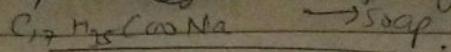


Soaps - $\text{R}_3\text{C}(\text{O})\text{Na}$ salts of higher fatty acids.



Sodium soap is soluble in hard water.

But Mg & Ca soap is not soluble in hard water.

TDS - Total dissolved solids (present in H₂O systems).

Hardness

Soluble salts of Mg & Ca present in water make the water hard.

The most insoluble salts are carbonates & phosphates.

The water becomes hard on presence of soluble salts of Mg & Ca, some heavy metals, ~~SO₄²⁻~~ etc.

Q. Why hard water does not give lather with soap?
(Explain & give reactions).

Hard water cannot be called impure water.

Types of Hardness

Permanent hardness

* Non-Carbonate hardness.

Chlorides & sulphates of Mg^{2+} & Ca^{2+} etc.

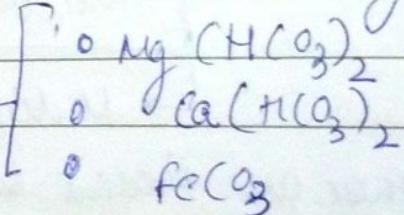
* temporary hardness.

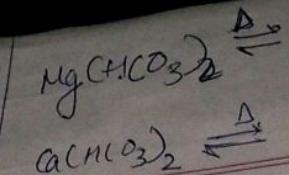
(Can be removed by boiling).

* Carbonate hardness

\rightarrow bicarbonates of Ca^{2+} & Mg^{2+}

3 salts
that cause
Temp.
hardness.





(Reactions from book)

degree of hardness: how hard the water is.
It is measured in ppm (parts per million)

e.g. hard water which contains:

$$\text{CaCl}_2 = 10 \text{ ppm}$$

$$\text{MgSO}_4 = 2 \text{ ppm}$$

$$\text{NaCl} = 5 \text{ ppm} \rightarrow \text{won't cause hardness}$$

$$\text{K}_2\text{SO}_4 = 5 \text{ ppm.} \rightarrow \text{won't cause hardness.}$$

(No salt of potassium causes hardness).

Convert the salts into equivalents of CaCO_3 & then add them. (by equating moles).

$$111 \text{ g } \text{CaCl}_2 = 100 \text{ g } \text{CaCO}_3.$$

$$80.5 \text{ g } \text{CaCl}_2 = \left[\frac{80.5}{111} \times 100 \right] \text{ CaCO}_3$$

↳ Multiplication factor.

To convert Amount of any hardness causing salt into equivalents of CaCO_3 ,

$$\frac{\text{Amount of salt} \times \text{Molecular weight of } \text{CaCO}_3}{\text{Molecular weight of salt}}$$

↳ Multiplication factor.

(These are bivalent salts ~~(dilute)~~)

Q. NaAlO_2 multiplication factor?
(Molecular weight = 82).

→ $\text{Na}^+ \text{ AlO}_2^-$ (this is monovalent salt).

$$\text{multiplication factor} = \frac{100}{82 \times 2}$$

Q. $\text{AlO}_3^- = 43 \text{ ppm}$: multiplication factor?

$$\rightarrow \frac{43 \times 100}{61 \times 2} \quad \begin{array}{l} \text{[As } \text{AlO}_3^{2-} \text{ is a monovalent salt,} \\ \text{so divide by 2]} \end{array}$$

Q. $\text{Mg}^{2+} = 30 \text{ ppm}$ multiplication factor

$$\rightarrow \frac{30 \times 100}{24} \quad \begin{array}{l} \text{(a bivalent salt).} \\ \text{(here we take atomic weight as} \\ \text{given instead of} \\ \text{molecular weight).} \end{array}$$

Exception:

Q. $\text{Al}_2(\text{SO}_4)_3 = (\text{mol wt} = 342)$,
(x ppm).

$$\rightarrow \left(\begin{array}{c} \text{Ca}^{2+} \\ | \\ \text{SO}_4^{2-} \end{array} \right) \text{ so, } \text{Al}_2(\text{SO}_4)_3 = x \times \frac{100}{342/3}$$

$$= x \times \frac{100}{\frac{114}{3}} \quad \begin{array}{l} \text{Multiplication} \\ \text{factor.} \end{array}$$

$$\frac{12 + 32}{3} = 14$$

Q. $\text{CO}_2 = 2 \text{ ppm}$

Convert to equivalent of calcium carbonate.

$$\rightarrow = \frac{2 \times 100}{44}$$

⇒ Units of hardness.

① ppm ② mg/L

2/1/17 Seminar

Date _____

Page _____

Imp. Prove that mg/L is same as ppm.

→ PPM. 1 part of $\text{CaCO}_3 / 10^6$ part of water.

mg/L : 1mg of $\text{CaCO}_3 / 1\text{L}$ of water

$$1\text{L} = 1000\text{g.} = 1000000 \text{ mg.} = 10^6 \text{ mg.}$$

∴ 1 part of $\text{CaCO}_3 \rightarrow 1/10^6$ part of water.

① Degree Clarke (${}^{\circ}\text{C}$)

→ It is the number of grains of CaCO_3 present per gallon of water where in 1 grain $\frac{1}{7000} \text{ lbs}$

$$\& 1 \text{ gallon} = 10 \text{ lbs.}$$

$$\text{No. of grains of } \text{CaCO}_3 / \text{gallons of water} = \frac{1}{7000 \times 10} = \frac{1}{70000}$$

Hence, it can be said that Degree Clarke is
1 part CaCO_3 per 70000 parts of water

② Degree French. (${}^{\circ}\text{F}$)

→ It is defined as no. of parts of CaCO_3 present per 10^5 parts of water

Relation b/w different Units

classmate

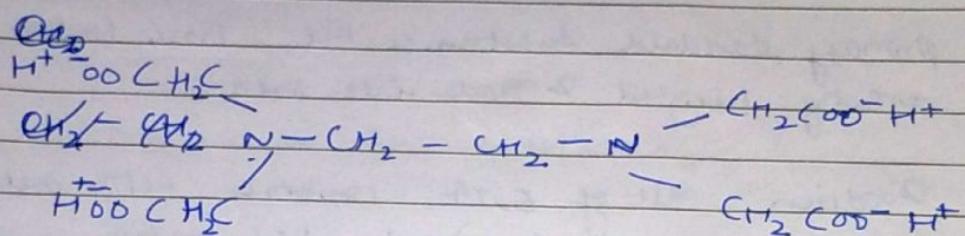
Date _____

Page _____

$$1 \text{ ppm} = 1 \text{ mgs/L} = 0.07^\circ \text{cl} = 0.1^\circ \text{Fr}$$

\Rightarrow Determination of hardness by EDTA method of water
By EDTA Method.

(Ethylenediamine tetraacetic acid)

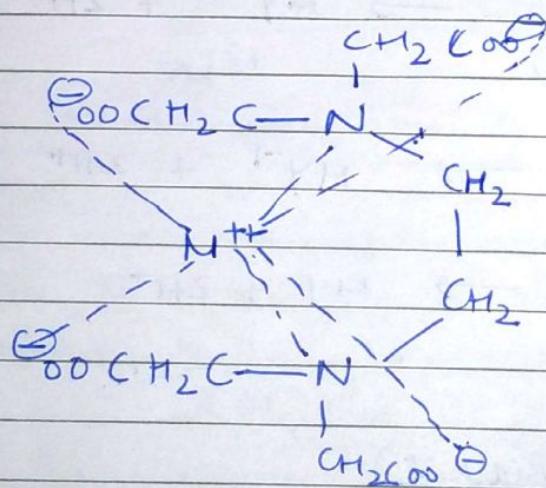


EDTA $\xrightarrow{\quad}$ Titrant.

EBT (Eriochrome Black T) $\xrightarrow{\quad}$ Indicator

~~EDTA~~ $\xrightarrow{\quad}$ Hexadentate Ligand.

Complex formed by metal ion.



Structure of EDTA / Mⁿ⁺ ion

Q: Why disodium salt of EDTA is used / preferred over EDTA?

→ ① Disodium salt of EDTA can be obtained in large amounts

of purity

② It is a primary standard (EDTA is secondary)

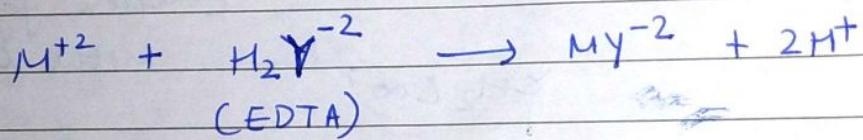
standard soln. → whose molarity, normality is known

secondary standard substances are those which cannot be directly weighed & made into solution.

