(ii) *Calculation of non-carbonate hardness* :

50 mL boiled hard water $\equiv$ 10 mL EDTA soln.

$\equiv 10 \times (50/48)$ mg $CaCO_3$ eq.

$= 10.417$ mg $CaCO_3$ eq.

$\therefore$ 1,000 mL boiled hard water $\equiv \dfrac{10.417 \times 1000}{50}$ mg $CaCO_3$ eq.

$= 208.3$ mg $CaCO_3$ eq.

$\therefore$ Non-carbonate hardness = 208.3 mg/L or **208.3 ppm**

Hence, carbonate hardness = (312.5 – 208.3) = **104.2 ppm.**

Example 18. *The hardness of 50,000 litres of a sample was removed by passing it through a zeolite softener. The softener then required 200 litres of NaCl solution, containing 125 g/litre of NaCl for regeneration. Calculate the hardness of the sample of water.* (UPT, Dec. 03)

Solution. 200 L of NaCl solution

$\equiv 200\ L \times 125\ g/L = 25{,}000$ g NaCl $= (25{,}000 \times 50)/585$ g $CaCO_3$ eq.

$= 21{,}368$ g $CaCO_3$ eq.

$\therefore$ Hardness of 50,000 L water $\equiv 21{,}368$ g $CaCO_3$ eq.

or hardness of 1 L water $\equiv \dfrac{21{,}368}{50{,}000} = 0.4274$ g $CaCO_3$ eq.

$= 427.4$ mg $CaCO_3$ eq.

Hence, hardness of water = **427.4 mg/L (or ppm).**

Example 19. *50 mL of water sample during each time of titration against soap solution gave the following results :*

(i) *Lather factor = 0.5 mL.* (ii) *Total hardness volume = 15.5 mL.*

(iii) *Permanent hardness volume = 12.5 mL.* (iv) *Standard hard water volume = 40.5 mL,*

Standard hard water is prepared by dissolving 0, 2 g of $CaCO_3$ per litre. Calculate total, temporary and permanent hardness of water sample in ppm. (Amravati, Dec. 2K)

Solution. 1 L of SHW = 200 mg $CaCO_3$ eq

$\therefore$ 50 mL of SHW = $200 \times (50/1{,}000)$ mg $CaCO_3$ eq

= 20 mg $CaCO_3$ eq.

Now 50 mL SHW $\equiv$ 20 mg$CaCO_3$ eq $\equiv 40.5 - 0.5 = 40$ mL soap soln.

$\therefore$ 40 mL soap solution $\equiv$ 20 mg $CaCO_3$ eq.

or 1 mL soap solution $\equiv$ 20/40 or 0.5 mg $CaCO_3$ eq.

(i) Calculation of total hardness of water :

50 mL HW $\equiv 15.5 - 0.5$ or 15 mL of soap soln.

$\equiv 15 \times 0.5$ mg $CaCO_3$ eq = 7.5 mg $CaCO_3$ eq.

$\therefore$ 1 L HW $\equiv 7.5 \times 1{,}000/50$ or 150 mg $CaCO_3$ eq.

Hence, total hardness = **150 mg/L** or **150 ppm**

(ii) Calculation of permanent hardness of water :

50 mL BHW = (12.5 – 0.5) or 12 mL soap soln.

$\equiv 12 \times 0.5$ or 6 mg $CaCO_3$ eq

$\therefore$ 1 L BHW = $6 \times 1{,}000/50$ 120 mg $CaCO_3$ eq

$\therefore$ Permanent hardness = **120 mg/L** or **120 ppm.**

Hence, temporary hardness = (150 – 120) = **30 ppm.**

Example 20. *100 mL of water sample on titration with N/50 HCl requires 8.0 mL of the acid to phenolphthalein end-point and 9.0 mL of the acid to methyl orange end point. Calculate the type and extent of alkalinity present in the water sample.* (RGT, June 04)

Solution. 100 mL of water upto phenolphthalein end-point ≡ 8.0 mL of N/50 HCl

∴ $100 \text{ mL} \times N_P = 8.0 \text{ mL} \times (N/50)$

or normality, $N_P = \dfrac{8.0 \text{ mL}}{100 \text{ mL}} \times \dfrac{N}{50} = 0.0016 \text{ N}$

∴ Strength of alkalinity upto phenolphthalein end-point as $CaCO_3$ eq,

$$P = 0.0016 \times (50 \text{ g/L}) = 0.08 \text{ g/L} = 80 \text{ mg/L} = 80 \text{ ppm}$$

