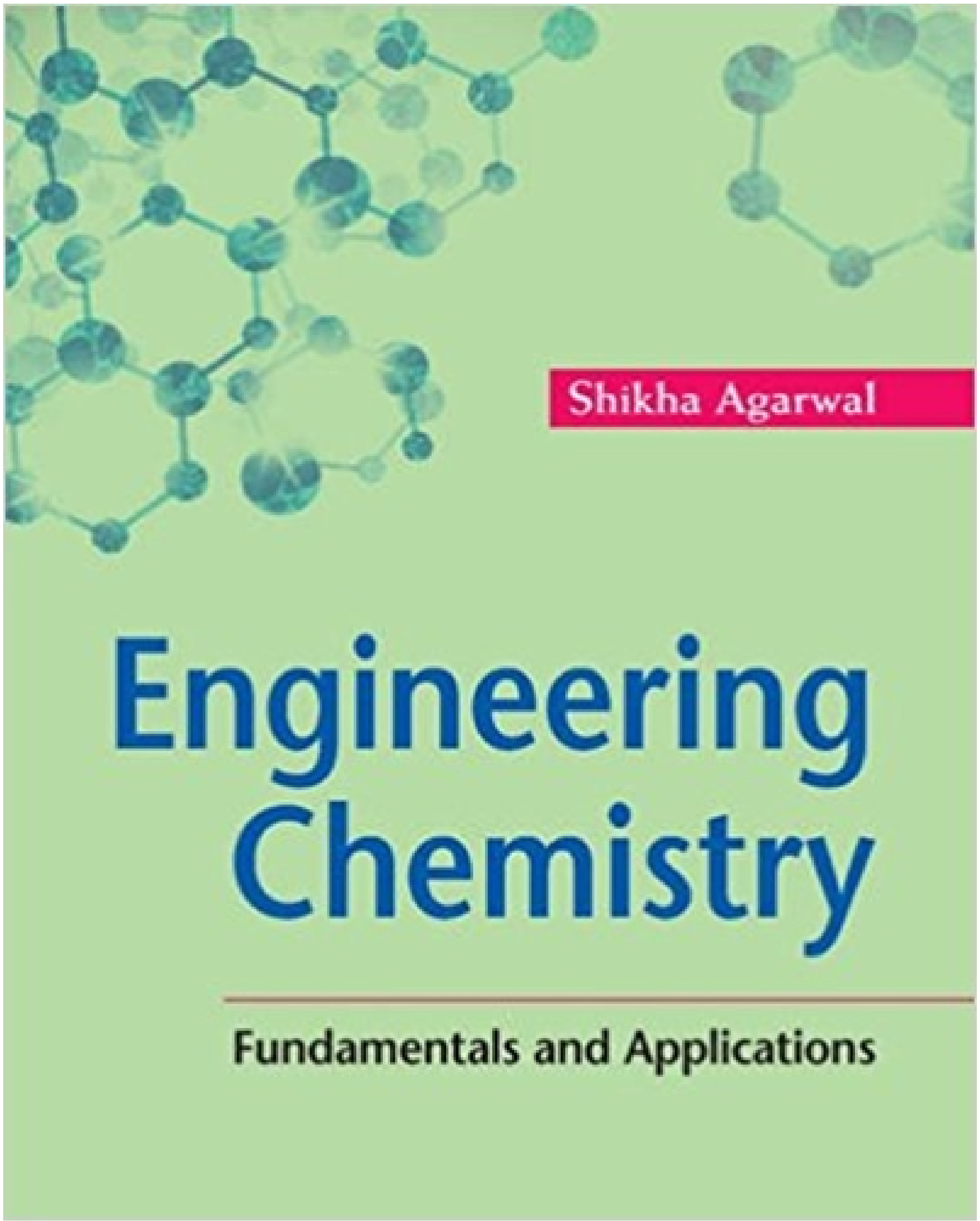
Solutions for Engineering Chemistry Fundamentals and Applications 1st Edition by Agarwal



Solutions

Chapter 2

WATER

Practice problems

1. A water sample contains $Ca(HCO_3)_2 = 32.4$ mg/L, $Mg(HCO_3)_2 = 29.2$ mg/L, $CaSO_4 = 13.5$ mg/L. Calculate the temporary and permanent hardness of water.

Solution:

Conversion into $CaCO_3$ equivalent

Constituent	**Amount**	**Equivalent of $CaCO_3$**
$Ca(HCO_3)_2$	32.4 mg/L	$\frac{32.4 \times 100 / 2}{162 / 2} = 20$ mg/L
$Mg(HCO_3)_2$	29.2 mg/L	$\frac{29.2 \times 100 / 2}{146 / 2} = 20$ mg/L
$CaSO_4$	13.5 mg/L	$\frac{13.5 \times 100 / 2}{136 / 2} = 9.926$ mg/L

Temporary hardness is due to Ca $(HCO_3)_2$ & Mg $(HCO_3)_2$ as $CaCO_3$ equivalent

Hence Temporary hardness = 20 + 20 = 40 ppm,

Permanent hardness is due to salt of $CaSO_4$ as $CaCO_3$ equivalent

Permanent hardness = 9.926 ppm

[Ans. Temporary hardness = 20 + 20 = 40 ppm; Permanent hardness = 9.926 ppm]

2. A sample of water on analysis gives the following data:

$Ca(HCO_3)_2 = 24.1°$ French; $CaSO_4 = 3.2°$ French; $MgCl_2 = 9.5°$ French; $SiO_2 = 2.1°$ French; $MgSO_4 = 8.2°$ French

Calculate the temporary and permanent hardness on °Clarke and ppm scale.