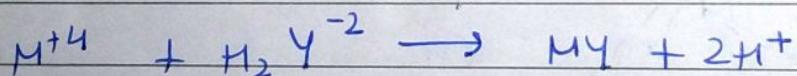
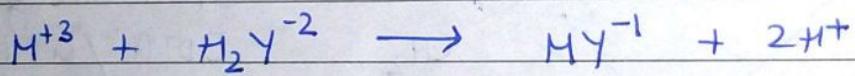
primary standard substances are those which can be directly weighed & made into soln.

③ Disodium salt of EDTA combines with metal ions (hardness causing ions) in 1:1 ratio.

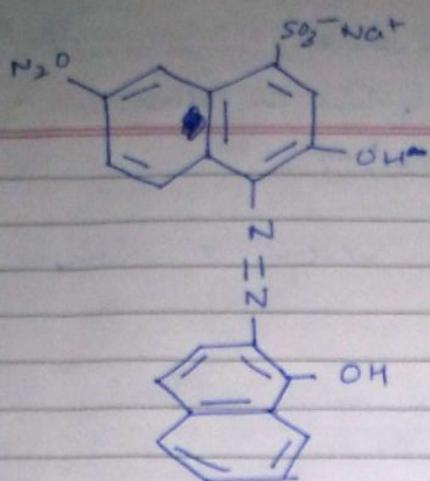
④ Irrespective of the charge on cation, resultant complexes have similar structure but differ in charges they carry. This can be indicated as below:



(EDTA)



⇒ EBT (Eriochrome Black T)



Special points about

- * It has 1 ~~sulphonic~~ ^{aromatic} acid group \rightarrow completely ionized
- * 2 phenolic groups \rightarrow partially ionized
- * It acts as a weak acid

Q: Why does it behave as an indicator?

\rightarrow Color.

In aqueous solution, it shows diff. colours at diff. pH values.

5 - 5.5 \rightarrow Red

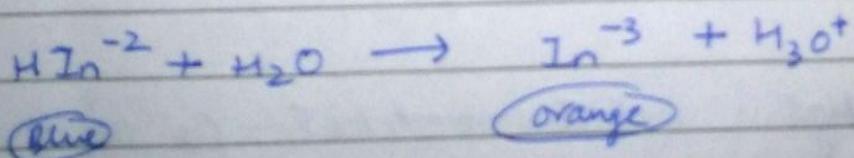
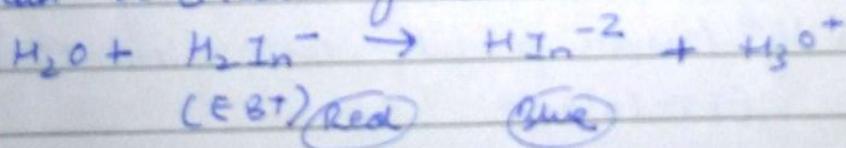
7 - 11 \rightarrow Blue

Above 11.5 \rightarrow yellowish orange

* Colour of $\text{EBT}^{\text{M}^{++}}$ complex is wine red.

* Show that EBT is pH sensitive indicator?

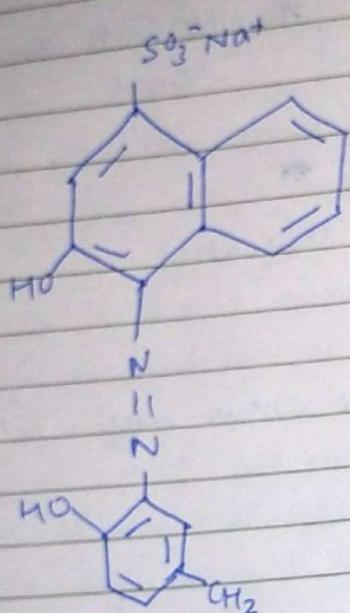
\rightarrow This can be shown by its reaction with water.



Q:

EBT has a T-shape structure & the powder form of EBT is black in colour.

Q. What is alternative to EBT?
Ans. Calmagite (it is more stable as it does not decompose on standing like EBT).

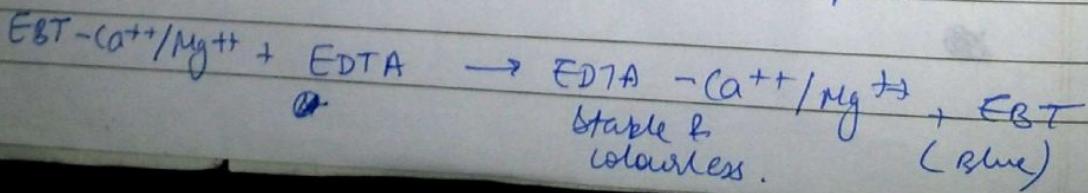
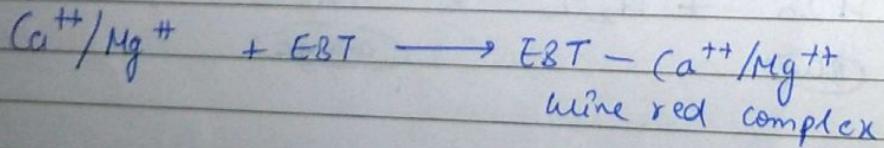


⇒ Methods of determination of hardness

(Complexo titration or EDTA method)

Principle of EDTA method

The hardwater in which hardness causing ions like Ca^{++} & Mg^{++} ions are present react with EBT to form $\text{EBT} - (\text{Ca}^{++}/\text{Mg}^{++})$



End point \rightarrow colour change from blue red

W.M.F.

Why EBT- $\text{Ca}^{++}/\text{Mg}^{++}$ Complex breaks up & EDTA- $\text{Ca}^{++}/\text{Mg}^{++}$ Complex is formed?

(Why EDTA Complex is more stable than EBT Complex)
EDTA is a hexadentate complex

① EDTA- $\text{Ca}^{++}/\text{Mg}^{++}$ complex is more stable as it has got six coordinate bonds in its structure.
EBT Complex has only three coordinate bonds.

② Dissociation constant of EDTA $\text{Ca}^{++}/\text{Mg}^{++}$ complex is more than EBT complex.

Q: Why the soln is blue?

\rightarrow Due to EBT formed in reaction. Not due to EDTA- $\text{Ca}^{++}/\text{Mg}^{++}$ Complex

\Rightarrow Methods of determination

1. Preparation of standard ^(SHW) ~~titration~~ hard water & knowing its strength in mgs/mL.

2. Determination of strength of unknown EDTA

- By titrating against known SHW

SHW v/s unknown EDTA (v_1)

3. Determination of total hardness of unknown water sample
- water sample v/s known EDTA. (v_2)

4. Determination of permanent hardness

- Boiled water v/s known EDTA (v_3)

$$\text{Total hardness} = \frac{V_2}{V_1} \times \frac{\text{Vol of SHW} \times \text{Strength of SHW (mg/mL)}}{\text{Vol of Sample water}}$$

$$\times \frac{1000}{1} = \text{_____ ppm}$$

$$\text{Permanent hardness} = \frac{V_2}{V_1} \times \frac{\text{Vol of SHW} \times \text{Strength of SHW (mg/mL)} \times 1000}{\text{Vol of Boiled water}} = \text{_____ ppm}$$

$$\text{Temporary hardness} = \text{Total} - \text{Permanent}$$

\Rightarrow in case strength of EDTA is given,

$$\text{Total hardness} = V_2 \times \frac{\text{Strength of EDTA (mg/mL)} \times 1000}{\text{Vol. of sample water}}$$

$$\text{Permanent hardness} = \frac{V_2}{V_1} \times \frac{\text{Strength of EDTA (mg/mL)} \times 1000}{\text{Vol. of boiled water}}$$

Q: Why strength of salts is converted into equivalents of CaCO_3 ?

- \rightarrow ① for ease of calculation, its mol. wt is 100g.
- ② during softening processes, (removal of hardness), most of the hardness causing salts are precipitated in form of CaCO_3 .

