

1.1. Introduction

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Water analysis—

1. Water is a clear, tasteless and odorless liquid that we find everywhere on earth.
2. It's made of two molecules first is hydrogen atom and second is an oxygen atom which chemists write H_2O .
3. The earth's 71% surface area is occupied by water and the remaining 29% by land.
4. This water is 97% available on earth's surface.
5. This water cannot be used directly for drinking, agricultural and industrial purposes.
6. Hence, we are totally dependent on rain water and it is necessary to store water available from rain.
7. In our daily life water is used for drinking, bathing, cooking and washing purposes.

1.2 Importance of water:-

1. Water is super important for plants, animals and even humans need it to survive we drink it to stay hydrated and it helps plants grow too.
2. Without food human being can survive for a number of days, but water is such an essential thing without one cannot survive.

1.3 Properties of water

Water can exist as solid ice, liquid water or gas vapor depending on the temperature.

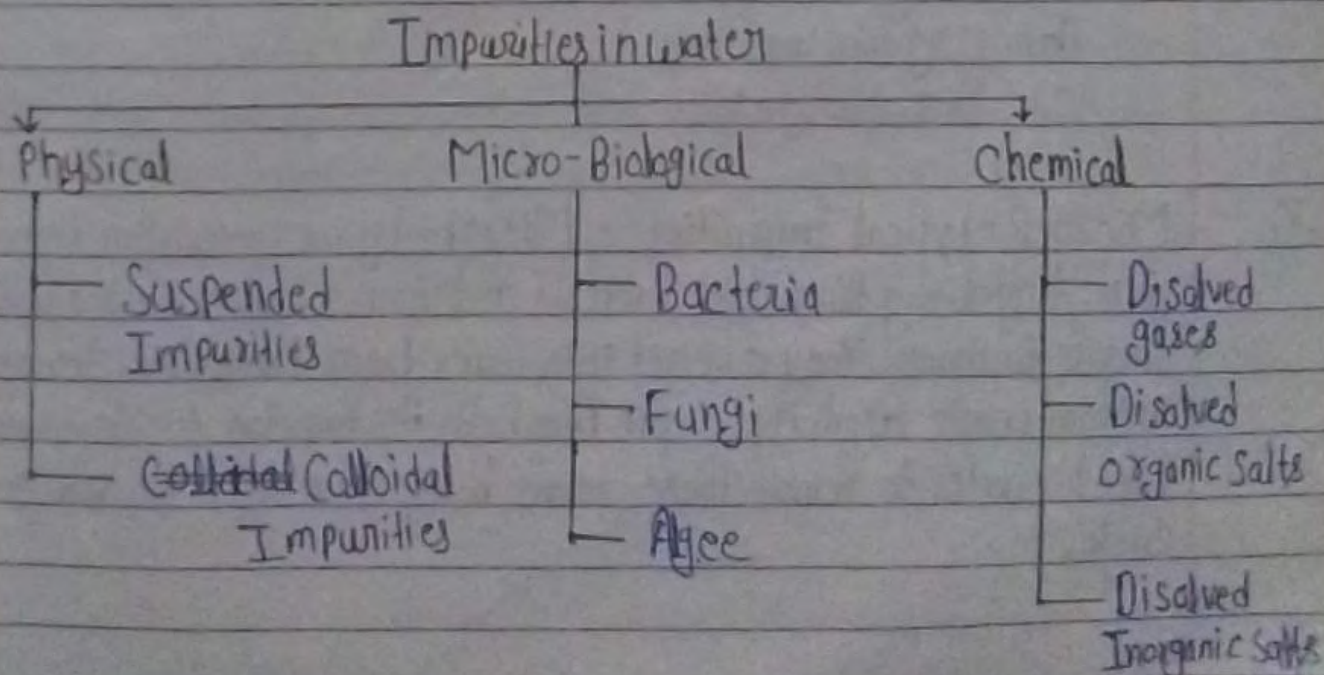
- (a) Liquid at Room Temperature — water is usually found as a liquid at room temperature, which means it flows easily and take the shape of its container.
- (b) Transparent — water is clear and ~~is~~ transparent, allowing us to see through it to the bottom of lakes, rivers and oceans.
- (c) Tasteless and Odorless — Pure water does not have a taste or smell, making it pleasant to drink and use in cooking.

1.4

USE OF WATER

- (a) Drinking — we drink water to satisfy our thirst and keep our body healthy.
- (b) Cooking — water is used for boiling, steaming, and preparing food like rice, pasta and soups.
- (c) Cleaning — water is used for washing dishes, clothes and surfaces to keep them clean.
- (d) Bathing — we use water for showering and bathing to stay clean and fresh.
- (e) Watering Plants — water is used to give plants the moisture they need to grow.

1.5

IMPURITIES IN WATER

1. **Physical Impurities:**— Physical Impurities in water refer to substances or particles that are physically present in the water but are not dissolved. These impurities can include:

(a) **Suspended Solids**— Solid particle that float or sink in water but are not dissolved. These can include sediment, sand and other debris.

(b) **Floating Debris (colloidal impurities)**— Larger objects like leaves, twigs, plastic or other debris that can be seen floating on the surface of water.

2. **Chemical Impurities**— Chemical impurities in water are things that mix into the water and change its properties. They can be minerals, like salt or iron or things from pollution like pesticides or oil. These impurities can make the water taste different or even unsafe to drink.

These impurities are three types, they are—

(a) Inorganic impurities.

(b) Organic impurities.

