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RTU ROLL NO. ....

ARYA GROUP OF COLLEGES

I MID TERM EXAMINATION 2018-19 (I Sem.)

1FY2-03_Engineering Chemistry

BRANCH: Common to All

Max Marks:- 80 **Time:- 2 hrs.**

PART A (Attempt All)

Q.1
(b) Explain the terms Priming & Foaming.
(c) What is Galvanization?
(d) Write down requisites of potable water. 5*2
(d) Explain Pilling Bedworth Rule
(e) What are different units in which the hardness of water can be expressed?

PART B (Attempt any Four)

Q.2
(a) Discuss the Zeolite process of water softening.
(b) Calculate the quantity of lime and soda required for softening 50,000 litres of water containing the following salts per litre. $Ca(HCO_3)_2$ = 8.1 mg/lit.; $Mg(HCO_3)_2$ = 7.5 mg/lit.; $CaSO_4$ = 13.6 mg/lit. $MgSO_4$ = 12 mg/lit.; MgCl = 2 mg/lit.; NaCl = 4.7 mg/lit. 4*10
(c) Explain the Break point Chlorination in detail.
(d) Explain Deionization method of water softening in detail.
(e) Discuss caustic embrittlement.
(f) Write short note on (any two):
    (i) Galvanic Cell Corrosion
    (ii) Pitting Corrosion
    (iii) Scale & Sludge Formation

PART C (Attempt any Two)

Q.2
(a) What is corrosion? Explain the mechanism of electrochemical corrosion in detail.
(b) Discuss EDTA Complexometric titration of hardness determination. 2*15
(c) Discuss various methods used for protection from corrosion.

Solution of I Mid-term Engineering Chemistry (1FY2-03)

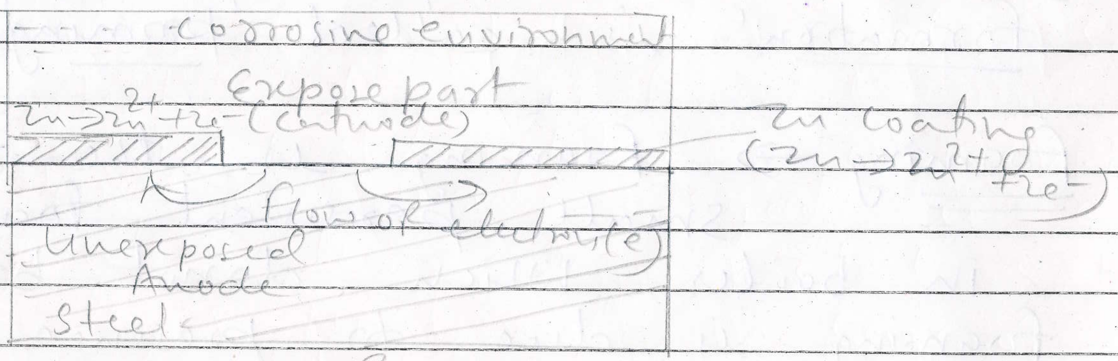
PART-A

Q.1 a) **Priming** → When a boiler is Steaming (producing steam) rapidly, some particles of the liquid water are carried along with the steam. This process of 'wet steam formation' is called 'priming'.

Foaming → Foaming is the formation of small persistent foam or bubbles in boiler, which donot break easily. Foaming is due to presence of substance like oils (which greatly reduce the surface tension of water.

Disadvantages → Dissolved salts in boiler water are carried by the wet steam to super heater parts where get deposited and reduces the efficiency of boiler.

b) **Galvanization** → Galvanization means zinc coating on the iron metal surface, as zinc coating is anodic to iron, it is corroded sacrificially while exposed iron being cathodic is protected. Moreover anode area (coating surface) is large while cathode area is small, therefore corrosion occurs at a slow and uniform rate.



functioning of anodic coating

Ⓒ Requisites of Potable Water →

Physical → i) It should be colourless & odourless.
ii) It should be pleasant in taste.
iii) It should be perfectly cool.
iv) Its turbidity should be less than 10 ppm.

Chemical → i) It should be free from harmful gases like H_2S, CO etc.

ii) It should be free from harmful minerals such as lead, arsenic, chromium etc.

iii) Total hardness should be less than 500 ppm

iv) TDS should be less than 500 ppm.

v) Chlorides, fluorides & Sulphate should be less than 250 ppm, 1.5 ppm & 250 ppm resp.

vi) Its alkalinity should be range of 7.00 - 8.5.

