Sample Questions for reference (Engineering Chemistry)

Answers till page no 10

Water

- How caustic embrittlement occurs due to the use of hard water? Explain with suitable reactions involved.

'Caustic embrittlement is a type of boiler corrosion which makes boiler material brittle'. This is caused by highly alkaline water in boiler in the boiler. During lime soda process free Na_2CO_3 is usually present in small proportion which decomposed to NaOH under pressure. The water containing NaOH flows into minute hair cracks by capillary action where water evaporates and concentration of NaOH increases progressively.This caustic soda aatckks the metals thereby dissolving the iron in the form of sodium ferroate. This causes embrittlement of boiler parts.

$Na_2CO_3 + H2O$ ------> $2\ NaOH + CO_2$

$2\ NaOH + Fe$ ------> $Na_2FeO_2 + H_2$

Sodium hypoferrite

$6\ Na_2FeO_2 + 6\ H_2O + O_2$ ------> $12\ NaOH + 2\ Fe_3O_4$ (Black rust)

Caustic embrittlement can be avoided by

1. By using sodium phosphate as a softening agent instead of sodium carbonate.

2. By adding tannin or lignin to the boiler water, since these substances block the hair cracks, thereby preventing the infiltration of the caustic soda solution in to these.

- What are the disadvantages of hard water in atleast six industries?

Textile Industry	It causes wastage of soap and forms precipitate which stick to cloth giving patch or spot and uneven colour of cloth.
Sugar Industry	Water containing sulphates, nitrates interfere in crystallization of sugar. Ans sugar so produced may undergo decomposition during storage.
Dyeing industry	It causes imperfect shades and uneven spots on fabric
Paper Industry	It causes pigmentation on paper due to presence of heavy metal ions and transition metals.
Concrete Industry	It causes slowdown in hydration of cement and hence final strength of cement reduces.
Food industry	It causes formation of certain undesirable products and thereby reducing the shelf life.
Laundary	Wastage of soaps and water

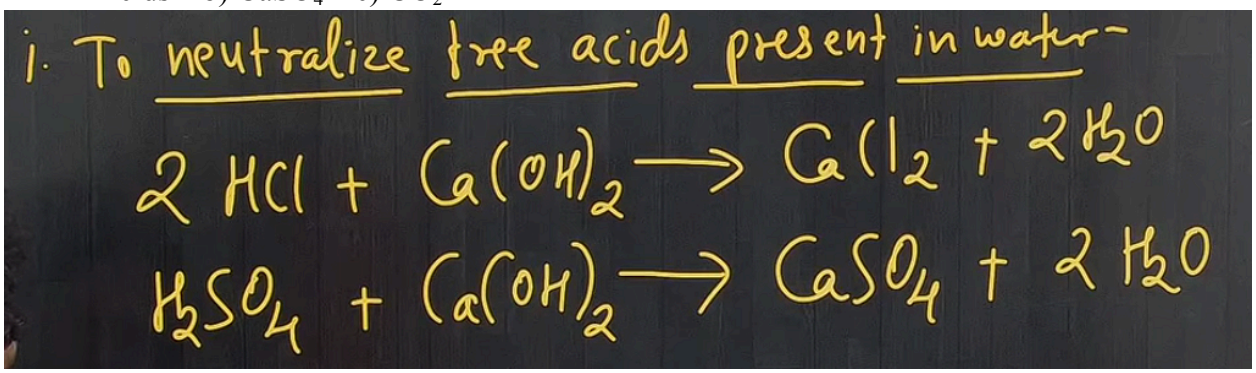
- Distinguish between temporary and permanent hardness.

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

- Distinguish between hard water and soft water

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

- Write the reactions of lime and soda with following impurities present in hard water; a) Acids b) $CaSO_4$ c) CO_2



Followed by

CaSO4 +Na2CO3
>CaCO3+ Na2SO4

Cacl2 + na2co3 □ caco3 + 2nacl

For CaSO4
Same

CaSO4 +Na2CO3
>CaCO3+ Na2SO4

For CO2

6. CO2	CO2 + Ca(OH)2 --------> 2 CaCO3 + 2H2O	No Reaction	L

- A sample of water on hardness estimation, found to contain:

Impurity	$Ca(HCO_3)_2$	$Mg(HCO_3)_2$	$CaCl_2$	$MgSO_4$	$CaSO_4$
Quantity (mg/L)	1.62	14.6	1.11	24	13.6

Calculate the temporary and permanent hardness of above sample.