Ans 7. (1)

Tutorial Sheet - I

Water Treatment

classmate

Date _____
Page _____

~~$\times 1000$~~

Ans 7. (i) total hardness = $\frac{V_2}{V_1} \times \frac{V_{straw} \times Straw (mg/L)}{V_{sample water}} \times 1000$

permanent hardness = $\frac{V_3}{V_1} \times \frac{V_{straw} \times Straw (mg/L)}{V_{sample water} V_{boiled water}} \times 1000$

$$V_1 = 20 \text{ mL}$$

$$V_2 = 30 \text{ mL}$$

$$V_3 = 10 \text{ mL}$$

$$Straw = 100 \text{ mL}$$

$$Straw = 0.5 \text{ g / } 500 \text{ mL} = \frac{0.5 \times 1000}{500} = 1 \text{ mg/mL}$$

$$V_{sample water} = 100 \text{ mL}$$

$$V_{boiled water} = 100 \text{ mL}$$

$$T.H = \frac{30}{20} \times \frac{100 \times 1}{100} \times 1000 = \frac{3000}{2} \\ = 1500 \text{ ppm}$$

$$P.H = \frac{10}{20} \times \frac{100 \times 1}{100} \times 1000 = 500 \text{ ppm}$$

$$\text{Temp. H} = 1500 - 500 \\ = 1000 \text{ ppm}$$

An alternative to EBT - Calgonite

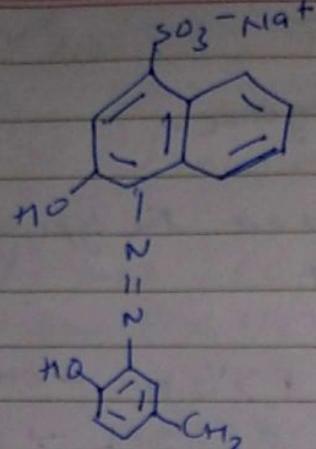
(A/Equivalent to EBT)

it is more stable & doesn't decompose on standing

9/11/17
classmate

Date _____

Page _____



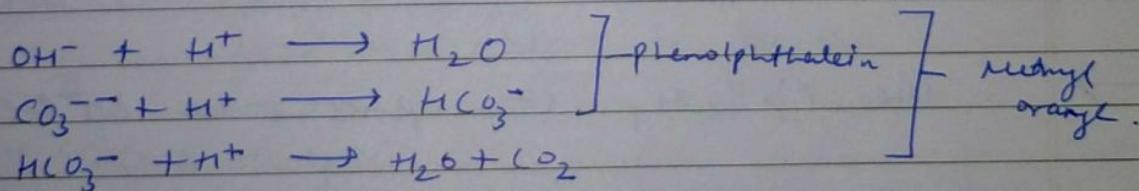
ALKALINITY

- ① Caustic alkalinity — OH^- , CO_3^{--}
- ② Temporary hardness — HCO_3^-

Drinking water is always slight alkaline.
pH should always be a lit above \neq not below.

Determination of ALKALINITY

Acid-Base titration



Indicators used \rightarrow Phenolphthalein (slightly acidic)

pH range is different for both.

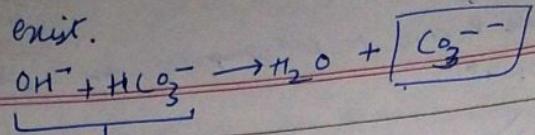
methyl orange has a wider pH range.

methyl orange (slightly basic)

V.V. TITRATES

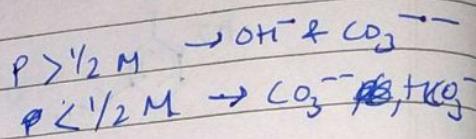
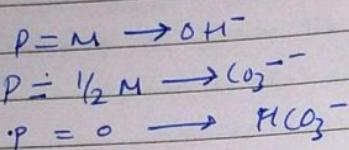
Q: Is it possible that all three ions are present together? And Why?

→ All three ions cannot exist as one combination cannot exist.



This comb. can't exist together.

Phenolphthalein is used to detect the type of ion
(alkalinity causing ion) present.



Reading	OH^-	CO_3^{2-}	HCO_3^-
$p = 0$	Nil	Nil	M
$p = M$	Nil	Nil	Nil
$p = \frac{1}{2}M$	Nil	Nil	Nil
$p > \frac{1}{2}M$	($2p - M$)	$2(M - p)$	Nil
$p < \frac{1}{2}M$	Nil	$2p$	$M - 2p$

Q:

$$\text{Prove that } \text{CO}_3^{2-} = 2(M-p) \& \text{OH}^- = 2p - M$$

when $p > \frac{1}{2}M$

→

When $p > \frac{1}{2}M$, ions present are $\text{OH}^- \& \text{CO}_3^{2-}$

$$P = \text{OH}^- + \frac{1}{2} \text{CO}_3^{2-}$$

$$M = \text{OH}^- + \text{CO}_3^{2-}$$

$$P - M = -\frac{1}{2} \text{CO}_3^{2-}$$

$$M - P = \frac{1}{2} \text{CO}_3^{2-}$$

$$2M - 2P = \text{CO}_3^{2-}$$

$$\cancel{2} (M - P) = \text{CO}_3^{2-}$$

1.

$$M = OH^- + 2(M - P)$$

$$\checkmark \boxed{2P - M = OH^-}$$

hence, proved.

a) Prove that $CO_3^{2-} = 2P$ & HCO_3^- is $M - 2P$
where $P < 1/2 M$

$$\rightarrow \cancel{M = 1/2 CO_3^{2-}} \quad P = \cancel{\frac{1}{2} CO_3^{2-}} + \cancel{OH^-} \\ \cancel{P = \frac{1}{2} CO_3^{2-}} + HCO_3^- \\ \cancel{P - \cancel{P}} = \cancel{\frac{1}{2} CO_3^{2-}}$$

$$P = 1/2 CO_3^{2-} \Rightarrow \boxed{2P = CO_3^{2-}}$$

$$M = CO_3^{2-} + HCO_3^-$$

~~$$M = 2P + HCO_3^-$$~~

$$\boxed{M - 2P = HCO_3^-}$$

Boiler feed water problems

if we feed hard water in boilers:

- scale & sludges
- Boiler corrosion
- Caustic Embrittlement
- Priming & foaming
- Carry over

1. Scale & sludges

Sludge: it is a soft, loose, slimy precipitate formed

in the colder portions of the boiler by salts whose solubility is more in hot water & may get precipitated in colder portions.

Eg: MgCl_2 , MgCO_3 , MgSO_4 etc.

removal: By using wire brush

disadvantages of sludge: ① Poor conductor of heat
② blocks pipe connections, plug openings thereby causing choking of pipes

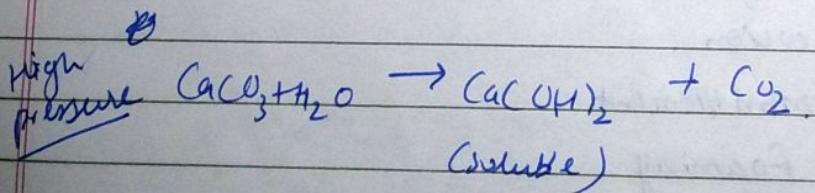
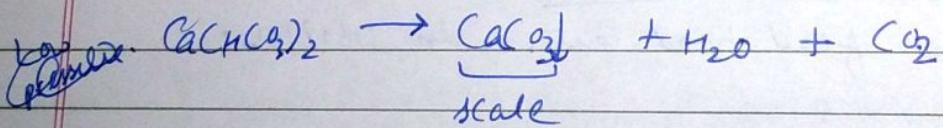
prevention: ① By using softened water
② By blow down operation

scales: scales are hard deposits sticking firmly to the walls of the boiler.

Reasons for scale formation:

1) Due to $\text{Ca}(\text{HCO}_3)_2$.

This scale is formed only in low pressure boilers but not in high pressure boilers.



In high pressure, scale dissolves to form $\text{Ca}(\text{OH})_2$

2) $\text{CaCO}_3 + \text{H}_2\text{O} \rightarrow \text{Ca}(\text{OH})_2 + \text{CO}_2$

3)

Q.
Ans

4)

Q.
Ans

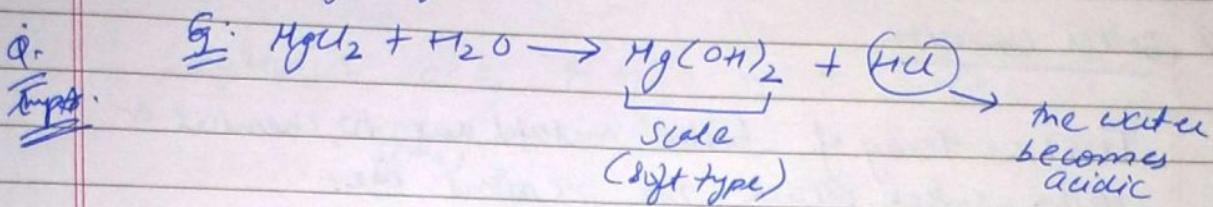
5)

2) Due to presence of CaSO_4

Q. Ans. ~~Ans.~~ classmate
Date _____
Page _____
 CaSO_4 forms a hard scale in the hotter portions of the boiler as it is less soluble in hot water than in cold water.

Precipitation occurs when ionic product $>$ solubility product. In hot water, ionic product increases.