Biological → Potable water should be free from disease producing micro-organisms.

ⓓ **Pilling Bedworth Rule** → The oxide layer can be protective or non-protective depending upon the ratio of volume of metal oxide to the volume of metal consumed. This is known as "pilling bedworth ratio"

$$\text{Pilling Bedworth Ratio} = \boxed{\frac{\text{Volume of the metal oxide formed}}{\text{Volume of metal Consumed}}}$$

Eg → ① volume of oxide layer is less than the volume of metal consumed sothat non-protective layer is formed in the case of alkali & alkaline earth metals.

Eg - ② volume of oxide layer is equal or greater than the metal sothat protective layer is formed in case of Al, Cr, W etc.

ⓔ <u>Different units of hardness</u> →

1) <u>Parts per million (ppm)</u> → It is defined as the 1 part of $CaCO_3$ eq. hardness in 10^6 parts of water.

2) **Milligrams Per litre (mg/lit)** → It is defined as the number of mg of $CaCO_3$ present in one lit of water.

$1 \, mg/lit = 1 \, ppm$

$(1L = 1kg = 10^6 mg)$

3) **Degree Clarke (°cl)** → It is defined as the parts of $CaCO_3$ eq hardness per 70,000 parts of water.

4) **Degree French (°fr)** → It is defined as the parts of $CaCO_3$ eq hardness 10^5 part water

$$\boxed{1 \, ppm = 1 \, mg/lit = 0.1°fr = 0.07°cl}$$

PART - B

Q.2

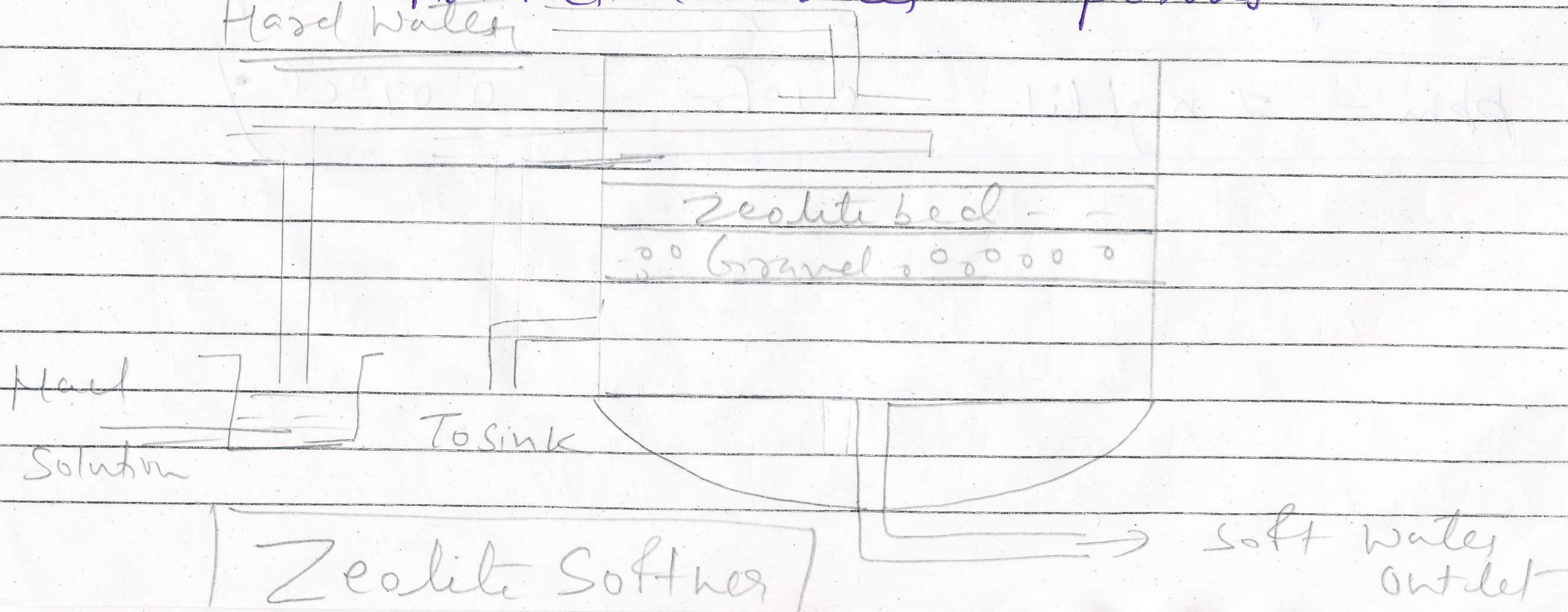
ⓐ Zeolite Process → In this process, water is softened with the help of a natural or artificial zeolite. Zeolites are hydrates of sodium aluminium orthosilicates.