Now 100 mL of water upto methyl orange end-point

≡ 9.0 mL of N/50 HCl

∴ $100 \text{ mL} \times N_M = 9.0 \text{ mL} \times (N/50)$

or normality, $N_M = \dfrac{9.0 \text{ mL}}{100 \text{ mL}} \times \dfrac{N}{50} = 0.0018 \text{ N}$

∴ Strength of alkalinity upto methyl orange end-point as $CaCO_3$ eq,

$$M = 0.0018 \times (50 \text{ g/L}) = 0.09 \text{ g/L} = 90 \text{ mg/L} = 90 \text{ ppm}$$

∴ Now $P\,(= 80 \text{ ppm}) > \dfrac{1}{2} M \left(= \dfrac{1}{2} \times 90 \text{ ppm} \right)$

so the *alkalinity is due to OH^- and CO_3^{2-}.*

Now alkalinity due to CO_3^{2-} ions $= 2\,(M - P) = 2\,(80 - 80)$ ppm $=$ **20 ppm.**

and alkalinity due to OH^- ions $= (2P - M) = (2 \times 80 - 90)$ ppm $=$ **70 ppm.**

Example 21. *100 mL water sample required 4 mL of N/50 H_2SO_4 for neutralization to phenolphthalein end-point. Another 16 mL of the same acid was needed for further titration to methyl orange end-point. Determine the type and amount of alkalinity.* (Ku, Jan. 04)

Solution. 100 mL of water upto phenolphthalein end-point

≡ 4 mL of N/50 H_2SO_4

∴ $100 \text{ mL} \times N_P = 4 \text{ mL} \times (N/50)$

or normality, $N_P = \dfrac{4 \text{ mL} \times N}{100 \text{ mL} \times 50} = 0.0008 \text{ N}$

∴ Strength of alkalinity upto phenolphthalein end-point at $CaCO_3$ eq,

$$P = 0.0008 \times (50 \text{ g/L}) = 0.04 \text{ g/L} = 40 \text{ mg/L} = 40 \text{ ppm}$$

Now 100 mL of water upto methyl orange end-point,

≡ (4 + 16) mL of N/50 H_2SO_4

∴ $100 \text{ mL} \times N_M = 20 \text{ mL} \times N/50$

or normality, $N_M = \dfrac{20 \text{ mL} \times N}{100 \text{ mL} \times 50} = 0.0040 \text{ N}$

∴ Strength of alkalinity upto methyl orange end-point as $CaCO_3$ eq,

$$M = 0.004 \times (50 \text{ g/L}) = 0.2 \text{ g/L} = 200 \text{ mg/L}$$

Now $P\,(= 40 \text{ ppm}) < \dfrac{1}{2} M \left(\dfrac{1}{2} \times 200 \text{ ppm} = 100 \text{ ppm} \right)$,

so *carbonate and bicarbonate are present.*

Now alkalinity due to $CO_3^{2-} = 2P = 2 \times 40$ ppm $=$ **80 ppm**

Alkalinity due to HCO_3^- $= (M - 2P) = (200 - 2 \times 40) =$ **120 ppm.**

K_{sp} = solubility product of $CaCO_3 = [Ca^{2+}][CO_3^{2-}]$

K_s = dissociation constant for : $HCO_3^- \rightleftharpoons H^+ + CO_3^{2-}$

$[Ca^{2+}]$ = calcium hardness expressed as $CaCO_3$ equivalent in mg/L (or ppm) ;

$[HCO_3^-]$ = bicarbonate alkalinity expressed as $CaCO_3$ equivalent in mg/L (or ppm)

and operation 'p' = logarithm to the base 10 of reciprocal,

e.g., $p\,K_{sp} = \log_{10}(K_{sp})^{-1} = -\log_{10} K_{sp}$, etc.

Significance of L.I. : If (*i*) L.I. = 0, the water is stable (i.e., neither deposits scales of $CaCO_3$ or nor dissolve thin protective coating of $CaCO_3$), (*ii*) L.I. = positive, then water has scale forming tendancy, (*iii*) L.I. = negative, then water has corrosive tendency.

Note : L.I. of water used for cooling purposes is, usually, adjusted between 0.6 and 1.0 so that no corrosion can take place.

Solved Examples

Example 1. *How many grams of $FeSO_4$ dissolved per litre gives 210.5 ppm of hardness ? (Fe = 56, S = 32, O = 16, Ca = 40, C = 12).* (Jadavpur, 96 ; Anna, Dec. 03)

Solution. $FeSO_4 \equiv CaCO_3$

$56 + 16 + 64 = 136$ g $\quad$ 100 g

$\therefore$ 100 ppm of hardness $\equiv$ 136 ppm of $FeSO_4$

or 210.5 ppm of of hardness $\equiv \dfrac{136 \times 210.5}{100} = 286.3$ ppm of $FeSO_4$

$= 286.3$ mg/L or 0.2863 g/L of $FeSO_4$.