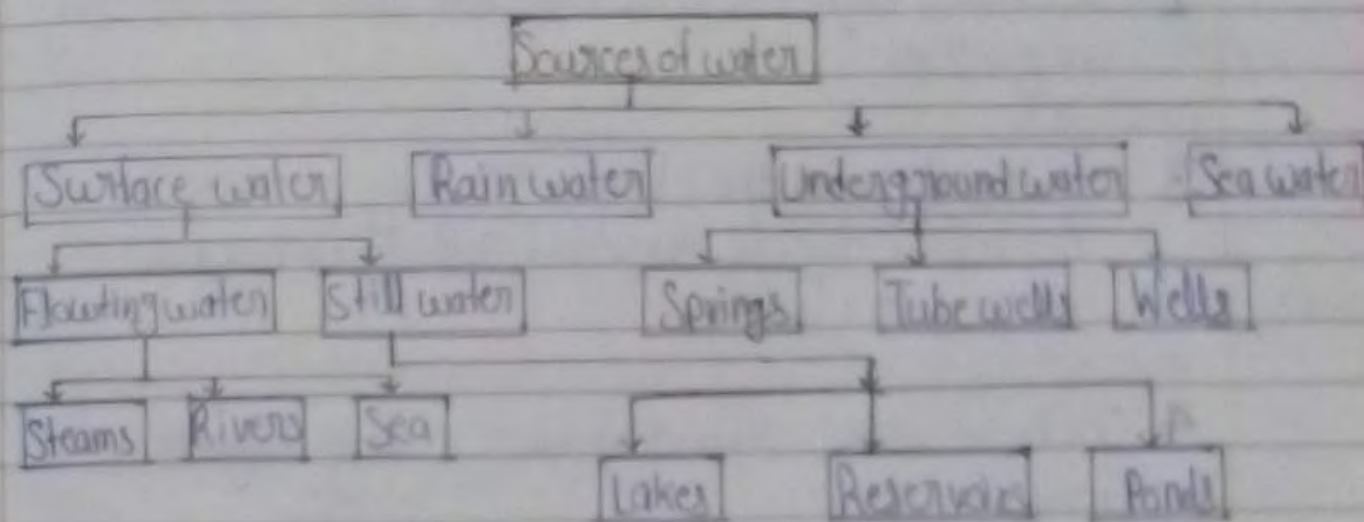
(c) Dissolved gases.

3. **Micro-Biological Impurities**— Microbiological impurities in water are tiny living things like bacteria and viruses that can make water unsafe to drink. They can get into water from things like sewage, animal waste or dirty runoff from fields. It's important to clean or treat water to remove these germs before drinking it to avoid getting sick.

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Sources of water

Sources of water are places where we can find water. They include things like rivers, lakes, streams, ponds, wells and even rain. These sources provide us with the water we need for drinking, cooking, washing and many other daily activities.



(a) Surface water— This includes water found on the surface of Earth. Such as rivers, lakes, streams and ponds.

(b) Rain water— water that falls from the sky as precipitation including rain, snow, sleet and hail.

(c) Underground water— water that is stored beneath the Earth's surface in soil and rock formations, accessed through wells and aquifers.

Hard Water and Soft WaterHARD WATERDefination :-

1. Water which does not produce foam with Soap is known as hard water.
2. Contains high levels of minerals like Calcium and magnesium
3. In hard water the cleaning property of soap is depressed due to dissolved salt. It is Bad for washing & cleaning.
4. In hard water, skin and hair, causing dryness and irritation.

Soft WaterDefination :-

1. Water which produce foam with Soap is known as soft water.
2. Contains low level of minerals.
3. Soft water is used to daily action like cooking, washing and cleaning.
4. In soft water, skin and hair feeling smooth and moisturized.

Types of Hardness

① Temporary Hardness

by-carbonate Hardness

Alkaline Hardness

ex- CaCO_3 , MgCO_3 ,
 $\text{Ca(HCO}_3)_2$, $\text{Mg(HCO}_3)_2$

② Permanent Hardness

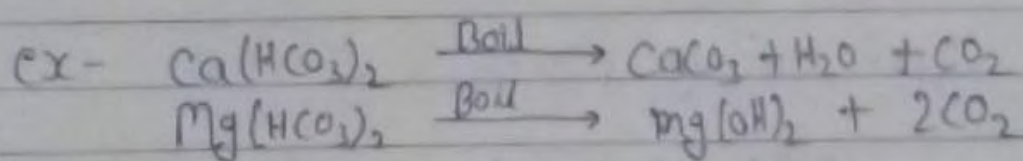
Carbonate Hardness

Non-Alkaline Hardness

ex- MgCl_2 , CaSO_4 , MgSO_4 ,
 FeSO_4 , $\text{Al}_2(\text{SO}_4)_3$ Temporary Hardness

1. It is due to the presence of soluble carbonate and by-carbonate of calcium and magnesium is known as temporary hardness.

2. The hardness of water which can easily removed by simple boiling of water is known as temporary hardness



3. It is also known as carbonate hardness or Alkaline Hardness

(4) It is determine by titration with HCl using methic orange as indicator.

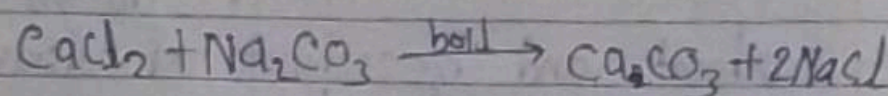
Permanent Hardness:-

1. It is due to the ~~present~~ presence of dissolve chloride and sulphate of Ca, Mg and Al is known as permanent hardness.

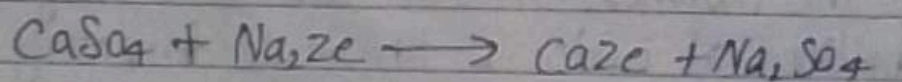
2. The hardness of water which still remain after boiling of water is known as permanent hardness.

