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Subject: Engineering Chemistry

Unit:I

Topic: Water Analysis, Treatments and Industrial Applications

Water is essential for all living beings, water is very crucial. Almost all human activities – domestic, agricultural and industrial use water. Although water is nature's most wonderful and abundant compound but only less than 1% of the world's water resources is available for ready use. Hence, water has to be used carefully and economically. As an engineering tool water is mainly used for steam generation and it is also used as a coolant although different uses of water demand different specifications –

(i) Textile industry needs frequent dying of clothes and the water used by this industry should be soft and free from organic matter. Hard water decreases the solubility of acidic dyes.

(ii) Laundries require soft water, free from colour, Mn and Fe, because hardness increases consumption of soaps, salts of Fe and Mn impart a grey or yellow shade to the fabric.

(iii) For boilers water should be free from hardness otherwise efficient heat transfers is prevented by scale formation. Untreated water can lead to corrosion of boiler material.

(iv) Paper industry requires water free from SiO_2 as it produces cracks in paper; turbidity as it can affect brightness and colour of paper; alkalinity as it consumes more alum; hardness as it increases the ash content of the paper.

(v) Sugar industry requires water free from hardness because hard water causes difficulty in the crystallization of sugar.

(vi) Dairies and pharmaceutical industry require ultra pure water, which should be colorless, tasteless, odorless and free from pathogenic organisms.

Therefore water needs to be treated to remove undesirable impurities. "Water treatment" is the process by which all types of undesirable impurities are removed from water and making it fit for domestic or industrial purposes.

Impurities present in Water can be categorized as;

- Physical may be Suspended or Colloidal
- Chemical like Dissolved gases, Dissolved organic Salts, Dissolved inorganic Salts
- Biological like Bacteria, Fungi, Algae

Sources of Water:

- Rain Water
- Surface Water

  Flowing Water like Streams, Rivers
  Still Water like Lakes, Reservoirs, Ponds
- Underground Water like Springs, Tube wells, Wells
- Sea Water

River water contains dissolved minerals like chlorides, sulphates, bicarbonates of sodium, magnesium, calcium and iron. Its composition is not constant. Lake water has high quantity of organic matter present in it. Its chemical composition is also constant. Rain water, is the purest form of natural water. When it comes down, it dissolves organic and inorganic suspended particles and some amount of industrial gases. Underground water is free from organic impurities and is clearer in appearance due to filtering action of the soil. It has large amount of dissolved salts. Sea water is very impure due to continuous evaporation and impurity thrown by rivers as they join sea.

Hardness of Water:

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Hardness is defined as soap consuming capacity of water sample. It is that characteristic "which prevent the lathering of soap." It is due to presence of certain salts of Ca, Mg and other heavy metal ions like Al^{3+}, Fe^{3+} and Mn^{2+} dissolved in water. A sample of hard water, when treated with soap (K or Na salt of higher fatty acids like oleic, palmitic or stearic acid), does not produce lather, but forms insoluble white scum or ppt of calcium and magnesium soaps.

$$2C_{17}H_{35}COONa + CaCl_2 \longrightarrow (C_{17}H_{35}COO)_2Ca\downarrow + 2\,NaCl.$$

Soap (Hardness) — Calcium Sterate
(Sodium Sterate) — (Insoluble)

$$2C_{17}H_{35}COO\,Na + MgSO_4 \rightarrow (C_{17}H_{35}COO)_2Mg + Na_2SO_4$$

Soap (Hardness) — Magnesium Sterate (Insoluble)

S.No	HARD WATER	SOFT WATER
1.	Water which does not produce lather with soap solution readily, but forms a ppt.	Water which lather easily on shaking with soap solution, is called soft water.
2.	It contains dissolved Ca & Mg salts in it.	It does not contain Ca & Mg salts in it.
3.	Cleansing quality in depressed and lot of soap is wasted.	Cleansing quality is not depressed and so not soap is wasted.
4.	Boiling point of water is elevated, and more fuel and time are required for cooking.	Less fuel and time are required for cooking in soft water.
5.	Water is said to hard when hardness is above 100 mg. / ltr.	In soft water hardness is below 100 mg. / ltr.

