**Important Qs of Engg Chemistry For first Mid term Examination:-**

1)Define Hardness, what is temporary and permanent hardness explain with examples.

2)Explain Complexometric Titration (EDTA method) for determining hardness of water.

**3)**Define Alkalinity, discuss the method and principle of alkalinity titration., Why combination of $OH^-$ and $HCO_3^-$ is not possible in alkalinity.

4)Explain Units of hardness, mention relationship between them.

5) Boiler Corrosion by dissolved $O_2$, $CO_2$

6)Explain Lime Soda Method of water softening under following heads

1) Principle 2) Reaction 3) Advantages

7) Write short note on

1) Scale 2) Caustic Embrittlement 3) Priming

8)Explain Zeolite Method of water softening under following heads 4)

1) Principle. 2) Process

9) Write short note on.

(1) Disadvantages of Lime Soda Method lime

(2) Regeneration process in Zeolite method.

10) Differentiate between hot lime soda and cold lime soda method.

# CHEM Mid Sem-1

Q1> Define Hardness, what is temporary and permanent hardness explain with examples.

Ans * Hardness is the amount of soluble salts present in water.

* Hardness is that property of water due to which it is unable to give lather / foam with soap.

* Hard water do not give lather with soap due to the presence of dissolved salts of Ca, Mg and other heavy metal ions like $Al^{3+}$, $Fe^{3+}$ & $Mn^{2+}$.

There are two types of hardness:-

i> Temporary Hardness

* It is caused by presence of dissolved bicarbonates of Ca & Mg and carbonate of iron
Salts mainly responsible for temporary hardness are $Ca(HCO_3)_2$, $Mg(HCO_3)_2$.

* It is also called carbonate hardness / alkaline hardness.

* It can be removed by boiling of water
i.e

$$Ca(HCO_3)_2 \xrightarrow{\Delta} \underset{\text{(insoluble)}}{CaCO_3} + H_2O + CO_2\uparrow$$

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

bicarbonate decompose to insoluble ppt which gets diposited and we get soft water.

ii> Permanent Hardness

* It is caused by the presence of dissolved chlorides & sulphates of Ca, Mg, iron & other heavy metals
i.e $CaCl_2$, $MgCl_2$, $CaSO_4$, $MgSO_4$, $FeSO_4$, $Al_2(SO_4)_3$

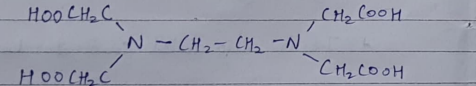
* It cannot be removed by boiling but by following methods:
→ Lime Soda method
→ zeolite Method
→ Ion exchange method

* Permanent hardness is also called non carbonate / non alkaline hardness

Q 2> Explain Complexometric Titration (EDTA method) for determining hardness of water.

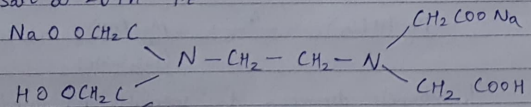
Ans Water hardness is caused by $Ca^{2+}$ & $Mg^{2+}$ ions. The estimation of water hardness is done by complexometric titration using disodium salt of EDTA as titrant and EBT as indicator.

Structure of EDTA:



ethylene diammine tetraacetic acid $\{H_4Y\}$

$\{H_4Y\}$ EDTA has less solubility in water therefore we use Disodium salt of EDTA i.e



$\{Na_2H_2Y \cdot 2H_2O\}$



This Disodium salt of EDTA gives anion of EDTA $(H_2Y^{2-})$
i.e

$$Na_2H_2Y \cdot 2H_2O \xrightarrow{H_2O} \text{anion of EDTA } (H_2Y^{2-})$$

and this $(H_2Y^{2-})$ reacts with Ca, Mg salts or ions to form a complex whose quantity tells us about the estimation of hardness in water.
i.e

$$Ca^{2+} + H_2Y^{2-} \longrightarrow \underset{\text{(Complex)}}{CaY^{2-}} + 2H^+$$