3) Hydrolysis of Mg salts



4) Presence of Silica

Q. Ans. Why water purified through sand filter is not fit for boilers?
Hard & brittle scales of CaSiO_3 & MgSiO_3 are formed.

Disadvantages of scale formation:

① Wastage of fuel.

(Scales are poor conductors of heat, so more heat is required)

② Lowering of boiler safety

(Because of over heating, boiler material gets ~~badly~~ destructed / weakening of boiler material which increases the chance of explosion)

③ Decrease in efficiency of boiler due to choking of pipes

④ Danger of explosion

(Due to uneven expansion caused by cracking of scales, water suddenly comes in contact with over heated surface of the boiler, large amount of steam is formed suddenly leading to sudden rise in pressure causing explosion)

removal of scales. Depends on type of scale formed.

1) Loosely scale: Can be removed by wire brush.

2) Brittle scales (like silica scales), by thermal shocks.

Hard adherent scales can be removed by using 5-10% H_2 EDTA solution.

Q: Differences b/w scale & sludge?

2. Boiler Corrosion

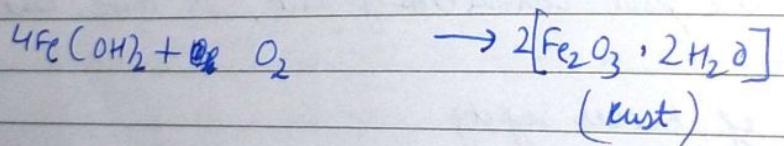
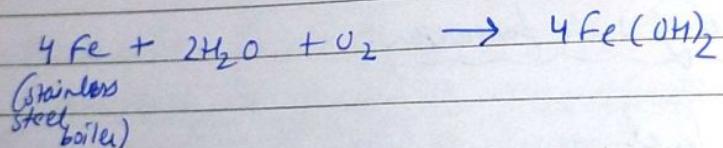
It is the decay of boiler material due to chemical or electrochemical attack. The reasons are:

Dissolved O_2

Dissolved CO_2

Mineral acids

Dissolved O_2 :

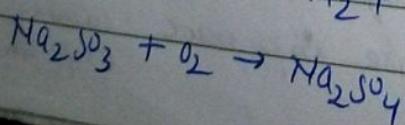
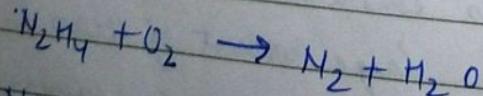


How to remove oxygen?

(a) Mechanical deaeration

(b) By adding chemicals

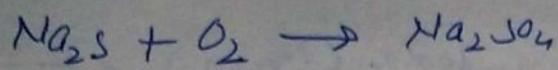
Hydrazine (N_2H_4), Na_2SO_3 , Na_2S etc



(a)
(b)

(c)

3.



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Date _____

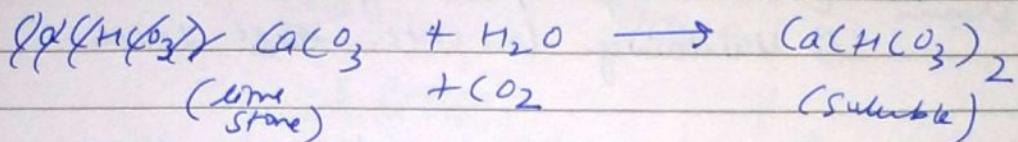
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Presence of CO_2

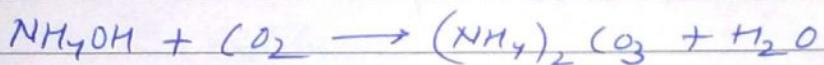
CO_2 forms H_2CO_3 (carbonic acid) with water which is corrosive in nature.

How to remove CO_2 ?

- Mechanical deaeration
- Filtering water through limestone



- Addition of Ammonium hydroxide



Presence of Mineral Acids

Source of mineral acids in water is presence of Mg salts.

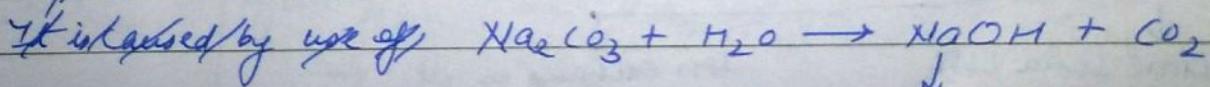
How to remove Mineral Acids?

- Removing Mg salts
- By adding alkali salts.

3. Caustic Embrittlement

Caustic soda is sodium hydroxide

Cause of this is highly alkaline water in high pressure boilers like ⚡



\downarrow
NaOH dissolves boiler material in the form of sodium ferrate causing embrittlement

classmate

Prevention: ① Avoid using soda (Na_2CO_3) during softening. Other conditioning methods can be used.

4. Priming Foaming

Priming: is the formation of wet steam which is caused by high steam velocities, sudden boiling or faulty design of the boiler.

Prevention: ① Controlling rapid change in steam velocities
② Maintaining low water ~~full~~ level

Foaming: formation of persistent foam or bubbles on the surface. It is caused due to presence of oil and alkali which react to form soap.

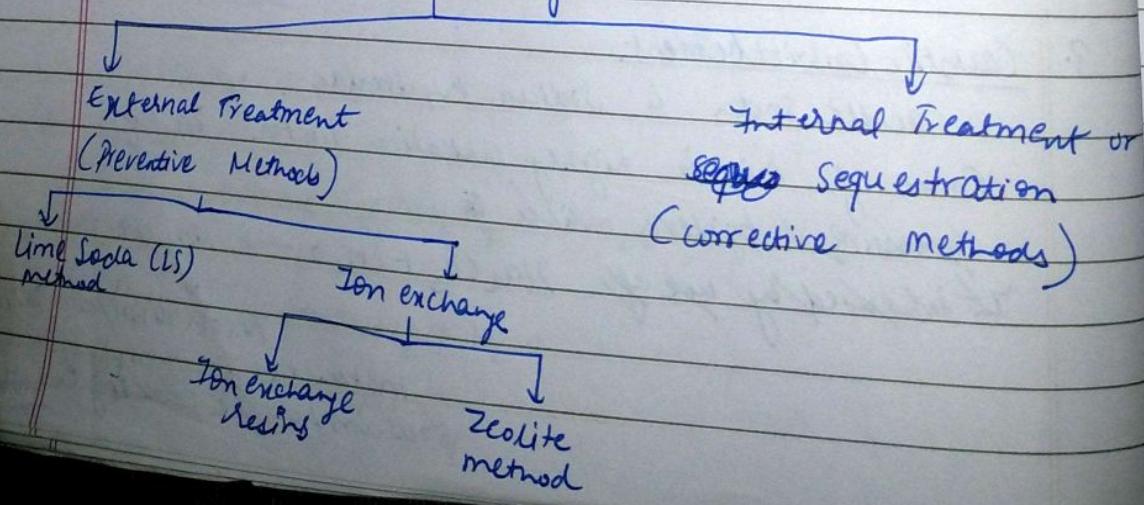
Prevention: ① Addition of anti-foaming agents
② Removing oil from water.

5. Carry over

It is the carrying over of impurities in water by steam to the boiler parts where they deposit & decrease the efficiency of the boiler.

16/11/17.

Water Softening



Colloidal conditioning

water

Batch process

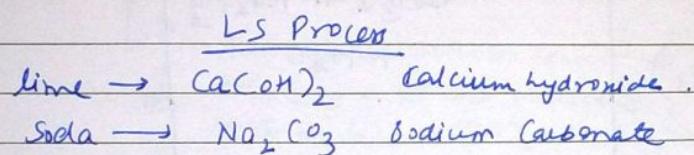
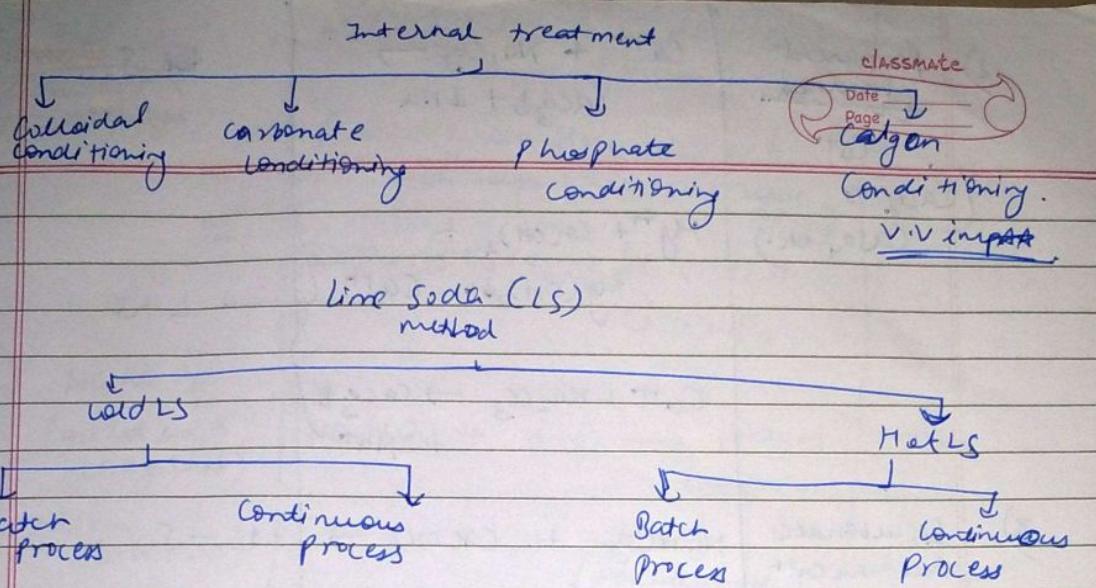
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Principle: lime & soda react with hardness causing salts & convert them to insoluble precipitates of carbonates & hydroxides which can be easily removed from water.