Problem 1: Calculate temporary hardness and permanent hardness of water sample from the following data:

$Mg(HCO_3)_2$ = 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

Solution: Conversion into $CaCO_3$ equivalent:

Constituents	Quantity in mg/L	Multiplication factor	$CaCO_3$ equivalent
$Mg(HCO_3)_2$	16.8	100/146	11.5
$MgCl_2$	19	100/95	20
$MgSO_4$	24	100/120	20
$Mg(NO_3)_2$	29.6	100/148	20
$Ca\ CO_3$	04	100/100	4
$MgCO_3$	10	100/84	11.9

Temporary Hardness = Hardness due to $[Mg(HCO_3)_2 + CaCO_3 + MgCO_3]$
= 11.5 + 04 + 11.9
= 27.4 mg $CaCO_3$ equivalent / litre

Permanent Hardness = Hardness due to $[MgCl_2 + MgSO_4 + Mg(NO_3)_2]$
= 20 + 20 +20
= 60 mg $CaCO_3$ equivalent / litre

Thus,

Temporary hardness = 27.4 mg $CaCO_3$ equivalent / litre
Permanent hardness = 60 mg $CaCO_3$ equivalent / litre

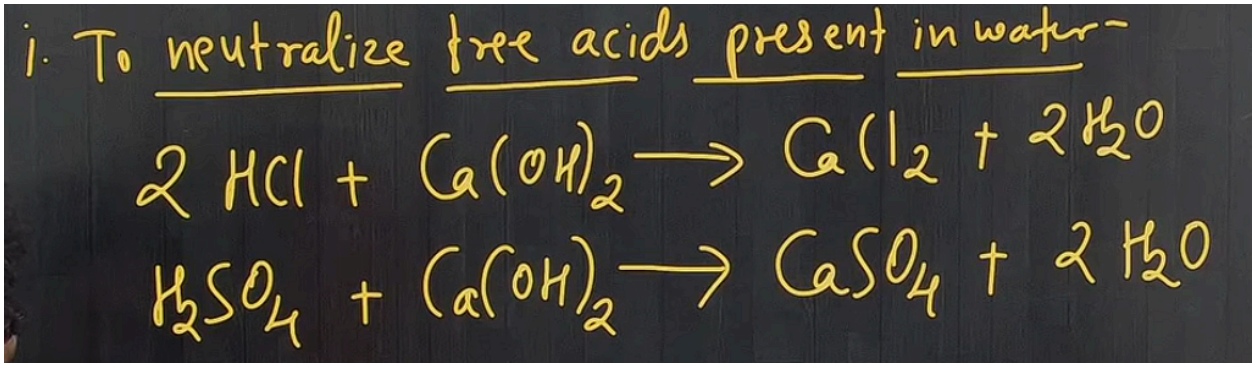
Question is similar to this

- Write the reaction of lime and soda with following impurities
A) $Mg(HCO_3)_2$ B) CO_2 C) $Al_2(SO_4)_3$ D) H_2SO_4

2. Temp Mg	$Mg(HCO_3)_2$ + 2 $Ca(OH)_2$ --------> Mg(OH)2 + 2CaCO3 + 2 H20	No Reaction	2L

6. CO2	CO2 + Ca(OH)2 --------> 2 CaCO3 + 2H2O	No Reaction	L

4.Perm Al	3Ca(OH)2 +Al2(SO4)3 --------> 2Al(OH)3+ **3 CaSO4**	**CaSO4** +Na2CO3 -------- >CaCO3+ Na2SO4	L + S



Followed by

CaSO4 +Na2CO3
>CaCO3+ Na2SO4

- What is equivalence of $CaCO_3$ hardness?

Calcium carbonate is chosen particularly for reporting the hardness of water since it simplifies the calculations as its molecular weight is 100. Moreover, it is the most insoluble salt that can be precipitated in water treatment.