⇒ Principle of EDTA method:-

1> In this method, buffer solution is added in hard water to maint pH of ~10 by using $NH_4OH + NH_4Cl$ solution. Then EBT (Eriochrome black T) indicator (few drops of) is added to above solution which form weak complex with metal ions and gives a wine red colour solution.
i.e

$$Ca^{2+} \text{ or } Mg^{2+} + EBT \xrightarrow[\text{buffer}]{(NH_4Cl + NH_4OH)} \underset{\text{unstable wine red complex.}}{[Ca^{2+}-EBT] \text{ or } [Mg^{2+}-EBT]}$$

ions from hard water indicator

2> Now the wine red sol$^n$ is titrated using EDTA which combines with $Ca^{2+}$ or $Mg^{2+}$ ions to give a stable colourless sol$^n$

i.e $Ca^{2+}$ or $Mg^{2+}$ + EDTA $\longrightarrow$ $[Ca^{2+}-EDTA]$ or $[Mg^{2+}-EDTA]$
Hardness causing ions stable colourless complex.

Then the EDTA sol$^n$ displaces the indicator EBT from metal-EBT complex and forms a sky blue colour

i.e $[Ca^{2+} - EBT]$ + EDTA ⟶ $[Ca^{2+} - EDTA]$ + EBT
or $[Mg^{2+} - EBT]$ or $[Mg^{2+} - EDTA]$ + EBT
wine red complex colourless free indicator (sky blue colour)

This is the endpoint, where readings are noted.

⇒ Procedure for total hardness determination by EDTA:

* 20 ml of hard water is pipetted out into clean conical flask and 5 ml buffer along with 1-2 drops of EBT are added in the conical flask.
* Wine red coloured sol$^n$ is obtained
* Above sample of conical flask is titrated with EDTA from burette until wine red changes to sky blue colour at the end point and readings are noted.
* Above procedure is repeated until same readings are obtained.

⇒ Procedure for permanent hardness determination by EDTA:

* 100 ml of hard water is pipetted out into clean beaker and boiled for 20 minutes and then filtered to remove precipitate formed due to decomposition of temoporary hardness producing salts.
* The filtrate is made up to 100 ml again by adding distilled water.
* 20 ml of the 100 ml filtrate is pipetted out into conical flask and 5 ml buffer with 1-2 drops of EBT is added in it to form a wine red sol$^n$.
* Above wine red sol$^n$ is titrated with EDTA until endpoint at which wine red changes to sky blue colour and the titration is repeated to get same reading.

⇒ Temporary hardness = Total hardness − Permanent hardness

Q 3> Define Alkalinity, discuss method & principle of alkalinity titration, Why combination of $OH^-$ and $HCO_3^-$ is not possible in alkalinity

Ans * Alkalinity can be ~~difined~~ defined as the total content of all those substances in water which increase the concentration of hydroxyl ion ($OH^-$) by dissociation or hydrolysis.

* Ions that cause alkalinity are
i> Hydroxyl ion ($OH^-$)
ii> Carbonate ion ($CO_3^{2-}$)
iii> Bicarbonate ion ($HCO_3^-$)

* Possible combination of ions causing alkalinity are:
i> $OH^-$ only <ii> $CO_3^{2-}$ only <iii> $HCO_3^-$ only

iv> $OH^-$ and $CO_3^{2-}$ <v> $CO_3^{2-}$ and $HCO_3^-$

* Combination of ions that is not possible:
i> Combination of $OH^-$ & $HCO_3^-$ ion together is not possible because they combine to form $CO_3^{2-}$ ion
i.e

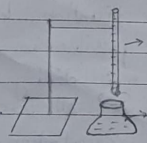
$$OH^- + HCO_3^- \longrightarrow CO_3^{2-} + H_2O$$

ii> $OH^-$, $CO_3^{2-}$ and $HCO_3^-$ also cannot exist together due to same above rxn.

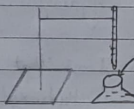
* Determination and estimation of alkalinity causing ions is done by titration with acid like $H_2SO_4$ and using phenopthalein and methyl orange as indicators.

## Procedure / principle of alkalinity titration :-

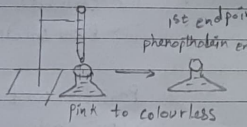
1> Firstly $\frac{N}{50}$ $H_2SO_4$ is taken in burette and 100 ml of alkaline water sample is pipetted into a clean titration flask.



