LECTURE NOTES

ON

WATER TECHNOLOGY

ENGINEERING CHEMISTRY

B.Tech 1st year

By

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1. Hardness of water

Water which does not produce lather with soap is termed as hard water. The hardness is usually expressed in terms of Ca & Mg salts like bicarbonate, carbonate, sulphate, chloride etc.

Formation of Hard water:

Hard water is formed due to presence of minerals like Ca and Mg. they are not removed or separated by sedimentation or filtration. When hard water reacts with soap (sodium salt of stearic acid or pametic acid) gives curdy precipitate.

$$2C_{17}H_{35}COONa + CaCl_2 \rightarrow Ca(C_{17}H_{35}COO)_2\downarrow + NaCl$$

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

In above reaction hard water react with sodium salt of stearic acid to form calcium stearate or magnesium stearate which being insoluble and separate out without producing lather.

2. Types of hardness

a) Temporary hardness:

Temporary hardness of water is caused by Ca and Mg bicarbonate. This can be removed by simply boiling of water. Due to boiling bicarbonate is converted into carbonate (insoluble precipitate)

$$Ca(HCO_3)_2 \rightarrow CaCO_3\downarrow + H_2O + CO_2\uparrow$$

$$Mg(HCO_3)_2 \rightarrow Mg(OH)_2\downarrow + 2CO_2\uparrow$$

Temporary hardness can also be removed by adding hydrated lime to precipitate insoluble carbonate.

$$Ca(HCO_3)_2 + Ca(OH)_2 \rightarrow 2CaCO_3\downarrow + 2H_2O$$
$$Mg(HCO_3)_2 + Ca(OH)_2 \rightarrow Mg(OH)_2\downarrow + 2CaCO_3\downarrow + 2H_2O$$

b) Permanent hardness:

Permanent hardness is caused by the presence of soluble salt of Ca and Mg other than bicarbonate such as chloride and sulphate. Permanent hardness cannot be removed by boiling of water or hydrated lime. It can be eliminate by water softening techniques like Lime-soda process, Zeolite, Ion-exchange resin, reverese osmosis etc.

3. Degree of hardness

The unit in which hardness is usually expressed, known as degree of hardness. Degree of hardness is expressed in terms of calcium carbonate ($CaCO_3$) equivalent because $CaCO_3$ have molecular weight 100 and it is easily precipitate. Degree of hardness may be expressed as follows-

$$\text{Equivalent of } CaCO_3 = \frac{\left[\textit{strength of substance producing hardness}\left(\frac{mg}{lit}\right)\right]\times[\textit{ chemical equvalent of } \text{CaCO3}]\times 2}{[\textit{ chemical equivalent of hardness producing substance}]\times 2}$$

OR

$$\text{Equivalent of } CaCO_3 = \frac{\left[\textit{strength of substance producing hardness}\left(\frac{mg}{lit}\right)\right]\times 100}{[\textit{ chemical equivalent of hardness producing substance}]\times 2}$$

Unit of hardness:

i) **Parts per million (ppm):** it is the number of equivalent part $CaCO_3$ present per million (10^6) part of water by weight.

ii) **Milligram per litre (mg/lit):** it is the number of milligram of $CaCO_3$ present in one litre of water.

iii) **Degree Clarke (°Cl):** it is the number of equivalent part of $CaCO_3$ present per 70,000 part of water.

iv) **Degree French (°Fr):** it is the number of equivalent part of $CaCO_3$ present per 10^5 part of water.

Correlation between ppm, mg/lit, °Cl and °Fr:

[1ppm= 1mg/lit=0.07 °Cl= 0.1 °Fr]

4. Boiler Trouble

Boilers are used in industries and power station to generate steam. During conversion of water into steam in boiler, the dissolve and suspended solids are not removed. All the impurities are deposited in form of **scale** and **sludge** within the boiler and causes boiler troubles.

a) Scales formation:

Scales are hard deposits, which stick on the inner wall of the boiler. These are formed by $CaCO_3$, $CaSO_4$, $Ca(HCO_3)_2$, $Mg(OH)_2$ etc. in hot portion of boiler.

b) Sludge formation:

Sludge form loose, slimy and soft precipitate in the colder area of the boiler. The sludge formed by the $CaCl_2$, $MgCl_2$, $MgCO_3$, $MgSO_4$ etc.

