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.

$$Ca^{2+} + RCOONa \rightarrow RCOOCa \atop Soap} \rightarrow RCOOCa \atop Calcium salt(Scum)} + 2Na^{+}$$

$$Mg^{2+} + RCOONa \rightarrow RCOOMg \atop Soap} + 2Na^{+}$$

$$Magnesium salt(Scum)$$

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

Solution Volume of water sample for titration = 100 mL

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

- Calculation becomes easy as Mol. Wt. of CaCO<sub>3</sub> is 100.
- ii. Insoluble CaCO3 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<sub>2</sub>SO<sub>4</sub> 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.

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 mLPhenolphthalein alkalinity (in terms of CaCO, equivalent)  $N_1V_1 = N_2V_2$ (Water) (Acid)  $N_1 \times 100 = \frac{N}{50} \times 4$ Strength =  $N_1 \times Eq$ . wt of CaCO,  $\frac{4}{50\times100}\times50$ Phenolphthalein alkalinity (P) =  $\frac{4}{50\times100}\times50\times1000$  ppm

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

Similarly, for methyl orange alkalinity,

$$N_3 V_3 = N_4 V_4$$
Water Acid
$$N_3 \times 100 = \frac{N}{50} \times 20$$

$$N_3 = \frac{N}{50} \times \frac{20}{100}$$

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

M = 200 ppm

Hence.

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

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  $M_1V_{1 \text{ (water)}} = M_2V_{2 \text{ (EDTA)}}$   $100 \times 0.01 = 90 \times M_2$  $M_2 = 1/90$ 

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

 $100 \times M_{1(water)} = 36 \times 0.011$   $M_{1(water)} = 0.00396$ Total Hardness of water sample =  $M_1 \times M.W.$  of CaCO<sub>3</sub> × 1000  $0.00396 \times 100 \times 1000 = 396$  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 x 100x1000 = 198 mg/l or ppm

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

 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

 $\begin{aligned} M_1 V_{1 \text{ (Water)}} &= M_2 V_{2 \text{ (EDTA)}} \\ &\quad 50 \text{ x } M_{1 \text{(Water)}} = 15 \text{ x } 0.01 \\ M_1 &= 15 \text{ x } 0.01/50 = 0.003 \text{ M} \end{aligned}$ 

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

 $0.003 \times 100 \times 1000 = 300 \text{ mg/l or ppm}$ 

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

 $M_1V_{1 \text{ (Water)}} = M_2V_{2 \text{ (EDTA)}}$   $50 \times M_1 = 5 \times 0.01$  $M_1 = 5 \times 0.01/50 = 0.001 \text{ M}$ 

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

 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



Note the EDTA volume used by burette reading

Appearance of wine red color signify the formation of unstable complex of EBT with Ca<sup>2+</sup> or Mg<sup>2+</sup> ions

$$Ca^{2+}/Mg^{2+}$$
 + EBT  $\xrightarrow{pH \ 10}$   $Ca^{2+}/Mg^{2+}$  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

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 (106) parts of water.

1 ppm = 1 part of CaCO<sub>3</sub> equivalent hardness in 10<sup>6</sup> parts of water.

2) mg/l:

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

1 mg/l = 1 mg of CaCO<sub>3</sub> in 1 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.

1ppm= 1 mg/l = 
$$0.07$$
 °Clark = $0.1$  °F  
50 ppm= 50 mg/l= $3.5$  °Cl =  $5$  °F

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

70,000 Clark=10<sup>6</sup> ppm 70,000 Clark=10<sup>5</sup> °F