Solution:

Conversion into $CaCO_3$ equivalents:

Constituent	**Amount**	**$CaCO_3$ equivalents**
$Ca(HCO_3)_2$	24.1°French	$\frac{24.1 \times 100 / 2}{162 / 2}$ = 14.88°French
$CaSO_4$	3.2°French	$\frac{3.2 \times 100 / 2}{136 / 2}$ = 2.35 °French
$MgCl_2$	9.5 °French	$\frac{9.5 \times 100 / 2}{95 / 2}$ = 10°French
$MgSO_4$	8.2°French	$\frac{8.2 \times 100 / 2}{120 / 2}$ = 6.83 °French
SiO_2	2.1°French	Does not impart hardness

Relation used in Conversion = 1°French = 0.7°Clarke = 10 ppm

Temporary hardness = Hardness due to $Ca(HCO_3)_2$ as $CaCO_3$ equivalents = 14.88°Fr

Since 1°French = 0.7 °Clarke

Therefore 14.88°French = 14.88 × 0.7 = 10.41 °Clarke

As 1°Fr = 10 ppm

Therefore 14.88°Fr = 14.88 × 10 = 148.88 ppm

Temporary hardness = 14.88°French = 10.41 °Clarke = 148.88 ppm

Permanent Hardness = Hardness due to ($CaSO_4 + MgCl_2 + MgSO_4$) as $CaCO_3$ eq

= 2.35 + 10 + 6.83 = 19.18 °French

= 19.18 × 0.7 = 13.426 °Clarke

= 19.18 × 10 = 191.8 ppm

Permanent Hardness = 19.18 °Fr = 13.426 °Cl = 191.8 ppm

[Ans. Temporary hardness = 14.88°French = 10.41 °Clarke = 148.88 ppm; Permanent Hardness = 19.18 °Fr = 13.426 °Cl = 191.8 ppm]

3. A sample of water on analysis has been found to contain the following impurities:

$Mg(HCO_3)_2$ = 14.6 mg/l; $Mg(NO_3)_2$ = 44.4 mg/l; $MgSO_4$ = 36 mg/l; $MgCl_2$ = 19.0 mg/l and $CaCO_3$ = 30 mg/l.

Calculate the temporary and permanent hardness in ppm and °Clarke.

Conversion into $CaCO_3$ equivalents:

Constituent	**Amount**	**$CaCO_3$ equivalents**
$Mg(HCO_3)_2$	14.6 mg/l	$\frac{14.6 \times 100 / 2}{146 / 2}$ = 10 mg/l.
$Mg(NO_3)_2$	44.4 mg/l	$\frac{44.4 \times 100 / 2}{148 / 2}$ = 30 mg/l.
$MgSO_4$	36 mg/l	$\frac{36 \times 100 / 2}{120 / 2}$ = 30 mg/l.
$MgCl_2$	19.0 mg/l	$\frac{19.0 \times 100 / 2}{95 / 2}$ = 20 mg/l.
$CaCO_3$	30 mg/l.	$\frac{30 \times 100 / 2}{100 / 2}$ = 30 mg/l.

Temporary hardness = Hardness due to $Mg(HCO_3)_2 + CaCO_3$ as $CaCO_3$ equivalents

$$10 + 30 = 40 \text{ mg/l}$$

$$= 40 \times 0.07 = 2.8\ ^\circ\text{Clarke}$$

Permanent Hardness = Hardness due to $(Mg(NO_3)_2 + MgSO_4 + MgCl_2)$ as $CaCO_3$ eq

$$30 + 30 + 20 = 80 \text{ mg/l}$$

$$= 80 \times 0.07 = 5.6\ ^\circ\text{Clarke}$$

[Ans. Temporary hardness = 40 ppm & 2.8 °Clarke;
Permanent hardness = 80 ppm & 5.6 °Clarke]

Practice Problems

1. Calculate the amount of lime required for softening 50,000 litres of hard water containing; $CaCO_3$ = 20 ppm; $MgCO_3$ = 190 ppm; $CaCl_2$ = 120 ppm; $MgCl_2$ = 100 ppm; Na_2SO_4 = 20 ppm; Fe_2O_3 = 30 ppm.

Solution:

Conversion into $CaCO_3$ equivalents:

Constituent	**Amount**	**$CaCO_3$ equivalents**	
$CaCO_3$	20 ppm	$20 \times \frac{100}{100} = 20$ ppm	L
$MgCO_3$	190 ppm	$\frac{190 \times 100 / 2}{84 / 2} = 226.19$ ppm	2L
$CaCl_2$	120 ppm	$\frac{120 \times 100 / 2}{111 / 2} = 108.108$ ppm	S
$MgCl_2$	100 ppm	$\frac{100 \times 100 / 2}{95 / 2} = 105.263$	L + S
Na_2SO_4	20 ppm	-	
Fe_2O_3	30 ppm	-	

$$V = 50000 \text{ litre}$$

$$\text{Lime} = \frac{74}{100}\left[20 + 2 \times 226.19 + 105.263\right] \times 50000$$

$$= 2137279 \text{ mg} = 21.37 \text{ kg}$$

[Ans. Lime Required = 21.37 Kg]

2. A sample of water was analysed and found to contain temporary magnesium hardness = 25 mg/l; permanent magnesium chloride hardness = 15 mg/l; permanent calcium sulphate hardness = 20 mg/l and SiO_2 = 300 mg/l. Calculate the lime and soda required for softening 30,000 litres of hard water.

Solution:

Conversion into $CaCO_3$ equivalents:

Constituent	**Amount**	**$CaCO_3$ equivalents**	
$Mg(HCO_3)_2$	25 mg/l	$\frac{25 \times 100}{146} = 17.123$	2L
$MgCl_2$	15 mg/l	$\frac{15 \times 100}{95} = 15.789$	L + S
$CaSO_4$	20mg/l	$\frac{20 \times 100}{136} = 14.705$	S

$$\text{Lime} = \frac{74}{100}\left[2 \times 17.123 + 15.789\right] \times 30000$$

$$= 1110777 \text{ mg} = 1.11 \text{ kg}$$

$$\text{Soda} = \frac{106}{100}\left[15.789 + 14.705\right] \times 30000$$

$$= 969709.2 \text{ mg} = 0.9697 \text{ kg}$$

[Ans. Lime = 1.1107 Kg; Soda = 0.9697 Kg]

3. Calculate the quantities of lime and soda required for softening 3,00,000 litres of water using 164 ppm of sodium aluminate as coagulant. The analytical result of raw water is Ca^{+2} = 240 ppm; Mg^{+2} = 96 ppm; HCO_3^- = 732 ppm; CO_2(dissolved) = 44 ppm; NaCl = 60 ppm; Fe_2O_3 = 160 ppm

Solution:

Conversion into $CaCO_3$ equivalents :

Constituent	**Amount**	**$CaCO_3$ equivalents**	
Ca^{2+}	240 ppm	$240 \times \frac{100}{40} = 600$ ppm	S
Mg^{2+}	96 ppm	$96 \times \frac{100}{24} = 400$ ppm	L + S
HCO_3^-	732 ppm	$732 \times \frac{100}{2 \times 61} = 600$ ppm	L–S
CO_2	44 ppm	$44 \times \frac{100}{44} = 100$ ppm	L
$NaAlO_2$	164 ppm	$164 \times \frac{100}{82 \times 2} = 100$ ppm	–L

$$V = 300000 \text{ litre}$$

$$\text{Lime} = \frac{74}{100}\left[400 + 600 + 100 - 100\right] \times 300000$$

$$= 222000000 \text{ mg} = 222 \text{ kg}$$

$$\text{Soda} = \frac{106}{100}\left[600 + 400 - 600\right] \times 300000$$

$$= 127200000 \text{ mg} = 127.2 \text{ kg}$$

[Ans. Lime = 222 Kg; soda = 127.2 Kg]

4. Calculate the quantity of lime and soda required to soften 25000 gallons of hard water containing $Ca(HCO_3)_2$ = 20 grains; $Mg(HCO_3)_2$ = 15 grains; $CaSO_4$ = 5 grains by lime soda process.