3. It cannot be destroy by boiling. It can be removed by-

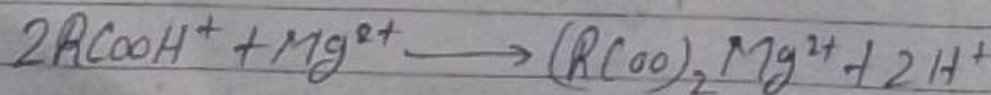
(i) Lime Soda process



(ii) Zeolite process -



(iii) Anion exchange process



Total Hardness:- Total hardness is the measure of the concentration of calcium (Ca^{2+}) and magnesium (Mg^{2+}) ions present in water.

$$\text{Total Hardness (mg/L as CaCO}_3\text{)} = \text{Calcium hardness} + \text{Magnesium hardness}$$

or

$$\text{Total Hardness} = \text{Temporary Hardness} + \text{Permanent Hardness}$$

Table for multiplication factor of
Salts/ions

Constituent Solution	molar mass	n-factor	Chemical equivalent $= \frac{\text{molar mass}}{\text{n-factor}}$	multiplication factor for converting into eq. of CaCO_3
$\text{Ca}(\text{HCO}_3)_2$	162	2	$162/2 = 81$	$100/(2 \times 81) = 100/162$
$\text{Mg}(\text{HCO}_3)_2$	146	2	$146/2 = 73$	$100/(2 \times 73) = 100/146$
CaSO_4	136	2	$136/2 = 68$	$100/(2 \times 68) = 100/136$
MgSO_4	120	2	$120/2 = 60$	$100/(2 \times 60) = 100/120$
CaCl_2	111	2	$111/2 = 55.5$	$100/(2 \times 55.5) = 100/111$
MgCl_2	95	2	$95/2 = 47.5$	$100/(2 \times 47.5) = 100/95$
CaCO_3	100	2	$100/2 = 50$	$100/(2 \times 50) = 100/100$
MgCO_3	84	2	$84/2 = 42$	$100/(2 \times 42) = 100/84$
CO_2	44	2	$44/2 = 22$	$100/(2 \times 22) = 100/44$
$\text{Mg}(\text{NO}_3)_2$	148	2	$148/2 = 74$	$100/(2 \times 74) = 100/148$
HCO_3^-	61	1	$61/1 = 61$	$100/(2 \times 61) = 100/122$
OH^-	17	1	$17/1 = 17$	$100/(2 \times 17) = 100/34$
NaAlO_2	82	1	$82/1 = 82$	$100/(2 \times 82) = 100/164$
$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$	278	2	$278/2 = 139$	$100/(2 \times 139) = 100/278$
H^+	1	1	$1/1 = 1$	$100/(2 \times 1) = 100/2$
CO_3^{2-}	60	2	$60/2 = 30$	$100/(2 \times 30) = 100/60$
$\text{Al}_2(\text{SO}_4)_3$	342	6	$342/6 = 57$	$100/(2 \times 57) = 100/114$

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Formula of Degree of Hardness:-

$$\text{CaCO}_3 \text{ eq} = \frac{\text{mass of hardness producing substance}}{\text{X multiplication factor}}$$

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Degree of Hardness:-

Degree of hardness define as the term of equivalent amount of CaCO_3 because of taken of CaCO_3 it is insoluble in water easily calculated, easily filtered its molecular weight is 100.

$$1 \text{ mole of } \text{CaCO}_3 = 100 \text{g of } \text{CaCO}_3$$

$$1 \text{ mole of } \text{Mg}(\text{HCO}_3)_2 = 146 \text{g of } \text{Mg}(\text{HCO}_3)_2$$

$$1 \text{ mole of } \text{MgCl}_2 = 95 \text{g of } \text{MgCl}_2$$

4 Types of Degree of Hardness:-

① PPM(Parts per Million):-

- Part of CaCO_3 in 1 million part of water.
- It's define as the number of parts of the CaCO_3 equivalent.
- Present in 10^6 part of water

$$1 \text{ ppm} = 1 \text{ part of } \text{CaCO}_3 \text{ in } 10^6 \text{ parts of water}$$

⑩ Calcium Hardness

- Number of milligram of calcium carbonate (CaCO_3) present in 1 liter of water.

1 mg/L = 1mg of CaCO_3 eq. hardness in 1 liter of water

$$\text{1 ppm} = 1 \text{ mg/L}$$

$$m = D \quad \rightarrow \text{in case of water } D = 1$$

$$m = V$$

$$11 = 1 \text{ mg} \times 1000 = 1000 \times 1000 \text{ mg}$$

$$11 = 10^6 \text{ mg}$$

$$1 \text{ mg/L} = \frac{1 \text{ mg}}{10^6 \text{ mg}} = \frac{1}{10^6} = 1 \text{ ppm}$$

$$\boxed{1 \text{ mg/L} = 1 \text{ ppm}}$$

⑪ $^{\circ}\text{CL}$ (Degree Clarke):

- Number of parts of calcium carbonate (CaCO_3) present in 70000 parts of water.
- It is define as the number of parts of CaCO_3 eq. if 1000000 parts of the water is known as Clarke.
 $1^{\circ}\text{CL} = 1 \text{ Part of } \text{CaCO}_3 \text{ eq. per } 70000 \text{ part of water}$

(iv) °Fr (Degree French) :-

- Number of parts of calcium carbonate (CaCO_3) present in 10^5 part of water.
- It is define as the number of part of the CaCO_3 eq it is tendency power. 10^5 parts of the water is known as French.

$1^\circ\text{Fr} = 1 \text{ part of } \text{CaCO}_3 \text{ eq per } 10^5 \text{ part of water}$

Note:-

Relationship between various units of hardness:-

$1 \text{ ppm} = 1 \text{ part per } 10^6 \text{ parts of water}$
 $1^\circ\text{Fr} = 1 \text{ part per } 10^5 \text{ parts of water}$
 and $1^\circ\text{Cl} = 1 \text{ part per } 70,000 \text{ parts of water}$

$\therefore 10^6 \text{ ppm} = 10^5 \text{ }^\circ\text{Fr} = 70,000 \text{ }^\circ\text{Cl}$

Hence, $1 \text{ ppm} = 0.1^\circ\text{Fr} = \frac{70,000}{10^6} = 0.07^\circ\text{Cl} = 1 \text{ mg/l}$