The equivalents of $CaCO_3$

$$= \frac{[\text{Mass of hardness producing substance}] \times [\text{Chemical equivalent of } CaCO_3]}{\text{Chemical equivalent of hardness producing substance}}$$

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

- Find the equivalence of $CaCO_3$ hardness in ppm and degree Clarke from following data;

a) 73 mg of $Ca(CO_3)_2$ dissolved in 500 ml water
b) 34 mg of $CaSO_4$ dissolved in 1 lit water

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

- Concentration = 73 mg in 500 mL = $\frac{73\,\text{mg}}{0.5\,\text{L}} = 146\,\text{mg/L}$.

Since the molecular weight of $Ca(CO_3)_2$ is the same as $CaCO_3$, the ppm value is directly:

146 ppm
Degree Clarke: 10.22

b)
34 mg of CaSO4 is 0.5 milli grams equivalents
Which gives us 50 x 0.5 mgm of CaCO3 in 1 Lit
= 25 ppm = 1.75 degree clark

- Define hardness of water.

Hardness of Water (5 Marks Answer in Points):

1. **Definition of Hardness**:
   - Hardness of water is the characteristic that prevents it from lathering easily with soap.
   - It is primarily caused by dissolved salts of **calcium** and **magnesium**, as well as trace amounts of heavy metals like iron.
2. **Effect on Soap**:
   - The metal ions in hard water react with the fatty acid components of soap, forming **insoluble precipitates**.
   - This reduces the **detergent efficiency** of soap, as the insoluble compounds prevent lather formation.
3. **Types of Salts Involved**:
   - Soap generally consists of sodium salts of long-chain fatty acids like **oleic acid**, **palmitic acid**, and **stearic acid**.
   - The dissolved calcium and magnesium ions in hard water form insoluble compounds with these soap components.

4. **Chemical Reactions:**

   - **Reaction with Calcium Chloride:**

   $$2\,C_{17}H_{35}COONa + CaCl_2 \rightarrow (C_{17}H_{35}COO)_2Ca\,(ppt) + 2\,NaCl$$

     - Sodium stearate (soap) + calcium chloride (hardness) → calcium stearate (insoluble precipitate) + sodium chloride.

   - **Reaction with Magnesium Sulfate:**

   $$2\,C_{17}H_{35}COONa + MgSO_4 \rightarrow (C_{17}H_{35}COO)_2Mg\,(ppt) + Na_2SO_4$$

     - Sodium stearate (soap) + magnesium sulfate (hardness) → magnesium stearate (insoluble precipitate) + sodium sulfate.

5. **Result of Hardness**:
   - Due to these reactions, hard water **loses its detergent value** as the formation of insoluble calcium or magnesium salts prevents soap from lathering effectively, making the water hard.

- Determine temporary, permanent and total hardness of water having following impurities; $Mg(NO_3)_2$= 7.4 mg/L, CO_2= 22 mg/L, KNO_3= 10 mg/L, $MgCO_3$= 2.05 mg/L, $CaCl_2$= 3.33 mg/L, $NaHCO_3$= 12 mg/L

Problem 7: The water sample contains the following impurities in mg/L.

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

Calculate the temporary permanent and total hardness. **[Dec 2009]**

Solution: Conversion into $CaCO_3$ equivalent:

Constituents	Quantity in mg/L	Multiplication factor	$CaCO_3$ equivalent
$Mg(HCO_3)_2$	7.3	100/146	05
$MgCl_2$	9.5	100/95	10
$Ca(HCO_3)_2$	16.2	100/162	10
$CaSO_4$	13.6	100/136	10

Temporary Hardness = Hardness due to $[Mg(HCO_3)_2 + Ca(HCO_3)_2]$

= 5 + 10

= 15 ppm

Permanent Hardness = Hardness due to $[MgCl_2 + CaSO_4]$

= 10 +10

= 20 ppm

Total Hardness = Temporary Hardness + Permanent Hardness

= 15 + 20

= 35 ppm

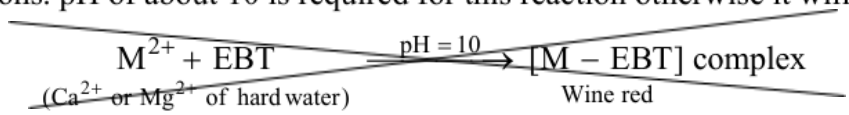
Thus,

Temporary hardness = 15 ppm, Permanent hardness = 20 ppm, Total hardness = 35 ppm

Similar to this, pay attention to which one's temporary, permanent and no hardness

- Explain the process of determining all types of hardness using EDTA titrations derive the necessary formula.