Solution:

Conversion into $CaCO_3$ equivalents:

Constituent	**Amount**	**$CaCO_3$ equivalents**	
$Ca(HCO_3)_2$	20 grains	$20 \times \frac{100}{162} = 12.345$ grains	L
$Mg(HCO_3)_2$	15 grains	$15 \times \frac{100}{146} = 10.273$ grains	2L
$CaSO_4$	5 grains	$5 \times \frac{100}{136} = 3.676$ grains	S

$$V = 25000 \text{ gallons}$$

$$\text{Lime} = \frac{74}{100}\left[12.345 + 2 \times 10.273\right] \times 25000$$

$$= 608483.5 \text{ grains}$$

1lb = 7000 grains or 1 grain = 1/7000 pound = 608483.5/7000 = 86.9 lbs

$$\text{Soda} = \frac{106}{100}\left[3.68\right] \times 25000 = \frac{97520}{7000} = 13.93 \text{ pounds}$$

[Ans. Lime = 86.9 lbs (pounds); Soda = 13.93 lbs(pound)]

5. Calculate the quantity of lime and soda required for softening 60,000 litres of hard water. The analysis is as follows:

Temporary hardness = 55.5 ppm

Permanent calcium hardness = 42.5 ppm

Permanent magnesium hardness = 48 ppm

Solution:

$$\text{Lime} = \frac{74}{100}\left[55.5 + 48\right] \times 60000 = 4.595 \text{ kg}$$

$$\text{Soda} = \frac{106}{100}\left[42.5 + 48\right] \times 60000 = 5.755 \text{ kg}$$

[Ans. Lime = 4.60 Kg; Soda = 5.755 Kg]

6. Calculate the amounts of lime (90% pure) and soda (98% pure) required for the treatment of one million litres of water containing:

$Ca(HCO_3)_2$ = 8.1 ppm; $CaCl_2$ = 33.3 ppm; HCO_3^- = 91.5 ppm; $MgCl_2$ = 38ppm; $Mg(HCO_3)_2$ = 14.6 ppm. The coagulant $Al_2(SO_4)_3$ was added at a rate of 17.1 mg/l of water.

Solution:

Conversion into $CaCO_3$ equivalents:

Constituent	**Amount**	**$CaCO_3$ equivalents**	
$Ca(HCO_3)_2$	8.1 ppm	$\frac{8.1 \times 100}{162} = 5$ ppm	L
$CaCl_2$	33.3 ppm	$\frac{33.3 \times 100}{111} = 30$ ppm	S
HCO_3^-	91.5 ppm	$\frac{91.5 \times 100}{2 \times 61} = 75$ ppm	L – S
$MgCl_2$	38 ppm	$\frac{38 \times 100}{95} = 40$ ppm	L + S
$Mg(HCO_3)_2$	14.6 ppm	$\frac{14.6 \times 100}{146} = 10$ ppm	2L
$Al_2(SO_4)_3$	17.1 mg/l	$\frac{17.1 \times 100 \times 3}{342} = 15$ ppm	L + S

$$\text{Lime} = \frac{74}{100}\left[5 + 75 + 40 + 20 + 15\right] \times 10^6 \times \frac{100}{90} = 127.44 \text{ kg}$$

$$\text{Soda} = \frac{106}{100}\left[30 - 75 + 40 + 15\right] \times 10^6 \times \frac{100}{98} = 10.82 \text{ kg}$$

[Ans. Lime = 127.44 Kg; Soda = 10.82 Kg]

7. A sample of water on analysis gave the following results:

H_2SO_4 = 147 mg/l; $MgCl_2$ = 95mg/l; $MgSO_4$ = 24 mg/l; $CaSO_4$ = 170 mg/l and KCl = 20 mg/l.

Water is to be supplied to the town of the population of one lakh only. The daily consumption of water is 100 litres per head. Calculate the cost of lime and soda required for softening hard water for the town for one month (November). If lime is 90% pure and Rs 5.00 per Kg and soda is 92% pure and costs Rs 8.00 per Kg.

Solution:

Conversion into $CaCO_3$ equivalents :

Constituent	**Amount**	**$CaCO_3$ equivalents**	
H_2SO_4	147 mg/l	$\frac{147 \times 100 / 2}{98 / 2} = 150$ ppm	L + S
$MgCl_2$	95 mg/l	$\frac{95 \times 100}{95} = 100$ ppm	L + S
$MgSO_4$	24 mg/l	$\frac{24 \times 100}{120} = 20$ ppm	L + S
$CaSO_4$	170 mg/l	$\frac{170 \times 100}{136} = 125$ ppm	S

$$V = 10^5 \times 100 = 10^7 \text{ Litres}$$

$$\text{Lime} = \frac{74}{100}[150 + 100 + 20] \times 10^7 \times \frac{100}{90} = 222 \times 10^7 \text{ mg}$$

$$\text{Cost} = \frac{222 \times 10^7}{10^6} \times 30 \times 5 = 333000 \text{ Rs}$$

$$\text{Soda} = \frac{106}{100}[150 + 100 + 20 + 125] \times 10^7 \times \frac{100}{92} \times 30 = 13653.2 \text{ kg}$$

$$\text{Cost} = 13653.2 \times 8 = 1092260.87 \text{ Rs}$$

[Ans. Cost of lime = Rs 3,33,000; Cost of soda = Rs 1092260.87]

8. Calculate the amount of lime and soda needed for softening 75,000 litres of hard water. The results of analysis of raw water and treated water are as follows:

Analysis of raw water:

HCO_3^- = 212 mg/l; H^+ = 3 mg/l; Ca^{+2} = 55.5 mg/l; Mg^{+2} = 42 mg/l; CO_2 = 66 mg/l;

Analysis of treated water:

CO_3^{2-} = 90 mg/l; OH^- = 45 mg/l.

In this treatment 20 mg/l of $NaAlO_2$ was used as a coagulant.