Hence, 0.2863 g of $FeSO_4$ dissolved per litre gives 210.5 ppm of hardness.

Example 2. *Three samples A, B and C were analysed for their salt contents :*

(*i*) *Sample A was found to contain 168 mg of magnesium carbonate per litre.*

(*ii*) *Sample B was found to contain 820 mg of calcium nitrate and 2 mg of silica per litre.*

(*iii*) *Sample C was found to contain 20 g of potassium nitrate and 2 g of calcium carbonate per 500 mL. Determine the hardness in all the above three samples in ppm and in grains per gallon.* (RGT, June 04)

Solution. *Calculation of $CaCO_3$ equivalents :*

Sample	*Constituent*	*Multiplication factor*	*$CaCO_3$ equivalent*
A	$MgCO_3$ = 168 mg/L	100/84	168 × 100/84 = 200 mg/L
B	$Ca(NO_3)_2$ = 820 mg/L	100/164	820 × 100/164 = 500 mg/L
C	$CaCO_3$ = 2 g/500 mL or 4,000 mg/L	100/100	4,000 × 100/100 = 4,000 mg/L

$\therefore$ Hardness of sample *A* = 200 mg/L or **200 ppm.**

Hardness of sample *B* = 500 mg/L or **500 ppm.**

Hardness of sample C = 4,000 mg/L or **4,000 ppm.**

Now 1 ppm = 0.07° Cl = 0.07 grain/gallon

$\therefore$ Hardness of sample *A* = 200 × 0.07 = **14 grains/gallon.**

Hardness of sample *B* = 500 × 0.07 = **35 grains/gallon.**

Hardness of sample C = 4,000 × 0.07 = **280 grains/gallon.**

Example 3. *Calculate the temporary hardness and permanent hardness of a sample of water containing : $Mg(HCO_3)_2 = 7.3$ mg/L ; $Ca(HCO_3)_2 = 16.2$ mg/L ; $MgCl_2 = 9.5$ mg/L ; $CaSO_4 = 13.6$ mg/L. (Atomic weights of Mg and Ca are 24 and 40 respectively.)* (UPT, Dec. 03)

Solution. *Conversion into $CaCO_3$ equivalents :*

Constituent	*Multiplication factor*	*$CaCO_3$ equivalent*
$Mg(HCO_3)_2 = 7.3$ mg/L	100/146	$7.3 \times 100/146 = 5$ mg/L
$Ca(HCO_3)_2 = 16.2$ mg/L	100/162	$16.2 \times 100/162 = 10$ mg/L
$MgCl_2 = 9.5$ mg/L	100/95	$9.5 \times 100/95 = 80$ mg/L
$CaSO_4 = 13.6$ mg/L	100/136	$13.6 \times 100/136 = 10$ mg/L

∴ Temporary hardness, due to $Mg(HCO_3)_2$ and $Ca(HCO_3)_2$

$= (5 + 10)$ mg/L = 15 mg/L or **15 ppm.**

Permanent hardness, due to $MgCl_2$ and $CaSO_4$

$= (10 + 10)$ mg/L = 20 mg/L or **20 ppm.**

Example 4. *Calculate the temporary and total hardness of a sample of water containing $Mg(HCO_3)_2 = 73$ mg/L ; $Ca(HCO_3)_2 = 162$ mg/L, $MgCl_2 = 95$ mg/L, $CaSO_4 = 136$ mg/L.* (Anna, May 04)

Solution. *Calculation of $CaCO_3$ equivalents :*

Constituent	*Multiplication factor*	*$CaCO_3$ equivalent*
$Mg(HCO_3)_2 = 73$ mg/L	100/146	$73 \times 100/146 = 50$ mg/L
$Ca(HCO_3)_2 = 162$ mg/L	100/162	$162 \times 100/162 = 100$ mg/L
$MgCl_2 = 95$ mg/L	100/95	$95 \times 100/95 = 100$ mg/L
$CaSO_4 = 136$ mg/L	100/136	$136 \times 100/136 = 100$ mg/L

