1. Soap's molecular composition is "sodium salt of long chain fatty acid". However, when salts of calcium or magnesium are present in water, its cleansing action is reduced. Why?

Soaps are sodium or potassium salts of long chain fatty acids. When soap is added to hard water, the Ca<sup>2+</sup> and Mg<sup>2+</sup> ions present in hard water react with soap. The sodium salts present in soaps are converted to their corresponding calcium and magnesium salts which are precipitated as scum. The insoluble scum sticks on the clothes and so the cleaning capacity of soap is reduced.

$$\begin{array}{c} Ca^{2+} + RCOONa & \rightarrow \begin{array}{c} RCOOCa \\ Soap \end{array} \begin{array}{c} + 2Na^{+} \end{array}$$
 
$$Mg^{2+} + RCOONa & \rightarrow \begin{array}{c} RCOOMg \\ Magnesium \ salt(Scum) \end{array} \begin{array}{c} + 2Na^{+} \end{array}$$

2. Why hardness of water is expressed in equivalents of calcium carbonate?

The hardness of water is expressed in equivalents of calcium carbonate due to the fact that:

- i. Calculation becomes easy as Mol. Wt. of CaCO<sub>3</sub> is 100.
- ii. Insoluble CaCO<sub>3</sub> precipitated out from water therefore it is easy to calculate its amount in water
- 3. 100 ml of water sample required 4 mL of N/50  $H_2SO_4$  for neutralization of phenolphthalein end point. Another 16 mL of the same was needed for further titration to the methyl orange end point. Determine the type of alkalinity and amount of alkalinity.

Solution Volume of water sample for titration = 100 mL Volume used to phenolphthalein end point (A) = 4 mL Volume used to methyl orange end point (B) = 16 mL Total volume used to methyl orange end point (A + B) = 20 mL Phenolphthalein alkalinity (in terms of CaCO $_3$  equivalent)

$$\begin{aligned} N_1 V_1 &= N_2 V_2 \\ (Water) & (Acid) \\ N_1 \times 100 &= \frac{N}{50} \times 4 \\ N_1 &= \frac{4}{50 \times 100} \end{aligned}$$

Strength = 
$$N_1 \times Eq$$
. wt of CaCO<sub>3</sub>

$$\frac{4}{50 \times 100} \times 50$$

Phenolphthalein alkalinity (P) = 
$$\frac{4}{50 \times 100} \times 50 \times 1000$$
 ppm  
= 40 ppm

Similarly, for methyl orange alkalinity,

$$\begin{aligned} N_3 V_3 &= N_4 V_4 \\ \text{Water} & \text{Acid} \end{aligned}$$
 
$$N_3 \times 100 = \frac{N}{50} \times 20$$
 
$$N_3 = \frac{N}{50} \times \frac{20}{100}$$

Methyl orange alkalinity (M) =  $\frac{1}{50} \times \frac{20}{100} \times 50 \times 1000$  ppm

$$M = 200 \text{ ppm}$$

Hence,

$$P < \frac{1}{2}M$$

$$P(40) < \frac{1}{2}M(100)$$

So CO<sub>3</sub><sup>2-</sup> and HCO<sub>3</sub> ions are present.

Now, alkalinity due to  $CO_3^{2-}$  ions =  $2P = 2 \times 40$  ppm = 80 ppm alkalinity due to  $HCO_3^{-}$  ions = M - 2P = 200 - 80 = 120 ppm

4. 0.5 g of CaCO3 was dissolved in dil. HCl and diluted to 500 ml. Then, 100 ml of this solution required 90 ml of EDTA solution for titration. Also, 100 ml of a water sample required 36 ml of the same EDTA solution for titration. After boiling, titration of 100 ml of same water sample required 18 ml of EDTA. Calculate total, permanent and temporary hardness.

**Step 1:** 1 M CaCO<sub>3</sub> water solution =100 gm of CaCO<sub>3</sub> disolved in 1 liter of water =50 gm of CaCO<sub>3</sub> in 0.5 liter water

if disolved 0.5 gm in 500 mL water than concentration will be 0.01 M.

**Step 2:** 100 ml of this solution required 90 ml of EDTA solution for titration

After applying  $M_1V_{1 \text{ (water)}} = M_2V_{2 \text{ (EDTA)}}$  $100 \text{ x } 0.01 = 90 \text{ x } M_2$ 

 $M_2 = 1/90$ 

Concentration of EDTA=1/90 M = 0.011 M

Step 3: 100 ml of a water sample required 36 ml of the same EDTA solution for titration

 $100 \text{ x } M_{1(\text{water})} = 36 \text{ x } 0.011$   $M_{1(\text{water})} = 0.00396$ Total Hardness of water sample =  $M_1 \text{ x } M.W.$  of  $CaCO_3 \text{ x } 1000$  0.00396 x 100x 1000 = 396 mg/l or ppm

**Step 4:** After boiling, titration of 100 ml of same water sample required 18 ml of EDTA

 $100 \times M_1 = 18 \times 0.011$  $M_1 = 0.00198$ 

Permanent Hardness of water sample= $0.00198 \times 100 \times 1000 = 198 \text{ mg/l or ppm}$ 

Temporary hardness= Total Hardness- Permanent Hardness= 396-198 = **198 mg/l or ppm** 

5. 50 mL of a water sample consumed 15 mL of 0.01 M EDTA before boiling and 5 mL of the same EDTA after boiling. Calculate total, permanent and temporary hardness of water sample.

