = 20$
$MgCl_2$	95	95	100/95	$95 \times (100/95) = 100$
$NaCl$	20	-	-	-

b. Total hardness = Hardness due to

$Ca(HCO_3)_2 + CaCl_2 + MgCl_2 = 100 + 20 + 100 = 220\ ppm$

7) Classify the following impurities into temporal, permanent & non-hardness causing impurities:

$Ca(HCO_3)_2$, $MgSO_4$, $CaCl_2$, CO_2, HCl, $Mg(HCO_3)_2$, $CaSO_4$ & $NaCl$.

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

a. Tempo. hardness causing impurities: $Ca(HCO_3)_2$, $Mg(HCO_3)_2$

b. Perm. Hardness causing impurities: $CaSO_4$, $MgSO_4$, $CaCl_2$

c. Non-hardness causing impurities: CO_2, HCl, $NaCl$

d. $CaCO_3 + 2HCl \rightarrow CaCl_2 + H_2O + CO_2 \uparrow$

    MW = 100   MW = 111

    (1 Mole)   (1 Mole)

    $\because$ 1 ppm $CaCO_3$ hardness $\equiv 1.11$ gm of $CaCl_2$

    $\therefore$ 150 ppm $CaCO_3$ hardness $\equiv \dfrac{150}{1} \times 1.11 = 166.5$ gm $CaCl_2$

e. Thus, 166.5 gm $CaCl_2$ dissolved per litre will give 150 ppm of hardness.

8) Classify the following salts into temporal & permanent hardness causing & also calculate their $CaCO_3$ equivalents.

$Ca(HCO_3)_2 = 16.2 \, mg/L$, $MgSO_4 = 1.2 \, mg/L$, $FeCl_2 = 12.7 \, mg/L$, $NaCl = 94 \, mg/L$

a. Tempo. hardness causing salts: $Ca(HCO_3)_2$

b. Perm. Hardness causing salts: $MgSO_4$, $FeCl_2$

c. Non-hardness causing salts: $NaCl$

d. $CaCO_3$ equivalents:

Salt	Qty. (ppm)	Mol. wt.	M.F.	CaCO₃ Equivalent (ppm)
$Ca(HCO_3)_2$	16.2	162	100/162	$16.2 \times (100/162) = 10$
$MgSO_4$	1.2	120	100/120	$1.2 \times (100/120) = 1$
$FeCl_2$	12.7	127	100/127	$12.7 \times (100/127) = 10$
$NaCl$	94	-	-	-

9) Two water samples A & B were analysed for their salt content.

a. Sample A was found to contain 168 mg $MgCO_3/lit$.

b. Sample B was found to contain 820 mg $Ca(NO_3)_2/lit$ & 2 mg SiO_2/lit.

Calculate the total hardness of each sample & state which sample is more-hard.

    i.   **Sample A:**

- It contains 168 mg $MgCO_3/lit$

- $CaCO_3$ e.g. $168 \times \dfrac{100}{84} = 200\ ppm$ = tempo. Hardness = total hardness.

ii. Sample B:

- It contains 820 mg $Ca(NO_3)_2/lit$

- $CaCO_3$ e.g. $820 \times \dfrac{100}{164} = 500\ ppm$ = perm. Hardness = total hardness

SiO_2 does not cause any hardness

Sample B is more hard.

❖ **Problems on EDTA method:**

1) Calculate the total hardness for given water sample:

   a. 50 ml SHW containing 1 mg pure $CaCO_3/ml$ consumed 20 ml. EDTA solutions.

   b. 50 ml water sample consumed 30 ml EDTA solution using EBT.

   a. Standardization of EDTA:

   ∵ 20 ml EDTA solution $\equiv$ 50 ml SHW

   ∴ 1 ml EDTA solution $\equiv \dfrac{1}{20} \times 50\ ml$ SHW $= \dfrac{50}{20}\ CaCO_3$ equivalent

   b. Calculation of total hardness:

   ∵ 50 ml HW sample $\equiv 30\ ml$ EDTA solution

   ∴ 1 ml HW $\equiv \dfrac{1}{50} \times 30\ ml$ EDTA solution $= \dfrac{30}{50} \times \dfrac{50}{20}\ mg\ CaCO_3$ eq

   ∴ 1000 ml HW $\equiv \dfrac{30}{\cancel{50}} \times \dfrac{\cancel{50}}{20} \times 1000\ mg\ CaCO_3$ eq

   ∴ Total hardness = 1500 ppm

2) A SHW contains 15 g/L $CaCO_3$. 20 ml of this water required 25 ml EDTA solution. 100ml of sample water required 18 ml EDTA solution. The same sample after boiling required 12 ml of EDTA solution. Calculate temporal hardness of the water sample.

   a. Concentration of SHW = 15 g/l = 15 mg/ml $CaCO_3$.

   b. ∴ 20 ml of SHW = $20 \times 15 = 300\ mg$ of $CaCO_3$

   20 ml of SHW = 25 ml of EDTA solution

   ∴ 1 ml of EDTA solution $= \dfrac{20}{25} \times 15 = 12\ mg$ of $CaCO_3$

c. 100 ml of water sample = 18 ml of EDTA

∴ 1000 ml of water sample $= \dfrac{1000}{100} \times 18 = 180$ ml of EDTA

1 ml of EDTA = 12 mg of $CaCO_3$

∴ 180 ml of EDTA $= 180 \times 12 = 2160\, mg$ of $CaCO_3 / L$

∴ Total hardness = 2160 mg /L

d. 100 ml of boiled water = 12 ml of EDTA of $= 12 \times 12 = 144\, mg$ of $CaCO_3$

∴ 1000 ml of boiled water $= \dfrac{1000}{100} \times 144 = 1440\, mg / l\; CaCO_3$

∴ Perm. Hardness = 1440 mg/ L.

e. Tempo. Hardness = total hardness – perm. hardness

$\qquad$ = 2160-1440= 720 mg/L or ppm

3) 0.5 gm. of $CaCO_3$ was dissolved in HCI & the solution mode up-to 500 ml. with distilled water. 50ml of the solution required 45 ml of EDTA solution for titration. 50 ml of hard water sample required 15 ml of EDTA & after boiling & filtering required 10 ml of EDTA solution. Calculate total & tempo. hardness of the hard water sample.

a. Concentration of SHW = 0.5 g $CaCO_3$ / 500 ml of distilled water

$\qquad$ = 500 mg in 500 ml = 1 mg / ml $CaCO_3$

b. 50 ml of SHW $\equiv 4.5\, ml.$EDTA

i.e. 45 ml EDTA $\equiv$ 50 mg $CaCO_3$ eq. hardness

Now, 50 ml water sample $\equiv$ 15 ml EDTA

Hardness of sample $= \left(15 \times \dfrac{50}{45} \right) mg\; CaCO_3$eq. for 50 ml hardness

Hardness/L of sample $= \left(15 \times \dfrac{50}{45} \right) \times \dfrac{1000}{50} = 333.33\, ppm$

∴ Total hardness = 333.33 ppm

c. 50 ml water sample after boiling $\equiv$ 10 ml EDTA

Perm. Hardness of sample $= \left(10 \times \dfrac{50}{45} \right) mg\; CaCO_3$ eq. for 50 ml

Perm hardness of 1 litre sample $= \left(10 \times \dfrac{50}{45} \right) \times \dfrac{1000}{50} = 222.22\, mg / L$

∴ Perm. Hardness = 222.22 ppm

d. ∴ Tempo. Hardness = total hardness – perm. hardness

$\qquad$ = 333.33 – 222.22 = 111.11 ppm

4) 50 ml of SHW containing 1mg of pure $CaCO_3/ml$ consumed 20 ml of EDTA. 50 ml of the water sample consumed 30 ml. of the same EDTA solution using EBT. After boiling & filtering, 50 ml of the water sample required 10 ml of the same EDTA for titration. Calculate the total & perm. Hardness of the water sample.

a. Concentration of SHW = 1mg/ml $CaCO_3$

b. 50 ml of SHW = 50 mg of $CaCO_3$

50 ml of SHW = 20 ml of EDTA

$\therefore 1$ ml of EDTA $= \dfrac{1}{20} \times 50 = \dfrac{50}{20}$ of $CaCO_3$ eq. = 2.5 mg of $CaCO_3$ eq.

c. 50 ml water sample = 30 ml of EDTA

$\therefore 1000$ ml of water sample $= \dfrac{1000}{50} \times 30 = 600\, ml$ of EDTA

$\because 1000$ ml of EDTA = 2.5 mg of $CaCO_3$ eq.