→ Zeolites are represented by $Na_2O.\overset{Al_2O_3}{\underline{R_2O_3}}\,xSiO_2.yH_2O$

→ Zeolites are of two types -

Natural Zeolites - non-porous

Artificial Zeolites - porous



Zeolite Softner

→ The zeolite or permutit is put in suitable columnn and hard water is percodated through it.

→ The permutit can be represented as Na_2Z and after base exchange it is converted into CaZ & MgZ. Thus hardness causing ions (Ca^{2+} / Mg^{2+}) are retained by the bed & equivalent amt. of Na^+ ions released in water.

$$Na_2Z + Ca(HCO_3)_2 \longrightarrow 2NaHCO_3 + CaZ$$
$$Na_2Z + MgCl_2 \longrightarrow 2NaCl + MgZ$$

→ Regeneration → After sometimes, the zeolite is completely converted into Ca^{2+}/Mg^{2+} zeolite and gets exhausted. The zeolite conbe represented by passing 10% NaCl solution into the bed.

$$CaZ + 2NaCl \longrightarrow Na_2Z + CaCl_2$$
$$MgZ + 2NaCl \longrightarrow Na_2Z + MgCl_2$$

$CaCl_2$ / $MgCl_2$ are rinsed out from the zeolite bed by passing soft water through it. Soft water obtained by this method is used mostly for laundry purpose.

Merits of Zeolite Process → ① Softening Plant occupies small area.

② Softening plant is of 10 ppm hardness only.

③ There is no risk of sludge formation in water.

④ It requires less maintenance.

Demerits of Zeolite Process → ① Turbid water Cannot be treated satisfactorily as it may choke zeolite bed.

② Treated water contains higher concentration of sodium salts.

③ This method only replaces Ca^{2+}/Mg^{2+} & not all others ions (eg HCO_3^-/CO_3^{2-})

ⓑ **Solution:-** Conversion of $CaCO_3$ equivalent

S.N	Substance	Amount of	Multiplication factor	$CaCO_3$ equivalent
1	$Ca(HCO_3)_2$	8.1 mg/lit	100/162	$8.1 \times \frac{100}{162} = 5$ mg/lit
2.	$Mg(HCO_3)_2$	7.5 mg/lit	100/146	$7.5 \times \frac{100}{146} = 5.137$ mg/lit
3.	$CaSO_4$	13.6 mg/lit	100/136	$13.6 \times \frac{100}{136} = 10$ mg/lit
4.	$MgSO_4$	12 mg/lit	100/120	$12 \times \frac{100}{120} = 10$ mg/lit
5.	$MgCl_2$	2 mg/lit	100/95	$2 \times \frac{100}{95} = 2.105$ mg/lit
6	NaCl	4.7 mg/lit	Does not impart hardness	

Lime Required $= \frac{74}{100}\left[Ca(HCO_3)_2 + 2 \times Mg(HCO_3)_2 + MgSO_4 + MgCl_2 \text{ as } CaCO_3 \text{ eq.}\right]$