Problems caused in boilers:

i) Scales and sludge is poor conductor of heat & therefore prevent effective transfer of heat to water.

ii) In this condition excessive heat is required which increase fuel consumption.

iii) Scale often crack due to their uneven expansion allowing the water to come immediately in contact with overheated metal. This suddenly result in the formation of large quantity of steam which in turn leads to excess pressure and then to explosion.

5. Boiler trouble removal by internal treatment

Internal treatment:

i) Sludge formation can be removed by blow down operation. In this case impurities can be removed by an outlet present at the bottom of boiler.

ii) Scale formation can be prevented by internal treatment that involve addition of chemical to the boiler water either to ppt the scale forming impurities in the form of sludge so that they can be removed by blow down method or to convert them into soluble compounds.

a) Calgon treatment:

Calgon is sodium meta hexa phoaphate, which can be used to covert CaSO4 into soluble complex.

$$\underset{\textbf{Calgon}}{Na_2[Na_4(PO_3)_6]} + 2CaSO_4 \longrightarrow \underset{\textbf{soluble}}{Na_2[Ca_2(PO_3)_6]} + 2Na_2SO_4$$

b) Phosphate treatment:

Scale formation can be removed by adding sodium phosphate, which reacts with hardness of water and form soft sludge of Ca and Mg phosphates which can be removed by blow-down operation.

$$3CaCl_2 + 2Na_3PO_4 \longrightarrow Ca_3(PO_4)_2\downarrow + 6NaCl$$

$$MgSO_4 + 2Na_3PO_4 \longrightarrow Mg_3(PO_4)_2\downarrow + 3Na_2SO_4$$

6. Techniques for water softening (External treatment)

a) Zeolite process

Zeolite is a three-dimensional silicate. The chemical formula of zeolite is hydrated sodium aluminum silicate represented as $Na_2OAl_2O_3.xSiO_2.yH_2O$ (x = 2-10 & y = 2-6). Zeolites are capable exchanging ions with sodium ions. So it is capable of exchanging hardness producing icons present in water. This process also called as permutit process. Zeolite can be written as Na_2Ze The two Na^+ icons is replaced by one Ca^{2+} or Mg^{2+} ions.

$$Na_2Ze + Ca^{2+} \longrightarrow CaZe + 2Na^+$$

Process:-

The apparatus is made of cylindrical metallic vessel several beds are made inside it where zeolite salt is kept. Raw water is poured inside the apparatus through inlet that passes through beds and thus chemical ion exchange reactions are takes place. After the use of this process for a certain time, Zeolite is exhausted i.e all Na^+ ions are replaced by Ca^{2+} or Mg^{2+} and therefore this will not be used for soften the water.

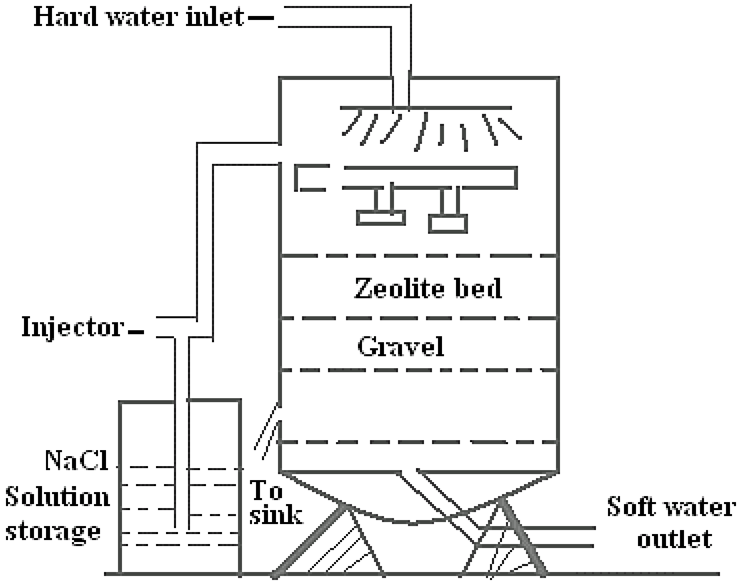
$$Na_2Ze + CaCl_2/CaSO_4/\ Ca(HCO_3)_2 \longrightarrow CaZe + 2NaCl/Na_2SO_4/2NaHCO_3$$