Solution:

Conversion into $CaCO_3$ equivalents:

Constituent	**Amount**	**$CaCO_3$ equivalents**	**Requirement (L/S)**
HCO_3^-	212 mg/l	$\frac{212 \times 100}{61 \times 2} = 173.77$ ppm	L – S
H^+	3 mg/l	$\frac{3 \times 100}{2} = 150$ ppm	L + S
Ca^{+2}	55.5 mg/l	$\frac{55.5 \times 100}{40} = 138.75$ ppm	S
Mg^{+2}	42 mg/l	$\frac{42 \times 100}{24} = 175$ppm	L + S
CO_2	66 mg/l	$\frac{66 \times 100}{44} = 150$ppm	L
CO_3^{2-}	90 mg/l	$\frac{90 \times 100}{60} = 150$ppm	L + S
OH^-	45 mg/l	$\frac{45 \times 100}{2 \times 17} = 132.35$ppm	L
$NaAlO_2$	20 mg/l	$\frac{20 \times 100}{82 \times 2} = 12.195$ppm	–L

$$V = 75000 \text{ litres}$$

$$\text{Lime} = \frac{74}{100}[173.77 + 150 + 175 + 150 + 132.35 - 12.195] \times 75000$$

$$= 42675337.50 \text{ mg} = 42.67 \text{ Kg}$$

$$\text{Soda} = \frac{106}{100}\left[150 - 173.77 + 138.75 + 175 + 150 + 132.35\right] \times 75000$$

$$= 45500235 \text{ mg} = 45.5 \text{ kg}$$

[Ans. Total Lime = 42.67 Kg Total Soda = 45.5 Kg]

Practice problems

1. A zeolite softener was completely exhausted and was regenerated by passing 100 litres of NaCl solution containing 120 g/litre of NaCl. How many litres of sample of water of hardness 500 ppm can be softened by this softener.

Solution:

V_1 = volume of water softened = ?

V_2 = Volume of NaCl solution used for regeneration

= 100 litres

m = Amount of NaCl = 120g/l

Hardness (H) = 500 ppm

$$\text{Formula: Hardness} = \frac{50 \times m \times V_2 \times 10^3}{58.5 \times V_1}$$

$$500 = \frac{50 \times 120 \times 100 \times 10^3}{58.5 \times V_1}$$

$$V_1 = \frac{50 \times 120 \times 100 \times 10^3}{58.5 \times 500}$$

$$= 20512.8 \text{ litres}$$

Total volume of hard water softened = 20512.8 litres [Ans. 20512.8 litres]

2. A zeolite softener was completely exhausted after softening 145,000 litres of hard water. To regenerate the zeolite softener 540 litres of NaCl solution containing 110 g/litre of NaCl is required. Calculate the hardness of one litre water sample in ppm.

Solution:

$$\text{Hardness} = \frac{50 \times m \times V_2 \times 10^3}{58.5 \times V_1}$$

Hardness in ppm = ?

m = Amount of NaCl in gm/litre = 110 g/l

V_2 = Volume of NaCl solution used for regeneration

= 540 litres

V_1 = Total volume of water softened

= 145000 litres

$$\text{Hardness} = \frac{50 \times 110 \times 540 \times 10^3}{58.5 \times 145000} = 350.13 \text{ mg/l}$$

Hardness = 350.13 ppm [Ans. 350.13 ppm]

3. 200 litres of NaCl solution containing 85 g/litre of NaCl was required to regenerate a completely exhausted zeolite softener. How many litres of hard water of hardness 600 ppm can be softened by the softener.

Solution:

$$\text{Hardness} = \frac{50 \times m \times V_2 \times 10^3}{58.5 \times V_1}$$

Hardness in ppm = 600 ppm

m = Amount of NaCl in gm / litre = 85g/l

V_2 = Volume of NaCl solution used for regeneration

= 200 litres

V_1 = Total volume of water softened = ?

Placing these values in the formula we have

$$600 = \frac{50 \times 85 \times 200 \times 10^3}{58.5 \times V_1}$$

$$V_1 = \frac{50 \times 85 \times 200 \times 10^3}{58.5 \times 600} = 24216.5 \text{ litre}$$

Volume of hard water softened = 24216.5 litres [Ans. 24216.5 litres]

4. When a zeolite softener was completely exhausted it was regenerated by passing 200 litres of NaCl solution containing 120 g/litre of NaCl. How many litres of a sample of water of hardness 550 mg/litre can be softened by the zeolite softener before regenerating it again?

Solution:

V_1 = Total volume of water softened = ?

V_2 = Volume of NaCl solution used for regeneration

= 200 litres

m = Amount of NaCl in gm / litre = 120 g/l

Hardness (H) = 550 mg/l = 550 ppm

$$\text{Hardness} = \frac{50 \times m \times V_2 \times 10^3}{58.5 \times V_1}$$

$$550 = \frac{50 \times 120 \times 200 \times 10^3}{58.5 \times V_1}$$

$$V_1 = \frac{50 \times 120 \times 200 \times 10^3}{58.5 \times 550} = 37296.037 \text{ litres}$$

Total volume of hard water softened = 37296.037 litres [Ans. 37296.037 litres]

Practice Problems

1. 100 ml of tap water was titrated with N/50 HCl with methyl orange as an indicator. If 28 ml HCl were required,calculate the hardness as parts of $CaCO_3$ per 10,000 parts of water. The hardness is temporary.

Solution:

Volume of water sample V_1 = 100 ml

Normality of water sample N_1 = ?

Normality of HCl $N_2 = N/50$

Volume of HCl V_2 = 28 ml

Hardness as $CaCO_3$ equivalent per 10000 parts of water

$$\underset{water}{N_1V_1} = \underset{HCl}{N_2V_2}$$

$$N_1 \times 100 = \frac{N}{50} \times 28$$

$$N_1 = \frac{28}{50 \times 100}$$

$$\text{Strength} = \frac{28}{50 \times 100} \times \text{Equivalent wt } CaCO_3 \times 10000$$

$$= \frac{28}{50 \times 100} \times 50 \times 10000$$

= 2800 mg per 10000 parts of water

[Ans. 2800 parts per 10000 parts of water]

2. In an experiment to determine the hardness of a sample of water, 25 ml of N/50 Na_2CO_3 solution was added to 100 ml of water sample. After completion of precipitation of the insoluble carbonates the unreacted Na_2CO_3 was titrated against N/50 H_2SO_4 solution when 10 ml of the acid was required. Calculate the degree of hardness and comment on the nature of hardness so determined.