Types of Hardness: It is of following types

1. Temporary Hardness: It is caused by presence of dissolved bicarbonates of Ca, Mg and other heavy metals and the carbonates of Iron. Example – Ca $(HCO_3)_2$ and Mg $(HCO_3)_2$. It can be removed by boiling of water, bicarbonates decompose to yield insoluble carbonates or hydroxides, which gets deposited as scale at the bottom of vessel. It is also known as carbonate hardness or alkaline hardness.

$$Ca(HCO_3)_2 \longrightarrow CaCO_3 + H_2O + CO_2$$

$$Mg(HCO_3)_2 \longrightarrow Mg(OH)_2 + 2CO_2$$

2. Permanent Hardness: It is due to presence of dissolved chlorides and sulphates of calcium, magnesium, iron and other heavy metals, eg. $CaCl_2$, $MgCl_2$, $CaSO_4$, $MgSO_4$, $FeSO_4$, $Al_2(SO_4)_3$ etc. It cannot be destroyed by boiling. Permanent hardness is also known as non-carbonate or non-alkaline hardness.

3. Total Hardness = Carbonate Hardness (Temporary) + Non-carbonate Hardness (Permanent)

Equivalent Amount of $CaCO_3$: To make uniformity or similarity impurities are expressed in terms of equivalent amount (equivalents) of $CaCO_3$ i.e., the mg $CaCO_3$ / Litre. The $CaCO_3$ is chosen as standard because it is the most insoluble salt of Ca in water and it is having great convenience to calculate as the molecular weight is 100 and its equivalent weight is 50. Therefore, all the hardness-causing impurities are first converted in terms of their respective weights equivalent to $CaCO_3$ and is expressed in parts per million or mg/L and calculated by;

Equivalent Amount of $CaCO_3$= Mass of salt × Chemical equivalent wt. of $CaCO_3$

Chemical equivalent wt. of the salt

Multiplication factors for different salts are:

Constituent Salt / ion	Molar Mass (a)	n – factor (b)	Chemical equivalent=(a)/(b)	Multiplication factor for converting into equivalents of $CaCO_3$
$Ca(HCO_3)_2$	162	2 (divalent)	162/2 = 81	100/2 x 81 = 100/162
$Mg(HCO_3)_2$	146	2	146/2 = 73	100/2 x 73 = 100/146
$CaSO_4$	136	2	136/2 = 68	100/2 x 68 = 100/136
$MgSO_4$	120	2	120/2 = 60	100/2 x 60 = 100/120
$CaCl_2$	111	2	111/2 = 47.5	100/2 x 47.5 = 100/111
$MgCl_2$	95	2	95/2 = 47.5	100/2 x 50 = 100/95
$CaCO_3$	100	2	100/2 = 50	100/2 x 50 = 100/100
$MgC0_3$	84	2	84/2 = 42	100/2 x 42 = 100/84
CO_2	44	2	44/2 = 22	100/2 x 22 = 100/44
$Mg(NO_3)_2$	148	2	148/2 = 74	100/2 x 74 = 100/148
HCO_3	61	1 (monovalent)	61/1 = 61	100/2 x 61 = 100/122
OH^-	17	1	17/1 = 17	100/2 x 17 = 100/34
CO_3^{2-}	60	2	60/2 = 30	100/2 x 30 = 100/60
$NaAlO_2$	82	1	82/2 = 82	82/2 x 82 = 100/164
$Al_2(SO_4)_3$	342	6	342/6 = 57	100/2 x 57 = 100/114
$FeSO_4 \cdot 7H_2O$	278	2	278/2 = 139	100/2 x 139 = 100/278
H^+	1	1	1/1 = 1	100/2 x 1 = 100/2

UNITS OF HARDNESS:

1. Parts per million (ppm): ppm is the parts of calcium carbonate equivalent hardness present per 10^6 parts of water.
2. Milligrams per litre (mg/L): It is the number of milligrams of $CaCO_3$ equivalent hardness present per litre of water.