$\therefore 600$ ml of EDTA $= 600 \times 2.5 = 1500\, mg$ of $CaCO_3$ eq.

$\therefore$ Total hardness = 1500 ppm

d. 50 ml of boiled water = 10 ml of EDTA = $10 \times 2.5\, mg\ CaCO_3$

$\therefore 1000$ ml of boiled water $= \dfrac{1000 \times 10 \times 2.5}{50} = 500\, mg\ CaCO_3$

$\therefore$ Perm hardness = 500 ppm

5) 1 gm. of $CaCO_3$ was dissolved in 1 lit. of distilled water. 50 ml of solution required 45 ml EDTA for titration. 50 ml of hard water required 25 ml of EDTA for titration. The same sample of water after boiling consumed 15 ml of EDTA for titration. Calculate the total, perm. & tempo. hardness of water.

a. Concentration of distilled i.e SHW water = 1 gm / lit = 1 mg/ml.

50 ml of SHW = 50 mg of $CaCO_3$

50 ml of SHW = 45 ml EDTA

1 ml of EDTA $= \dfrac{50}{45}\, mg\ CaCO_3$ eq.

b. 50 ml of hard water sample – 25 ml EDTA

1000 ml of hard water sample $= \dfrac{1000}{50} \times 25\, ml$ EDTA = 500 ml EDTA

$= 500 \times \dfrac{50}{45} = 555.55$ of $CaCO_3$ eq.

Total hardness = 555.55 ppm

c. 50 ml of boiled water = 15 ml EDTA

$$1000 \text{ ml of boiled water} = \frac{1000}{50} \times 15 \, ml$$

$$= \frac{1000}{50} \times 15 \times \frac{50}{45} = 333.33$$

Perm hardness = 333. 33 ppm

d. Tempo hardness = Total hardness – Perm. Hardness

$$= 555.55 - 333.33 = 222.22 \text{ ppm}$$

6) A standard hardware contains 15 gm/l calcium carbonate. 20 ml of this water required 25 ml of EDTA solution. 100 ml of sample water required 18 ml of EDTA solution. The same sample after boiling required 12 ml of EDTA solution. Calculate temporary hardness of water.

Solution:

Given: Concentration of SHW = 15 g/lit

$$= 15000 \text{ mg}/1000 \text{ ml}$$

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

Volume of std. water = 20 ml

Volume of EDTA for SHW = 25 ml = V_1

Volume of water sample = 100 ml

Volume of EDTA for sample = 18 ml = V_2

Volume of water sample (after boiling) = 100 ml

Volume of EDTA for sample (after boiling) = 12 ml = V_3

$$20 \text{ ml SHW} \equiv 25 \text{ ml EDTA Soln}$$

$$1 \text{ ml EDTA} \equiv \left\lceil \frac{20}{25} \times 15 \right\rceil \text{ mgs of } CaCO_3 \text{ Equivalent hardness}$$

$$\equiv \frac{300}{25} \text{ Mgs of } CaCO_3 \text{ Equivalent hardness}$$

$$\equiv 12 \text{ mgs of } CaCO_3 \text{ equivalent hardness}$$

Now,

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

$$\equiv (18 \times 21) \text{ Mgs of } CaCO_3 \text{ Equivalent hardness}$$

$$\equiv 216 \text{ mgs of } CaCO_3 \text{ Equivalent hardness}$$

Per litre $\equiv 2160 \text{ mgs of } CaCO_3 \text{ Equivalent hardness}$

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

Now,

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

$$\equiv [12 \times 12] \text{ mgs of } CaCO_3 \text{ equation}$$

$$\equiv 144 \text{ mgs of } CaCO_3 \text{ Equation}$$

$$\text{Per litre} \equiv 1440 \text{ ppm}$$

$$\therefore \text{Permanent Hardness} \equiv 1440 \text{ ppm}$$

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

Ans.:   Total hardness = 2160 ppm

Permanent Hardness = 720 ppm

Temporary Hardness = 1440 ppm

7) 0.5 gm of $CaCO_3$ was dissolved in HCI and the solution made up-to 500 ml with distilled water. 50 ml of the solution required 48 ml of EDTA solution for titration. 50 ml of water sample required 15 ml of EDTA and after boiling and filtering required 10 ml of EDTA solution. Calculate temporary hardness of water.

Solution:

Concentration of S.H.W. = 0.5 gm $CaCO_3$ / 500 ml D.W.

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

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

Now,

50 ml SHW required $\equiv$ 48 ml EDTA solution.

i.e. 48 ml EDTA solution $\equiv$ 50 mgs $CaCO_3$ equivalent hardness

$$\therefore 1 \text{ ml EDTA solution} \equiv \left(\frac{50}{48}\right) \text{mgs } CaCO_3 \text{ equivalent hardness}$$

Now,

50 ml water sample $\equiv$ 15 ml EDTA solution

$$\therefore \text{Hardness of sample} \equiv \left(15 \times \frac{50}{48}\right) \text{ mgs } CaCO_3 \text{ equivalent for 50 ml Sample}$$

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

$$\equiv \left(\frac{750}{48}\right) \times 20 \text{ mgs / lit}$$

Now, $\therefore$ Total hardness $\equiv$ 312.50 ppm

50 ml water sample after boiling $\equiv$ 10 ml EDTA solution

$$\therefore \text{Permanent hardness of sample} \equiv \left(10 \times \frac{50}{48}\right) \text{mgs } CaCO_3 \text{ equivalent for 50 ml}$$

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

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

$\therefore$ Permanent hardness of sample = 208.33 ppm

$\therefore$ Temporary hardness = Total hardness – perm. Hardness

$$= 312.50 - 208.33$$

$\therefore$ Temporary hardness of sample = 104.17 ppm

Ans.:　　Total hardness = 312.50 ppm

Permanent hardness = 208.33 ppm

And Temporary hardness = 104.17 ppm

8) 1 gm of $CaCO_3$ was dissolved in 1 litre 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.

Solution:

Given: Concentration of SHW = 1g/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 =?

Standardization of EDTA:

Standard hardware has 1 g i.e. $1 \times 1000 = 100$ mg of $CaCO_3$ equivalent hardness per lit.

$$= 100 \, mgs / lit$$

$$= \frac{100}{1000} = 0.1 \, mg / ml \; CaCO_3 \text{ equivalent hardness}$$

$$50 \text{ ml SHW} = 50 \times 1 \, mg \; CaCO_3 \equiv 50 \, mgs \; CaCO_3$$

$$45 \text{ ml EDTA} = 50 \text{ ml SHW} \equiv 50 \, mgs \; CaCO_3$$

$$1 \text{ ml EDTA} = \frac{50}{45} = 1.11 \, mgs \text{ of } CaCO_3 \text{ equivalent hardness}$$

Calculation of total hardness:

50 ml of H.W. sample = 25 ml EDTA

= 25×1.11mgs of HW per 100 ml

= 0.2775 mgs of $CaCO_3$

Total H per litre = 277.5 mgs of $CaCO_3$

Calculation of permanent hardness:

50 ml of boiled water = 15 ml of EDTA

=15×1.11 mgs of $CaCO_3$ in 100 ml

= 0.1665 mgs of $CaCO_3$

Hence per litre = 166.5 mgs of $CaCO_3$

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

= 277.5 −166.5

= 111 mgs of $CaCO_3$

Total hardness = 277.5 ppm

Permanent hardness = 166.5 (mgs of $CaCO_3$) ppm

Temporary hardness = 111 ppm

9) 50 ml sample of water required 7.2 ml of N/20 disodium EDTA for titration. After boiling and filtration the same volume required 4 ml of EDTA. Calculated each type of hardness.