Regeneration:

Exhausted zeolite can be regenerated by treating it with brine solution (10% NaCl solution)

$$(Ca^{2+}/Mg^{2+})\ Ze + NaCl \longrightarrow Na_2Ze + CaCl_2\ (or)\ MgCl_2$$

Exhausted Zeolite on washing with cold water, $CaCl_2$ & $MgCl_2$ can be removed and regenerated zeolite is this ready to be reused.



b) Ion-exchange resin:

In this process cations and anions are completely removed by passing impure water into two different columns. First column contain sulphuric acid resin with acidic group $-SO_3H$. This column is known as cation exchange resin because it exchange only cations like Ca^{2+}, Mg^{2+}, Na^+ etc.

$$\text{Resin–}SO_3H + Na^+ \longrightarrow \text{resin- }SO_3^-Na^+ + H^+$$

$$2\text{Resin–}SO_3H + Ca^{2+} \longrightarrow (\text{resin- }SO_3)_2Ca + 2H^+$$

$$2\text{Resin–}SO_3H + Mg^{2+} \longrightarrow (\text{resin- }SO_3)_2Mg + 2H^+$$

Whereas, second column contain resin with basic group like $-NR_3^+OH^-$. It is known as anion exchange resin because it exchanges anions like Cl^-, SO_4^{2-} etc.

$$\text{resin–}NR_3^+OH^- + Cl^- \longrightarrow \text{resin–}NR_3^+Cl^- + OH^-$$

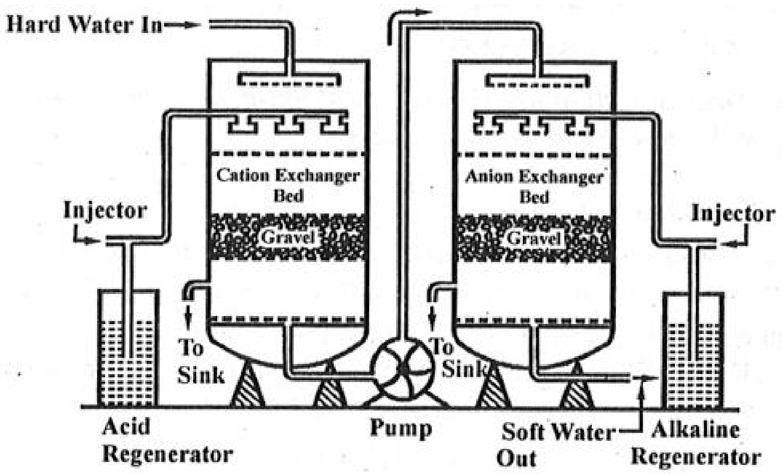
The removal of H^+ ions from the first column and OH^- ions from the second column react to form water.

Regeneration:

when both the column are exhausted, then first and second column are treated with dilute sulphuric acid or HCl (generate H^+ ions) and aqueous NaOH (generate OH^- ions) respectively. So, they have to be regenerated.

$$(\text{resin- }SO_3)_2Ca + 2H^+ \longrightarrow 2\text{Resin–}SO_3H + Ca^{2+}$$

$$(\text{resin- }SO_3)_2Mg + 2H^+ \longrightarrow 2\text{Resin–}SO_3H + Mg^{2+}$$



c) Lime-soda process:

In this process, hydrated lime & sada ash use to remove hardness from water.

i) Hydrated lime:

Hydrated lime is used to remove temporary hardness of water. It react with $Ca(HCO_3)_2$ & $Mg(CO_3)_2$ to form insoluble precipitate of calcium carbonate and magnesium hydroxide respectively.

$$Ca(HCO_3)_2 + Ca(OH)_2 \longrightarrow 2CaCO_3\downarrow + 2H_2O$$

$$Mg(HCO_3)_2 + 2Ca(OH)_2 \longrightarrow Mg(OH)_2\downarrow + 2CaCO_3\downarrow + 2H_2O$$