→ ↓	ppm	mg/l	$^\circ\text{Fr}$	$^\circ\text{Cl}$
ppm	1	1	0.1	0.07
mg/l	1	1	0.1	0.07
$^\circ\text{Fr}$	10	10	1	0.7
$^\circ\text{Cl}$	1/0.07	1/0.07	1/0.7	1

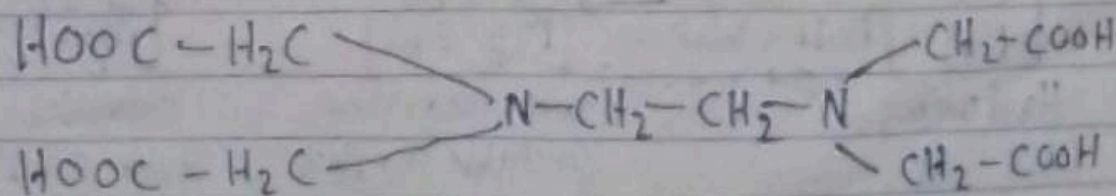
Classification of water hardness adapted from the WQA

Classification	Soft	Slightly hard	Moderately hard	Hard	Very hard
Ppm or mg/L	0-17	17-60	60-120	120-180	180 and above

110 Determination of Hardness by ~~Edta~~ EDTA method.

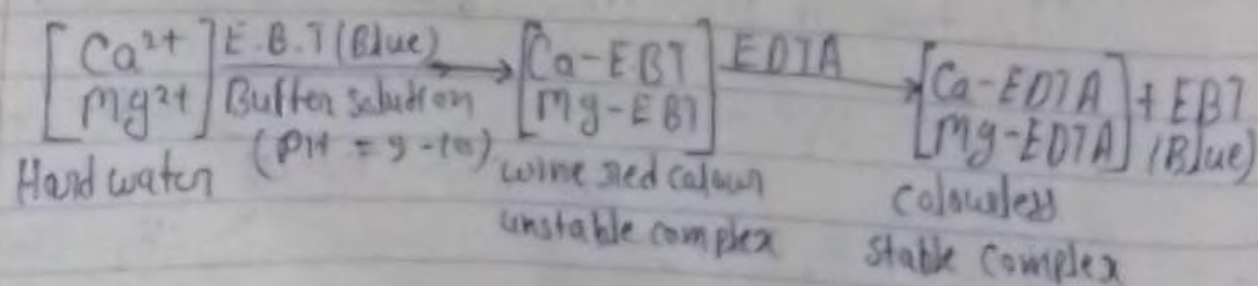
- EDTA is abbreviation of ethylene diamine tetra acetic acid.
- EDTA ~~dissolves~~ dissolves in water with great difficulty and in a very very small quantity.
- On the ~~contra~~ contrary it's di-sodium salt dissolves in water quickly and completely. Hence for common experimental purpose, in place of EDTA. It's di-sodium derivative is used.
- EDTA is a hexadentate ligand. It binds the metal ions in water i.e. Ca^{2+} or Mg^{2+} to give highly stable chelate complex (These metal ions are bonded via oxygen or nitrogen from EDTA molecule). Therefore this method is called as Complexometric Titration.

Structure of EDTA (Ethylenediamine tetraacetic acid)



Principle of EDTA method:

- The di-Sodium Salt of EDTA forms complexes with Ca^{2+} and Mg^{2+} as well as with many other metal cations in aqueous solution.
- Thus the total hardness of a hardwater sample, can be determined by ~~test~~ titrating Ca^{2+} and Mg^{2+} present in the sample with di-sodium salt of EDTA (Na_2EDTA) solution, using ammonical buffer solution containing NH_4Cl , NH_4OH of pH 10 using Eriochrome Black-T (EBT) as the metal indicator.
- At pH 10, EBT indicator forms wine red coloured unstable complex with Ca^{2+} and Mg^{2+} ions in hard water.
- This complex is broken by EDTA solution during titration, giving stable complex with ions and releasing EBT indicator solution which is blue in color. Hence the colour change is from wine red to blue (EBT's own colour).
- Thus noting noting the colour change, the point of equivalence can be trapped and hardness of water can be determined by this method.



Advantages of EDTA method:-

- Greater accuracy
- Highly rapid
- Highly convenient

Alkalinity and its determination:-

Alkalinity

- It can be defined as "the concentration of the salts present in water which increases the concentration of OH^- ions due to the hydrolysis thereby rising pH of water to alkaline range".
- Natural water when found alkaline, it is generally due to the presence of HCO_3^- , SiO_3^{2-} and sometimes CO_3^{2-} ions. In addition to the above the alkalinity of boiler water is also due to the presence of OH^- & PO_4^{3-} ions.

The extent of alkalinity depends on the presence of ions which broadly can be categorized as presence of.

(i) OH^- only (ii) CO_3^{2-} only (iii) HCO_3^- only (iv) OH^- & CO_3^{2-} together (v) HCO_3^- & CO_3^{2-} together.

bicarbonates

hydroxyle

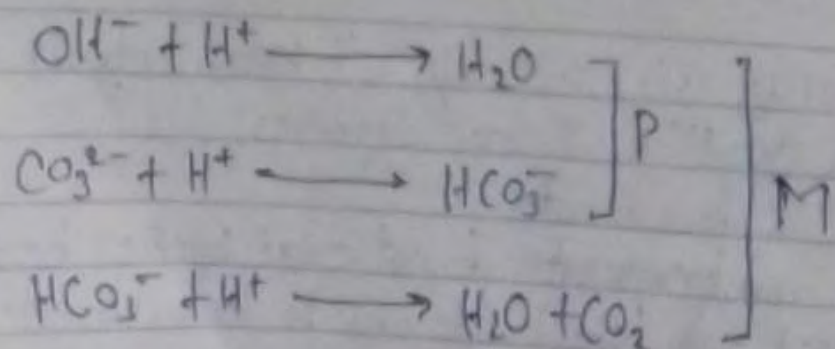
- Hydroxide and bicarbonates do not exist together because hydroxide ions react with bicarbonate ions to form carbonate ions. Therefore existence of hydroxyle and bicarbonate ions together is ruled out.