∴ Temporary hardness, due to $Mg(HCO_3)_2$ and $Ca(HCO_3)_2$

$= (50 + 100)$ mg/L = 150 mg/L or **150 ppm.**

Total hardness, $= (50 + 100 + 100)$ mg/L = 350 mg/L or **350 ppm**

Example 5. *Calculate the amount of lime required for softening 50,000 litre of hard water containing : $CaCO_3 = 25$ ppm, $MgCO_3 = 144$ ppm, $CaCl_2 = 111$ ppm, $MgCl_2 = 95$ ppm, $Na_2SO_4 = 15$ ppm $Fe_2O_3 = 25$ ppm.* (UPT, May 04)

Solution. *Calculation of $CaCO_3$ equivalents :*

Constituent	*Multiplication factor*	*$CaCO_3$ equivalent*
$CaCO_3 = 25$ ppm	100/100	$25 \times 100/100 = 25.0$ mg/L
$MgCO_3 = 144$ ppm	100/84	$144 \times 100/84 = 171.43$ mg/L
$CaCl_2 = 111$ ppm	100/111	$111 \times 100/111 = 100.0$ mg/L
$MgCl_2 = 95$ ppm	100/95	$95 \times 100/95 = 100.0$ mg/L

∴ Lime requirement for softening 50,000 L of hard water

$= 74/100\ [CaCO_3 + 2 \times MgCO_3 + MgCl_2 \text{ as } CaCO_3 \text{ eq}] \times$ Vol. of water

$= 74/100\ [25.0 + 2 \times 171.43 + 100.0]$ mg/L × 50,000 L

$= 74/100\ [467.86$ mg/L$] \times 50,000$ L = 1,73,10,820 mg

$= (1,73,10,820/10^6)$ kg = **17.311 kg.**

Reactions involved to get excess OH^- and CO_3^{2-} ions :

$$Ca(OH)_2 \rightarrow Ca^{2+} + 2\,OH^- ;\; Ca^{2+} + Na_2CO_3 \rightarrow CaCO_3 + 2\,Na^+ ;\; Na_2CO_3 \rightarrow 2\,Na^+ + 2OH^-$$

∴ Lime required for excess OH^- ions in treated water

$$= 74/100\,[OH^-] = 74/100\,[191.2 \text{ ppm}] = 141.5 \text{ ppm or mg/L}$$

and soda required for excess OH^- and CO_3^{2-} ions in treated water

$$= 106/100\,[OH^- + CO_3^{2-} \text{ as } CaCO_3 \text{ eq}] = 106/100\,[191.2 + 66.7\,]\text{ppm}$$

$$= 273.4 \text{ ppm or mg/L} \qquad ...(iii)$$

Total lime (80% pure) required for 10^6 L water

$$[(i) + (iii)] \times 100/80 \times 10^6 \text{ L} = (730 + 141.5)\text{mg/L} \times 100/86 \times 10^6 \text{ L}$$

$$= 1{,}089 \times 10^6 \text{ mg} = \mathbf{1{,}089 \text{ kg.}}$$

∴ Total soda (90% pure) required for 10^6 L water

$$= [(ii) + (iii)] \times 100/90 \times 10^6 \text{ L} = [1{,}272 + 273.4 \text{ mg/L} \times 100/90 \times 10^6 \text{ L}]$$

$$= 1{,}717 \times 10^6 \text{ mg} = \mathbf{1{,}717 \text{ kg.}}$$

(*ii*) Since zeolite softer removes all Ca^{2+} and Mg^{2+} and Al^{3+} ions, so total hardness in the raw water.

$$= [750 + 625] \text{ ppm} = 1{,}375 \text{ ppm or mg/L}$$

Total hardness in 10,000 L water $= 1{,}375 \times 10{,}000$ mg as $CaCO_3$ eq

$= 13{,}750$ g as $CaCO_3$ eq

Now 50 g of $CaCO_3$ eq ≡ 58.5 g of NaCl

∴ 13,750 g of $CaCO_3$ eq ≡ $58.5 \times 13{,}750$ g NaCl

$=$ **16,088 g NaCl or 16.088 kg NaCl.**

Example 14. *100 mL of a sample of hard water neutralizes exactly 12 mL of 0.12 N HCl using methyl orange as indicator. What kind of hardness is present ? Express the same in terms of an equivalent of CaCO3 ?*

(Madras, April 97)

Solution. Hardness of water is temporary, since methyl orange indicator does not give the value for permanent hardness.