Solution:

As $\dfrac{1}{20}$ EDTA solution = $\dfrac{N}{20}$

$CaCO_3$ And 1000 ml of 1 normal, $CaCO_3$ corresponding to 50 gm $CaCO_3$

1 ml of $\dfrac{N}{20}$ $CaCO_3$ correspond to $\dfrac{0.005}{20}$ of $CaCO_3$

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

i.e. correspond to $(0.005/20 \times 1/20 \times 7.2$ (outside gms. of $CaCO_3$))

1000 ml of hard water correspond to $0.005/20 \times 1/20 \times 7.2 \times 1000$ gm $CaCO_3$

Hardness is equal to,

$$\frac{0.005/20 \ \times 1/20 \ \times 7.2}{1000} \times 1000 = \frac{0.036}{1000}$$

= 360 PPM or m gm/lit

10) 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 hardness.

Solution:

Given: Weight of $CaCO_3$ = 1.2 gm / litre

Voltage of SHW = 20 ml

Voltage of EDTA solution for SHW = 35 ml

Voltage of EDTA (V_2) = 30 ml

Voltage of EDTA (V_3) = 25 ml (for 100 ml sample)

To calculate the all types of hardness,

20 ml SHW = 35 ml. EDTA

Concentration of SHW = 1.2 g/lit

$$= 1200 \text{ mg}/100 \text{ ml}.$$

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

20 ml SHW $\equiv 20 \times 1.2 \, mgs$ hardness

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

Thus, 35 ml EDTA $\equiv 24$ mgs equivalent $CaCO_3$ eq. hardness

1 ml SHW $\equiv \dfrac{24}{35}$ mgs equivalent $CaCO_3$ eq. hardness

Total hardness is per 50 ml $= \left(V_1 \times \dfrac{24}{35} \right)$ mgs of equivalent $CaCO_3$ eq. hardness

$$= \left(30 \times \dfrac{24}{35} \right) \text{ mgs of equivalent } CaCO_3 \text{ eq. hardness}$$

$$= 20.57$$

$$\text{Per litre} = \left(20.57 \times \dfrac{1000}{50} \right) = 411.4 \, ppm$$

Permanent hardness per 100 ml $= \left(V_2 \times \dfrac{24}{35} \right)$ mgs of equivalent $CaCO_3$ eq.

hardness

$$= \left(25 \times \dfrac{24}{35} \right) \text{ mgs of equivalent } CaCO_3 \text{ eq.}$$

hardness

$$= 17.14$$

$$\text{Per litre} = \left(17.14 \times \dfrac{1000}{1000} \right) = 171.4 \, ppm$$

Temporary hardness = Total H – Perm. Hardness

= 441.4-171.4

= 240.0 ppm

Ans.: Total Hardness   = 411.4 ppm

Permanent hardness = 171.4 ppm

Temporary hardness = 240.0 ppm

❖ **Unsolved Problems:**

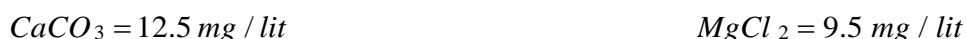1) What is the carbonate and non-carbonate hardness of a sample of water which has the following impurities per litre?

$Ca(HCO_3)_2 = 50.25\ mg$ $\qquad\qquad$ $Ca(NO_3)_2 = 8.2\ mg$

$CaCl_2 = 22.2\ mg$ $\qquad\qquad\qquad$ $KNO_3 = 20.2\ mg$

$MgCO_3 = 16.8\ mg$ $\qquad\qquad\qquad$ $FeSO_4 = 3.8\ mg$

$MgSO_4 = 6.0\ mg$
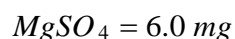
Express the results as ppm, Clarke degree and French degree.

Ans.: [Carbonate hardness = 51 ppm or $5.1^0 Fr\ or\ 3.56\ ^\circ C$

   Non-carbonate hardness = 27.5 ppm or $2.75^0\ Fr\ or\ 1.92\ ^\circ CI$]

2) Find carbonate and non-carbonate hardness of a sample of water which has the following impurities per lit?

$CaCO_3 = 12.5\ mg\ /\ lit$ $\qquad\qquad\qquad$ $MgCl_2 = 9.5\ mg\ /\ lit$

$MgCO_3 = 16.8\ mg\ /\ lit$ $\qquad\qquad\qquad$ $CO_2 = 22\ mg\ /\ lit$

$CaCl_2 = 11.1\ mg\ /\ lit$ $\qquad\qquad\qquad$ $NaHCO_3 = 13.6\ mg\ /\ lit$

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

3) 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 Eriochrome 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]

4) 0.25 gm of $CaCO_3$ is dissolved in dilute HCI and diluted to 250 ml. 25 ml of this solution required 24.0 ml of EDTA using Eriochrome Black –T indicator. 50 ml of a hard water sample required 22.55 ml of the same EDTA. 100 ml of the water after boiling and filtering required 120 ml of the said EDTA. Calculate the hardness in the sample (permanent and temporary).

Ans.: [Total Hardness = 468 ppm, Permanent hardness = 333 ppm &
   Temporary hardness = 135 ppm]

5) What is carbonate and non-carbonate hardness of a sample of water which has the following impurities per litre :

$Mg(HCO_3)_2 = 146 \, mg \, / \, lit$ $\qquad\qquad\qquad MgCl_2 = 95 \, mg \, / \, lit$

$NaCl = 50 \, mg \, / \, lit$ $\qquad\qquad\qquad Ca(HCO_3)_2 = 81 \, mg \, / \, lit$

$CaCl_2 = 111 \, mg \, / \, lit$ $\qquad\qquad\qquad CaSO_4 = 68 \, mg \, / \, lit$

Express the results as ppm,

Ans.: [Carbonate hardness = 150 ppm =15 $^\circ Fr = 10.5 \, ^\circ Cl$

   Non carbonate hardness = 250 ppm = 25 $^\circ Fr = 17.5 \, ^\circ Cl$]

6) What is the carbonate and non-carbonate hardness of a sample of water which has the following impurities per litre?

$Ca(HCO_3)_2 = 81 \, mg \, / \, lit$ $\qquad\qquad\qquad MgCl_2 = 95 \, mg \, / \, lit$

$NaCl = 38.5 \, mg \, / \, lit$ $\qquad\qquad\qquad CaCl_2 = 22.2 \, mg \, / \, lit$

$Mg(HCO_3)_2 = 58.2 \, mg \, / \, lit$ $\qquad\qquad\qquad CO_2 = 4.4 \, lit$

Express the results as ppm,

Ans.: [Carbonate hardness = 89.86 ppm = 6.29 $^\circ Cl = 8.986 \, ^\circ Fr$

   Non carbonate hardness = 250 ppm = 8.4 $^\circ Cl = 12 \, ^\circ Fr$]

7) 0.1 g of $CaCO_3$ was dissolved in dil. HCI 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.