The alkalinity of natural water is due to the presence of hydroxides, carbonates and bicarbonates of calcium and magnesium. Alkalinity is a measure of the ability of water to neutralize the acids. The constituents causing alkalinity in natural water are as follows:-

This is determined by titrating the sample with a standard solution of a strong acid. When the pH of the sample is above 8.3, titration is first carried out using phenolphthalein indicator. At the end point when indicator changes from pink to colourless, the pH is lowered to about 4.5 due to addition of HCl. At this point complete neutralization of hydroxide and conversion of all the carbonate into bicarbonate occurs. The alkalinity measured upto this point is called phenolphthalein alkalinity. [P] titration is continued using methyl orange indicator. The color changes from yellow to red and shows complete neutralization of all the bicarbonate ions.

When standard acid solution is added to alkaline water following reaction takes place



The total volume of acid used in both the stages corresponds to the neutralization of hydroxide, carbonate and bicarbonate and is thus a measure of total alkalinity. [11]

Calculation of Alkalinity of water by following table:-

Alkalinity	OH^- (PPm)	CO_3^{2-} (PPm)	HCO_3^- (PPm)
$P=0$	0	0	M
$P = \frac{1}{2}M$	0	2P	0
$P < \frac{1}{2}M$	0	2P	$(M-2P)$
$P > \frac{1}{2}M$	$(2P-M)$	$2(M-P)$	0
$P=M$	$P=M$	0	0

Significance:-

- (1) For calculating the amount of lime and soda required for water softening.
- (2) In Conditioning boiler feed water highly alkaline water may to caustic embrittlement and also may cause deposition of precipitates and sludge in boiler tubes and pipes.

(3) Bicarbonates of calcium and magnesium induce temporary hardness in water. which if untreated, cause scale formation in boilers.

Numerical based on Hardness & strength :-

Formula

Formula for Determination of Hardness

$$\text{Hardness} = \frac{\text{Strength (in mg/L)} \times \text{chemical equivalent wt. of } \text{CaCO}_3}{\text{chemical equivalent wt. of hardness producing salt}}$$

$$\text{CaCO}_3 \text{ eq} = \frac{\text{mass of hardness producing substance} \times \text{multiplication factor}}{100}$$

- Q- A water sample contain 408 mg/L of CaSO_4 per liter. Calculate the hardness in term $\text{CaCO}_3 \text{ eq}$.

Solution Given that

Water sample = 408 mg/L of CaSO_4

and $\text{CaCO}_3 \text{ eq} = ?$

$$\therefore \text{CaCO}_3 \text{ eq} = \frac{\text{mass of hardness}}{\text{Producing substance}} \times \frac{\text{multiplication factor}}{\text{Producing substance}}$$

$$\text{CaCO}_3 \text{ eq} = \frac{408 \times 100}{136} \text{ mg/L}$$

$$\text{CaCO}_3 \text{ eq} = 300 \text{ mg/L}$$

- Q- Find the $\text{CaCO}_3 \text{ eq}$, Temporary Hardness, Permanent Hardness and Total Hardness of these salts and its value in mg/L , $^\circ\text{Cl}$ and $^\circ\text{F}$.

Salts	Amount in mg/L
$\text{Ca}(\text{HCO}_3)_2$	5
$\text{Mg}(\text{HCO}_3)_2$	7
MgCO_3	4
MgCl_2	8
CaCl_2	3
CaSO_4	9

Solution	Salt	Amount in mg/L	multiplication factor	CaCO ₃ eq
	Ca(HCO ₃) ₂	5	100/162	3.08 mg/L
	Mg(HCO ₃) ₂	7	100/146	4.79 mg/L
	MgCO ₃	4	100/84	4.76 mg/L
	MgCl ₂	8	100/95	8.42 mg/L
	CaCl ₂	3	100/111	2.7 mg/L
	CaSO ₄	9	100/136	6.61 mg/L

Temporary Hardness = 7.88 mg/L

Permanent Hardness = 22.5 mg/L

Total Hardness = 30.38 mg/L

Hardness	in mg/L	in °F	in °C
Temporary	7.88 mg/L	0.78	0.55
Permanent	22.5	2.24	1.57
Total	30.38	3.03	2.12

Numerical Problems

Q - 60 ml of Standard hardwater, calculate 1mg of pure CaCO_3 per litre consumed 30 ml of EDTA. 60 ml water sample consumed 35 ml of EDTA solution using the EBT as Indicator calculate the total hardness of water sample in ppm.

Solve - Given that

$$\begin{aligned}\text{Standard hardwater} &= 60 \text{ ml} \\ \text{EDTA} &= 30 \text{ ml} \\ \text{Water Sample} &= 60 \text{ ml} \\ \text{EDTA} &= 35 \text{ ml}\end{aligned}$$

$$\frac{\text{S.H.W}}{\text{S.H.W}} = 1 \text{ mg} = 1 \text{ ml}$$

(i) Standardization of EDTA solution -

1 ml of Standard hardwater contains 1 mg of CaCO_3

Now

$$30 \text{ ml of EDTA} = 60 \text{ ml of S.W.H}$$

$$30 \text{ ml of EDTA} = 60 \times 1 \text{ mg of } \text{CaCO}_3$$

$$1 \text{ ml of EDTA} = \frac{60}{30} \text{ mg of } \text{CaCO}_3$$

$$1 \text{ ml of EDTA} = 2 \text{ mg of } \text{CaCO}_3$$

(ii) Determination of Permanent hardness -

(i) Determination of total Hardness of water -

$$60 \text{ ml of water sample} = 35 \text{ ml of EDTA}$$

$$60 \text{ ml of water sample} = 35 \times 1 \text{ ml of EDTA}$$

$$60 \text{ ml of water sample} = 35 \times 2 \text{ mg of } \text{CaCO}_3$$

$$60 \text{ ml of water sample} = 70 \text{ mg of } \text{CaCO}_3$$

$$1 \text{ ml of water sample} = \frac{70 \text{ mg of } \text{CaCO}_3}{60}$$

$$1 \text{ L of water sample} = \frac{70 \times 1000 \text{ mg of } \text{CaCO}_3}{60}$$

$$1 \text{ L of water sample} = 1166 \text{ mg of } \text{CaCO}_3$$

$$\text{Hence, total hardness of water} = 1166 \text{ mg} = 1166 \text{ PPM}$$

Q. 100 ml of standard hardwater contains 1.5 mg of pure CaCO_3 per litre consumed 44 ml of EDTA. 50 ml of water sample consumed 20 ml of the same EDTA solution using the EBT indicator. Calculate the total hardness of water in ppm and $^\circ\text{Cl}$ unit.

