Hardness

- property of water which prevents formation of lather with soap. is called Hardness.
- Hardness in water is due to presence of bicarbonate, $Cl^{\ominus}$, SO_4^{2-} of Ca, Mg and other heavy metal.
- Soap is composed of Na or K-salt of long fatty acid chain, when in hard water sample soap is used, it does not form lather (झाग), due to presence of Ca^{2+} and Mg^{2+} ion.

Reaction:- $2\,C_{17}H_{35}COO^{\ominus}Na^{\oplus}$ (soap) + Ca^{2+}/Mg^{2+} (from water) $\rightarrow$ $Ca(C_{17}H_{35}COO)_2\downarrow + 2Na^{\oplus}$ insoluble

④ Difference b/w hard and soft water:-

Hard water	soft water
① Does not form lather (झाग) with soap but form white particles.	② It forms lather easily with soap.
② It contains dissolved Ca, Mg salts.	③ It doesn't contain dissolved Mg and calcium salt.
③ Due to presence of Ca, Mg-salt its boiling point is high. so, more time taking + energy loss while cooking	③ Less time + less fuel to cook with soft water
④ While washing of cloth with hard there is loss of soap. (extra amt soap ka use hota है।)	④ No wasting of shop.

⊛ Types of hardness:-

(i) Temporary hardness (ii) permanent hardness.

(i) Temporary hardness is due to presence of bicarbonate of Ca, Mg and carbonate of Fe. (also called as carbonate Hardness)

- It can be easly remove by boiling the water, which convert bicarbonate into insoluble carbonate or hydroxide, which gets deposited at the bottom of vessel.

Rxn:- $Ca(HCO_3)_2 \xrightarrow{\Delta} CaCO_3\downarrow + H_2O + CO_2\uparrow$

$Mg(HCO_3)_2 \xrightarrow{\Delta} \underset{\text{insoluble}}{Mg(OH)_2\downarrow} + 2CO_2\uparrow$

(ii) Permanent hardness:- Due to presence of $Cl^{\ominus}$, SO_4^{2-} of Ca, Mg, Fe and other heavy metals. (non-carbonate hardness, which can't be remove by just boiling the water, but removed by chemical methods like

A) Lime-soda method
B) Zeolite process
C) Ion-exchange process.

⊛ Alkaline and Non-alkaline hardness:

It is Bicarbonate, carbonate and hydroxy of hardness producing cations. This is determine by titration of H_2O with HCl using methyl orange indicator.

$HCO_3^{\ominus}/CO_3^{2-}/OH^{\ominus}$ of $M^{\oplus}$

Rxn:-
$HCO_3^{\ominus} + H^{\oplus}/HCl \rightarrow H_2O + CO_2$
$CO_3^{2-} + H^{\oplus} \rightarrow HCO_3^{\ominus}$
$OH^{\ominus} + H^{+} \rightarrow H_2O$

For numericals on water

① ppm (part per million) 1 ppm means 1 part in 10^6 part

- 1 ppm = 1 part of $CaCO_3$ equivalent hardness in 10^6 part of H_2O.
- 1 mg/L

$1\ Kg = 1000\ g$

$1\ g = 1000\ mg$ ∴ $1\ Kg = 10^6\ mg$

- 1 mg/L = 1 ppm

⊛ Calcium carbonate Equivalent:-

$CaCO_3 = [40 + 12 + (16\times3)] = 40+12+48 = 100$

= Molecular wt of $CaCO_3$ = 100

Eq. wt. of $CaCO_3$ = $\frac{M.wt}{n\text{-factor}}$ (60)

$= \frac{100}{2} = 50$

n factor = (charge of cation / " " anion)

- Eq. of $CaCO_3$ = $\frac{\text{wt of hardness producing substance}}{\text{Eq. wt of "}} \times$ Eq. wt of $CaCO_3$
- Eq. of $CaCO_3$ = $\frac{\text{wt. of hardess substance (in mg/L) or ppm}}{\text{Eq. wt of "}} \times 50$
- [where as equivalent wt of hardness producing substance = $\frac{M.wt}{n\text{-factor}}$]

Examples:- $Ca(HCO_3)_2$ ⇒ M.wt = 40+2+24+96 ⇒ 162

Eq. wt = $\frac{162}{n\text{-factor}} = \frac{162}{2} = 81$

n-factor = total (+ve) charge or total -ve charge or cation or anion part of compound.