$\times$ vol. of water

$$= \frac{74}{100}\left[5 + (2 \times 5.137) + 10 + 2.105\right] \times 50{,}000 \text{ lit of water}$$

$$= \frac{74}{100}\left[27.379\right] \text{mg/lit} \times 50{,}000 \text{ lit}$$

$$= 1010\,30\,23 \text{ mg} = 1.0130 \text{ kg}$$

<u>Soda Required</u> →

$$\frac{106}{100}\left[CaSO_4 + MgSO_4 + MgCl_2\right] \text{ as } CaCO_3 \text{ eq} \times 50{,}000 \text{ lit } H_2O$$

$$= \frac{106}{100}\left[10 + 10 + 2.105\right] \text{mg/lit} \times 50{,}000$$

$$= \frac{106}{100}\left[22.105\right] \text{mg/lit} \times 50{,}000$$

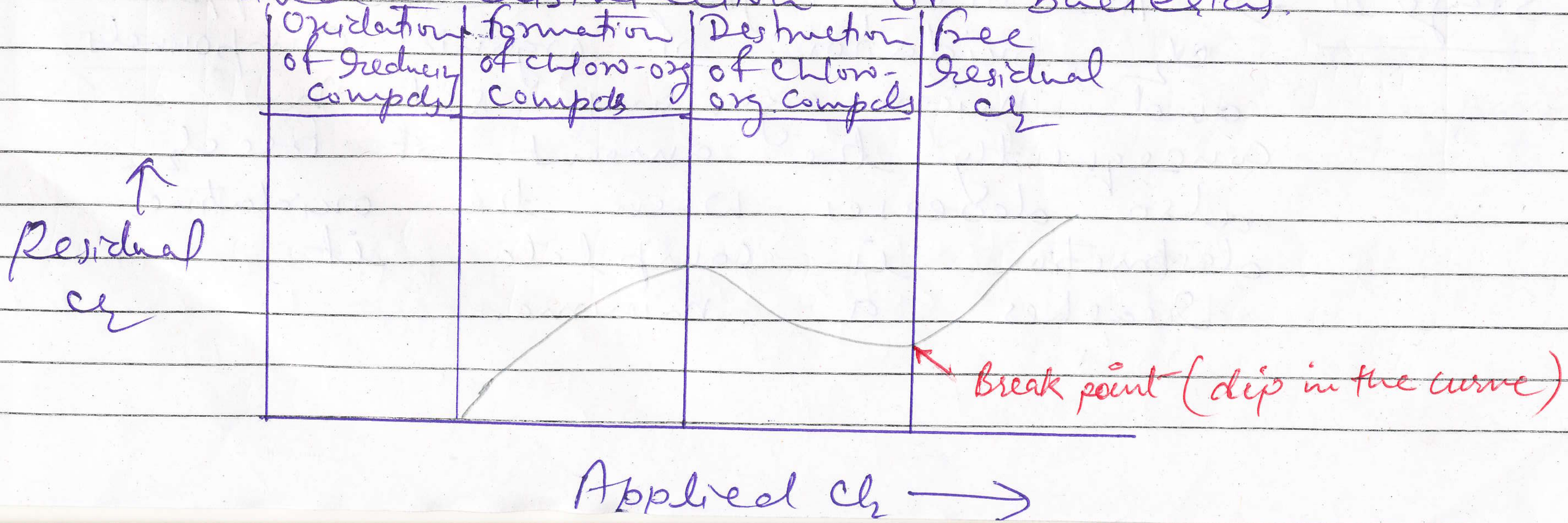
$$= 1171565 \text{ mg} \times \frac{1 \text{ kg}}{10^6} = 1.171 \text{ kg}$$

ⓒ Break Point Chlorination →

Chlorination of water to such an extent that not only the living organisms, but other impurities in water are completely destroyed is called "Break Point Chlorination" It is also known as Free Residual

Chlorination.

→ When in water Cl_2 is added it is consumed for different reactions, such as oxidation of reducing species present, chlorination of any organic substances and free ammonia and disinfection of bacteria.



Stage I → Initially for lower dosage of Cl_2, there is no free residual Cl_2, since all the added Cl_2 get consumed in complete oxidation of reducing substances present in water.

Stage II → As the amount of Cl_2 dosage is increased, amount of residual Cl_2 also show steady increase. This stage corresponds to formation of chloro-organic compounds without oxidising them.

Stage III → At still higher dose of applied Cl_2, oxidation of organic compounds and micro-organisms set in. Consequently the amount of free Cl_2 also decreases when the oxidative destruction is complete it reaches a minima.

Stage IV → After minima, the added cl_2 is not used in any reaction. Thus the residual cl_2 keep on increasing in direct proportion to added cl_2.