Solve Given that

$$\text{Standard hardwater} = 100 \text{ ml}$$

$$\text{EDTA} = 44 \text{ ml}$$

$$\text{Water sample} = 50 \text{ ml}$$

$$\text{EDTA} = 20 \text{ ml}$$

~~Ind. Shw~~

$$1 \text{ ml Shw} = 1.5 \text{ mg } \text{CaCO}_3$$

Step-1 Standardization of EDTA Solution

$$1 \text{ ml of Standard hardwater contains } 1.5 \text{ mg of } \text{CaCO}_3$$

Now

$$44 \text{ ml of EDTA} = 100 \text{ ml of S.H.W}$$

$$44 \text{ ml of EDTA} = 100 \times 1.5 \text{ mg of } \text{CaCO}_3$$

$$44 \text{ ml of EDTA} = 150 \text{ mg of } \text{CaCO}_3$$

$$1 \text{ ml of EDTA} = \frac{15.44}{1000} \text{ mg of CaCO}_3$$

$$1 \text{ ml of EDTA} = 3.40 \text{ mg of CaCO}_3$$

(ii) Determination of total hardness of water -

$$50 \text{ ml of water sample} = 20 \text{ ml of EDTA}$$

$$50 \text{ ml of water sample} = 20 \times 1 \text{ ml of EDTA}$$

$$50 \text{ ml of water sample} = 20 \times 3.40 \text{ mg of CaCO}_3$$

$$50 \text{ ml of water sample} = 68 \text{ mg of CaCO}_3$$

$$1 \text{ ml of water sample} = \frac{68}{50} \text{ mg of CaCO}_3$$

$$1 \text{ L of water sample} = \frac{68}{50} \times 1000 \text{ mg of CaCO}_3$$

$$1 \text{ L of water sample} = 1360 \text{ mg of CaCO}_3$$

$$\text{Hence, Total hardness of water} = 1360 \text{ mg} = 1360 \text{ ppm}$$

$$\text{Total hardness} = 95.2^\circ \text{Cl}$$

Q. Calculate the hardness of a water sample, whose 20 ml required 30 ml EDTA. 10 ml of standard calcium chloride solution, whose strength is equivalent to 300 mg of CaCO_3 per 20 ml, required 20 ml of the same EDTA solution.

Ans. 20 ml of EDTA = 200 ml of hard water
 $= 200 \times 300$ mg of CaCO_3 eq hardness
 $= 6 \times 10^4$ mg of CaCO_3 eq hardness

Thus, 1 ml of EDTA = $\frac{6 \times 10^4}{20} = 3000$ of CaCO_3 eq

Determination of hardness of water sample

20 ml of Sample water = 30 ml of EDTA = 30×3000

Thus, 1 L of Sample water = $\frac{30 \times 3000}{20}$

= 4500 mg of CaCO_3 eq hardness

Q One gm of CaCO_3 was dissolved in dilute HCl and the solution was made to one litre by dist. dilution. 50 ml of this solution required 40 ml of EDTA solution, while 50 ml of the sample water required 20 ml of EDTA solution. Calculate total hardness of water sample.

Soln - We Calculate the total hardness in two steps -

(i) Standardization of EDTA solution

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

Now, 40 ml of EDTA solution = 50 ml of standard water

40 ml of EDTA solution = 50×1 mg of CaCO_3 ↑

∴ 1 ml of EDTA solution = $\frac{50}{40}$ mg of CaCO_3

(ii) Determination of total hardness of water sample

Further, 50 ml of sample water = 20 ml of EDTA solution
 = $\frac{20 \times 50}{40}$ mg of CaCO_3 ↑

1000 ml of sample water = $\frac{20 \times 50 \times 1000}{40 \times 50}$ mg of CaCO_3 ↑

= 500 mg of CaCO_3

Total hardness = 500 mg/L or 500 ppm

Q - 10ml CaCO_3 of strength 1gm/litre required 8ml EDTA on titration. 10 ml of a water sample requires 6ml of the same EDTA solution on titration. Calculate the total hardness of water sample.

Sol: (i) Standardization of EDTA solution

$$1\text{L of Standard water} = 1\text{g of CaCO}_3$$

$$\therefore 1\text{ml of standard water} = 1\text{mg of CaCO}_3$$

$$\text{Now, } 8\text{ml of EDTA} = 10\text{ml of standard water}$$

$$\therefore 8\text{ml of EDTA sol.} = 10 \times 1\text{mg of CaCO}_3$$

$$\therefore 1\text{ml of EDTA sol.} = \frac{10}{8} \text{ mg of CaCO}_3$$

(ii) Determination of total hardness of water sample

$$\text{Further, } 10\text{ml of sample water} = 6\text{ml of EDTA solution}$$

$$= 6 \times \frac{10}{8} \text{ mg of CaCO}_3$$

$$10\text{ ml of sample water} = 6 \times \frac{10}{8} \times 10 \text{ mg of CaCO}_3$$

$$= 75 \text{ mg of CaCO}_3$$

$$\text{Total hardness} = 75 \text{ mg/L or } 75 \text{ ppm}$$

Q- 50 ml of standard hard water containing 1000 mg of pure CaCO_3 per litre, consumed 20 ml of EDTA solution. Using ~~erio~~eriochrome black-T as indicator, calculate the total hardness of water sample in ppm.