CO_3^{2-} ⇒ Eq. wt of CO_3^{2-} = $\frac{60}{2} = 30$

" $OH^{\ominus}$ = $\frac{17}{1} = 17$

$FeSO_4.7H_2O$ = $\frac{278}{2} = 139$

$H^{\oplus}$ = $\frac{1}{1} = 1$

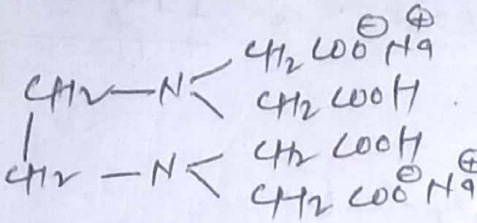
HCl = $\frac{1+35.5}{1} = \frac{36.5}{1} = 36.5$

Determination of Hardness

(i) EDTA method
(ii) Soap titration method

- **EDTA :-** Ethylene Diamine Tetra-acetic Acid

EDTA or [H_4Y]



Disodium salt [Na_2H_2Y]

- Generally Disodium salt of EDTA is used.

⑤ Theory for titration with EDTA :-

Ca^{2+}/Mg^{2+} present in water forms a complex with EDTA, EBT Indicator is used in titration at PH = 10, ~~if EDTA~~

Ca^{2+}/Mg^{2+} + EBT $\xrightarrow[(NH_4Cl + NH_4OH)]{PH=10}$ $\left[\begin{matrix} Ca^{2+} \\ Mg^{2+} \end{matrix} - EBT\right]$

from water (indicator) — wine-red colour unstable

↓ when EDTA added

EBT (Blue) + $\left[\begin{matrix} Ca^{2+} - EDTA \\ Mg^{2+} - EDTA \end{matrix}\right]$

now free indicator — stable complex colourless.

Q. Sample of water contains 204 mg of $CaSO_4$ per litre (5)
calculate hardness in terms of $CaCO_3$ equivalent.

Soln:- $CaCO_3$ equivalent (in terms of hardness) = $\frac{\text{wt of substance causing hardness}}{\text{Eq. wt}} \times 50$

$= \frac{204}{68} \times 50$

$= 150$ mg

| $CaSO_4$
| Mol. $40 + 32 + 64 = 136$
| Eq. wt $= \frac{136}{2} = 68$
| total +ve charge on cation

or, 150 mg in 1L
or, 150 mg in 10^6 µL
or 150 ppm

| 1L = 1000 mL
| 1 mL = 1000 micro L
| ∴ 1L = 10^6 µL

{ mg को µL, g को mL, kg को L के साथ लेंगे }

~~10^6 ppm = 10^6 µL~~

(2) How many gram of $MgCl_2$ dissolved in 1 litre, giving 190 ppm of hardness.

Soln. $CaCO_3$ equivalent = $\frac{wt}{Eq.wt} \times 50$

190 ppm (given) = $\frac{wt}{95/2} \times 50$

$190 = \frac{(wt)}{95/2} \times 50$

$wt = 190 \times \frac{95}{2} \times \frac{1}{50} = 180.5$ mg of $MgCl_2$ present

| $MgCl_2$
| $24 + (35.5 \times 2)$
| $24 + 71 = 95$
| Eq. wt of $MgCl_2$ $\frac{95}{2}$

• in gm ⇒ $\frac{180.5 mg}{1000} = 0.1805$ g | 1gm = 1000 mg

Q. Sample of water having $Ca(HCO_3)_2$ = 4mg
$Mg(HCO_3)_2$ = 6mg
$CaSO_4$ = 8mg
$MgSO_4$ = 10mg
calculate temproary, and permanent and total hardness of water in ppm?

soln Note: Temproary hardness is due to prerence of bicarbonate/$HCO_3^{\ominus}$
permanent " " " SO_4^{2-} and $Cl^{\ominus}$ of M

∴ Temproary Hardness ⇒
$= Ca(HCO_3)_2 + Mg(HCO_3)_2$

$= \left(\frac{4}{81} \times 50\right) + \left(\frac{6}{73} \times 50\right)$

$= 2.469 + 4.109$

$= \boxed{6.578 \text{ ppm}}$

* $Ca(HCO_3)_2$
↓
40 + 2 + 24 + 96 = 162
Eq.wt = 162/2 = (81)

* $Mg(HCO_3)_2$
24 + 2 + 24 + 96 = 146
Eq wt = 146/2 = (73)

* $CaSO_4$
40 + 32 + 64 = 136
Eq.wt = $\frac{136}{2}$ = (68)

* $MgSO_4$ = 24 + 32 + 64
120
Eq.wt = 120/2 = (60)

• permanent Hardness : $CaSO_4 + MgSO_4$

$= \left(\frac{8}{68} \times 50\right) + \left(\frac{10}{60} \times 50\right)$

$= 5.882 + 8.333$

$= \boxed{14.215 \text{ ppm}}$

∴ Total hardness = 6.578
14.215
20.793 ppm

Note Relation b/w various unit

$\boxed{1 \text{ ppm} = 1 \text{ mg/L} = 0.1^{\circ} \text{ Fr}}$ Fr = Degree French.