Solution:

Volume of Na_2CO_3 added = 25 ml

Excess Na_2CO_3 = 10 ml

Volume of N/50 Na_2CO_3 solution used for removing permanent hardness in 100 ml water sample = 25 – 10 = 15 ml

$$\underset{\text{water sample}}{N_1V_1} = \underset{\text{Acid}}{N_2V_2}$$

$$N_1 \times 100 = \frac{N}{50} \times 15$$

$$N_1 = \frac{15}{50 \times 100}$$

Strength of water = $\dfrac{15}{50 \times 100} \times 50 \times 1000 = 150$ ppm

[Ans. Permanent hardness 150 ppm]

Practice Problems

1. A standard hard water contains 15 g of $CaCO_3$ per litre. 20 ml of this water sample required 25 ml of EDTA solution,100 ml of sample water required 18 ml of EDTA solution. The sample after boiling required 12 ml EDTA solution. Calculate total,permanent and temporary hardness of the given water sample in ppm.

Solution:

Step 1: Standardisation of EDTA **Solution:**

Given 1 litre of standard hard water contains 15 g of $CaCO_3$

Or, 1000 ml of standard hard water contains 15000 mg of $CaCO_3$

∴ 1 ml of std hard water contains 15 mg of $CaCO_3$ equivalent of hardness … (1)

Now, 25 ml of EDTA solution = 20 ml of std hard water

Or, 25 ml of EDTA solution = 20 × 15 mg of $CaCO_3$ equivalent hardness

Or 1 ml of EDTA solution = $\dfrac{20 \times 15}{25} = 12$ mg of $CaCO_3$ equivalent hardness … (2)

Step 2: Determination of Total hardness of water :

100 ml of sample water = 18 ml of EDTA

= 18 × 12

= 216 mg of $CaCO_3$ equivalent hardness

(From eq 2)

1000 ml (1 litre) of sample hard water = $\dfrac{216 \times 1000}{100} = 2160$ mg/L

Total Hardness = 2160 ppm

Step 3: Determination of permanent hardness:

$$100 \text{ ml of boiled water} = 12 \text{ ml of EDTA}$$

$$= 12 \times 12 = 144 \text{ mg of } CaCO_3 \text{ eq hardness}$$

(From eq 2)

$$1000 \text{ ml (or 1 litre) of boiled water} = \frac{144 \times 1000}{100} = 1440 \text{ mg/L of } CaCO_3 \text{ eq hardness}$$

Permanent hardness = 1440 ppm

Step 4: Determination of temporary hardness:

Temporary hardness = Total hardness – Permanent hardness

$$= 2160 - 1440 = 720 \text{ ppm}$$

[Ans. Total hardness = 2160 ppm; Permanent hardness = 1440 ppm; Temporary hardness = 720 ppm].

2. The EDTA was used to find out permanent and temporary types of hardness in a given hard water sample. Following observations were recorded:

(i) 22 ml of EDTA was consumed by 50 ml of standard hard water (containing 1 mg of $CaCO_3$ per ml).

(ii) 50 ml water sample consumed 27 ml EDTA solution.

(iii) 50 ml water sample after boiling, filtering consumed 20 ml of EDTA solution.

Solution:

Step 1: Standardisation of EDTA **Solution:**

$$22 \text{ ml of EDTA solution} = 50 \text{ ml of standard hard water}$$

$$= 50 \times 1$$

$$= 50 \text{ mg of } CaCO_3$$

(as 1 ml of hard water has 1 mg of $CaCO_3$ - given in question)

$$1 \text{ ml of EDTA solution} = \frac{50}{22} \text{ mg of } CaCO_3 \text{ equivalent hardness} \quad \ldots (1)$$

Step 2: Determination of Total hardness of water:

$$50 \text{ ml of sample water} = 27 \text{ ml of EDTA}$$

$$= 27 \times \frac{50}{22} \text{ mg of } CaCO_3 \text{ equivalent hardness}$$

(as 1 ml of EDTA = $\frac{50}{22}$ mg of $CaCO_3$ (From eq 1)

$$1000 \text{ ml of water sample} = 27 \times \frac{50}{22} \times \frac{1000}{50} = 1227.27 \text{ mg/l}$$

Total Hardness = 1227.27 ppm

Step 3: Determination of permanent hardness:

50 ml of boiled water = 20 ml of EDTA

$$= 20 \times \frac{50}{22} \text{ mg of } CaCO_3 \text{ equivalent hardness}$$

$$\left(\text{as 1 ml of EDTA} = \frac{50}{22} \text{ mg of } CaCO_3 \text{ (From eq 1)}\right)$$

$$1000 \text{ ml of water sample} = 20 \times \frac{50}{22} \times \frac{1000}{50} = 909 \text{ mg/l}$$

Permanent hardness = 909 ppm

Step 4: Determination of temporary hardness:

Temporary hardness = Total hardness – Permanent hardness

= 1227.2 – 909 = 318.2 ppm

[Ans. Total hardness = 1227.27 ppm; Permanent hardness = 909 ppm;
Temporary hardness = 318.2ppm]

3. 1.0 g of $CaCO_3$ was dissolved in hydrochloric acid and made upto 1000 ml. 50 ml of this solution required 46 ml of EDTA solution for titration. 50 ml of hard water sample required 20 ml of the same EDTA solution. After boiling the sample of hard water,50 ml of it consumed 12 ml of EDTA solution. Calculate the carbonate and non- carbonate hardness of the water sample.

Solution:

1000 ml of standard hard water = 1 g or 1000 mg of $CaCO_3$

∴ 1 ml of standard hard water = 1mg of $CaCO_3$ …(1)

Step 1: Standardisation of EDTA solution:

50 ml of std hard water = 46 ml of EDTA

Or, 46 ml of EDTA = 50 mg of $CaCO_3$ eq hardness

$$1 \text{ ml of EDTA solution} = \frac{50}{46} \text{ mg of } CaCO_3 \text{ equivalent hardness} \quad \ldots(2)$$

Step 2: Determination of total hardness of water:

50 ml of sample water = 20 ml of EDTA

$$= 20 \times \frac{50}{46} \text{ mg of } CaCO_3 \text{ equivalent hardness}$$

(From eq 2)

$$1000 \text{ ml (1 litre) of sample hard water} = 20 \times \frac{50}{46} \times \frac{1000}{50} = 434.78 \text{ mg/l}$$