Ans (i) Standardization of EDTA solution.

50 ml of standard water = 1000 mg of CaCO_3

1 ml of standard water = 20 mg of CaCO_3

Now, 20 ml of EDTA = 50 ml of standard hard water
 = 50×20 mg of CaCO_3 eq hardness

Hence 1 ml of EDTA = $\frac{50 \times 20}{20}$ = 50 mg of CaCO_3 eq hardness

(ii) Determination of total hardness of water sample

50 ml of sample water = 25 ml of EDTA

= 25×50 mg of CaCO_3 eq hardness

Hence, 1000 ml of sample water = $\frac{25 \times 50 \times 1000}{50}$

= 25000 mg of CaCO_3 eq hardness

Thus, total hardness of water = 25000 ppm

Q. 100 ml of standard hard water containing 1.5 mg of pure CaCO_3 , per ml consumed 44 ml of EDTA. 50 ml of a water sample consumed 20 ml of the same EDTA solution, using Eriochrome black-T as indicator, calculate the total hardness of water sample in ppm and $^\circ\text{Cl}$ units.

Solve (i) Standardization of EDTA solution

100 ml of standard water = 1.5 mg of CaCO_3

1 ml of standard water = 0.015 mg of CaCO_3

Now 44 ml of EDTA = 100 ml of standard hard water
= 100×0.015 mg of CaCO_3

1 ml of EDTA = $\frac{100 \times 0.015}{44} = \frac{15}{44} = 0.34$ mg of CaCO_3

(ii) Determination of total hardness of water sample

50 ml of sample water = 20 ml of EDTA

= 20×0.34 mg of CaCO_3

Hence, 100 ml of sample water = $\frac{20 \times 0.34 \times 100}{50}$

= 13.6 mg of CaCO_3 eq. hardness

1 PP = 1 mg/L

So, = 13.6 ppm

1 ppm = 0.07°Cl

So, 13.6 ppm = $13.6 \times 0.07^\circ\text{Cl}$
= 0.952°Cl

Q. One gram of CaCO_3 was dissolved in dil. HCl and the solution diluted to one litre. 100 mg of this solution required 30 ml of EDTA solution, while 100 ml of the sample water required 40 ml of EDTA. On the other hand, 100 ml of boiled water sample when titrated against EDTA consumed 20 ml of the solution. Calculate total permanent and temporary hardness of water sample in ppm.

Solve (i) Standardization of EDTA solution

$$1000 \text{ ml of Standard water} = 1 \text{ g of } \text{CaCO}_3$$

$$1 \text{ ml of standard water} = 1 \text{ mg of } \text{CaCO}_3$$

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

$$30 \text{ ml of EDTA} = 100 \times 1 \text{ mg of } \text{CaCO}_3$$

$$1 \text{ ml of EDTA} = \frac{100}{30} \text{ mg of } \text{CaCO}_3$$

(i) Determination of hardness

$$\text{Further, } 100 \text{ ml of sample water} = 40 \text{ ml of EDTA solution}$$

$$= 40 \times \frac{100}{30} \text{ mg of } \text{CaCO}_3$$

$$1000 \text{ ml of Sample water} = \frac{40 \times 100}{30} \times \frac{1000}{100} \text{ mg of } \text{CaCO}_3$$

$$\text{Total hardness} = \frac{4000}{9} = 444.44 \text{ mg/L} = 444.44 \text{ ppm}$$

$$\text{Also, } 100 \text{ ml of boiled Sample water} = 20 \text{ ml of EDTA solution}$$

$$= 20 \times \frac{100}{30} \text{ mg of } \text{CaCO}_3$$

$$1000 \text{ ml of boiled Sample water} = 20 \times \frac{100}{30} \times \frac{1000}{100} \text{ mg of } \text{CaCO}_3$$

$$\text{Permanent hardness} = \frac{2000}{90} = 222.22 \text{ PPM}$$

Hence,

$$\text{temporary hardness} = 444.44 - 222.22 = 222.22 \text{ PPM}$$

- Q- 0.5g of CaCO_3 was dissolved in HCl and the solution was made to 500 ml with distilled water. 50 ml of this solution required 25 ml of EDTA solution for titration. 50 ml of hard water sample required 20 ml of EDTA. After boiling 50 ml of boiled water sample required 15 ml of the same EDTA. Calculate each type of hardness in mg/L .

Solution (i) Standardization of EDTA solution

$$500 \text{ ml of standard water} = 0.5 \text{ g of } \text{CaCO}_3$$

$$\text{or } 1 \text{ ml of standard water} = 1 \text{ mg of } \text{CaCO}_3$$

$$\text{Now, } 25 \text{ ml of EDTA solution} = 50 \text{ ml of standard water}$$

$$\therefore \text{Also, } 25 \text{ ml of EDTA solution} = 50 \times 1 \text{ mg of } \text{CaCO}_3$$

$$1 \text{ ml of EDTA solution} = \frac{50}{25} \text{ mg of } \text{CaCO}_3$$

(ii) Determination of total hardness of water sample

$$\begin{aligned} \text{Further, } 50 \text{ ml of sample water} &= 20 \text{ ml of EDTA solution} \\ &= \frac{20 \times 50}{25} \text{ mg of } \text{CaCO}_3 \end{aligned}$$

$$500 \text{ ml of sample water} = \frac{20 \times 50 \times 500}{25 \times 50} = 400 \text{ mg of } \text{CaCO}_3$$

$$\text{Total hardness} = 400 \text{ mg/L}$$

$$50 \text{ ml of boiled water sample} = 15 \text{ ml of EDTA solution} \\ = \frac{15}{50} \text{ mg of } \text{CaCO}_3$$

$$\text{Thus 1L of water sample} = \frac{15}{50} \times 1000 = 300 \text{ mg of } \text{CaCO}_3$$

$$\text{Permanent Hardness} = 300 \text{ mg/L}$$

$$\begin{aligned} \text{Temporary hardness} &= \text{Total hardness} - \text{Permanent hardness} \\ &= 400 - 300 \\ &= 100 \text{ mg/L} \end{aligned}$$

- Q - 0.28 g of CaCO_3 was dissolved in 1 litre of water 100 ml of this water on titration required 28 ml of EDTA 100 ml of unknown hard water sample required 33 ml of EDTA after boiling and cooling 100 ml of this sample required 10 ml of EDTA. Calculate the temporary hardness of water.