Now 100 mL of sample $= 12$ mL of 0.12 N HCl

$= 12 \times 0.12$ mL of 1 N HCl

$= 1.44$ mL of 1 N HCl or 1 N $CaCO_3$ eq

$= 1.44 \times 10^{-3}\,\text{L} \times 50\,\text{g } CaCO_3 \text{ eq L}^{-1}$

$= 0.072$ g $CaCO_3$ eq or 72 mg $CaCO_3$ eq

$$\therefore \quad 1{,}000 \text{ mL (or 1 L) of water} = \frac{72 \text{ mg } CaCO_3 \text{ eq} \times 1{,}000 \text{ mL}}{100 \text{ mL}} = 720 \text{ mg } CaCO_3 \text{ eq}$$

Hence, the temperary hardness of water is **720 ppm.**

Example 15. *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 insoluble carbonate, the unreacted Na_2CO_3 was titrated against N/50 H_2SO_4 solution, when 10 mL of the acid was required. Calculate the hardness and comment on the nature of hardness so-determined.*

(Jodhpur, May 99)

Solution. 100 mL of water

$$\equiv 25 \text{ mL of N/50 } Na_2CO_3 + 10 \text{ mL of N/50 } H_2SO_4$$

$$\equiv (25 - 10) \text{ mL of N/50 } Na_2CO_3 = (15/50) \text{ mL of N-}Na_2CO_3$$

$\therefore$ 1,000 mL of water

$$= (15/50) \times 10 \text{ mL of N–}Na_2CO_3 = 3 \text{ mL of N–}Na_2CO_3$$

$$= \frac{3 \times 50 \text{ g}}{1{,}000} \text{ of } CaCO_3 \text{ eq} = 0.150 \text{ g of } CaCO_3 \text{ eq}$$

$\therefore$ Hardness of water = 0.150 g/L or 150 mg/L or **150 ppm.**

Since sodium carbonate removes permanent hardness causing ions, so the above result represents permanent hardness of water.

Example 16. *50 mL of a sample water consumed 15 mL of 0.01 M-EDTA before boiling and 5 mL of the same EDTA after boiling. Calculate the degree of total hardness, permanent hardness and temperature hardness.* (Anna, Nov. 2K)

Solution. 50 mL of water sample $\equiv$ 15 mL *of* 0.01 M-EDTA

$$= \frac{15 \times 100}{50} \text{ mL of 0.01 M-EDTA} = 300 \text{ mL of 0.01 M-EDTA}$$

$$= 2 \times 300 \text{ mL of 0.01 N-EDTA}$$

($\because$ Molarity of EDTA = 2 × Normality of EDTA)

$$\equiv 600 \text{ mL (or 0.6 L) of 0.01 eq } CaCO_3$$

$$\equiv 0.6 \times 0.01 \times 50 \text{ g } CaCO_3 \text{ eq}$$

Hence, total hardness $= 0.30$ g or 300 mg of $CaCO_3$ eq

= **300 mg/L** or **300 ppm.**

Now 50 mL of boiled water $\equiv$ 5 mL of 0.01 M–EDTA

$\therefore$ 1,000 mL of boiled water $= \frac{5 \times 1{,}000}{50}$ mL of 0.01 M–EDTA

= 100 mL of 0.01 M-EDTA

= 200 mL (or 0.2 L) of 0.01 N–EDTA

$= 0.2 \times 0.01 \times 50$ g of $CaCO_3$ eq

$= 0.1$ g or 100 mg of $CaCO_3$ eq

Hence, permanent hardness = **100 mg/L or ppm**

$\therefore$ Temporary hardness = (300 – 100) ppm = **200 ppm.**

Example 17. *0.5 g of $CaCO_3$ was dissolved in HCl and the solution made upto 500 mL with distilled water. 50 mL of the solution required 48 mL of EDTA solution for titration. 50 mL of hard water sample required 15 mL of EDTA and after boiling and filtering required 10 mL of EDTA solution. Calculate the hardness.* (Anna, May 04)

Solution. 500 mL of SHW $\equiv$ 0.5 g or 500 mg $CaCO_3$ eq

$\therefore$ 1 mL SHW $\equiv$ 1 mg $CaCO_3$

Now 48 mL of EDTA soln. $\equiv$ 50 mL SHW $\equiv$ 50 mg $CaCO_3$ eq

$\therefore$ 1 mL of EDTA soln. $\equiv$ 50/48 mg $CaCO_3$ eq.

(i) Calculation of the total hardness of water :

50 mL hard water $\equiv$ 15 mL EDTA $\equiv 15 \times (50/48)$ mg $CaCO_3$ eq

= 15.625 mg $CaCO_3$ eq.

$\therefore$ 1,000 mL of hard water $\equiv \frac{15.625 \times 1{,}000}{50}$ mg $CaCO_3$ eq.

= 312.5 mg/L $CaCO_3$ eq.

Hence, total hardness = 312.5 mg/L or 312.5 ppm