Hence, for effectively killing the micro-organism, sufficient cl_2 has to be added. Addition of cl_2 in such dosages is called Break Point Chlorination. This indicates the point at which free cl_2 begins to appear and resulting in appearence of water free from bad odour & taste.

Advantages → ① It ensures complete distruction of organic compounds which imparts colour, bad odour & unpleasant taste.

② It completely destroys all the disease producing bacterias.

ⓔ **Caustic Embrittlement** → Caustic embrittlement is predominately a type of stress corrosion initiated by caustic $NaOH$.

→ The rivets, joints of boiler plates, become brittle by the action of caustic alkalies formed during steam generation

→ The phenonmenon is more pronounced if water has been treated by L-S process, it is possible that some residual sodium carbonate may be still there in the water.

$$Na_2CO_3 + H_2O \longrightarrow 2NaOH + CO_2 \uparrow$$

→ The $NaOH$ so-formed makes the water alkaline. This caustic water enters the minute cracks present in the inner wall of the boilers.

→ On evaporation of water the conc. of dissolved NaOH increases, which attacks the iron converting it to sodium ferroate (Na_2FeO_2) by concentration cell reaction. It causes embrittlement of boiler walls, particularly in parts like joints, rivets, bends etc. which are under constant stress.

Anode (oxidation) Cathode (Reduction)

Iron at rivets, bends, joints	Conc. NaOH	Dilute NaOH	Iron at plane Surfaces

$$Fe + 2NaOH \longrightarrow Na_2FeO_2 + H_2\uparrow$$

$$3Na_2FeO_2 + 4H_2O \longrightarrow 6NaOH + Fe_3O_4 + H_2\uparrow$$

Prevention → ① Lagnin or tanin can be added to boiler water which block the cracks in the boiler wall thus preventing the entry and attack of NaOH into such areas.

② By using sodium phosphate instead of sodium carbonate for softening purpose.

③ It has been noted that caustic embrittlement can be prevented if Na_2SO_4 is added to the boiler water.
The ratio of $NaOH / Na_2SO_4$ is kept as 1:1, 2:1 and 3:1 in boilers working at pressure at 10, 20 & 30 atm.

Part-C

Q3 ⓐ **Corrosion** → Corrosion is the destruction of metal by the electrochemical reaction of metal with its natural environment. Metals are converted to their oxides, sulphides, carbonates etc by the process of corrosion.

$$\begin{tikzcd}
\text{Metal (A state of high energy)} \arrow[d, shift right, "\text{corrosion (oxidation)}"'] \\
\boxed{\text{Metallic compounds}} + \text{Energy} \arrow[u, shift right, "\text{metallurgy (reduction)}"']
\end{tikzcd}$$

(A state of lower energy)

Electrochemical Theory of corrosion →

→ Electrochemical theory is a most accepted theory and takes place under wet or moist conditions.

→ The essitial features of this theory →

i) The presence of a conducting medium.

ii) the formation of anodic and cathodic areas between which current flows through the conducting medium.

iii) occurence of oxidation (corrosion) at anodic area which generates metallic ions.

iv) formation of non-metallic ions like OH^- at cathode.

v) Diffusion of metallic & non-metallic

ion towards each other through conduction medium & formation of corrosion products somewhere between anodic & cathodic areas.

Mechanism → At anodic area $M \rightarrow M^{n+} + ne^-$ (oxidation)

The cathodic reaction consume electrons with either by -

① evolution of H_2 gas:

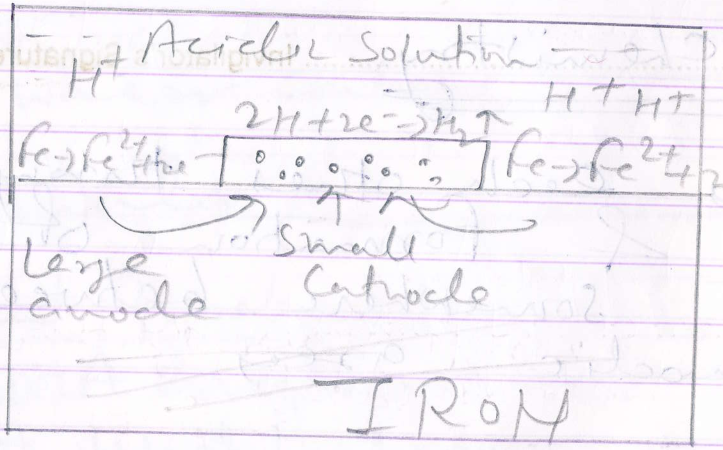
② Absorption of O_2 gas

ⓐ Evolution of hydrogen type corrosion

usually in anodic environment

In case of iron, the anodic Rxn

$Fe \longrightarrow Fe^{2+} + 2e^-$ (oxidation)



Mechanism of wet corrosion by H_2 evolution

The liberated electrons flow through the metal from anode to cathode where H^+ ions (of acidic solution) are eliminated as hydrogen gas.