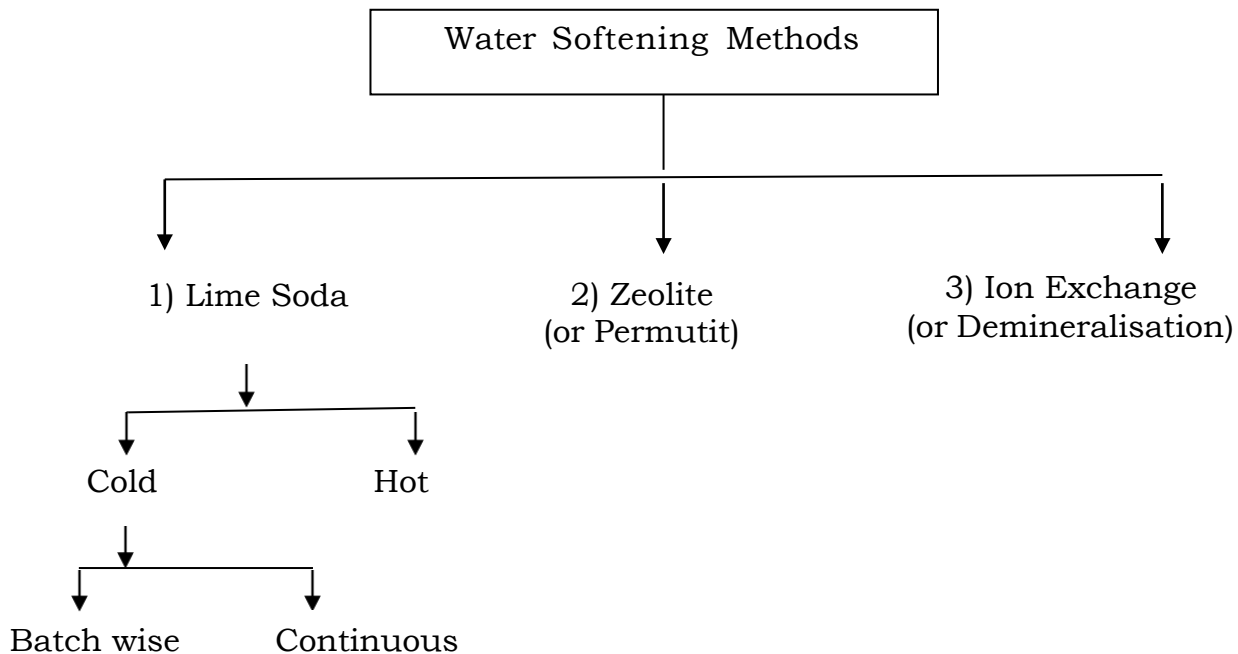Ans.: [Temporary hardness = 125 ppm, Permanent hardness = 500 ppm
   Total hardness = 625 ppm]

8) Calculate the hardness of water sample, whose 20 ml required 30 ml of EDTA. 10 ml of calcium solution, whose strength is equivalent to 300 mg of calcium carbonate per 200 ml required 20 ml of EDTA solution.

❖ **Softening of Hard Water:**

It means the process of removing or reducing concentration of hardness causing salts from water.

There are mainly 3 methods as follows:

```
                        ┌──────────────────────────┐
                        │ Water Softening Methods   │
                        └──────────────────────────┘
                                    │
        ┌───────────────────────────┼───────────────────────────┐
        ↓                           ↓                           ↓
   1) Lime Soda              2) Zeolite              3) Ion Exchange
                             (or Permutit)          (or Demineralisation)
        │
    ┌───┴───┐
    ↓       ↓
  Cold     Hot
    │
 ┌──┴──┐
 ↓     ↓
Batch wise   Continuous
```

❖ **Ion Exchange Process:**

- The process of removal of ions (both cations and anions) from water sample is known as ion-exchange process.
- 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.
- Water which is free from both cations and onions is known as deionised or demineralised water.

➤ **Cations- Exchange Resin:**

- Resin containing acidic functional group $(-COOH, -SO_3H)$ exchange their H^+ ions with other cations is known as cation exchange resin.

$$RH_2 + Ca^{2+} \rightarrow RCa + 2H^+$$

$$RH_2 + Mg^{2+} \rightarrow RMg + H$$
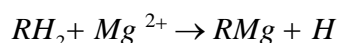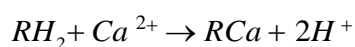
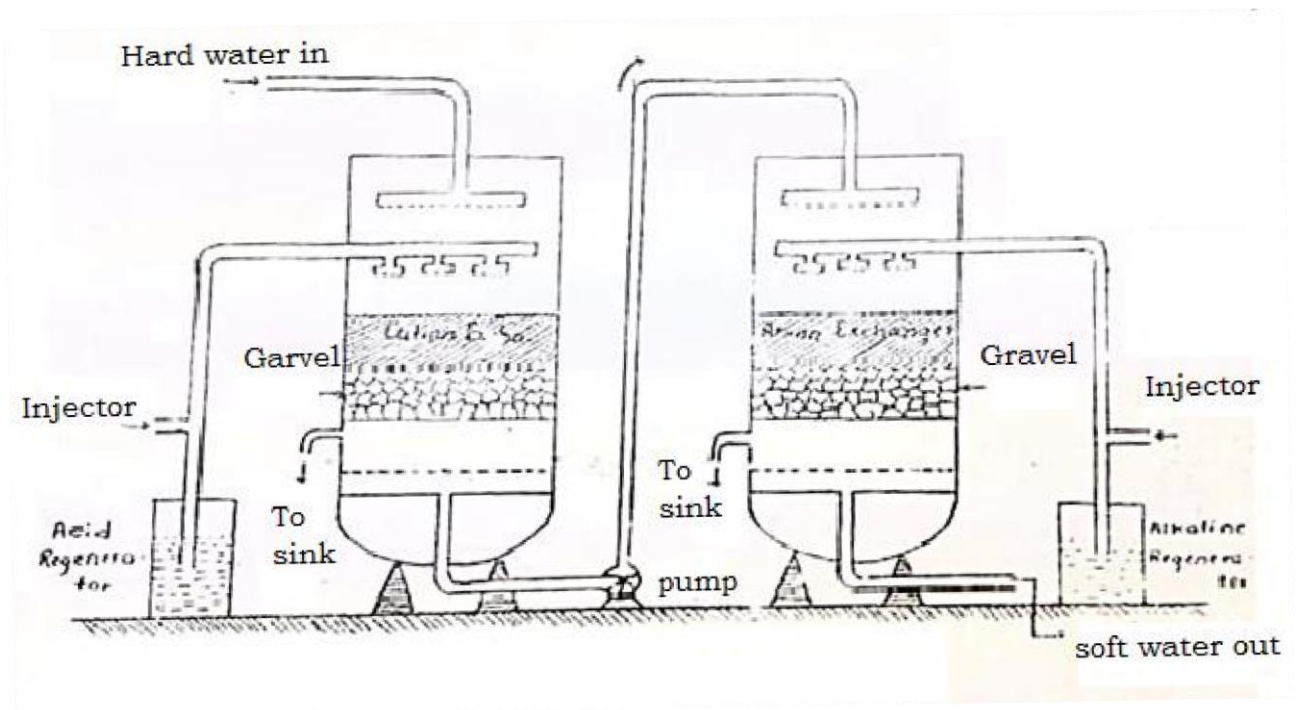- E.g. Divinyl benzene copolymer, dowex 50, Duolite etc.

➤ **Anion exchange Resin:**

▪ Resins containing basic functional groups $(-NH_2, -OH)$ exchange their anions with other is known as anion exchange resin.

▪ E.g. Amberlite 400, Zeolite – FF

$$R'(OH)_2 + H_2SO_4 \rightarrow R'SO_4 + 2H_2O$$

$$R'(OH)_2 + 2CHI \rightarrow R'Cl_2 + 2H_2O$$

$$R'(OH)_2 + H_2CO_3 \rightarrow R'CO_3 + 2H_2O$$
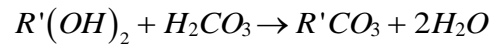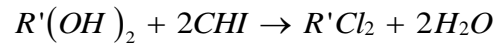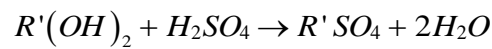
▪ When capacities of cation and anion exchangers to exchange H^+ and OH^- ions respectively are lost, they are then said to be exhausted.