Total Hardness = 434.78 ppm

Step 3: Determination of permanent hardness (Non carbonate hardness)

$$50 \text{ ml of boiled hard water} = 12 \text{ ml of EDTA}$$

$$= 12 \times \frac{50}{46} \text{ mg of } CaCO_3 \text{ eq hardness}$$

$$1000 \text{ ml of boiled hard water sample} = 12 \times \frac{50}{46} \times \frac{1000}{50} = 260.86 \text{ mg/l}$$

$$\text{Permanent hardness} = 260.86 \text{ ppm}$$

Step 4: Determination of temporary hardness:

$$\text{Temporary hardness} = \text{Total hardness} - \text{Permanent hardness}$$

$$= 434.78 - 260.86 = 173.92 \text{ ppm}$$

[Ans. Total hardness = 434.78 ppm; Permanent hardness (Non- carbonate hardness) = 260.86 ppm; Temporary hardness (Carbonate hardness) = 173.92 ppm]

4. 0.25 g of $CaCO_3$ was dissolved in HCl and diluted to 250 ml. 100 ml of this solution required 20 ml of EDTA solution for titration. 100 ml of a hard water sample required 30 ml of the same EDTA solution for titration. 100 ml of the sample water on boiling, cooling and filtering required 10 ml of EDTA. Calculate the total, permanent and temporary hardness of the water sample.

Solution:

250 ml of standard hard water contains 0.25 g or 250 mg of $CaCO_3$

$$\therefore \quad 1 \text{ ml of std hard water} = 1 \text{mg of } CaCO_3 \qquad \ldots.(1)$$

Step 1: Standardisation of EDTA solution:

$$100 \text{ ml of std hard water} = 20 \text{ ml of EDTA}$$

Or, $$20 \text{ ml of EDTA} = 100 \text{ mg of } CaCO_3 \text{ eq hardness}$$

(as 1 ml of std hard water = 1 mg of $CaCO_3$ eq hardness)

$$1 \text{ ml of EDTA solution} = \frac{100}{20} \text{ mg of } CaCO_3 \text{ equivalent hardness} \qquad \ldots (2)$$

Step 2: Determination of Total hardness of water:

$$100 \text{ ml of sample water} = 30 \text{ ml of EDTA}$$

$$= 30 \times \frac{100}{20} \text{ mg of } CaCO_3 \text{ equivalent hardness}$$

(From eq 2)

$$1000 \text{ ml (1 litre) of sample hard water} = 30 \times \frac{100}{20} \times \frac{1000}{100} = 1500 \text{ ppm}$$

$$\text{Total Hardness} = 1500 \text{ ppm}$$

Step 3: Determination of permanent hardness:

$$100 \text{ ml of boiled water} = 10 \text{ ml of EDTA}$$

$$= 10 \times \frac{100}{20} \text{ mg of CaCO}_3 \text{ eq hardness}$$

$$1000 \text{ ml of sample hard water} = 10 \times \frac{100}{20} \times \frac{1000}{100} = 500 \text{ ppm}$$

$$\text{Permanent hardness} = 500 \text{ ppm}$$

Step 4: Determination of temporary hardness:

$$\text{Temporary hardness} = \text{Total hardness} - \text{Permanent hardness}$$

$$= 1500 - 500 = 1000 \text{ ppm}$$

[Ans. Total hardness = 1500 ppm; Permanent hardness = 500 ppm;
Temporary hardness = 1000 ppm]

Practice problems

1. A standard hard water was prepared by dissolving 0.2 g of pure and dried $CaCO_3$ in one litre of distilled water. The soap solution was consumed for each titration against 50 ml of the water sample. Following observations were obtained -

(i) Volume with standard hard water = 20.5 ml.

(ii) Volume with hard water sample = 9.0 ml.

(iii) Volume for permanent hardness = 3.0 ml.

(iv) Lather factor = 1.0 ml.

Find out each type of hardness in ppm.

Solution:

Step 1: Standardisation of soap solution:

$$1000 \text{ ml of standard hard water} = 0.2 \text{ gm of CaCO}_3$$

$$50 \text{ ml of standard hard water} - \frac{0.2 \times 50}{1000} \text{ gm of CaCO}_3 \text{ equivalent hardness}$$

$$= 0.01 \text{ gm of CaCO}_3 \text{ equivalent hardness}$$

$$= 10 \text{ mg of CaCO}_3 \text{ equivalent hardness} \qquad \ldots(1)$$

Now,

$$50 \text{ ml of std hard water} = (20.5 - 1.0) \text{ ml of soap solution}$$

$$= 19.5 \text{ ml of soap solution}$$

$$10 \text{ mg of CaCO}_3 \text{ equivalent hardness} = 19.5 \text{ ml of soap solution}$$

[As 50 ml of standard hard water = 10 mg of $CaCO_3$ equivalent hardness] … from eq (1)

1 ml of soap solution = $\frac{10}{19.5}$ mg of $CaCO_3$ equivalent hardness …(2)

Step 2: Determination of total hardness

50 ml of given hard water sample = 9.0-1.0 = 8 ml of soap solution

$= 8 \times \frac{10}{19.5}$ mg of $CaCO_3$ equivalent hardness

= 4.1 mg of $CaCO_3$ equivalent hardness

1000 ml of hard water sample = $\frac{4.1 \times 1000}{50}$

= 82 mg of $CaCO_3$ equivalent hardness

Total hardness = 82 ppm

Step 3: Determination of Permanent hardness

50 ml of given boiled water sample = 3.0-1.0 = 2 ml of soap solution

$= 2 \times \frac{10}{19.5}$ mg of $CaCO_3$ equivalent hardness

= 1.026 mg of $CaCO_3$ equivalent hardness

1000 ml of hard water sample = $\frac{1.026 \times 1000}{50}$

= 20.5 mg of $CaCO_3$ equivalent hardness

Permanent hardness = 20.5 ppm

Step 4 : Determination of Temporary hardness

Temporary hardness = Total hardness – Permanent hardness

= 61.5 ppm

[Ans. Total hardness = 82 ppm; Permanent hardness = 20.5 ppm;
Temporary hardness = 61.5 ppm]

2. A standard hard water solution was prepared by 250 mg of $CaCO_3$ in 1000 ml of distilled water. 17.2 ml of soap solution was consumed,when titrated with 50 ml of standard hard water. Lather factor for 50 ml of distilled water is 0.6 ml. The 50 ml of given sample of hard water consumed 7.6 ml of soap solution. 6.8 ml of soap solution was consumed when titrated with 50 ml of boiled filtered hard water sample. Find out total, permanent and temporary hardness.