Calculation: Calculation of lime & soda quantity is very important. It is based on certain chemical reactions.

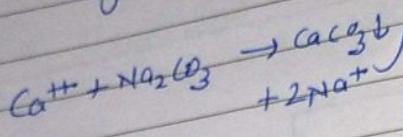
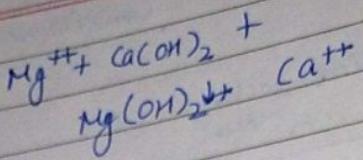
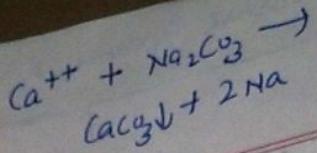
constituent / type of salt	chemical reaction	Requirement of L or S
I) temporary hardness $\text{Ca}(\text{CHCO}_3)_2$	$\text{Ca}(\text{HCO}_3)_2 + \text{Ca(OH)}_2 \rightarrow 2\text{CaCO}_3 \downarrow + \text{H}_2\text{O}$	L
$\text{Mg}(\text{HCO}_3)_2$	$\text{Mg}(\text{HCO}_3)_2 + 2\text{Ca(OH)}_2 \rightarrow \text{Mg}(\text{OH})_2 + 2\text{CaCO}_3 \downarrow + \text{H}_2\text{O}$	$2 \times L$ approx.

Q: Why $2 \times L$ is taken for $\text{Mg}(\text{HCO}_3)_2$

2) Permanent hardness.

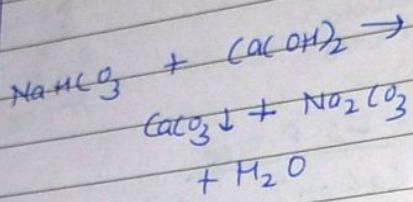
Ca^{++}

(CaCl_2 or
 CaSO_4 etc.)



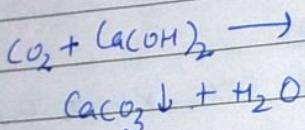
3) Bicarbonates
Other main Ca^{++}
 Mg^{++}

(e.g.: NaHCO_3)



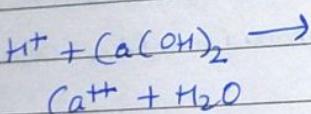
$\text{L} - \text{S}$

4) O_2

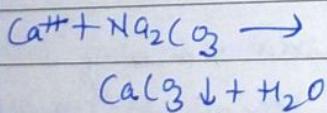


L

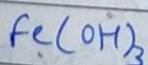
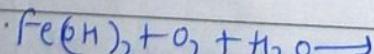
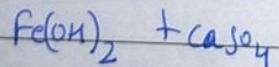
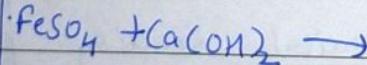
5) Free Acids (H^+)



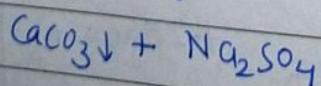
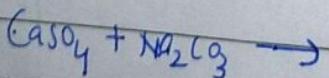
$\text{L} + \text{S}$



6) FeSO_4
(added as a coagulant)

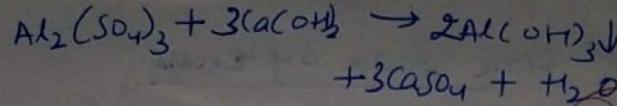


$\text{L} + \text{S}$



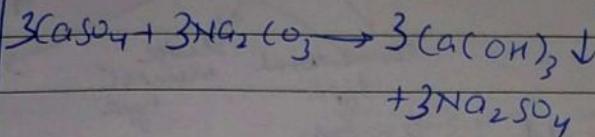
Soda

7) $\text{Al}_2(\text{SO}_4)_3$
(added as a coagulant)



CASSMATE
Date _____
Page _____

[$\text{Al}(\text{OH})_3$ is a flocculent ppt which helps other ppts to settle down]

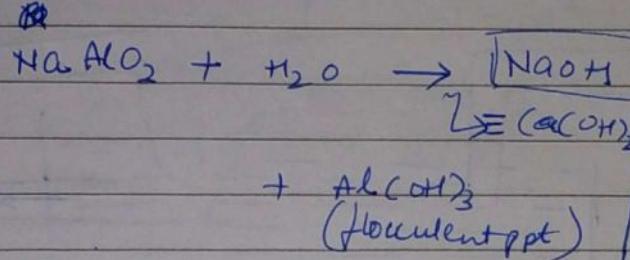


L + S

8) NaAlO_2

(added as a coagulant)

[Sodium Aluminate]



(Flocculent ppt)

- L

[NaOH is considered equivalent to Ca(OH)_2 . It was removed because like $\text{Ca}(\text{OH})_2$, but is avoided as it is highly alkaline].

$$\text{Lime Required} = \frac{74}{100} [\text{Temp-Ca}^{++} + 2 \times \text{Temp Mg}^{++} + \text{Perm. Mg}^{++} + \text{CO}_2 + \text{H}^+ (\text{free acids}) + \text{FeSO}_4 + \text{Al}_2(\text{SO}_4)_3 - \cancel{\text{NaAlO}_2}]$$

$$= \frac{\text{mg/L} \times \text{V litres of water to be softened}}{10^6}$$

$$= \frac{\text{kg of lime}}{\text{V litres of water}}$$

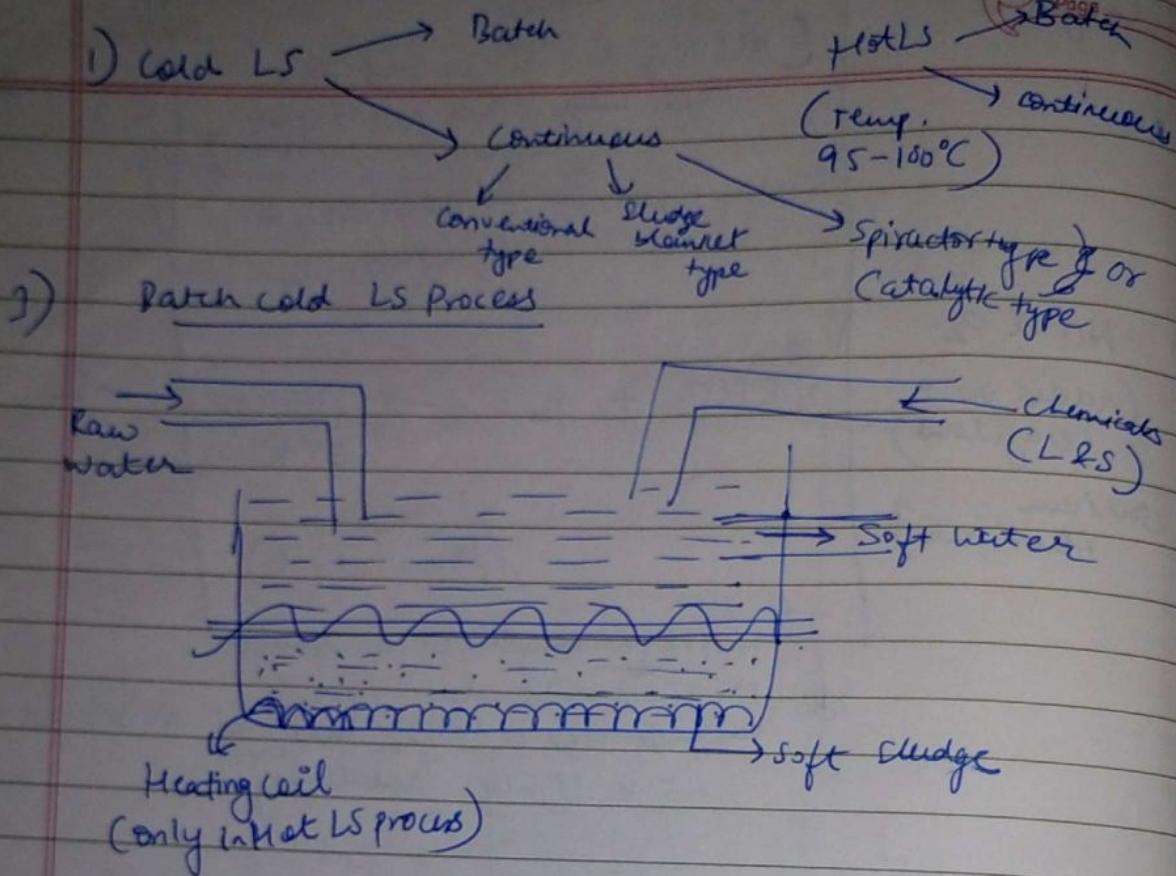
$$\text{Soda Required} = \frac{106}{100} [\text{Perm. Mg}^{++} + \text{Perm. Ca}^{++} + \text{H}^+ + \text{FeSO}_4 + \text{Al}_2(\text{SO}_4)_3 - \text{HCO}_3^- \text{ or } (\text{HCO}_3^- + \text{CO}_3^{2-}) \text{ (Corresponding Ca}^{++} \text{ & Mg}^{++}\text{)}]$$