➤ **Demineralization of water:**

Hard water in

Garvel   Cation & So/   Anion Exchanger   Gravel

Injector   Injector

Acid Regenirator   To sink   To sink   pump   Alkaline Regenerator

soft water out

▪ **Process**:

1) The hard water is passed through cation exchange column, which removes all cation like Ca^{2+}, Mg^{2+} etc. from it and equivalent amount of H^+ ions are released from this column to water.

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

$$2RH^+ + Mg^{2+} \rightarrow R_2Mg + 2H^+$$
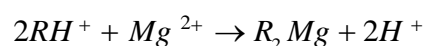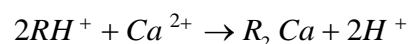
2) After cation exchange column, hard water passed through anion exchange resin, which removes all anions like SO_4^{2-}, Cl^- present in the water, and equivalent amount of released in water.

$$ROH^- + Cl^- \rightarrow RCl + OH^-$$
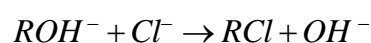
H^+ And OH^- released from both the columns get combined to produce water molecule.

$$H^+ + OH^- \rightarrow H_2O$$
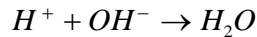
Water coming out from the exchange is free from cations as well as anions. It is called as demineralised or deionised water.

- **Regeneration:**

  When capacities of cation and anion exchanger to exchange H^+ and OH^- ions are lost, then they are said to be exhausted.

  1) The exhausted cation exchange column is regenerated by passing a solution of dil. HCl or dil. H_2SO_4.

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

  2) The exhausted anion exchange is regenerated by passing solution of dil. NaOH.

  $$R_2SO_4 + 2OH^- \rightarrow 2ROH^- + SO_4^{2-} \text{ (washing)}$$

  Regenerated ion exchange resins are then used again.

➤ **Advantages:**
   1) Process can be used to soften highly acidic or alkaline waters.
   2) Produces water with very low hardness (abt. 2ppm)

➤ **Disadvantages:**
   1) The equipment's are costly and more expensive chemicals are needed.
   2) If water contains turbidity, then the output of the process is reduced.

➤ **Mixed Bed Deioniser:**
   Mixed bed deioniser consist essentially a single cylinder containing an intimate mixture of hydrogen exchanger and strongly basic anion exchange.

➤ **Regeneration of mixed ion Exchange:**

Regeneration of mixed ion Exchange
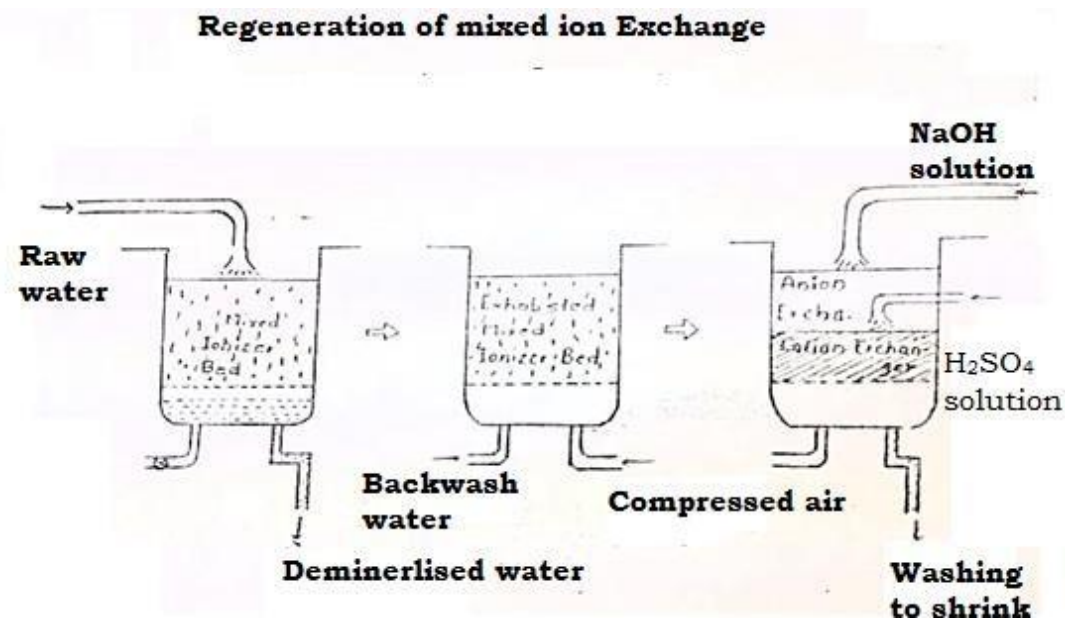
Desalination:

Water containing high concentration of dissolved soilds with a peculiar salty taste is called brackish water. The process of removing common salt (NaCl) from such water is known as desalination

Electrodialysis:

In Electrodialysis, ions present in the saline water migrate towards respective electrode through ion selective membrane by passing direct current.

a. In this method desalination is carried out by electro-dialysis method.

b. When direct current is passed through saline water the sodium ions (Na^+) start moving towards negative pole (cathode); while chloride ions (Cl) start moving towards positive pole (anode) through membranes.

c. As a result, the concentration of brine decreases in the central compartment, while increases in two side compartments.

d. Desalinated water (pure water) is removed from the central compartment from time to time, while conc. brine is replaced by sea water.

e. For more efficient separation, ion-selective membranes are employed.

Cation Selective membrane:

Cation selective membrane is permeable to cations only. They possess functional group like RSO_3^-, $RCOO^-$, etc....
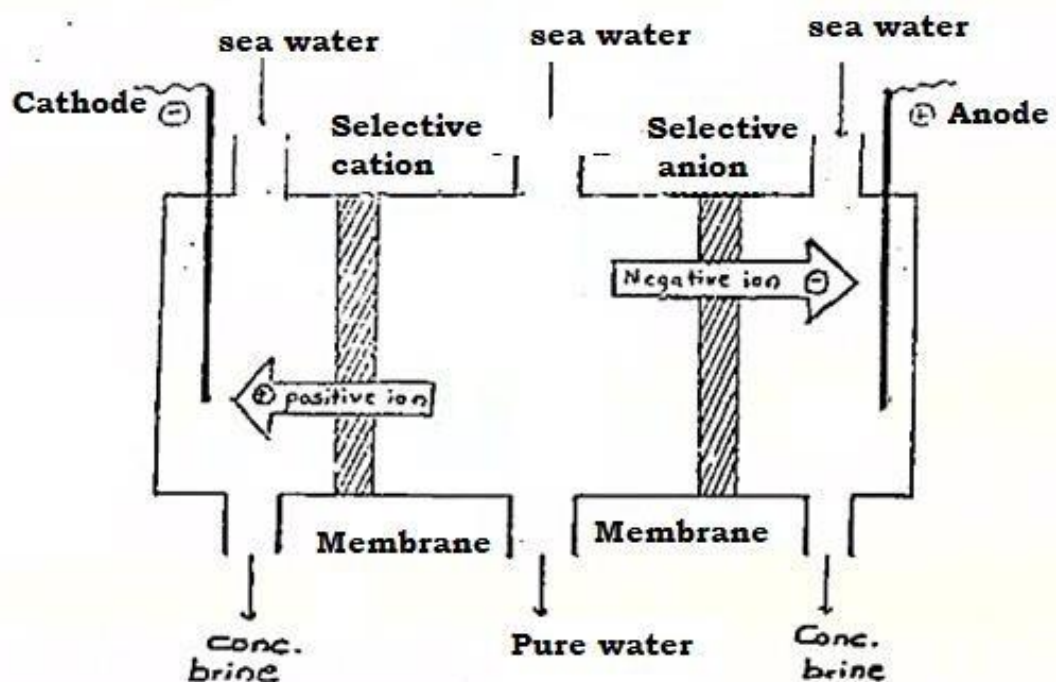
Anion Selective membrane:

Anion selective membrane is permeable to anions only. They possess functional group like $R_4N^\oplus$.