   1 mg / L. = 1 mg of $CaCO_3$ eq. Hardness / L of water

But 1 L of water weighs 1000 gms.
= 1000 x 1000 mg.
1 mg / L = 1 mg / 10^6 mg = 1 ppm.

3. Clarke's degree (^{0}Cl) or Grains per gallon: It is the number of grains of $CaCO_3$ equivalent hardness present per gallon of water. It is the parts of $CaCO_3$ equivalent hardness per 70,000 parts of water.
4. Degree French (^{0}Fr): It is the parts of $CaCO_3$ eq. Hardness present per 10^5 parts of water.

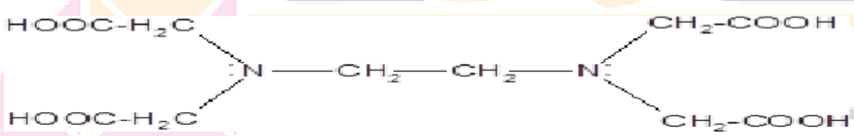
Relationship between units:

1 PPm	=	1 mg / L	=	0.1 ^{0}Fr	=	0.07 ^{0}Cl
1 ^{0}Fr	=	10 PPm	=	10 mg / L	=	0.7 ^{0}Cl
1 ^{0}Cl	=	14.3 PPm	=	14.3 mg/L	=	1.43 ^{0}Fr

Determination of Hardness by EDTA Method:

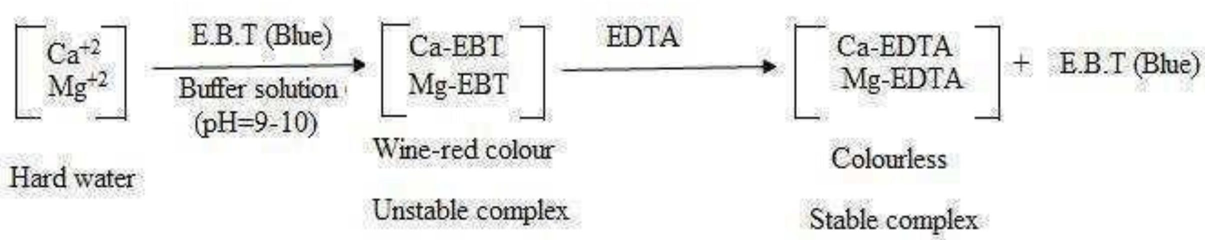
- EDTA is abbreviation of Ethylene diamine tetra acetic acid.
- EDTA dissolves in water with great difficulty and in a very very small quantity.
- On the contrary its di-sodium salt dissolves in water quickly and completely. Hence for common experimental purpose, in place of EDTA, its di-sodium derivative 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 (Ethylene diamine Tetra acetic 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 hard water sample, can be determined by titrating Ca^{2+} and Mg^{2+} present in the sample with di-sodium salt of EDTA (Na_2 EDTA) solution, using ammonical buffer solution containing NH_4Cl-NH_4OH of p^H 10 using Eriochrome Black-T (EBT) as the metal indicator.
- At p^H 10, EBT indicator form 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 colour. Hence the colour change is from wine red to blue (EBT's own colour).
- Thus 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

Formula for Determination of Hardness:

$$\text{Hardness(in mg/l)} = \frac{ENV}{\text{Vol of water sample}} \times 1000$$

Here E = Chemical equivalent wt. of $CaCO_3$

N= Normality of EDTA solution

V= Volume of EDTA solution used

Alkalinity and its determination:

- 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. It can be defined as "the concentration of the salts present in water which increases the concentration of OH^- ions due to hydrolysis thereby rising p^H 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^{2-} ions.
- The constituents causing alkalinity in natural water: 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) CO_3^{2-} & HCO_3^- together.
- Hydroxide and bicarbonates do not exist together because hydroxyl ions react with bicarbonate ions to form carbonate ions. Therefore existence of hydroxyl and bicarbonates ions together is ruled out.