Solution:

Step 1 - Standardisation of soap solution :

1000 ml of standard hard water = 250 mg of $CaCO_3$

50 ml of standard hard water – $\frac{250\times50}{1000}$ mg of $CaCO_3$ equivalent hardness

$= 12.5$ mg of $CaCO_3$ equivalent hardness …(1)

Now,

50 ml of std hard water = (17.2 – 0.6) ml of soap solution

= 16.6 ml of soap solution

12.5 mg of $CaCO_3$ equivalent hardness = 16.6 ml of soap solution

[As 50 ml of standard hard water = 12.5 mg of $CaCO_3$ equivalent hardness] …from eq (1)

1 ml of soap solution = $\frac{12.5}{16.6}$ mg of $CaCO_3$ equivalent hardness …(2)

Step 2: Determination of total hardness

50 ml of given hard water sample = 7.6 – 0.6 = 7 ml of soap solution

$= 7 \times \frac{12.5}{16.6}$ mg of $CaCO_3$ equivalent hardness

1000 ml of hard water sample = $7 \times \frac{12.5 \times 1000}{16.6 \times 50}$

$= 105.42$ mg of $CaCO_3$ equivalent hardness

Total hardness $= 105.42$ ppm

Step 3: Determination of Permanent hardness

50 ml of boiled water = 6.8 – 0.6 = 6.2 ml of soap solution

$= 6.2 \times \frac{12.5}{16.6}$ mg of $CaCO_3$ equivalent hardness

$= 1.026$ mg of $CaCO_3$ equivalent hardness

1000 ml of hard water sample = $\frac{6.2 \times 12.5 \times 1000}{16.6 \times 50}$

$= 93.373$ mg of $CaCO_3$ equivalent hardness

Permanent hardness = 93.373 ppm

Step 4: Determination of Temporary hardness

Temporary hardness = Total hardness – Permanent hardness

= 105.42 – 93.373 = 12.047 ppm

[Ans. Total hardness = 105.42 ppm; Permanent hardness = 93.373 ppm;
Temporary hardness = 12.047 ppm]

Practice problems

1. A water sample is alkaline to both phenolphthalein as well as methyl orange. 100 ml of a this water sample required 7.5 ml of N/50 HCl for neutralisation to phenolphthalein end point (P). At this stage a few drops of methyl orange were added. The acid required further was 14.5 ml of N/50 HCl for neutralisation to methyl orange end point (M). Calculate alkalinity of water as $CaCO_3$ due to the presence of carbonate and bicarbonate.

Solution:

100 ml of water upto phenolphthalein end point = 7.5 ml of N/50 HCl

$$100 \times N_P = 7.5 \times \frac{N}{50}$$

$$N_P = \frac{7.5}{100} \times \frac{N}{50}$$

Strength of alkalinity up to phenolphthalein end point in terms of $CaCO_3$

$$= N_p \times 50 \times 1000 \text{ ppm}$$

$$P = \frac{7.5}{100} \times \frac{1}{50} \times 50 \times 1000 = 75 \text{ ppm}; \ P = 75 \text{ ppm}$$

Now, 100 ml of water up to methyl orange end point

$$= 7.5 + 14.5 = 22 \text{ ml of N/50 HCl}$$

$$100 \times N_M = 22 \times \frac{N}{50}$$

$$N_M = \frac{22}{100} \times \frac{N}{50}$$

Strength of alkalinity up to methyl orange end point in terms of $CaCO_3$ equivalent hardness-

$$= N_M \times 50 \times 1000$$

$$= \frac{22}{100} \times \frac{1}{50} \times 50 \times 1000 = 220 \text{ ppm}; \text{ M} = 220 \text{ ppm}$$

As P < ½ M, hence CO_3^{2-} and HCO_3^- are present.

Alkalinity due to CO_3^{2-} = 2P = 2 × 75 = 150 ppm

Alkalinity due to HCO_3^- = M – 2P = 220 – 150 = 70 ppm

[Ans. Alkalinity due to $CO_3{}^{2-}$ = 150 ppm, Alkalinity due to $HCO_3{}^-$ = 70 ppm]

2. 100 ml of a raw water sample on titration with N/50 H_2SO_4 required 12.4 ml of the acid to phenolphthalein end point and 15.2 ml of the acid to methyl orange end point. Determine the type and extent of alkalinity present in the water sample

Solution:

100 ml of water up to phenolphthalein end point = 12.4 ml of N/50 H_2SO_4

$$100 \times N_P = 12.4 \times \frac{N}{50}$$

$$N_P = \frac{12.4}{100} \times \frac{N}{50}$$

Strength of alkalinity up to phenolphthalein end point in terms of $CaCO_3$

$$= N_p \times 50 \times 1000 \text{ ppm}$$

$$P = \frac{12.4}{100} \times \frac{1}{50} \times 50 \times 1000 = 124 \text{ ppm}$$

$$P = 124 \text{ ppm}$$

Now, 100 ml of water up to methyl orange end point requires 15.2 ml of $\frac{N}{50}$ H_2SO_4

$$100 \times N_M = 15.2 \times \frac{N}{50}$$

$$N_M = \frac{15.2}{100} \times \frac{N}{50}$$

Strength of alkalinity up to methyl orange end point in terms of $CaCO_3$ equivalent hardness

$$= N_M \times 50 \times 1000$$

$$= \frac{15.2}{100} \times \frac{1}{50} \times 50 \times 1000 = 152 \text{ ppm}$$

$$M = 152 \text{ ppm}$$

As P > ½ M, hence OH^- and CO_3^{2-} are present.

$$\text{Alkalinity due to } OH^- = 2P - M = 124 \times 2 - 152 = 96 \text{ ppm}$$

$$\text{Alkalinity due to } CO_3^{2-} = 2\,(M - P) = 2\,(152 - 124) = 56 \text{ ppm}$$

[Ans. Alkalinity due to OH^- = 96 ppm; Alkalinity due to CO_3^{2-} = 56 ppm]

3. 100 ml of a raw water sample required 25 ml of N/50 H_2SO_4 for neutralisation to phenolphthalein end point. After this methyl orange indicator was added to it and further acid required was 3.0 ml. Calculate the alkalinity of water as $CaCO_3$ in parts per million.