➤ **Advantages:**

  i.   It is most compact unit.
  ii.   Installation and operation of plant is economical.
  iii. If electricity is easily available, it is best suited.

❖ **Reverse Osmosis and Ultrafiltration:**

➤ **Reverse Osmosis:**

▪ **Normal Osmosis:**

In **Normal Osmosis Process**, solvent flows from low concentration solution to high concentration solution through the semipermeable membrane, until difference in water level creates a sufficient pressure to counteract the original flow. The difference in levels represents osmotic pressure of the solution.
In reverse osmosis, external pressure is applied on higher concentration solution slightly higher than its osmotic pressure. Hydrostatic Pressure in excess of osmotic pressure is applied on concentration side, the solvent flows reverses

▪ **In R.O. solvent is forced to move from conc. Side to dil. Side.**
▪ **In** R.O. Method, pure solvent (water) is separated from its contaminates, rather than removing contaminants from the water. This membrane filtration sometime also called **Super-Filtration** or **Hyper-Filtration.**
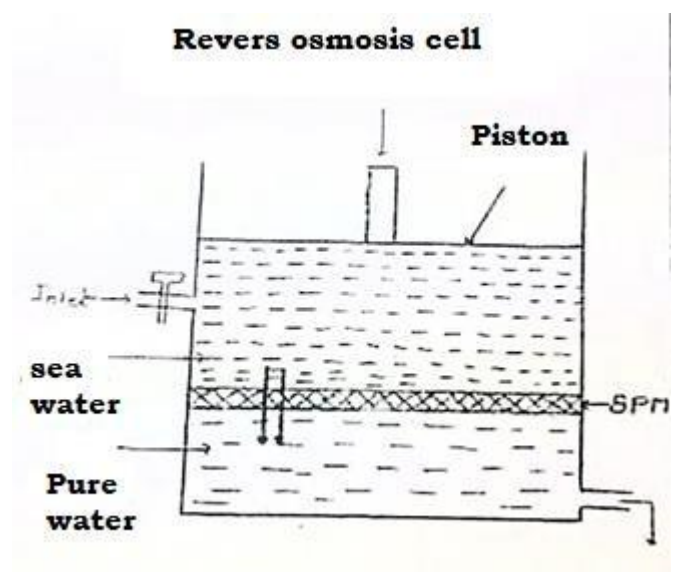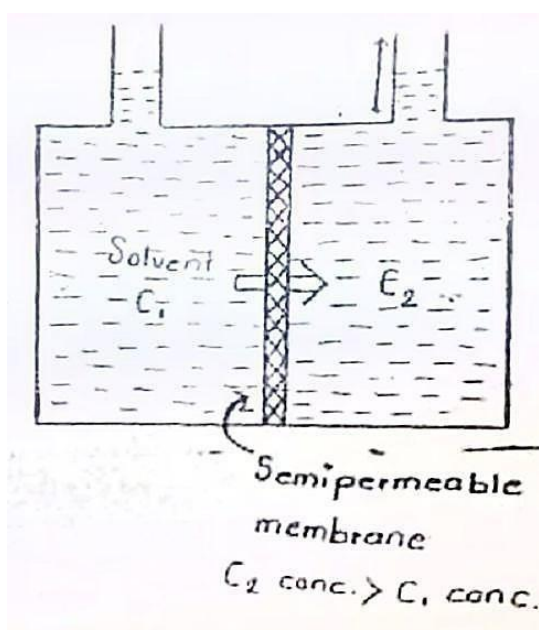
- **Method:**
  1) Pressure is applied to the sea water (impure water) to force its pure water out through the out through the semi-permeable membrane, leaving behind the dissolved solids.
 2) The membrane consists of very thin films of cellulose acetate, affixed to either side of a polymers are used.

- **Advantages:**
  1) This method removes ionic as well as non-ionic, colloidal and high molecular weight impurities.
  2) It removes colloidal silica, which is not removed by demineralization
  3) The life time of membrane is quite high about 2 years.
  4) Low capital cost simplicity, low operating cost and high reliability.

- **Applications of Reverse Osmosis:**
  1) Desalination of sea water
  2) For drinking water purification, as it provides pathogen free water
  3) Waste-water recovery in the food & beverages processing industries.
  4) Production of ultra-pure water for use in semiconductor industry
  5) Milk can be concentrated prior to cheese making at the farm level.

❖ **Ultrafiltration:**

Water
Suger
Protein
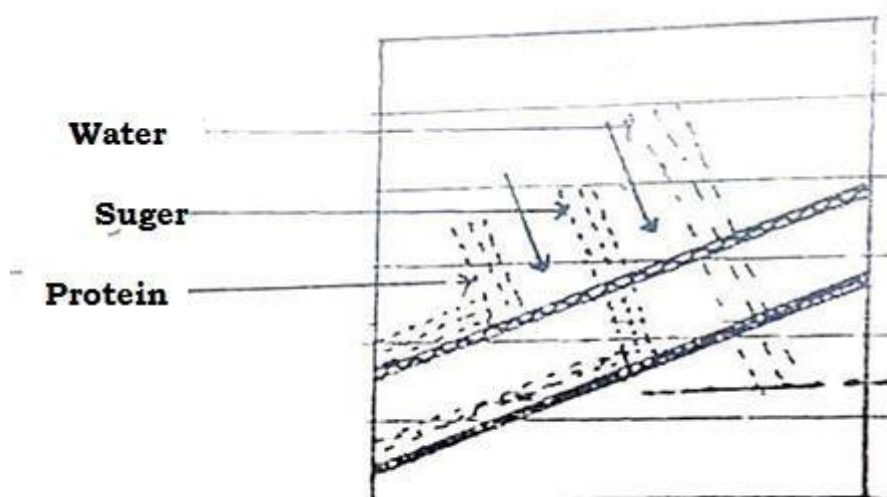
- Ultrafiltration is a variety of membrane filtration in which hydrostatic pressure forces a liquid against a semipermeable membrane.
- **Suspended solids and solutes of high molecular weight are retained, while water and low molecular weight solutes pass through the membrane.**

- **Ultrafiltration is cross flow filtration used in industries. It is pressurised flow of solution, which is tangential** to the surface of the supported membrane.
- **Membranes used having pure size 0.1 to 0.001 micron.**
- **In c**ross flow separation, membrane itself does not act as collector of ions, molecules or colloids but merely as a barrier to these species.

> **Ultrafiltration Application:**
>   1) Ultrafiltration is used in industry to separate suspended solid from solution
>   2) Paint recovery in automotive industry.
>   3) It is widely used in the fractionation of milk
>   4) Protein isolation
>   5) Removal of colloids.

BOD

"The Biochemical oxygen Demand (BOD) of water is a measure of amount of oxygen required for the biological oxidation of organic matter under aerobic conditions, at $20°c$ & for a period of five days."

Significance:

The higher the BOD of a sample, the higher amount of decomposable organic matter in the sample & higher the pollution of the sample.

∴ BOD
i. Gives an indication @ the extent of pollution at any time in the sewage sample
ii. Helps in pollution control.

❖ **Determination Of B.O.D:**
1) **Procedure:**
   a. A known volume of effluent sample is diluted with known volume of dilution water. The diluted sample is taken in two bottles.
   b. The dissolved oxygen content of the bottles is immediately determined (black). Another bottle is stored at $20°c$ for 5days after which unused oxygen content in the blank & unused oxygen of effluent water after 5days gives BOD.
   c. While carrying out the BOD test, water is diluted to ensure that sufficient O_2 is available for the complete oxidation of the organic matter.