Before boiling, 50 mL of a water sample consumed 15 mL of 0.01 M EDTA

 $M_1V_1$  (Water) =  $M_2V_2$  (EDTA)  $50 \times M_1$ (Water) = 15 x 0.01  $M_1$ = 15 x 0.01/50= 0.003 M

Total hardness of 50 mL of a water sample= 0.003 x M. W. of CaCO<sub>3</sub> x 1000

 $0.003 \ x \ 100 \ x \ 1000 = \!\! \textbf{300 mg/l or ppm}$ 

After boiling, 50 mL of same water sample consumed 5 mL of 0.01 M EDTA

 $\begin{aligned} M_1 V_{1 \text{ (Water)}} &= M_2 V_{2 \text{ (EDTA)}} \\ & 50 \text{ x } M_1 = 5 \text{ x } 0.01 \\ M_1 &= 5 \text{ x } 0.01 / 50 = 0.001 \text{ M} \end{aligned}$ 

Permanent hardness of 50 mL of a water sample= 0.001 x M.W. of CaCO<sub>3</sub> x 1000

 $0.001 \times 100 \times 1000 = 100 \text{ mg/l or ppm}$ 

Temporary hardness= Total hardness- Permanent hardness 300-100=**200 mg/l or ppm** 

6. Calculate the temporary and permanent hardness of a sample of water containing: Mg(HCO<sub>3</sub>)<sub>2</sub> = 7.3 mg/L; Ca(HCO<sub>3</sub>)<sub>2</sub> = 16.2 mg/L; MgCl<sub>2</sub> = 9.5 mg/L; CaSO<sub>4</sub> = 13.6 mg/L.

Temporary hardness = hardness due to  $Mg(HCO_3)_2$  and  $Ca(HCO_3)_2$  [7.3 x 100/146 + 16.2 x 100/162] mg/l [5 + 10] =15 mg/l or 15 ppm.

Permanent hardness= hardness due to MgCl<sub>2</sub> and CaSO<sub>4</sub> [9.5 x  $100/95 + 13.6 \times 100/136$ ] = [10 + 10]= **20 mg/l or 20 ppm.** 

7. Draw a flow chart diagram for the analysis of hard water using EDTA and EBT. Specify the role of colors in the flow chat diagram.

Take 10 mL of the hard water sample



Add 2-3 mL ammonium buffer solution to maintain pH~9-10



Add 2-3 drops of the EBT indicator (solution becomes wine red)



Titrate the hard water sample against the standard EDTA solution (till the color changes to blue)



Note the EDTA volume used by burette reading

Appearance of wine red color signify the formation of unstable complex of EBT with  $Ca^{2+}$  or  $Mg^{2+}$  ions

$$Ca^{2+}/Mg^{2+}$$
 + EBT  $\longrightarrow$   $Ca^{2+}/Mg^{2+}$  EBT complex Wine red (Unstable complex)

Disappearance of wine red color and appearance of blue color signify the formation of complex of EDTA with  $Ca^{2+}$  or  $Mg^{2+}$  ions

$$Ca^{2+}/Mg^{2+}$$
 EBT complex + EDTA  $\xrightarrow{pH \ 10}$   $Ca^{2+}/Mg^{2+}$  EDTA complex + EBT Wine red (Unstable complex) Colourless Blue dye

8. Write structure and full name of EDTA and EBT.

EBT =Eriochrome Black

## EDTA= Ethylenediaminetetraacetic acid

## 9. Write various units of hardness and what is the relationship among them.

1) Parts per million (ppm)

It is the number of parts of calcium carbonate equivalent hardness per million (10<sup>6</sup>) parts of water.

1 ppm = 1 part of  $CaCO_3$  equivalent hardness in  $10^6$  parts of water.

2) mg/l:

Usually defined as one milligram of calcium carbonate (CaCO<sub>3</sub>) per liter of water.

 $1 \text{ mg/l} = 1 \text{ mg of } CaCO_3 \text{ in } 1 \text{ liter water}$ 

3) Clark's Degree (°Cl)

One degree Clark is defined as one grain (64.8 mg) of CaCO<sub>3</sub> per imperial gallon (4.55 liters) of water.

*4) Degree French (°F):* 

One degree French is defined as 10 milligrams of calcium carbonate per liter of water.

Relationship among different units of hardness: 1ppm=1 mg/l = 0.07 °Clark =0.1 °F

10. Convert 50 ppm of CaCO3 into mg/L, degree Clarke and degree French.

11. Convert 70,000 °Clarke into ppm and °French.