Hydrated lime is also used to remove permanent hardness (magnesium salt impurities only) from water. It reacts with $MgSO_4$ & $MgCl_2$ to form insoluble precipitate of magnesium hydroxide.

$$MgCl_2 + Ca(OH)_2 \longrightarrow Mg(OH)_2\downarrow + CaCl_2$$

$$MgSO_4 + Ca(OH)_2 \longrightarrow Mg(OH)_2\downarrow + CaSO_4$$

In above reaction calcium based impurities like $CaCl_2$ & $CaSO_4$ also form, which are soluble in water. Therefore calcium based impurities ($CaCl_2$ & $CaSO_4$) are not removed by lime treatment.

ii) Soda ash:

Sodium carbonate (Na_2CO_3) is used to remove permanent hardness of water which caused by $MgSO_4$ & $MgCl_2$ or $CaCl_2$ & $CaSO_4$.

$$CaCl_2 + Na_2CO_3 \longrightarrow CaCO_3\downarrow + 2NaCl$$
$$CaSO_4 + Na_2CO_3 \longrightarrow CaCO_3\downarrow + Na_2SO_4$$
$$MgCl_2 + Na_2CO_3 \longrightarrow MgCO_3\downarrow + 2NaCl$$
$$MgSO_4 + Na_2CO_3 \longrightarrow MgCO_3\downarrow + Na_2SO_4$$

The amount of lime-sada required for the softening of hard water can be calculated by following formula-

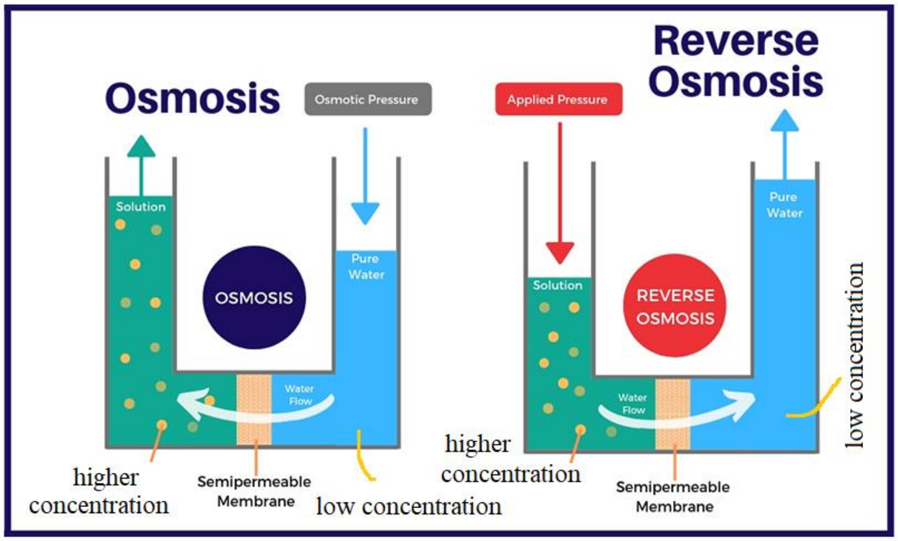
$$\text{Lime requirement} = \frac{74}{100}[\text{temporary hardness of Ca} + 2 \times \text{temporary hardness of Mg} + \text{permanent hardness of Mg in terms of } CaCO_3 \text{ equivalents}]$$

Soda requirement = $\frac{106}{100}$ [permanent hardness of $CaCl_2 + CaSO_4 + MgCl_2 + MgSO_4$

in terms of $CaCO_3$ equivalents]

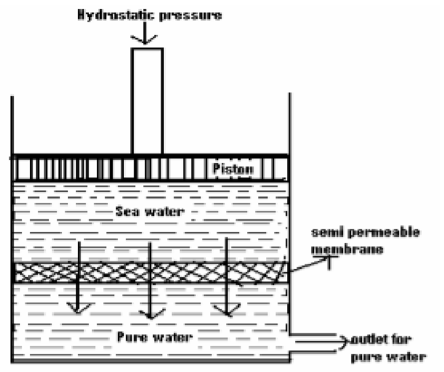
d) Reverse osmosis:

The minimum excess pressure yhat has to be applied on the solution to prevent the entry of the solvent molecule (pure water) into solution through semi permeable membrane is known as osmotic pressure (lower concentration to higher concentration).