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c. While carrying out the BOD test, water is diluted to ensure that sufficient O_2 is available for the complete oxidation of the organic matter.

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."

Significance:

v.   It helps in designing the water treatment plant.

vi. It helps in deciding the disposal of domestic effluents in various types of water streams.

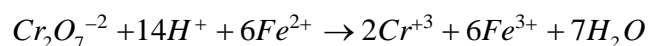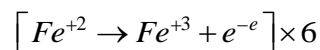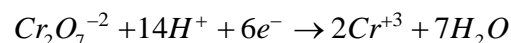❖ **Determination of COD:**

1) Procedure:

A known volume (250 ml) of waste water sample is refluxed with a known excess quantity of standard potassium dichromate $(K_2Cr_2O_7)$ (1N) & dilute H_2SO_4 in the presence of silver sulphate (Ag_2SO_4) for $1\frac{1}{2}$ hours. Ag_2SO_4 is used as a catalyst. The organic contents in the sample is oxidised to ammonia, CO_2 & water. The $K_2Cr_2O_7$ is used to calculate the equivalent oxygen required by the waste water for degradation of the pollutions.

2) Reactions:

$$C_xH_yO_z + (x + y/4 - z/2)O_2 \rightarrow X.CO_2 + y/2.H_2O$$
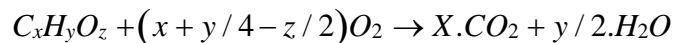
The unreacted dichromate solution is titrated against. $FeSO_4.(NH_4)_2.6H_2O$ using ferroin as indicator. At the end, blue colour changes to wine red.
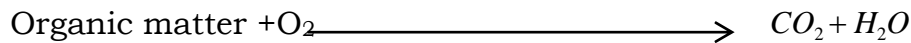
$$Cr_2O_7^{-2} + 14H^+ + 6e^- \rightarrow 2Cr^{+3} + 7H_2O$$

$$\left[Fe^{+2} \rightarrow Fe^{+3} + e^{-e}\right] \times 6$$

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

3) Calculation:

$$COD = \frac{(V_1 - V_2)N \times 8000}{Y} \text{ mg/l}$$

Where V_1 and V_2 are the volumes of ferrous ammonium sulphate in black & test experiments respectively N is the normality of ferrous ammonium sulphate. And Y= Volume of water sample taken for test.

3) **Reaction:**

$$\text{Organic matter} + O_2 \xrightarrow{\text{micro -organisms}} CO_2 + H_2O$$

The demand for oxygen is proportional to the amount of organic waste to be degraded.

The higher the value of BOD, higher will be the pollution.

Drinking water should have $BOD < 1ppm$

4) **Calculation:**

$$BOD = (DO_b - DO_i) \times \text{dilution factor}$$

Where,

DO_b = dissolved O_2 present in the sample before incubation

DO_i = dissolved O_2 present in the sample after incubation (incubation means storing)

Sr. No	BOD	COD
1.	It measures the oxygen demand of biodegradable pollutants only.	It measures the oxygen demand for biodegradable & non-biodegradable pollutants both.
2.	Slow process. It takes 5 days	Fast process. It takes 2-3 hours.
3.	Less stable measurements method, It uses micro-organisms which are easily influenced by pH, temperature & other variable. Pollutants in the water.	More stable method. It uses potassium dichromate which oxidises regardless of water conditions.
4.	BOD values< COD Valued	BOD values>COD Valued
5.	$$BOD = \left(\dfrac{DO_b - DO_i}{x}\right) ppm$$ Where, DO_b = DO in black titration DO_i = DO of the sample after include $x = \dfrac{\text{Volume of the sample}}{\text{Total volume to which it was diluted}}$	$$COD = \dfrac{(V_1 - V_2) N \times 8000}{Y} \text{ mg/l}$$ Where, V_1=volume of ferrous aluminium sulphate in black V_2=volume of ferrous aluminium sulphate in test N=Normality of ferrous aluminium sulphate Y=Volume of water sample

❖ **Broad Outline of Sewage Treatment by Activated Sludge Process:**
  o Sewage contains mineral and inorganic matter in suspension in solution. It also contains living organisms, some of which may be dangerous.
  o Hence, treatment of sewage has to be carried out. These treatment processes can be classified into the following categories:
   1) Preliminary treatment
   2) Primary treatment
   3) Secondary treatment
   4) Disinfection

  1) Preliminary treatment:
   a. Waste water contains floating suspended solids such as rages, wood, metal, plastic, etc. These have to be removed as they interfere with the treatment process or mechanical equipment's.
   b. In the preliminary treatment, these suspended impurities are removed.

  2) Primary treatment:
   a. Primary treatment to sewage mainly consists of the sedimentation process to remove suspended organic solids.
   b. Chemicals are sometimes added in primary clarifiers to assist in the removal of finely divided and colloidal solids or to precipitate phosphorous.

  3) Secondary Or Biological treatment:
   a. In this category, processes such as filtration or activated sludge process are included. Filtration is done in contact beds or intermittent sand filters or trickling filters.
   b. It removes finely divided sludge is added to the raw sewage together with oxygen which promotes coagulation of the suspended and colloidal matter.
   c. A part of the digested sludge is added to the raw sewage together with oxygen which promotes coagulation of the suspended and colloidal matter.
   d. The matter which settles down at the bottom after treatment is called sludge and the liquid is called effluent.
   e. The sludge is disposed-off in many ways such as drying beds, dumping into sea, etc.
   f. The effluent is also disposed of in many ways such as sewage farming, letting it into a natural drainage or sea. Stages in sewage treatments are as shown in fig.
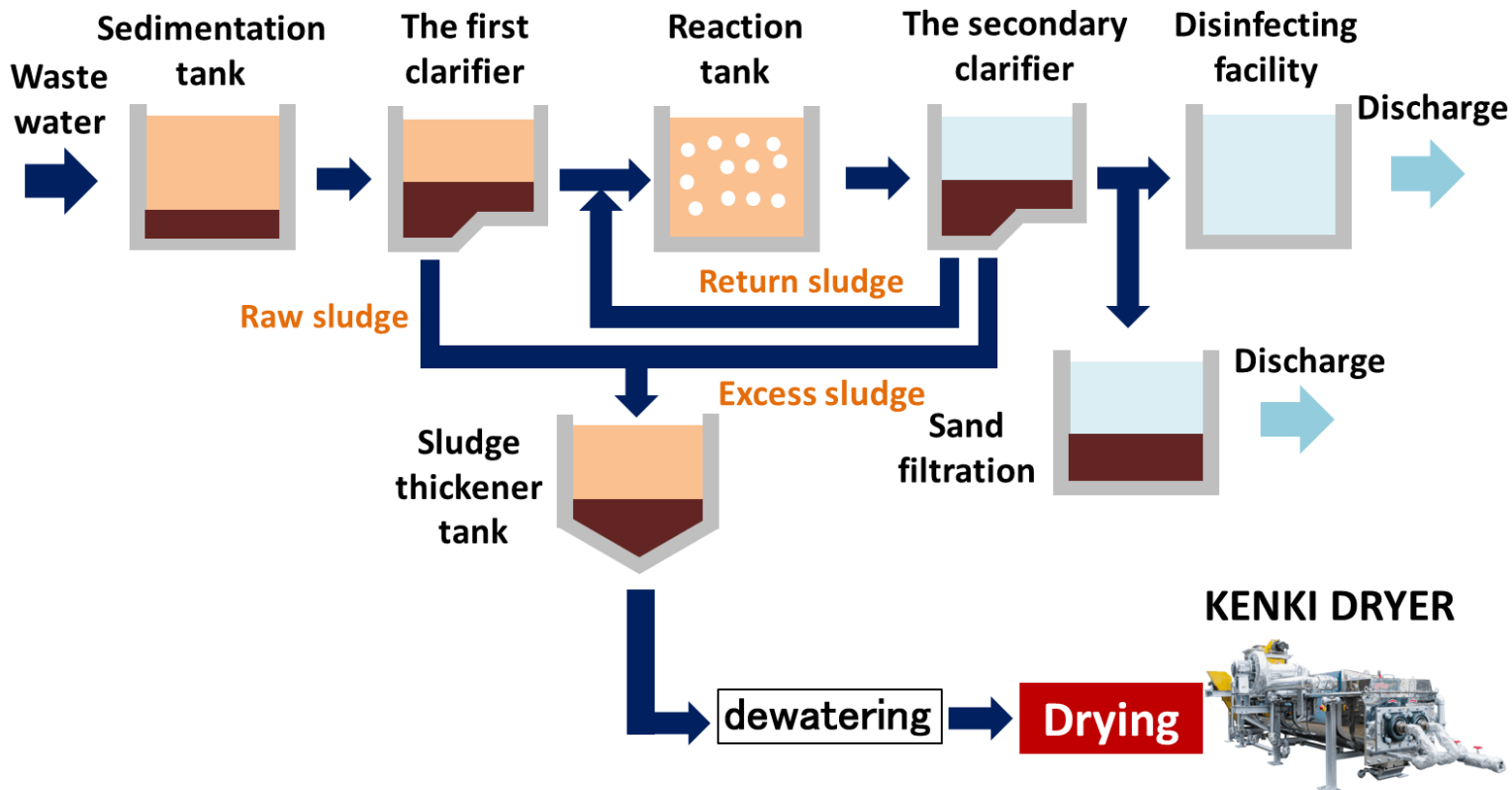
g. Trickling filters consists of circular beds, 2-5 m high, filled with porous lumpy materials, e.g. hard coke.