$2H^+ + 2e^- \longrightarrow H_2\uparrow$ (reduction)

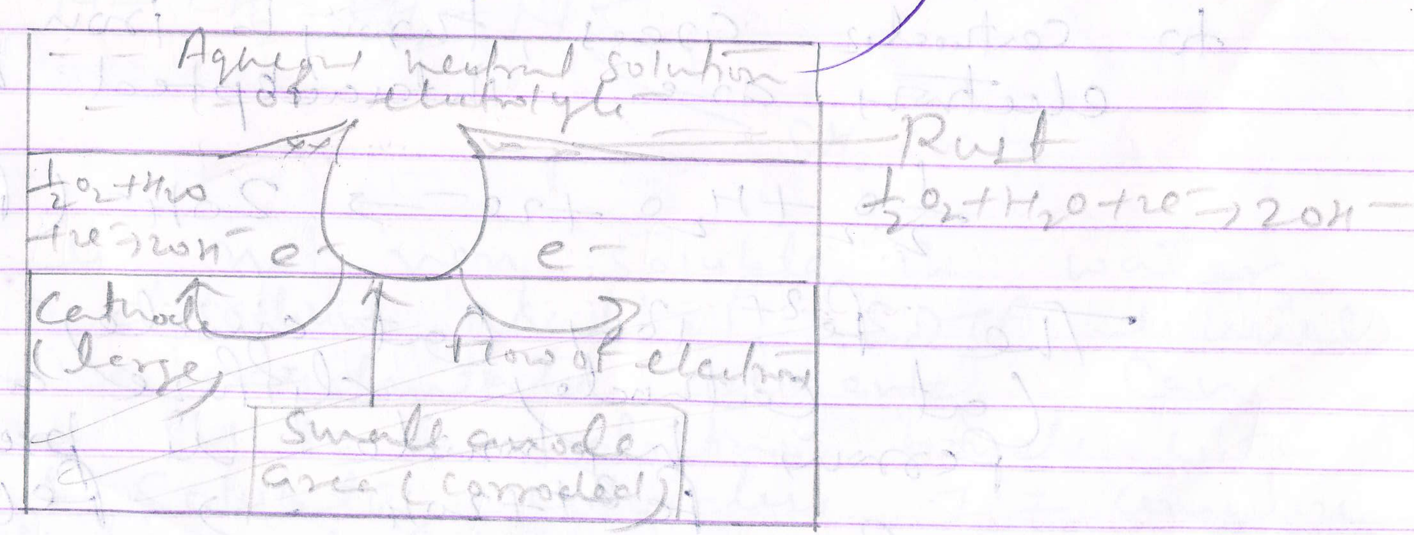
$Fe + 2H^+ \longrightarrow Fe^{2+} + H_2\uparrow$

Overall Rxn

Hydrogen Type Corrosion

ⓑ Absorption of oxygen occurs generally in neutral or weakly alkaline medium

Eg → Rusting of iron in neutral aqueous solution (like NaCl)



Mechanism of Wet Corrosion by Oxygen absorption

The surface of iron is usually coated with a thin film of iron oxide.

→ Anodic areas are coated on the surface of metal some cracks developed in oxide film, while the metal part act as cathode. In this case, the anodic areas are small surface parts while nearly the rest of metal surface act as cathode.