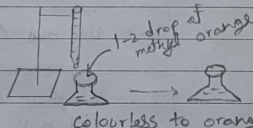

2> 1-2 drops of phenopthalein indicator is added in the conical flask due to which a pink coloured sol$^n$ is obtained



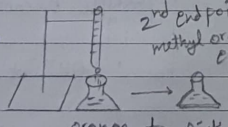

3> The pink coloured sol$^n$ is titrated with $\frac{N}{50}$ $H_2SO_4$ until a colourless sol$^n$ is obtained. It is the first endpoint / P / phenopthalein endpoint.




4> 1-2 drops of methyl orange indicator is added in the colourless sol$^n$ due to which orange coloured sol$^n$ is obtained




5> The orange coloured sol$^n$ is titrated with $\frac{N}{50}$ $H_2SO_4$ until orange colour changes to pink. It is the second endpoint / M / methyl orange endpoint.




### Reactions taking place are :-

i> $OH^- + H^+ \longrightarrow H_2O$ ]
ii> $CO_3^{2-} + H^+ \longrightarrow HCO_3^-$ ] P
iii> $HCO_3^- + H^+ \longrightarrow H_2O + CO_2$ ] M

| Condition | $OH^-$ | $CO_3^{2-}$ | $HCO_3^-$ |
|---|---|---|---|
| P = 0 | — | — | M |
| P = M | P or M | — | — |
| $P = \frac{1}{2}M$ | — | 2P | — |
| $P > \frac{1}{2}M$ | 2P − M | 2 (M − P) | — |
| $P < \frac{1}{2}M$ | — | 2P | M − 2P |



* For the determination and estimation of ion :

Q4> Explain units of Hardness, mention relationship between them.

Ans The units of hardness are as follows :-

1> Parts per million (ppm)
It is the no. of parts of weight of $CaCO_3$ present per million ($10^6$) parts by weight of water.

2> Milligram per litre ($mg/l$)
It is the no. of milligrams of $CaCO_3$ present in one litre of water i.e $\frac{1\ mg}{l} = 1$ ppm

3> Degree clarke (°Cl)
It is the parts of $CaCO_3$ equivalent hardness per 70000 parts of water.

4) Degree French (°fr)
It is parts of $CaCO_3$ equivalent per $10^5$ parts of water

5) $CaCO_3$ equivalent
Hardness of water is mostly expressed in terms of $CaCO_3$ equivalent because calculations become easy as its molecular weight is 100 and it is the most insoluble salt that can be precipitated in water treatment.

Formula to convert into $CaCO_3$ equivalent unit = strength of hardness producing substance in mg/l × 100 / molecular mass of hardness causing substance

* Relation between various units

$$1\ ppm = 0.1\ °fr = 0.07\ °cl = 1\ \frac{mg}{l}$$

Q5) Boiler Corrosion by dissolved $O_2$, $CO_2$.

Ans * Boiler corrosion refers to the damage and decay of boiler material (Iron) due to attack of chemicals present in its environment.

* Causes of boiler corrosion :-

1) By dissolved Oxygen

* Source : Water usually contains 8 ml of dissolved Oxygen per litre at room temperature

* Rxn of corrosion : $2Fe + 2H_2O + O_2 \longrightarrow 2Fe(OH)_2$

$4Fe(OH)_2 + O_2 \longrightarrow 2[Fe_2O_3 \cdot 2H_2O]$

Rust

* Removal of dissolved $O_2$ :

By adding chemicals,

$N_2H_4 + O_2 \longrightarrow N_2 + 2H_2O$

Hydrazine

Using hydrazine $O_2$ can be removed, because it produces $N_2$ which is harmless. and it is an ideal method

2> By dissolved Carbon dioxide

* Source : Bicarbonate salts present in water decompose to liberate $CO_2$

$Ca(HCO_3)_2 \xrightarrow{\Delta} CaCO_3 + H_2O + CO_2$

* Rxn of corrosion : Disolved $CO_2$ reacts with $H_2O$ to form $H_2CO_3$ (Carbonic acid) which causes boiler corrosion

i.e $CO_2 + H_2O \longrightarrow H_2CO_3$

Carbonic acid

$H_2CO_3$ + Boiler material $\longrightarrow$ Corrosion of boiler material

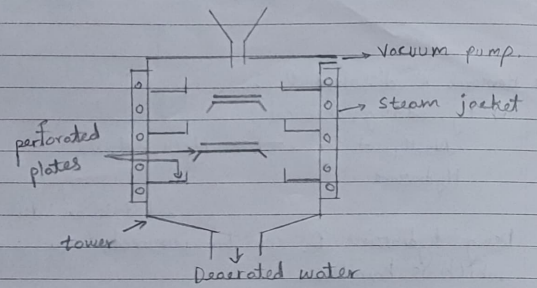
* Removal of dissolved $CO_2$ :