$$OH^- + HCO_3^- \longrightarrow CO_3^{2-} + H_2O$$

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 the indicator changes from pink to colorless, 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 up to this point is called phenolphthalein alkalinity. [P]

$$\text{Phenolphthalein alkalinity [P] (in mg/l)} = \frac{ENV_P}{\text{Vol of water sample}} \times 1000$$

Here E = Chemical equivalent wt. of CaCO3

N= Normality of Acid solution

V_P= Volume of Acid solution used at phenolphthalein end point

Titration is continued using methyl orange indicator. The color changes from yellow to red and shows complete neutralization of all the bicarbonate ions. 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. [M]

$$\text{Methyl orange alkalinity [M] (in mg/l)} = \frac{ENV_M}{\text{Vol of water sample}} \times 1000$$

Here V_M= Total Volume of Acid solution used

When standard acid solution is added to alkaline water following reactions takes place:-

$$\left.\begin{array}{l}\left.\begin{array}{l} OH^- + H^+ \longrightarrow H_2O \\ CO_3^{2-} + H^+ \longrightarrow HCO_3^- \end{array}\right\} P \\ HCO_3^- + H^+ \longrightarrow H_2O + CO_2 \end{array}\right\} M$$

Calculation of Alkalinity of water: The type and extent of alkalinity of water can be determined with the help of following table:

Alkalinity	OH^- (ppm)	CO_3^{--} (ppm)	HCO_3^- (ppm)
P = 0	0	0	M
P = 1/2M	0	2P	0
P < 1/2M	0	2P	(M-2P)
P > 1/2M	(2P-M)	2(M-P)	0
P = M	P = M	0	0

Significance:

1) For calculating the amounts of lime and soda required for water softening.
2) In conditioning boiler feed water, highly alkaline waters may lead 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, causes scale formation in boilers.

List of References;

Sr. No.	Title of the Book	Author/Publisher/Edition

1	Engineering Chemistry	rgpvnotes.in@gmail.com
2	Engineering Chemistry	Dara S.S & Singh A.K, S Chand & Co..
3	Engineering Chemistry	Jain & Jain, Dhanpat Rai & Co.
4	Engineering Chemistry	Chawla S. ,Dhanpat Rai & Co.

Questions based on Unit I:

1. Discuss the determination of hardness of water by the complexometric titration method along with relevant chemical reactions involved in titration.

2. What is Alkalinity of water? Discuss the principle and procedure used for determining alkalinity.

3. Give reason; (A) Alkalinity of water cannot be due to simultaneous presence of OH^-, CO_3^{--} and HCO_3^- ions.
   (B) Hard water consumes a lot of soap.

4. What is $CaCO_3$ equivalent? Why do we express hardness of water in terms of $CaCO_3$?

5. What is hardness of water? Discuss the types and units of hardness.

6. 100ml of water sample requires 4ml of 0.02N H2SO4 for neutralization to phenolphthalein end point. Another 16ml of the same acid was needed for further titration to methyl orange end point. Determine the type and amount of alkalinity.

7. 100 mL of water sample on titration with N/50 H_2SO_4 using phenolphthalein indicator gave the end point when 10.0 mL of acid were run.100 mL of same sample separately required 8.0 mL to obtain methyl orange end point. Find alkalinity of water sample in ppm.

8. 100 ml of water sample on titration with N/50 HCl required 8 ml of the acid to phenolphthalein end point and 9 ml of the acid to methyl orange end point. Calculate type and extent of alkalinity.

9. 100 mL of standard hard water containing 1.0 mg of pure $CaCO_3$ per mL consumed 25 mL of EDTA solution using EBT as indicator. 50 mL of water sample consumed 20 mL of same EDTA solution while after boiling, cooling and filtering 50 mL of water sample consumed 15 mL of same EDTA solution. Calculate temporary hardness of water sample in ppm, mg/L, °Cl and °Fr.
10. 1 gram of calcium carbonate was dissolved in acid and the solution was made to 1 litre. 100 mL of this solution required 90mL EDTA solution, while 100 mL of sample water required 40 mL of EDTA. Calculate total hardness present in hard water.