At Anode $Fe \rightarrow Fe^{2+} + 2e^-$ (oxidation)

The liberated electrons flows from anode to cathode areas, through iron metal, where electrons are interaccepted by dissolved O_2.

$$\frac{1}{2}O_2 + H_2O + 2e^- \rightarrow 2OH^- \text{ (Reduction)}$$

The Fe^{2+} ions (at anode) and OH^- ions (at cathode) diffuse and they combine Ferrous hydroxide is precipitated.

$$Fe^{2+} + 2OH^- \rightarrow Fe(OH)_2$$

If enough oxygen is present

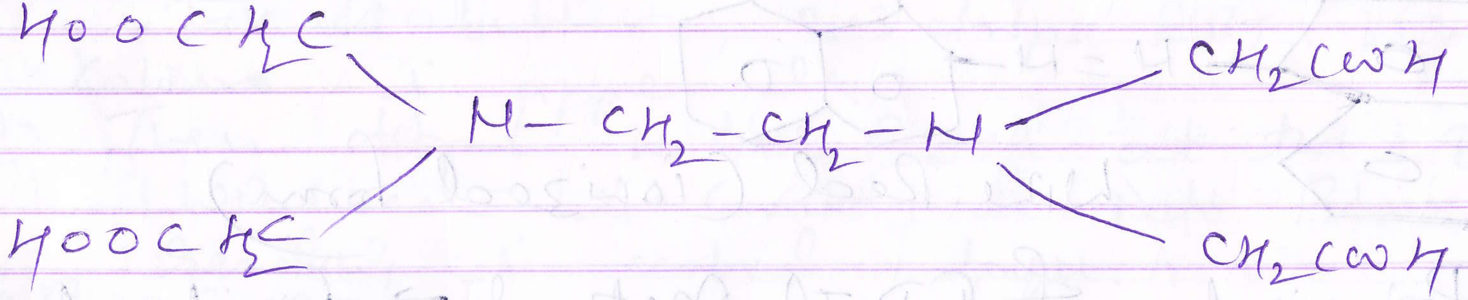
$$4Fe(OH)_2 + O_2 + 2H_2O \rightarrow \underline{4Fe(OH)_3} \text{ Yellow Rust}$$

is formed.

⑥ Estimation of water Hardness by EDTA Method

→ The estimation of water hardness is done by complexometric titration using standard EDTA as titrant and EBT as an indicator.

① **EDTA** → Ethylene diamine tetra acetic acid is a strong complexing agent.



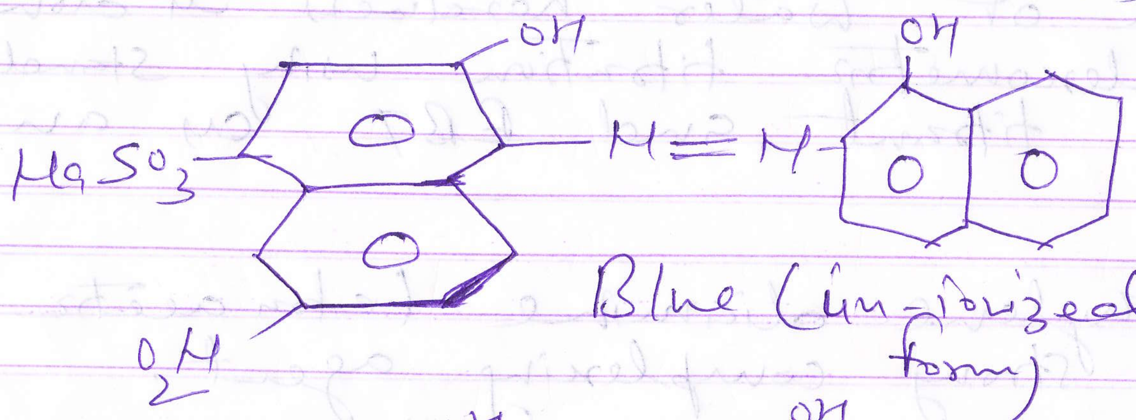
→ As it is not very soluble in water hence disodium salt of EDTA is used

→ EDTA is a hexadentate ligand can forms 4 to 6 dative bonds with metal & soluble, colourless, 1:1 complex is formed.