In order to determine the equivalence point, alcoholic solution of blue coloured dye Erichrome Black-T is used which forms unstable wine red complex with Ca^{2+} and Mg^{2+} ions. pH of about 10 is required for this reaction otherwise it will not go to completion.



During the course of titration against EDTA solution, EDTA combines with M^{2+} ions to form stable complex M-EDTA releasing EBT which combines with M^{2+} ions present in the solution and wine red colour is retained.

$$\underset{\text{Wine red}}{[M-EBT]\text{ complex}} + EDTA \xrightarrow{\text{titration}} [M\text{-}EDTA]\text{ complex} + \underset{\text{(Blue)}}{EBT}$$

$$M^{2+} + EBT \longrightarrow \underset{\text{Wine red}}{[M\text{-}EBT]\text{ complex}}$$

When all M^{2+} ions formed [M-EDTA] complex, the next drop of EDTA added displaces the EBT indicator from [M-EBT] complex and the wine red colour changes to blue. This is called the equivalence point. Thus, at equivalence point,

[M-EBT] complex + EDTA ⟶ [M-EDTA] complex + EBT (blue)

Thus, change of wine red colour to distinct blue marks the end point of titration.

Determination of Total Hardness, Temporary Hardness and Permanent Hardness:

Concentration of standard hard water = 1000 ppm = 1000 mg /L

1000 ml of standard hard water sample = 1000 mg of CaCO3

Therefore 1 ml of standard hard water sample = 1 mg of CaCO3

Part 1: Standardization:

$$50\text{ mL SHW} = V_1\text{ mL EDTA}$$

$$50 \times 1\text{ mg of } CaCO_3 = V1\text{ mL EDTA}$$

$$\text{Hence, 1 mL EDTA} = 50/V_1\text{ mg } CaCO_3\text{ eq.}$$

Part 2: Determination Of Total Hardness:

Now 50 mL of given hard water = V_2 mL of EDTA

= V_2 x 50/V_1 mg $CaCO_3$ eq.

1 L of given hard water = 20 x V_2 x 50/V_1 mg $CaCO_3$ eq.

Total Hardness of water = 1000 V_2/V_1 ppm

Part 3: Determination of Permanent Hardness

Now, 50 mL of boiled water = V_3 mL of EDTA

= V_3 x 50/V_1 mg $CaCO_3$ eq.

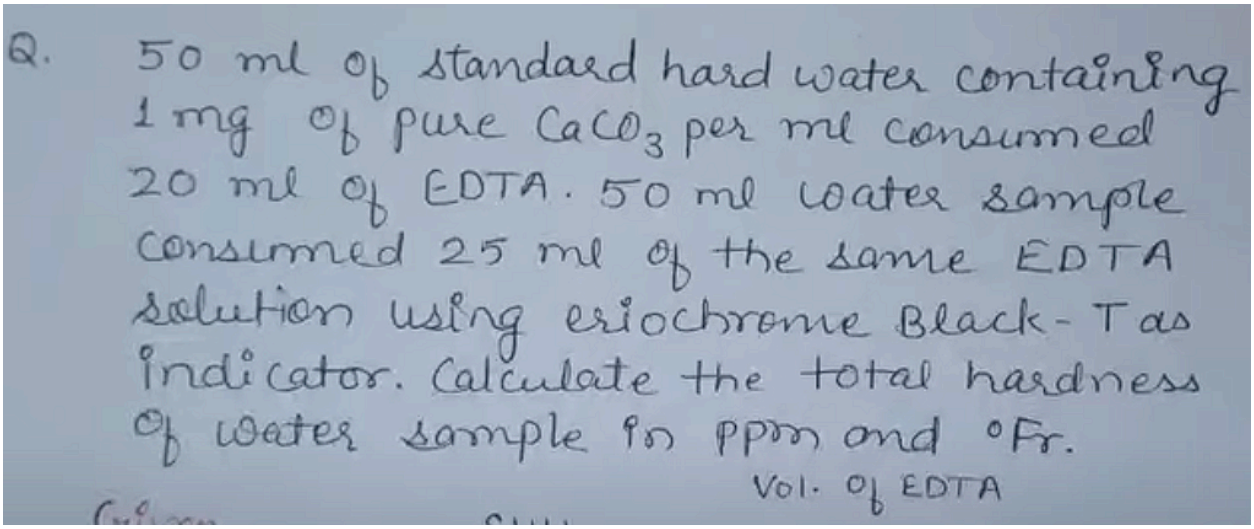
1 L of boiled hard water = 20 x V_3 x 50/V_1 mg $CaCO_3$ eq.