By adding chemical :

$2NH_4OH + CO_2 \longrightarrow (NH_4)CO_3 + 2H_2O$

Ammonium Hydroxide — Ammonium Carbonate

* Both dissolved $O_2$ & $CO_2$ can also be removed by using Mechanical deaeration.




In this, water is sprayed over hot metallic plates which removes the dissolved gases and the gases are then sucked out by vacuum pump

Q6) Explain Lime Soda method of water softening under following heads:

1) Principle

Ans * The basic principle of Lime soda method of water softening is to convert all the soluble hardness causing constituents into insoluble precipates by chemical reactions.

* In this method, lime i.e Calcium hydroxide ($Ca(OH)_2$) and Soda i.e Sodium carbonate ($Na_2CO_3$) is added in water which converts soluble salts of Ca & Mg into insoluble compound $CaCO_3$ & $Mg(OH)_2$ precipitate.

Then,

* The insoluble precipitate is filtered out to obtain soft water.



2) Reaction

The reactions involved are:

$$Ca^{2+} + Na_2CO_3 \longrightarrow CaCO_3 + 2Na^+$$
(Soda)

$$Mg^{2+} + Ca(OH)_2 \longrightarrow Mg(OH)_2 + Ca^{2+}$$
(Lime)

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

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

3) Advantages

Advantages of lime soda method are:

i) The soft water obtained has higher pH which prevents corrosion of distribution pipes.

ii) The amount of impurities like iron & manganese ~~are~~ is also decreased.

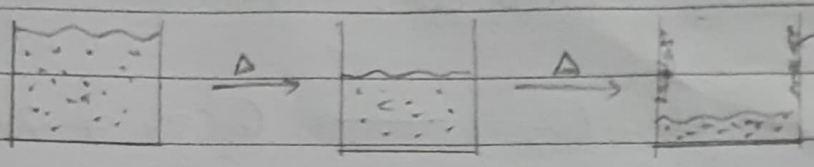
iii) Due to alkaline nature of treated water (soft water), amount of pathogenic bacteria also decreases.

iv) It is very economical method.

Q7) Write a short note on:

i) Scale

Ans *




→ When hard water boils in boiler, amount of water decreases & concentration of dissolved salt increases.

i) → At saturation point, salts are thrown out of water in form of precipitate on the inner walls of boiler.

ii) → If the layer of precipitate formed is hard, it is called scale.

* Disadvantage of scale:

i) → Wastage of fuel : scale have low thermal conductivity so they need constant heat supply which causes wastage of fuel.

ii) → Decrease in boiler efficiency : Sometimes, scale deposit in valves & condensers of boiler & choke them partially which leads to decrease in boiler efficiency.

* Removal of Scale

i) → Thermal shock treatment

ii) → Addition of chemicals like EDTA, HCl.

* Prevention of Scale

i) → External treatment : softening of water outside boiler.

ii) → Internal treatment : i) Colloidal conditioning
ii) Calgon conditioning
iii) Phosphate conditioning

2> Caustic Embrittlement

* Caustic embrittlement refers to the formation of brittle cracks in boiler shell due to accumulation of caustic substances.

* The causes of caustic embrittlement are:

i) → Presence of alkali-metal carbonate & bicarbonates in water.

ii) → Some of the $Na_2CO_3$ used in softening of water by lime soda method is left behind which reacts with water to give NaOH (caustic soda) which reacts with the boiler material and damages it.

* rxn is as follows:

$$Na_2CO_3 + H_2O \longrightarrow 2NaOH + H_2O$$

Sodium hydroxide

$$NaOH + Fe \longrightarrow \cancel{Na_2Fe_2O_3}$$ Sodium Ferroate

Caustic soda | boiler material | (makes boiler material brittle)

* Prevention of caustic embrittlement:

i) → By using $Na_3PO_4$ (Sodium phosphate) in place of $Na_2CO_3$ (Sodium carbonate)

ii) → By adding tanin or lignin that fill up the hairy cracks and thus preventing NaOH from penetrating inside the crack.