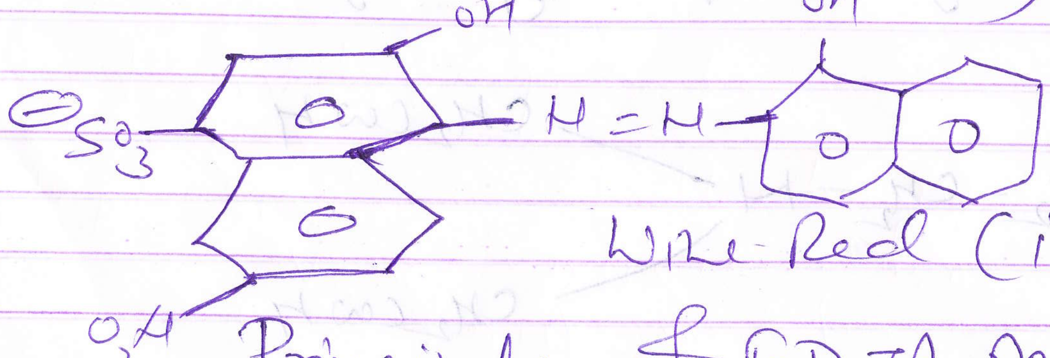
② **EBT** → Eriochrome Black-T

It is a azo dye, capable of

forming soluble wine wine red complex with metal ions (Ca^{2+}/Mg^{2+}) in water.



Blue (un-ionized form)



Wine Red (ionized form)

<u>Principle of EDTA Method</u> → first, the EBT which is blue in colour forms an unstable complex

$$[Ca^{2+}/Mg^{2+}] + EBT \xrightarrow[pH-9-10]{} M-EBT \text{ complex (wine Red)}$$

⑥ As this solution is titrated against EDTA the wine red colour is changed into blue

$$[M-EBT] + EDTA \longrightarrow [M-EDTA] + EBT \text{ (Blue)}$$

Preparation of solution → ① Standard Hard water →
1 gm $CaCO_3$ is dissolved in HCl and then heated on water bath, the residue left behind is dissolved in 1 lit dis. H_2O.

② **Preparation of EDTA** → 0.01 M EDTA is prepared by 3.78 gm of disodium EDTA in 1 lit dis H_2O.

③ **Buffer Solution EBT** → By dissolving 0.5gm EBT in 100ml alcohol.

④ **Buffer Solution** → 67.5 gm NH_4Cl in 570 ml NH_3 Solution

Procedure → ① fill the Burette with EDTA & add 3-4 ml buffer, 2-3 drops EBT wine-red colour is appeared

② Then titrate with EDTA at the End point wine red is converted into Blue, This reading is noted down.

OBSERVATION → Volume of standard hard water — 50ml

Volume of EDTA consumed — V_1 ml.

Step-I (Strength of EDTA Solution)

1 ml SHW contains — 1 mg $CaCO_3$

50 ml SHW contains — 50mg $CaCO_3$ eq

V_1 ml EDTA consumed for — 50mg $CaCO_3$ eq

1 ml EDTA used for — $\frac{50}{V_1}$ mg $CaCO_3$ eq

Step-II (Total Hardness)

V_2 ml EDTA consumed for —— 50 ml Tap water

1 ml EDTA used for —— $\frac{50}{V_1}$ mg $CaCO_3$ eq

V_2 ml EDTA used for —— $\frac{50}{V_1} \times V_2$ mg $CaCO_3$ eq

50 ml Tap water contains hardness —— $\frac{50}{V_1} \times V_2$ mg $CaCO_3$

1 ml Tap water contains —— $\frac{50}{V_1} \times \frac{V_2}{50}$

1000 ml Tap water —— $\frac{50}{V_1} \times \frac{V_2}{50} \times 1000 = \frac{V_2}{V_1} \times 1000$ ppm

Step-III (Permanent Hardness)

V_3 ml EDTA used for —— 50 ml Boiled water

1 ml EDTA used for —— $\frac{50}{V_1}$ mg $CaCO_3$ eq

V_3 ml EDTA used for —— $\frac{50}{V} \times V_3$ mg $CaCO_3$ eq

50 ml Boiled water contains hardness $\frac{50}{V_1} \times V_3$ mg $CaCO_3$

1 ml Boiled water —— $\frac{50}{V_1} \times \frac{V_3}{50} \times 1000$

1000 ml Boiled water —— $= \frac{V_3}{V_1} \times 1000$ ppm

Temporary Hardness = Total Hardness − Perm. Hardness

$= \frac{V_2}{V_1} \times 1000 - \frac{V_3}{V_1} \times 1000 = \frac{V_2 - V_3}{V_1} \times 1000$ ppm