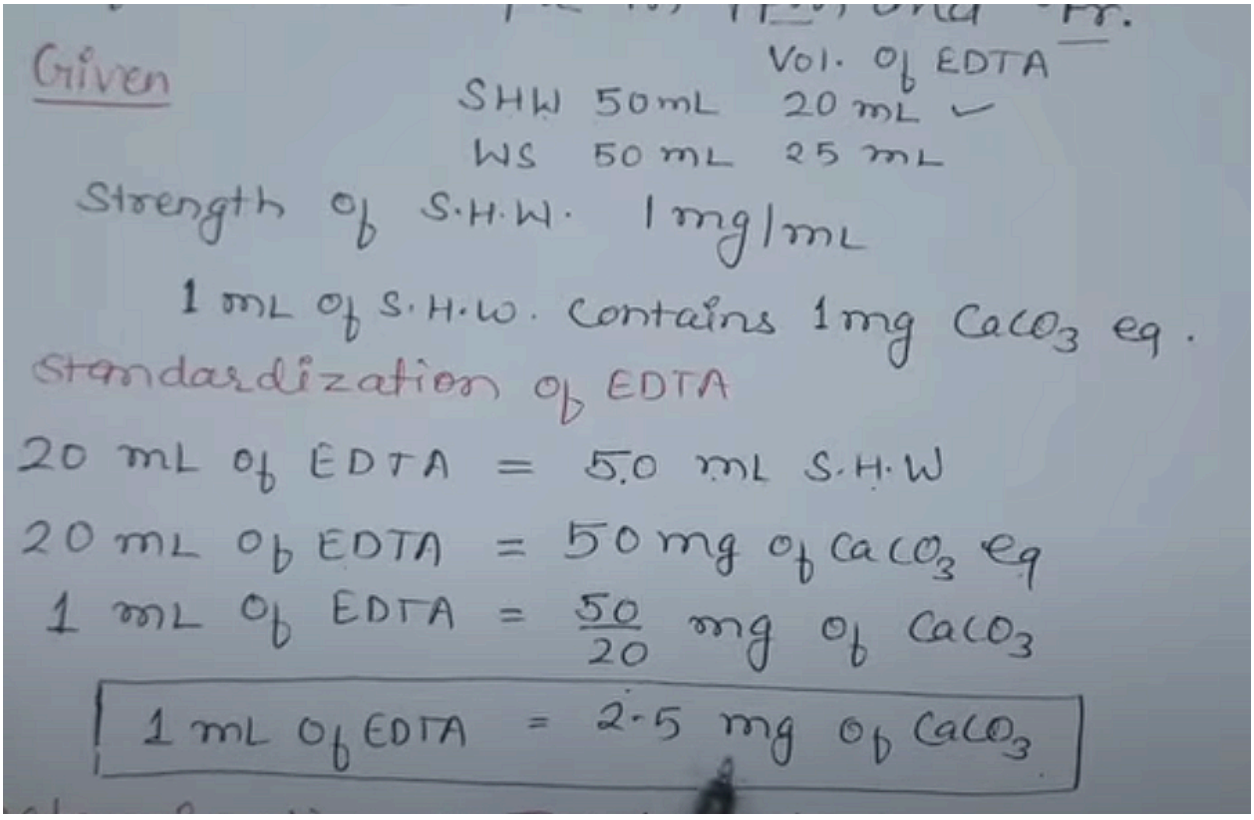
Permanent Hardness = 1000 V_3/V_1 ppm

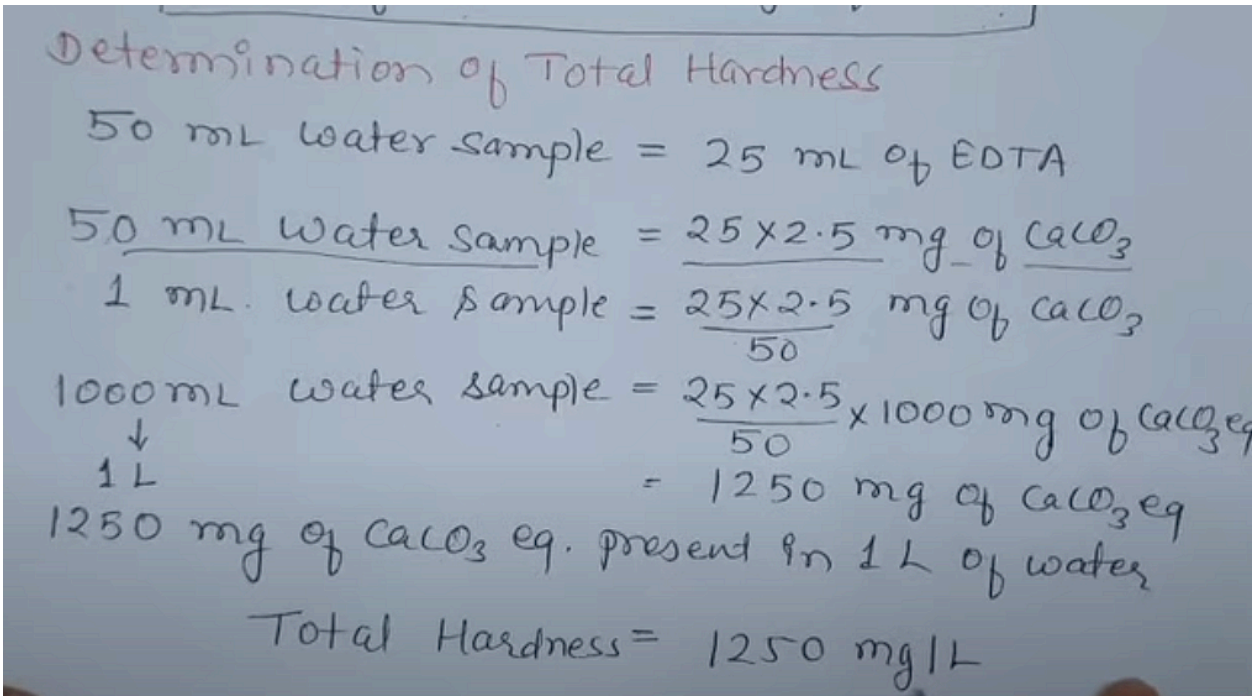
Part 4: Temporary Hardness

Temporary Hardness = Total Hardness – Permanent Hardness

= 1000 (V2 – V3)/V1







- If, 50 mL standard hard water having 1000 mg/L $CaCO_3$ equivalent hardness, requires 25 mL EDTA for titration. 50 mL unknown sample hard water requires 35 mL of same EDTA for titration. After boiling and filtration, 50 mL unknown sample hard water

requires 18 mL of same EDTA for titration. Calculate each type of hardness from the given information.

Total – 1400 ppm
Permanent – 720 ppm
Temporary – 680 ppm

- 50 ml of standard hard water (1.2 g/lit $CaCO_3$) required 13 ml of EDTA for titration using EBT indicator. 100 ml of water sample required 18 ml of same EDTA for titration while 50 ml of boiled water sample required 6 ml of EDTA. Calculate the temporary, permanent and total hardness.

