$$1 \text{ mg/L} = 1 \text{ mg of } CaCO_3 \text{ equivalent per } 10^6 \text{ mL of water}$$
$$= 1 \text{ part of } CaCO_3 \text{ equivalent per } 10^6 \text{ parts of water}$$
$$= 1 \text{ ppm}$$

Thus, mathematically both the units are equal.

3. Degree French (°Fr) : *It is defined as the number of parts of $CaCO_3$ equivalen*
resent per 10^5 parts of water.

$$1° \text{ Fr} = 1 \text{ part of } CaCO_3 \text{ equivalent hardness per } 10^5 \text{ parts of wate}$$

4. Degree Clark (°Cl) : It is the number of grains $\left(\frac{1}{7000}\text{ lb}\right)$ $CaCO_3$ equivalent pre
allon (10 lbs or 70,000 grains) of water

Always remember that,

$$1 \text{ lb} = 7000 \text{ grains and one gallon} = 70{,}000 \text{ grains}$$

It is defined as the number of parts of $CaCO_3$ equivalent hardness present per 70,000 p
ater.

1°Cl – 1 part of $CaCO_3$ equivalent hardness per 70,000 parts of water.

Relationship among various units of hardness

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

The above relation can be derived as follows:

We know that, 1 ppm = 1 part per 10,00,000 parts of water
1°Cl = 1 part per 70,000 parts of water
1°Fr = 1 part per 1,00,000 parts or water

∴ 10,00,000 ppm = 70,000°Cl = 1,00,000°Fr
or 110 ppm = 7°Cl = 10°Fr
or 1 ppm = 0.07°Cl = 0.1°Fr

Degree of hardness

It is the parts of calcium carbonate equivalent hardness in a definite number of parts of
pending upon the units in which hardness is expressed.

xample 4: ***A water sample contains 204 mg of $CaSO_4$/L. Calculate the hardness in terms of Ca***

lution:

$$CaSO_4 \equiv CaCO_3$$
$$136 \text{ g mol}^{-1} \equiv 100 \text{ g mol}^{-1}$$
$$\therefore \quad 136 \text{ mg/L of } CaSO_4 = 100 \text{ mg/L of } CaCO_3 \text{ equivalent}$$
$$\text{or} \quad 204 \text{ mg/L of } CaSO_4 = \frac{100 \times 204}{136} \text{ mg/L of } CaCO_3 \text{ equivalent} = 150 \text{ mg/L}$$
$$\therefore \quad \text{Hardness} = 150 \text{ mg/L or } 150 \text{ ppm}$$

Example 5: ***Calculate the temporary hardness, permanent magnesium hardness, total permanent hardness and total hardness in terms of calcium carbonate equivalents in a water sample containing following dissolved salts per litre: Calcium bicarbonate (12.2 mg), magnesium bicarbonate (8.2 mg); magnesium sulphate (5.6 mg), magnesium chloride (6.2 mg), calcium sulphate (10.3 mg) and sodium sulphate (7.5 mg). Given that atomic weight of Mg = 24 amu, Ca = 40 amu, S = 32 amu, S = 32 amu, O = 16 amu, Cl = 35.5 amu and C = 12 amu.***

Solution: The hardness of different salts in terms of calcium carbonate equivalent is:

(*a*) $Ca(HCO_3)_2$: 12.2 mg/l of $Ca(HCO_3)_2 = 12.2 \times \frac{100}{162} = 7.53$ mg/l of $CaCO_3$

(*b*) $Mg(HCO_3)_2$: 8.2 mg/l of $Mg(HCO_3)_2 = 8.2 \times \frac{100}{146} = 5.61$ mg/l of $CaCO_3$

(*c*) $MgSO_4$: 5.6 mg/l of $MgSO_4 = 5.6 \times \frac{100}{120} = 4.67$ mg/l of $CaCO_3$

(*d*) $MgCl_2$: 6.2 mg/l of $MgCl_2 = 6.2 \times \frac{100}{95} = 6.52$ mg/l of $CaCO_3$

(*e*) $CaSO_4$: 10.3 mg/l of $CaSO_4 = 10.3 \times \frac{100}{136} = 7.57$ mg/l of $CaCO_3$

Sodium sulphate does not contribute to the hardness of water. Therefore, using the above valu

we get

(*a*) Temporary hardness is caused by bicarbonates of calcium and magnesium = 7.53 + 5
= 13.14 mg/l.