If a pressure higher than the osmotic pressure is applied on the solution, the solvent (pure water) will flow reverse, higher concentration solution to low concentration solution, the process is known as reverse osmosis.

Reverse osmosis process can also be used in purification of sea water, for this purpose sea water is delivered under pressure through the semi-permeable membrane where water permeate the minute pores of the membrane & is delivered as purified water.



Advantages:

1) Reverse osmosis system have low maintenance requirement.

2) It removes colloidal silica, which is not removed by demineralization.

3) RO system required less energy as compare to other technology.

4) The reverse osmosis is gaining ground at present for converting sea water into drinking water and for obtaining water for very high pressure boilers.

7. Phase rule

Phase rule (Willard Gibbs in 1874), play an important role to know the behavior of heterogeneous system whereas as law of mass action is apply to know the behavior of homogenous system. If the equilibrium between any numbers of phases is not influenced by gravitational/electrical/magnetic forces but is influenced by pressure, temperature and concentration, then the number of degrees of freedom (F) is related to the number of components (C) and the number of phases (P) as:

$$F = C - P + 2$$

Explanation of terms used in phase rule:

1) Phase (P):

Phase is defined as “any homogeneous, physically distinct, mechanically separable portion of a system which is separated from other part of system by distinct interface”.

a) Gaseous phase:

All the gases are completely miscible and have no boundary between them. Hence all the gases constitute a single phase. For example O_2, N_2, H_2, CO_2 etc. form air, which constitute a single phase.

b) Liquid phase:

The number of liquid phase depends upon the number of liquid present and their miscibility. If two liquid are miscible then they form single phase eg. Alcohol in water. If two liquids are immiscible then they form two separate phase eg. Benzene in water, oil in water etc.

c) Solid phase:

All the solid phase constitutes the separate phase.

$$CaCO_3\,(s) \longleftrightarrow CaO\,(s) + CO_2\,(g) \qquad (C=3)$$

2) Component (P):

Component is defined as “number of independent variable like temperature, pressure and concentration by means of which composition of each phase can be expressed in terms of chemical equation”.

$$\mathbf{Ice(s)} \longleftrightarrow \mathbf{Water(l)} \longleftrightarrow \mathbf{Vapour(g)} \qquad \mathbf{(C= 1)}$$

$$H_2O \qquad H_2O \qquad H_2O$$

3) Degree of freedom (F):

Degree of freedom is defined as “number of independent variable like temperature, pressure and concentration must be fixed to define the system completely”.