Total – 830.77 ppm
Permanent – 553.84
Temporary – 276.93

- Give the formulae of finding the quantities of lime and soda requirement. What is the reaction of lime and/or soda with the following constituents in hard water:
  a) $Ca(HCO_3)_2$, b) $MgCl_2$, c) $Ca(NO_3)_2$

Name of Impurities	Reaction with Lime	Reaction With Soda	L & S Requirement
1.Temp Ca	$Ca(OH)_2$ +$Ca(HCO_3)_2$ --------> $2CaCO_3 + 2 H_20$	No Reaction	L
2. Temp Mg	$Mg(HCO_3)_2$ + 2 $Ca(OH)_2$ --------> Mg(OH)2 + 2CaCO3 + 2 H20	No Reaction	2L
3.Perm Mg	Ca(OH)2 +MgSO4 -------->**CaSO4**+ Mg(OH)2	**CaSO4** +Na2CO3 --------> CaCO3+ Na2SO4	L+ S
4.Perm Al	3Ca(OH)2 +Al2(SO4)3 --------> 2Al(OH)3+ **3 CaSO4**	**CaSO4** +Na2CO3 --------> CaCO3+ Na2SO4	L + S
5.Perm Fe	Ca(OH)2 +Fe(SO4) --------> Fe(OH)2+ **CaSO4**	**CaSO4** +Na2CO3 --------> CaCO3+ Na2SO4	L + S
6. CO2	CO2 + Ca(OH)2 --------> 2 CaCO3 + 2H2O	No Reaction	L
7. NaHCO3	2NaHCO3 + Ca(OH)2 --------> CaCO3 + **Na2CO3** +2H20	No Reaction	L - S
8. NaAlO2	NaAlO2 + H2O --------> Al(OH)3 + **NaOH**		**(-L)**eq to Ca(OH)2

- Calculate the quantities of lime and soda (both 100% pure) for softening of 4 x 10^6 liters of water containing the following constituents:
  $CaCl_2$= 2.22 ppm, $Mg(HCO_3)_2$ = 29.2 ppm, H_2SO_4 = 9.8 ppm, $MgCl_2$= 95 ppm, $CaSO_4$ = 2.72 ppm, KCl = 100 ppm

- Calculate the amount of lime (90 % pure) and soda (95 % pure) in kg, required for softening of 100000 litres of hard water having the following chemical constituents: $Ca(HCO_3)_2$ = 16.2 mg/L, $Mg(HCO_3)_2$ = 14.6 mg/L, $CaSO_4$ = 1.36 mg/L, $CaCl_2$ = 11.1 ppm, $MgCl_2$ = 9.5 ppm.

- Explain the principle, working of cold lime-soda method / hot lime-soda method with suitable diagram.

- Calculate the quantity of lime (80% pure) and soda (70% pure) for softening of 50000 liter of water having following impurities: $Ca(HCO_3)_2$= 8.1 ppm, $MgCO_3$ = 2.1 ppm, H_2SO_4= 4.9 ppm, $MgCl_2$= 1.9 ppm, $Ca(NO_3)_2$= 4.1 ppm, KNO_3= 10 ppm

- An exhausted zeolite softener was regenerated by passing 80 litres of 150 g/litre solution of NaCl. Calculate the volume of water softened (having 600 ppm hardness) using this zeolite softener.

- Explain the ion exchange process for removal of hardness with schematic diagram. Write the reactions during softening and regeneration process.

- Explain the demineralization process of softening hard water, with suitable reactions with suitable diagram.

- 50 ml of hard water (1 g $CaCO_3$/liter) required 22 ml of EDTA solution for titration using EBT. 50 ml of unknown water sample required 18 ml of same EDTA for titration. 100 ml of boiled water sample required 14 ml of same EDTA solution. Calculate temporary hardness.
- Explain with suitable diagram and reactions softening of hard water using Zeolite Permutit Method. Write its 2 advantages over lime soda Method.
- 25000 liter of hard water was softened by ion exchange column. For the regeneration of exhausted column 175 liter of 0.1 N HCl solution was used. Calculate the hardness of hard water.
- For BOD and COD numerical refer study material

Comparison:

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