Solution:

100 ml of water up to phenolphthalein end point = 25 ml of N/50 H_2SO_4

$$100 \times N_P = 25 \times \frac{N}{50}$$

$$N_P = \frac{25}{100} \times \frac{N}{50}$$

Strength of alkalinity up to phenolphthalein end point in terms of $CaCO_3$

$$= Np \times 50 \times 1000 \text{ ppm}$$

$$P = \frac{25}{100} \times \frac{1}{50} \times 50 \times 1000 = 250 \text{ ppm}$$

$$P = 250 \text{ ppm}$$

Now, 100 ml of water up to methyl orange end point

$$= 25 + 3 = 28 \text{ ml of N/50 } H_2SO_4$$

$$100 \times N_M = 28 \times \frac{N}{50}$$

$$N_M = \frac{28}{100} \times \frac{1}{50}$$

Strength of alkalinity up to methyl orange end point in terms of $CaCO_3$ equivalent hardness-

$$= N_M \times 50 \times 1000$$

$$= \frac{28}{100} \times \frac{1}{50} \times 50 \times 1000 = 280 \text{ ppm}; M = 280 \text{ ppm}$$

As P > ½ M, hence OH^- and CO_3^{2-} are present.

$$\text{Alkalinity due to } OH^- = 2P - M = 2 \times 250 - 280 = 220 \text{ ppm}$$

$$\text{Alkalinity due to } CO_3^{2-} = 2\,(M - P) = 2\,(280 - 250) = 60 \text{ ppm}$$

$$\text{Total alkalinity} = 220 + 60 = 280 \text{ ppm}$$

[Ans. Alkalinity due to OH^- = 220 ppm; Alkalinity due to CO_3^{2-} = 60 ppm; Total alkalinity = 280 ppm]

4. A water sample was alkaline to both phenolphthalein and methyl orange. 50 ml of the water sample required 18 ml of 0.02 N H_2SO_4 for phenolphthalein end point and another 6 ml for complete neutralisation. Describe the type and amount of alkalinity present.

Solution:

50 ml of water up to phenolphthalein end point = 18 ml of 0.02N H_2SO_4

$$50 \times N_P = 18 \times 0.02\text{N}$$

$$N_P = \frac{18}{50} \times 0.02$$

Strength of alkalinity up to phenolphthalein end point in terms of $CaCO_3$

$$= N_p \times 50 \times 1000 \text{ ppm}$$

$$P = \frac{18}{50} \times 0.02 \times 50 \times 1000 = 360 \text{ ppm } P = 360 \text{ ppm}$$

Now, 50 ml of water up to methyl orange end point

$$= 18 + 6 = 24 \text{ ml of 0.02N } H_2SO_4$$

$$100 \times N_M = 24 \times \frac{N}{50}$$

$$50 \times N_M = 24 \times 0.02\text{N}$$

$$N_M = \frac{24}{50} \times 0.02$$

Strength of alkalinity up to methyl orange end point in terms of $CaCO_3$ equivalent hardness-

$$= N_M \times 50 \times 1000$$

$$= \frac{24}{50} \times 0.02 \times 50 \times 1000 = 480 \text{ ppm}$$

$$M = 480 \text{ ppm}$$

As P > ½ *M*, hence OH^- and CO_3^{2-} are present.

$$\text{Alkalinity due to } OH^- = 2P - M = 2 \times 360 - 480 = 240 \text{ ppm}$$

$$\text{Alkalinity due to } CO_3^{2-} = 2\,(M - P) = 2\,(480 - 360) = 240 \text{ ppm}$$

$$\text{Total alkalinity} = 240 + 240 = 480 \text{ ppm}$$

[Ans. Alkalinity due to OH^- = 240 ppm; Alkalinity due to CO_3^{2-} = 240 ppm;
Total alkalinity = 480 ppm

Practice problems

1. 20 cm^3 of an industrial effluent consumed 4 cm^3 of 0.5 *N* $K_2Cr_2O_7$ solution of oxidation. Calculate the COD of the effluent.

   Solution:

   Volume of effluent = 20 cm^3

   Volume of 0.5 *N* $K_2Cr_2O_7$ consumed = 4 cm^3

   COD = ?

$$\begin{array}{ccc} \text{Sample} & & K_2Cr_2O_7 \\ N_1V_1 & = & N_2V_2 \end{array}$$

$$N_1 \times 20 = 0.5 \times 4$$

$$N_1 = \frac{0.5 \times 4}{20}$$

$$\text{COD} = \frac{0.5 \times 4}{20} \times 8 \times 1000 = 800 \text{ mg/l}$$

[Ans. 800mg/l]

2. 25 cm^3 of sewage water for COD is reacted with 20 cm^3 of potassium dichromate solution. The unreacted potassium dichromate requires 7.0 cm^3 of 0.5N ferrous ammonium sulphate solution under similar conditions. In blank titration, 12 cm^3 of ferrous ammonium sulphate is used up. Calculate the COD of the sample.

Solution:

Volume of sewage water = 25 cm^3

Volume of FAS for blank titration = 12 cm^3

Volume of FAS for sample = 7 cm^3

Volume of FAS required for the oxidation of sample = 12 – 7 = 5 cm^3

Normality of FAS = 0.5N

Now, Sample Ferrous ammonium sulphate

$$N_1V_1 = N_2V_2$$

$$N_1 \times 25 = 0.5 \times 5$$

$$N_1 = \frac{0.5 \times 5}{25}$$

$$\text{COD} = \text{Normality} \times \text{Equivalent weight of } O_2 \times 1000$$

$$\text{COD} = \frac{0.5 \times 5}{25} \times 8 \times 1000 = 800 \text{ mg/l}$$ [Ans. 800 mg/l]

3. 25 cm^3 of waste water sample is diluted to 500 cm^3 and equal volumes are filled into two BOD bottles. In a blank titration 100 cm^3 of waste water requires 8.8 cm^3 of 0.02N sodium thiosulphate solution. 100 cm^3 of incubated sample after 5 days requires 4.2 cm^3 of the same sodium thiosulphate solution. Calculate the BOD of the waste water.

Solution:

Initial volume of waste water = 25 cm^3

Volume after dilution = 500 cm^3

Initially $N_1V_1 = N_2V_2$

Sample $Na_2S_2O_3$

$$N_1 \times 100 = 0.02 \times 8.8 \qquad N_1 = \frac{0.02 \times 8.8}{100}$$

$$DO(D_1) = \frac{0.02 \times 8.8}{100} \times 8 \times 1000 = 14.08 \text{ mg/l}$$

AFTER 5 DAYS

$$\underset{\text{Sample}}{N_3V_3} = \underset{\text{Na}_2\text{S}_2\text{O}_3}{N_4V_4}$$

$$N_3 \times 100 = 0.02 \times 4.2$$

$$\text{N}_3 = \frac{0.02 \times 4.2}{100}$$

$$DO(D_2) = \frac{0.02 \times 4.2}{100} \times 8 \times 1000 = 6.72 \text{ mg/l}$$

$$BOD = (D_1 - D_2) \times \frac{\text{volume after dilution}}{\text{volume before dilution}}$$

$$= (14.08 - 6.72) \times \frac{500}{25} = 147.2 \text{ mg/l}$$