$$= \frac{\text{mg/L} \times \text{V litres of water}}{10^6}$$

$$= \frac{\text{kg of soda}}{\text{V litres of water}}$$

Lime-Soda Softener.

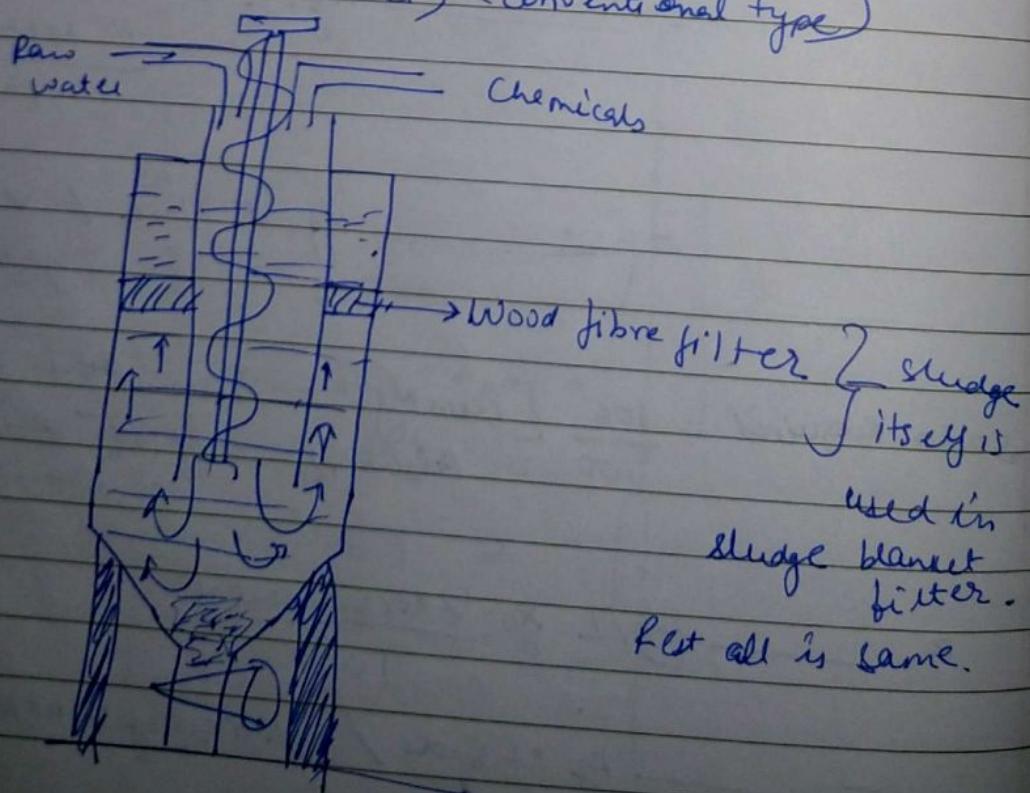
17/1/17 CLASSMATE
Date _____
Page _____



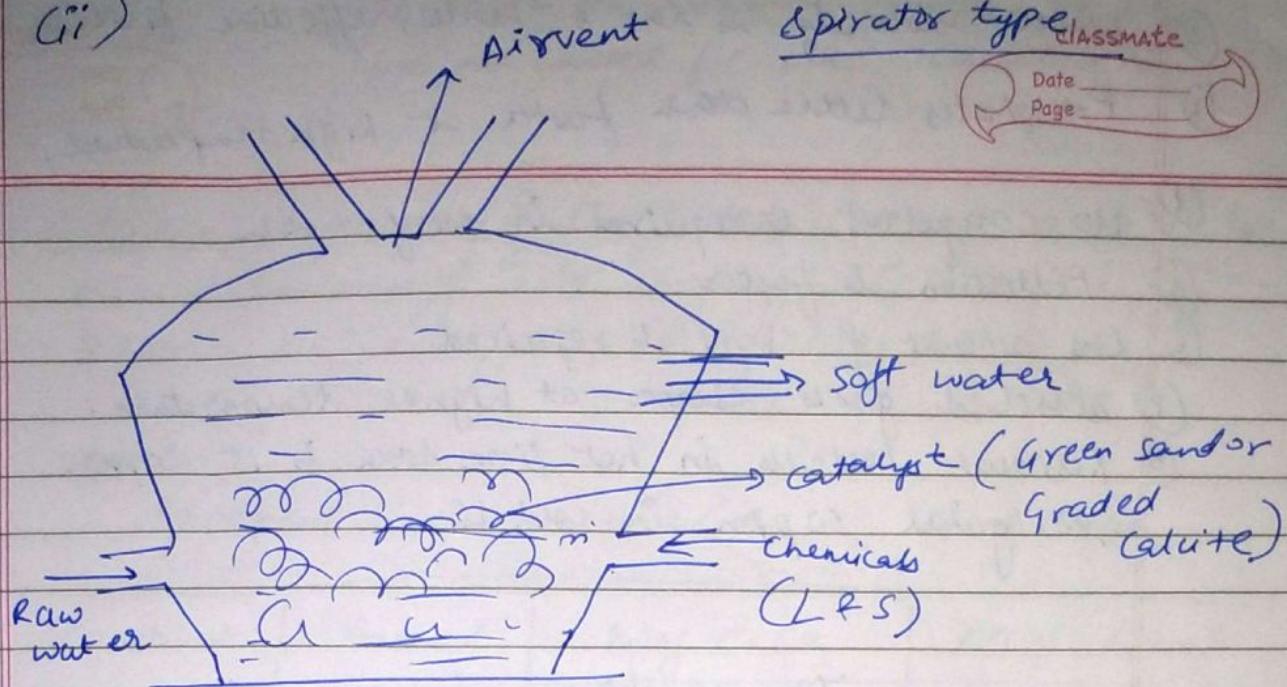
(Coagulant is also required in batch process. E.g. Alum, FeSO_4)