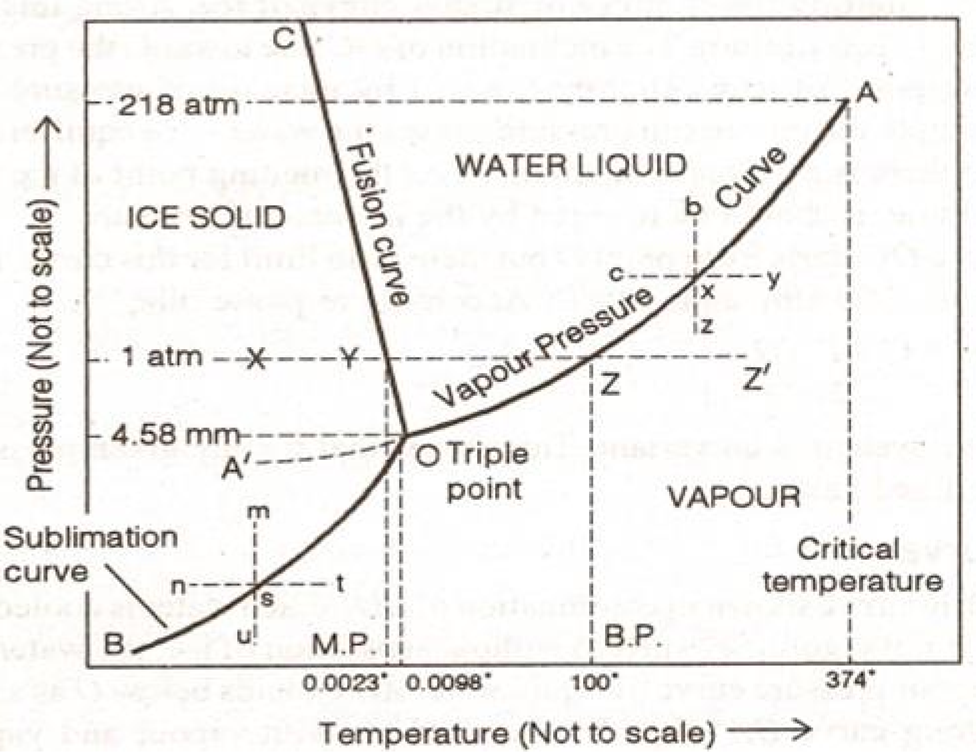
$$F=C-P+2$$

Where,
F=0 (Invarient)
F=1 (Univarient)
F=2 (Bivarient)………& so on

$$F \propto C$$

$$F \propto \frac{1}{P}$$

8. Application of phase rule one component water system



Water exists in 3 possible phases, namely solid ice, liquid water and water-vapour. Hence, there can be three forms of equilibria, each involving two phases such as.

Solid Ice ⟷ Liquid Water
Liquid Water ⟷ Water-vapour
Solid Ice ⟷ Water-vapour

The phase diagram for the water system is as follows and it contains curves, areas, and triple point.

Curve OA

The curve OA is called vapourisation curve, it represents the equilibrium between water and vapour. At any point on the curve the following equilibrium will exist.

Liquid Water ⟷ Water- vapour

This equilibrium (i.e. line OA) will extend upto the critical temperature (374°C). Beyond the critical temperature the equilibrium will disappear and only water vapour will exist

Curve OB

The curve OB is called sublimation curve of ice, it represents the equilibrium between solid ice and water-vapour. At any point on the curve the following equilibrium will exist.

Solid Ice ⟷ Water- vapour

This equilibrium (i.e.line OB) will extend up to the absolute zero (− 273°C). Beyond absolute zero only solid ice will exist and no water-vapour.

Curve OC

The curve OC is called melting point curve of ice, it represents the equilibrium between ice and water. At any point on the curve the following equilibrium will exist.

Solid Ice ⟷ Liquid Water

The curve OC is slightly inclined towards pressure axis. This shows that melting point of ice decreases with increase of pressure.

Curve OB′(Metastable Equilibrium)

The curve OB′ is called vapour pressure curve of the super-cooled water (or) metastable equilibrium where the following equilibrium will exist.

Super- cooled water ⟷ Water- vapour

Sometimes water can be cooled below it‟s freezing point (0°C) without the formation of ice, this water is called super-cooled water. Super cooled water is unstable and it can be converted into solid ice by "seeding" (or) by slight disturbance.

Along the curves OA,OB,OC and OB′

The no. of phases(P) is 2 ,component(C) is 1 and the degree of freedom of the system is one i.e., univariant. This is predicted by the phase rule:

$$F = C - P + 2; F = 1 - 2 + 2; F = 1$$

Therefore, either temperature (or) pressure must be fixed to define the system.

Point ‘O’ (Triple point)

The three curves OA, OB and OC meet at a point „O‟, where three phases namely solid ice, liquid water and water-vapour are simultaneously at equilibrium. This point is called triple point, at this point the following equilibrium will exist

Ice(s) ↔ Water(l) ↔ Vapour(g)

At this point the no. of phases (P) is 3, component(C) is 1 and the degree of freedom of the system is zero i.e., nonvariant. This is predicted by the phase rule:

$$\mathbf{F = C - P + 2;\ F = 1 - 3 + 2;\ F = 0}$$

This takes place only at a constant temperature (0.0075°C) and pressure (4.58 mm of Hg).

Areas

Areas AOC, BOC, AOB represent liquid water, solid ice and water-vapour respectively where the no. of phases (P) and component(C) are one. Hence the degree of freedom of the system is two i.e., bivariant. This is predicted by the phase rule:

$$\mathbf{F = C - P + 2;\ F = 1 - 1 + 2;\ F = 2}$$

Therefore, both temperature and pressure must be fixed to define the system at any point in the areas.