(*b*) Permanent magnesium hardness is due to magnesium chloride and magnesium sulp
= 4.67 + 6.52 = 11.19 mg/l.

(*c*) Total permanent hardness is permanent magnesium hardness + permanent calcium hard
(due to $CaSO_4$) = 11.19 + 7.57 = 18.76 mg/l.

(*d*) Total hardness = temporary hardness + permanent hardness = 13.14 + 18.76 = 31.9 m

Example 6: ***Calculate temporary hardness and permanent hardness of a sample of water whi analysis is found to contain the following data:***

$$Ca(HCO_3)_2 = 16.2 \text{ mg/L}$$
$$Mg(HCO_3)_2 = 7.3 \text{ mg/L}$$
$$MgCl_2 = 9.5 \text{ mg/L}$$
$$CaSO_4 = 13.6 \text{ mg/L}$$

Solution:

(*i*) Calculation for $Ca(HCO_3)_2$

Given mass of $Ca(HCO_3)_2$ = 16.2 mg/L

Molecular mass of $Ca(HCO_3)_2$ = 162

Hardness in terms of $CaCO_3$ equivalent = $\frac{16.2 \times 100}{162}$ = 10 mg/L (*ii*) Calculation for $Mg(HCO_3)_2$

Given mass of $Mg(HCO_3)_2 = 7.3$ mg/L

Molecular mass of $Mg\ (HCO_3)_2 = 126$

$$\text{Hardness in terms of } CaCO_3 \text{ equivalent} = \frac{7.3 \times 100}{126} = 5.0 \text{ mg/L}$$

(*iii*) Calculation for $MgCl_2$

Given mass of $MgCl_2 = 95$ mg/L

Molecular weight of $MgCl_2 = 95$

$$\text{Hardness in terms of } CaCO_3 \text{ equivalent} = \frac{9.5 \times 100}{95} = 10 \text{ mg/L}$$

iv) Calculation of $CaSO_4$

Given mass of $CaSO_4 = 13.6$ mg/L

Equivalent weight of $CaSO_4 = 68$

Hardness in terms of $CaCO_3$ equivalent = 10 mg/L

Temporary hardness in terms of $CaCO_3$ equivalent

= Hardness due to the carbonate ions = 15 mg/L = 15 ppm

Permanent hardness in terms of $CaCO_3$ equivalent

= Hardness due to Cl, SO_4^2 = 20 mg/L = 20 ppm

ALKALINITY AND ITS DETERMINATION

e alkalinity of natural water is ordinarily due to presence of carbonates, bicarbonates
esium. While the softened *water* may contain calcium hydroxide and sodium carbo
uring the process of softening. Thus alkalinity of water can be considered mainly

Hydroxide (*ii*) Carbonates

Bicarbonates

alkalinity of water can be estimated separately by titration against standard ac
ors used for detecting end points are phenolphthalein and methyl orange.
reactions can be represented by the following equations:

$$\left.\begin{array}{l}\left.\begin{array}{l} OH^- + H^+ \longrightarrow H_2O \\ CO_2^{2-} + H^+ \longrightarrow HCO_3^- \end{array}\right\} P \\ HCO_3^- + H^+ \longrightarrow H_2O + CO_2 \end{array}\right\} M$$

phenolphthalein is used as indicator, reaction (*i*) and (*ii*) takes place. Methy
ter the phenolphthalein end point corresponds to the neutralization of HCO_3^-
ans that at phenolphthalein end point, the OH^- ions are completely neutraliz
utralized *i.e.*, from CO_3^{2-} to HCO_3^- stage. When methyl orange is used as indic

5. When P < ½ M, then alkalinity of the solution is due to CO_3^{2-} and HCO_3^- ions.
   Alkalinity due to $CO_3^{2-} = 2P$
   ∴ Alkalinity due to $HCO_3^- = (M - 2P)$

Example 7: ***100 mL of a water sample consumed 20 ml of 0.01 N HCl in the absence of phenolp indicator. The resulting solution consumed another 10 ml of the same acid in the presence of orange indicator. Calculate the various types of alkalinities present in the above alkaline wate in ppm as CaCO₃ equivalent.***

Solution: Volume of acid consumed in case of phenolphthalein indicator = 20 ml

Volume of acid consumed in case of methyl orange indicator = 30 ml

Here, P = 20 ml and M = 30 ml

Therefore, $P > \frac{1}{2} M$

Hence, alkalinity is due to presence of OH^- and CO_3^{2-}.