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

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

j. It is necessary to maintain highly aerobic condition.

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

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

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

4) Disinfection:

a. After the secondary or biological treatment the effluent free from sledges is subjected to disinfection.

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

c. Through activated sludge process broadly consists of all above stages, the number of stages or treatments given/required by water also plays role.

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

Conventional activated sludge process

Waste water →

Sedimentation tank →

The first clarifier →

Reaction tank →

The secondary clarifier →

Disinfecting facility → **Discharge**

Raw sludge

Return sludge

Excess sludge

Sludge thickener tank

Sand filtration → **Discharge**

KENKI DRYER

dewatering → **Drying**

a. If the water is only to be safely disposed off, then the treatment steps are chosen accordingly and vice versa.
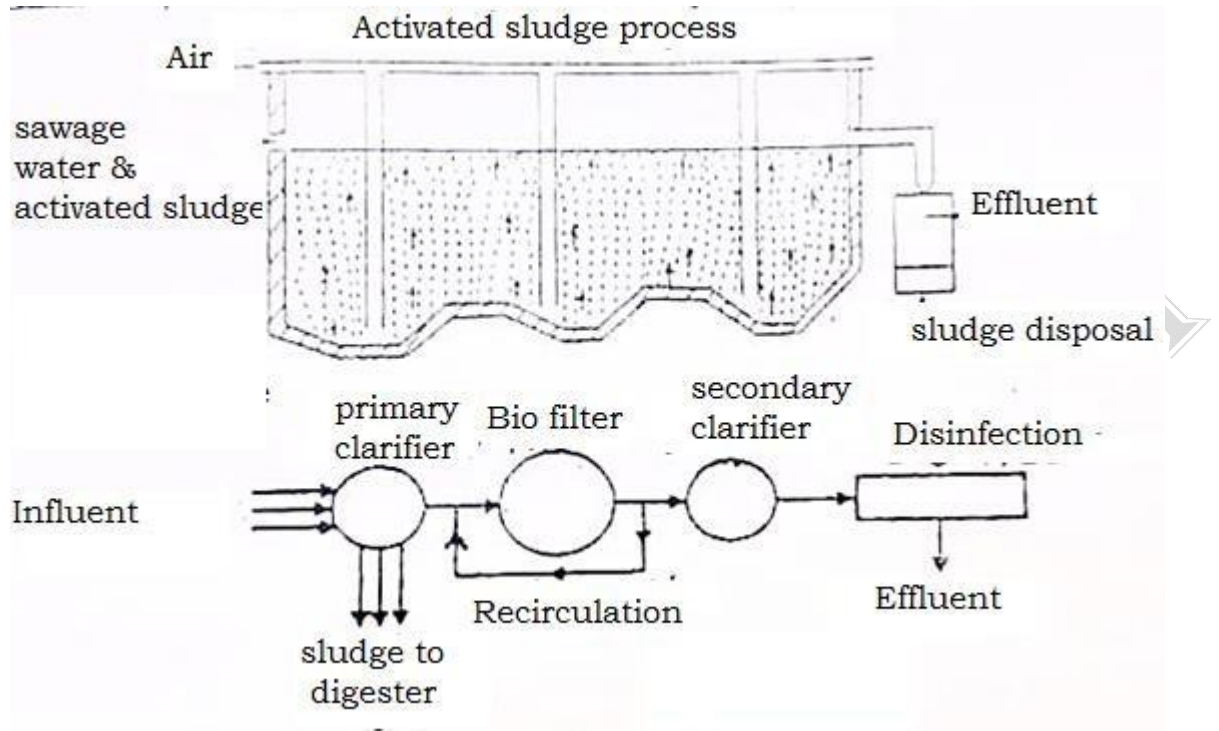
❖ Problems on COD & BOD:

1) Two BOD bottles contained each of 5ml of sewage sample & water diluted to distilled water to 300ml. One 100ml portion of the blank consumed 6.4 ml of 0.05 N thiosulphate, while the 100ml of the second bottle incubated of $20°c$ for the 5 days required 1.6 ml of the same thiosulphate solution. Calculate the BOD of the sample.

Solution:

a. Difference in the volume of thiosulphate solution required for the blank & sample solution=6.4-1.6=4.8 ml of 0.05 N thiosulphate

b. ∵ 1 litre of 1N thiosulphate solution=8 g oxygen

∴4.8 ml if 0.05 N thiosulphate solution $=\left[\left(8\times4.8\times0.05\right)/1000\right]\times\dfrac{100}{300}$

$=3.4\times10^{-4}$g of oxygen for 5ml sewage sample

c. Oxygen required for 1000ml of sewage sample= 0.1285g

d. ∴ BOD of sample=1285mg/l

2) A 50 ml sample contains 840 ppm of dissolved O_2. After 5 days the dissolved O_2 value becomes 230 ppm after the sample is diluted to 80 ml. Calculate the BOD of the sample.

Solution:

$BOD=\left(DO_b-DO_i\right)\times$dilution factor

$=\left(DO_b-DO_i\right)\times\dfrac{\text{ml. of sample after dilution}}{\text{ml. of sample before dilution}}$

$$= (840 - 230) \times \frac{80}{50}$$

$$= 976 \ ppm$$

3) A 5ml sample of waste water was refluxed with 30ml of potassium dichromate solution after refluxing the excess unreacted dichromate required 23ml of 0.1m. FAS solution. A blank of 5ml distilled water on refluxing with 30ml of dichromate solution required 36ml 0.1m FAS solution. Calculate COD value of the water

Solution:

a. Difference in volume of the FAS required for the blank & sample solution=36-23=13ml

b. $\because$ 1lit of 1M FAS=8g of O_2

   $\because$ 13ml of 0.1 M FAS $= 8 \times 13 \times 0.1/1000$

$$= 10.4 \times 10^{-3} g \ \text{of} \ O_2 \ \text{for 5ml of sample}$$

c. O_2 required for 1000ml of waste water=2.08g

   $\because$ COD for waste water sample=2080mg/lit.