Solve

(i) Standardization of EDTA Solution

Given, 1L of standard hardwater contains 0.28 gm CaCO_3 . Hence, each ml of standard hardwater contains 0.28 mg CaCO_3 .

As,

$$\begin{aligned} 28 \text{ ml of EDTA} &= 100 \text{ ml of standard hardwater} \\ &= 100 \times 0.28 \\ &= 28 \text{ mg of } \text{CaCO}_3 \end{aligned}$$

$$1 \text{ ml of EDTA} = \frac{28}{28} = 1 \text{ mg of } \text{CaCO}_3$$

(ii) Determination of hardness of water.

$$\begin{aligned} \text{Given, 100 ml of unknown hardwater sample} &= 33 \text{ ml of EDTA} \\ &= 33 \times 1 \\ &= 33 \text{ mg of } \text{CaCO}_3 \end{aligned}$$

$$1000 \text{ mg (or 1L) of unknown hard water sample} = \frac{330}{100} \times 1000$$

$$= 330 \text{ mg CaCO}_3 \text{ eq. hardness}$$

$$\text{Total hardness} = 330 \text{ ppm}$$

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

$$= 10 \times 1$$

$$= 10 \text{ mg of CaCO}_3 \text{ eq. hardness}$$

$$\therefore 1000 \text{ ml (or 1L) of boiled water} = \frac{10}{100} \times 1000 = 100 \text{ mg of CaCO}_3 \text{ eq. hardness}$$

$$\text{Permanent hardness of water} = 100 \text{ ppm}$$

$$\text{Hence, temporary hardness} = \text{Total hardness} - \text{Permanent hardness}$$

$$= 330 - 100 = 230 \text{ ppm}$$

Q. 100 ml of a water sample on titration with $N/50 \text{ H}_2\text{SO}_4$ gave a titre value of 8.5 ml to phenolphthalein end point and 17.0 ml to methyl orange end point. Calculate alkalinity of water sample.

Solve

$$100 \text{ ml water sample on titration with } \frac{N}{50} \text{ H}_2\text{SO}_4 \text{ requires}$$

$$= 8.5 \text{ ml } \frac{N}{50} \text{ H}_2\text{SO}_4$$

$$\therefore 100 \text{ ml} \times N_f = 8.5 \text{ ml} \times \frac{N}{50}$$

$$\text{Normality, } N_f = \frac{8.5}{100} \times \frac{1}{50} \text{ N}$$

Now, Strength of alkalinity of upto phenolphthalein end point in terms of CaCO_3 eq.

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

$$P = \frac{8.5}{100} \times \frac{1}{50} \times 50 \times 1000 = 85 \text{ ppm}$$

As, 100 ml of water sample upto methyl orange end point consumed

$$= 8.5 + 17 \text{ ml of } \frac{N}{50} \text{ H}_2\text{SO}_4$$

$$100 \times N_m = \frac{25.5 \times N}{50}$$

$$N_m = \frac{25.5 \times 1}{100 \times 50} \text{ N}$$

Strength upto methyl orange end point in terms of CaCO_3 equivalent,

$$M = N_m \times 50 \times 1000 \text{ ppm}$$

$$= \frac{25.5 \times 1}{100 \times 50} \times 50 \times 1000 \text{ ppm} = 255 \text{ ppm}$$

Since, $P > \frac{1}{2} M$ Hence, CO_3^{2-} and HCO_3^- ions present,

and alkalinity due to $\text{CO}_3^{2-} = 2P = 2 \times 85 = 170 \text{ ppm}$

and alkalinity due to $\text{HCO}_3^- = M - 2P = 255 - 170 = 85 \text{ ppm}$

Hence, the given water sample contains CO_3^{2-} alkalinity = 170 ppm and HCO_3^- alkalinity = 85 ppm

- ① 100 ml of a water sample required 20 ml of $\frac{N}{50}$ H_2SO_4 for neutralization to phenolphthalein end point. After this methyl orange indicator was added to this and further acid required was 15 ml. Calculate the type and extent of alkalinity.

Soln 100 ml of water sample on titration with $\frac{N}{50}$ H_2SO_4 required

$$= 20 \text{ ml of } \frac{N}{50} H_2SO_4$$

$$100 \text{ ml} \times N_p = 20 \times \frac{N}{50} H_2SO_4$$

$$100 \text{ ml} \times N_p = 20 \times \frac{N}{50}$$

$$N_p = \frac{20}{100} \times \frac{1}{50} N$$

Now, Strength of alkalinity upto phenolphthalein end point in terms of $CaCO_3$ eq

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

$$P = \frac{20}{100} \times \frac{1}{50} \times 50 \times 1000 \text{ ppm}$$

$$P = 200 \text{ ppm}$$

As, 100 ml of water sample upto methylorange end point consumed

$$= 20 + 15 = 35 \times \frac{N}{50} H_2SO_4$$

$$100 \times N_M = \frac{35 \times N}{50}$$

$$N_M = \frac{35 \times N}{100 \times 50}$$

Strength upto methyl orange endpoint in terms of CaO, eq

$$M = N_M \times 50 \times 1000 \text{ ppm}$$

$$M = \frac{35}{100} \times \frac{1N}{50} \times 50 \times 1000 \text{ ppm} = 350 \text{ ppm}$$