2) Cold Continuous Softener

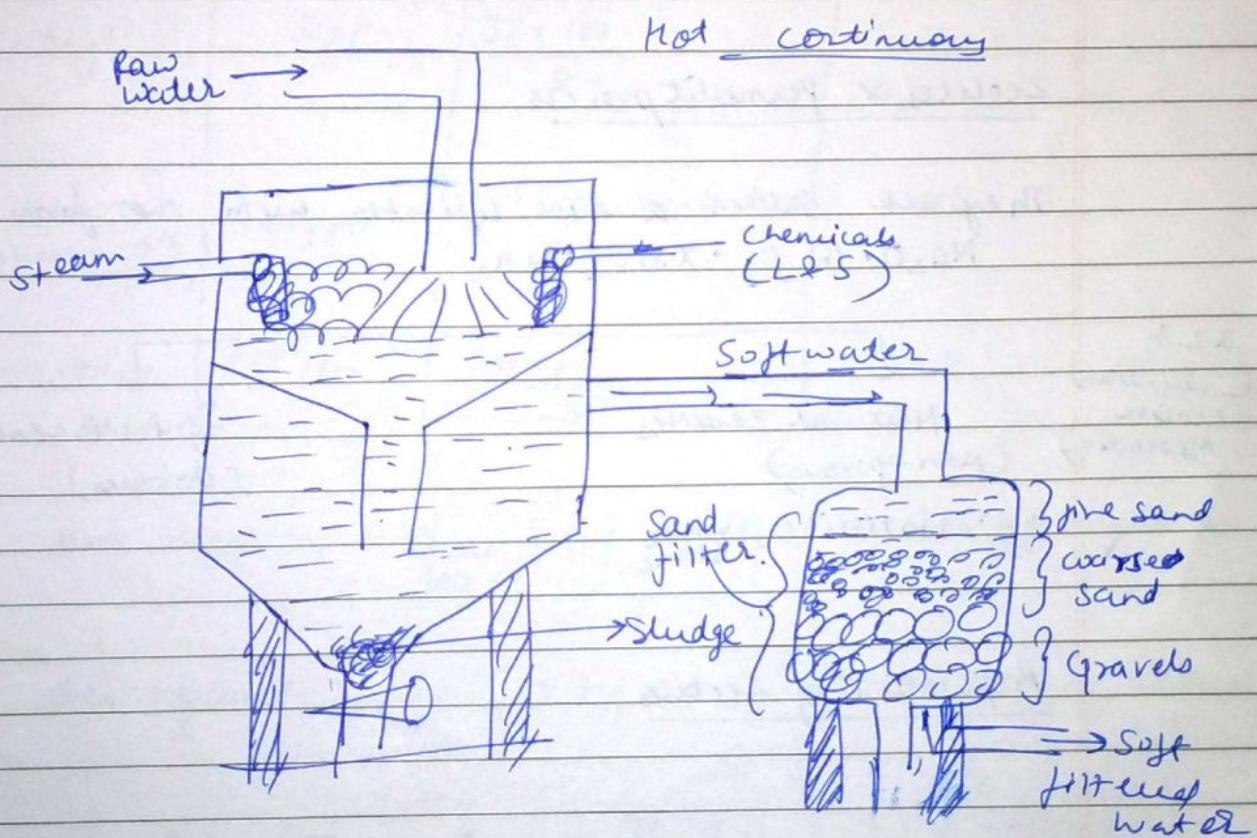
(i) (Conventional type)



(ii)



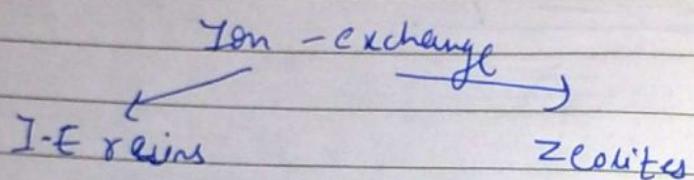
1)



Vivimex [®] Advantages of hot LS over cold LS

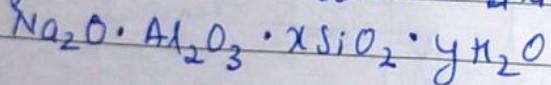
- ① chemical Reactions are faster & at a higher temp. in hot LS & they are take lesser time as compared to cold LS.

- Date _____
Page _____
- ② Water viscosity is low & hence, effective filtration.
 - ③ Precipitates settle down faster at high temperature.
 - ④ No coagulant is required in case of hot LS
 - ⑤ Filtration is faster
 - ⑥ Less amount of chemicals required
 - ⑦ Dissolved gases escape at higher temperature.
 - ⑧ Residual hardness in hot lime soda is 15-20 ppm as against 60 ppm in cold LS



Zeolites or permelit process

They are sodium-alumino silicates with the formula:



IZA
(International
Zeolite
Association)

Natural zeolites
(Non-porous)
Eg: Natrolite, Pumicite

Synthetic zeolites
(Porous)

Preparation of zeolites

* Phosphates do not cause hardness. So, they are not counted for L.S.C. calculation.

Date _____
Page _____

Q1

Calculate the quantity of lime & soda required per litre for chemical treatment of water containing $\text{Ca}^{++} = 80 \text{ ppm}$, $\text{Mg}^{++} = 2 \text{ ppm}$, $\text{HCO}_3^- = 195 \text{ ppm}$, $\text{FeSO}_4 \cdot 7\text{H}_2\text{O} = 735 \text{ ppm}$.

→

Ans

Constituent	Amount	Amount Eq. of CaCO_3	Eq. of Na_2O
Constituent	Amount	Eq. of CaCO_3	Eq. of Na_2O
Ca^{++}	80 ppm	$\frac{80 \times 100}{40} = 20$	5
Mg^{++}	2 ppm	$\frac{32 \times 100}{24} = 4$	L+S
HCO_3^- (concentration CaCO_3)	195 ppm	$\frac{195 \times 100}{61} = 2$	L-S
$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$	735 ppm	$\frac{735 \times 100}{278} = 264.38$	L+S

lime required = $\frac{74}{100} [y + z + a] = 236.46 \text{ mgs/litre}$

soda required = $\frac{106}{100} [x + y + a - z] = 211.89 \text{ mgs/litre}$

therefore $x = 200$ $y = 133.33$ $z = 319.67$

$a = 264.38$

$L.S. = \frac{74}{100} [133.33 + 319.67 + 264.38]$

=

Constituents	Amount	g of CaCO_3	(Ca^{++}) Loss
$\text{Mg}(\text{HCO}_3)_2$	73 mg/L	$\frac{73}{146} \times 100 = 50 \text{ mg/L}$	2 L
(Permanent alkalinity calc.) CaCO_3	222 mg/L	$\frac{222 \times 100}{111} = 200 \text{ mg/L}$	5
MgSO_4	120 mg/L	$\frac{120 \times 100}{120} = 100 \text{ mg/L}$	4 L + 5
(Permanent calc. hardness) $\text{Ca}(\text{NO}_3)_2$	164 mg/L	$\frac{164 \times 100}{164} = 100 \text{ mg/L}$	5

Nitrates are
soluble.

$$\text{Lime req} = \frac{74}{100} [100 + 100] = 74 \times 2 \\ = 148 \text{ mg/L}$$

$$= \frac{148 \times 5000}{100} = 0.74 \text{ kg/s}$$

$$\text{Soda req} = \frac{106}{100} [200 + 100 + 100] = \frac{106}{100} \times 400 \\ = 424 \text{ mg/L}$$

$$= \frac{424}{100} \times 5000 = 2.12 \text{ kg/s}$$

If purity is also given,

$$\text{then, Lime} = 0.74 \times \frac{1000}{74} = 1 \text{ kg}$$

$$\text{Soda} = 2.12 \times \frac{1000}{90} = 2.3 \text{ kg}$$

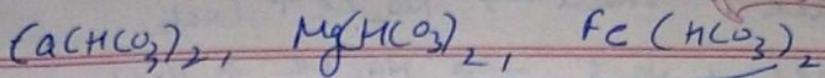
Cab & Tur II

(Neglect TDS for hardness).

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Date _____

Page _____



only may cause temp. hardness.

Also neglect NaCl as none of Na & K salts cause hardness.

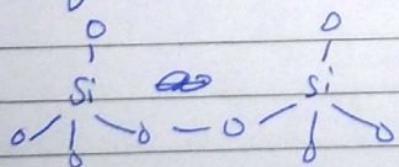
Lime soda ques come for Gmals in exam.

Preparation of zeolites

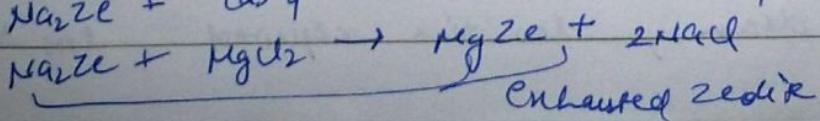
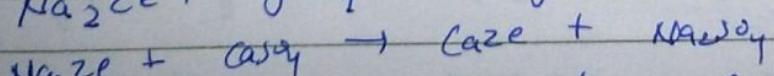
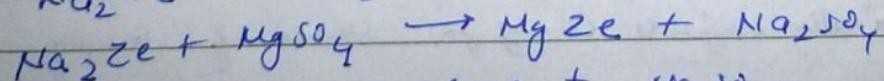
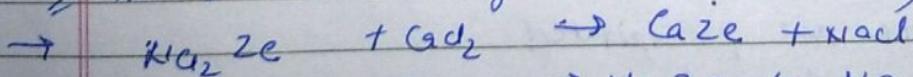
Chlorite clay (SiO_4), feldspar (Al_2O_3) & soda ash (Na_2O_3) are heated together which gives rise to the structure of a zeolite.