3> Priming

* When boiler produces steam rapidly then some of the liquid particles are also carried along with the steam, this formation of wet steam is called priming.

* Causes of priming are:-

i) → Improper boiler design

i) → High steam velocity
ii) → Sudden boiling and foaming
iv) → High amount of dissolved solid in water.

* Prevention of priming:
i) → Proper boiler design
ii) → Low steam velocity
iii) → Efficient softening of water
iv) → Using mechanical steam purifier.

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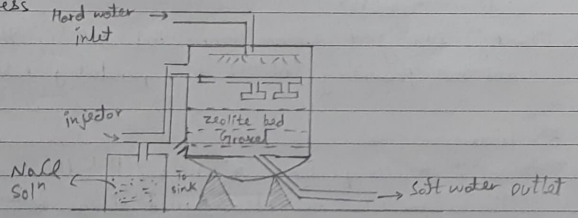
Q8) Explain Zeolite method of water softening under following heads:

1) Principle.

* In this method, hydrated sodium alumino silicate i.e $Na_2O \cdot Al_2O_3 \cdot x\,SiO_2 \cdot y\,H_2O$ which can also be written as $Na_2Ze$ i.e Sodium zeolite.

* Sodium zeolite is capable of exchanging reversibly its sodium ion for hardness producing ion in water ($Ca^{2+}/Mg^{2+}$).

2) Process




* For softening of water by zeolite process, hard water is allowed to flow at a specified rate through a bed of zeolite ($Na_2Ze$) kept in a cylinder.



* The hardness causing ions ($Ca^{2+}, Mg^{2+}$) in hard water are then retained by zeolite as $CaZe$ and $MgZe$ while the outgoing water contains sodium salts ($NaCl$, etc) which is stored in storage for regeneration of $Na_2Ze$

* The reactions taking place during softening process are:

$$Na_2Ze + CaCl_2 \longrightarrow CaZe + 2NaCl$$
$$Na_2Ze + MgSO_4 \longrightarrow MgZe + Na_2SO_4$$
$$Na_2Ze + Ca(HCO_3)_2 \longrightarrow CaZe + 2NaHCO_3$$

(Zeolite) (Sodium salt)

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Q9) Write short note on.

i) Disadvantages of Lime Soda Method.

i) The lime soda method cannot be used for domestic purpose because it is difficult to find amount of lime-soda required.

ii) Skilled and careful supervision is required for efficient and economical operation.

iii) It creates the problem of disposal of large amount of sludge.

iv) The hardness of water is not completely removed, 15-30 ppm hardness of water is obtained.

2) Regeneration process in Zeolite method

<Same diagram as previous Q8>

* When the zeolite is completely converted into calcium and magnesium zeolites, softening of water stops and zeolite gets exhausted.

* At this stage, supply of hard water is stopped and exhausted zeolite is regenerated by treating the zeolite bed with a concentrated 10% brine NaCl soln. i.e

$$CaZe \text{ (or } MgZe) + 2NaCl \longrightarrow Na_2Ze + CaCl_2 \text{ (or } MgCl_2)$$

exhausted zeolite — brine — regenerated zeolite — washings

The washings (containing $CaCl_2$ & $MgCl_2$) are led to drain and regenerated zeolite bed thus obtained is used again for softening purpose.

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Q 10> Differentiate between hot lime soda and cold lime soda method.

| Hot lime Soda method | Cold lime Soda method. |
|---|---|
| i> It is carried out at high temperature (80°-150°C) | i> It is carried out at room temperature (25°-30°C) |
| ii> It is a rapid process | ii> It is a slow process. |
| iii> No coagulent required | iii> Use of coagulent is necessary |
| iv> Filtration is easy as viscosity of water is low. | iv> Filtration is not easy. |
| v> Residual hardness is 15-30 ppm. | v> Residual hardness is 60 ppm |
| vi> Dissolved gases are removed. | vi> Dissolved gases are not removed. |
| vii> It has high softening capacity | vii> It has low softening capacity. |