Calculation of alkalinity due to OH^- in terms of $CaCO_3$ equivalent

Volume of acid used = 2 P – M = (2 × 20) – 30 ml = 10 ml

Applying normality equation

$$\underset{(\text{Water})}{N_1 V_1} = \underset{(\text{Acid})}{N_2 V_2}$$

$$N_1 \times 100 = \frac{1}{100} \times 10 \quad \text{or} \quad N_1 = \frac{1}{100} \times \frac{10}{100}$$

Therefore, alkalinity due to $OH^- = \frac{1}{100} \times \frac{1}{100} \times 50 \times 1000$ mg/L (∵ Eq. wt. of

$= 50$ ppm

Calculation of alkalinity due to CO_3^{2-} in terms of $CaCO_3$ equivalent

Volume of acid used = 2(M–P) = 2(30–20) ml = 20 ml

Applying normality equation,

$$\underset{(\text{Water})}{N_1 V_1} = \underset{(\text{Acid})}{N_2 V_2}$$

$$N_1 \times 100 = \frac{1}{100} \times 20 \quad \text{or} \quad N_1 = \frac{1}{100} \times \frac{20}{100}$$

Therefore, alkalinity due to $CO_3^{2-} = \frac{1}{100} \times \frac{20}{100} \times 50 \times 1000$ mg/L (∵ Eq. wt.

$= 1000$ ppm

Example 8: ***A water sample responds to both phenolphthalein and methyl orange ind of this water sample consumes 15.7 ml of N/20 HCl solution upto phenolphthalein resulting solution is titrated in the presence of methyl orange and consumes anoth above acid. Calculate the various types of alkalinities present in the alkaline water s CaCO₃ equivalent.***

Solution: Volume of acid consumed in case of phenolphthalein indicator = 15.7 ml

Volume of acid consumed in case of methyl orange indicator = 15.7 + 2.3 = 1

Here,

$$P = 15.7 \text{ ml}$$
$$M = 18.0 \text{ ml}$$

Since $P > \frac{1}{2}$ M alkalinity is due to presence of OH^- and CO_3^{2-}.

Calculation of alkalinity due to OH^- in terms of $CaCO_3$ equivalent

Volume of acid used = 2 P–M = (2 × 15.7) – 18.0 ml = 13.4 ml

Applying normality equation,

$$\underset{(\text{Water})}{N_1 V_1} = \underset{(\text{Acid})}{N_2 V_2}$$

$$N_1 \times 100 = \frac{1}{20} \times 13.4 \quad \text{or} \quad N_1 = \frac{1}{20} \times \frac{13.4}{100}$$

Therefore, alkalinity due to OH^-

$$= \frac{1}{20} \times \frac{13.4}{100} \times 50 \times 1000 \text{ mg/L} \qquad (\because \text{ Eq. wt of } CaCO_3 = 5$$
$$= 335 \text{ ppm.}$$

Calculation of alkalinity due to CO_3^{2-} in terms of $CaCO_3$ equivalent

Volume of acid used = 2(M–P) = 2(18–15.7) ml = 2 × 2.3 ml = 4.6 ml

Applying normality equation,

$$\underset{(\text{Water})}{N_1 V_1} = \underset{(\text{Acid})}{N_2 V_2}$$

$$N_1 \times 100 = \frac{1}{20} \times 4.6 \quad \text{or} \quad N_1 = \frac{1}{20} \times \frac{4.6}{100}$$

Therefore, alkalinity due to $CO_3^{2-} = \frac{1}{20} \times \frac{4.6}{100} \times 50 \times 1000$ mg/L $(\because$ Eq. wt. of $CaCO_3 =$

$$= 115 \text{ ppm}$$

ample 9: ***100 ml of water sample required 4 ml of $\frac{1}{50}$ H_2SO_4 for neutralization to phenolphth***

point. Another 1.6 ml of same acid was needed for further titration to methyl orange end p

termine the type and amount of alkalinity.

ution:

$$P = 4 \text{ ml}, \quad \text{and} \quad M = 4 + 16 = 20 \text{ ml}$$

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

∴ Alkalinity is due to the presence of CO_3^{2-} and HCO_3^-

The volume of acid in CO_3^{2-} type = 2P and volume of acid HCO_3^- type = M – 2P

For CO_3^{2-} alkalinity,

$$\underset{(\text{Water})}{N_1 V_1} = \underset{(\text{Acid})}{N_2 V_2}$$