Structure:

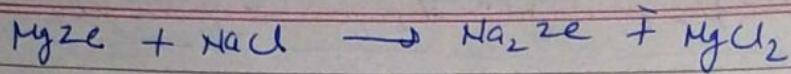
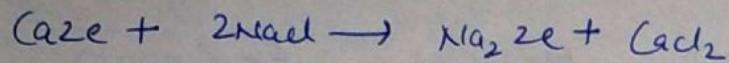
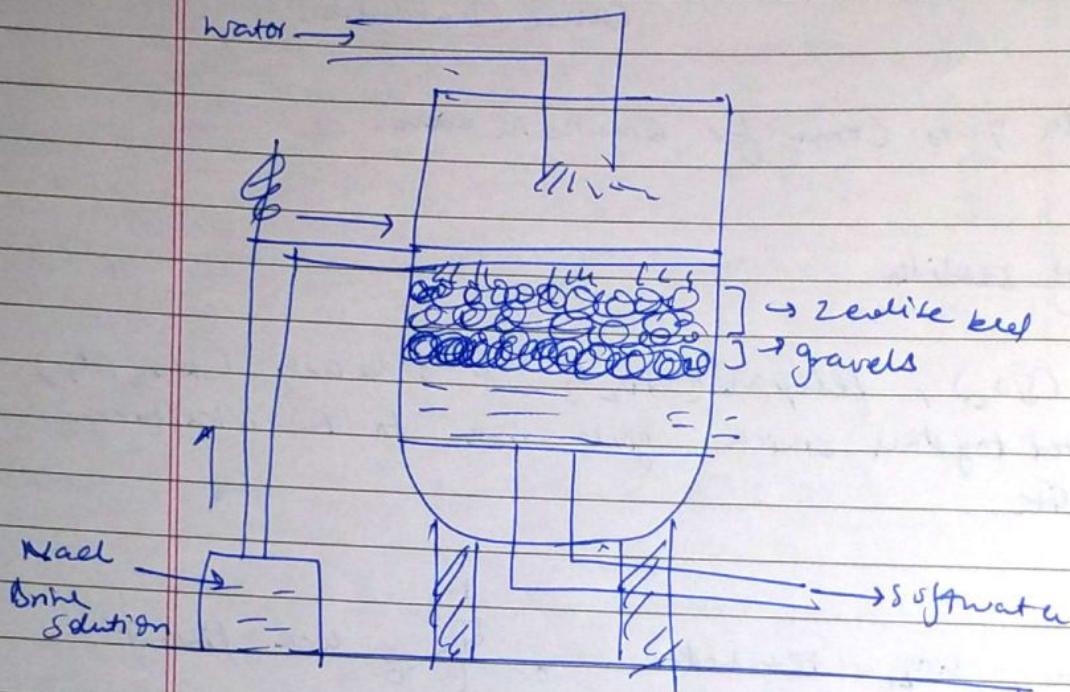
In zeolites, SiO_4 tetrahedra or Si_4O_10 are linked together. Each Oxygen is tetrahedra shared with adjacent one. Some Si^{+4} ions are replaced by Al^{+3} ions & equal no. of Na^+ & K^+ ions are added to balance the charges. This results in open cage like structure with cavities in which Na^+ & K^+ ions are loosely held & can be exchanged with other cations.



Q now does it exchange hardness? (reaction):



Exhausted zeolite

Regeneration:zeolite softener:Limitations:

- 1) suspended impurities if present clog the pores of zeolite & process cannot be conducted.
- 2) Fe or Mn if present in water forms $\text{Fe}_2\text{Ze}_2\text{Mn}_2\text{Ze}$ respectively, which cannot be regenerated & zeolite cannot be reused.
- 3) free acids destroy zeolite.

Advantages:

- 1) Residual hardness is 10 ppm
- 2) Equipment is compact
- 3) No impurities are precipitated
- 4) Automatically adjusts brine for water of varying hardness.
- 5) Process is clean, less time required, less NaCl

for maintenance & maintenance.

classmate

Date _____

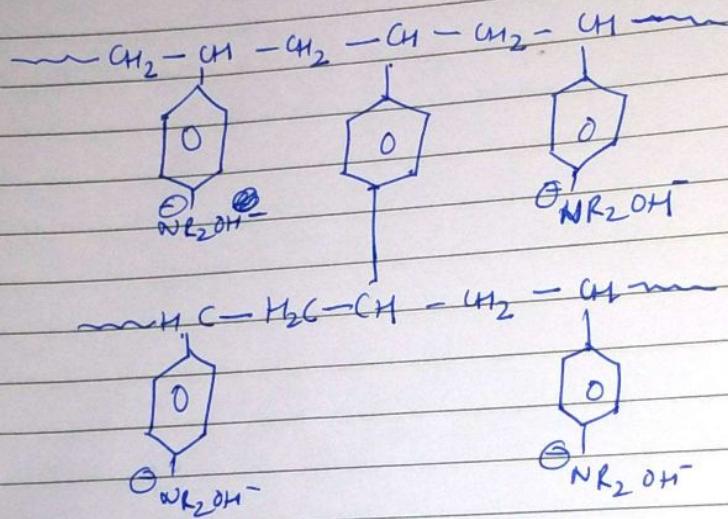
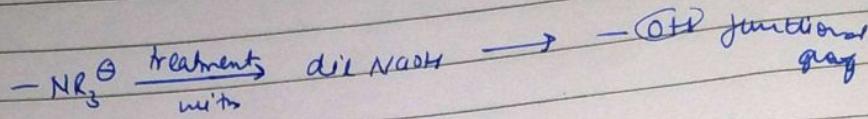
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Disadvantage:

- 1) Treated water contains high level of sodium salts
- 2) only cations are removed but some anions like CO_3^{2-} , HCO_3^- remain in water
- 3) Sulphate present in water clogs the holes of zeolite.

Anion exchange Resin

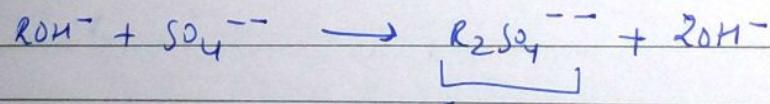
Example: Styrene di phenyl benzene copolymer resin
functional group $-NR_3^+$



Exchange process



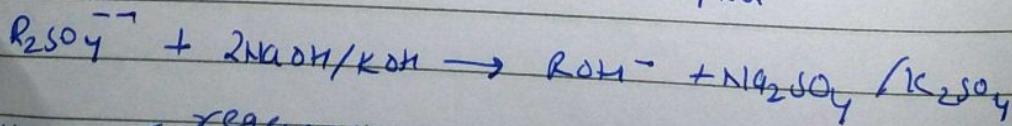
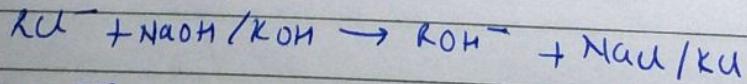
Rain



Exhausted resin

Exhausted resin
 \rightarrow whole OH- is removed.

Regeneration



After the regeneration process, the resin is washed with

demineralised water & used again.

classmate

Date _____

Page _____

Advantages:

- 1) Residual hardness is 2 ppm or less
- 2) Can be used for highly acidic ~~or~~ alkaline waters.

Disadvantages:

- 1) Equipment & chemicals are costly
- 2) Turbidity reduces efficiency.

Initial Treatment or Sequestration

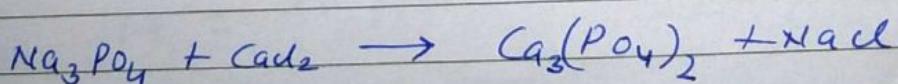
Hardness producing ions are prevented by exhibiting their original character by complexing & converting into more soluble salt by adding reagents which :

- 1) Converts ~~scale~~ forming impurities into sludge & remove
- 2) Converts into more soluble compounds which remain in water.

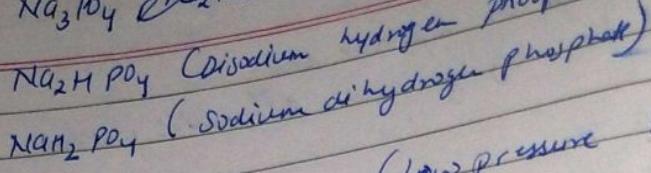
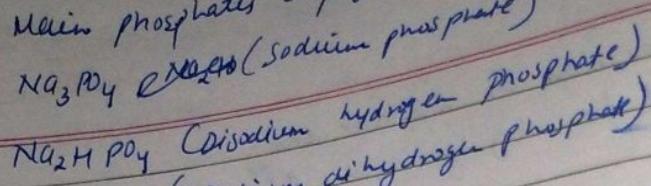
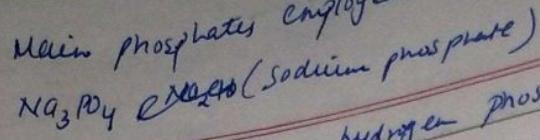
(1) Colloidal conditioning (for low pressure boilers)

In this method, some organic substances are added like tannin, kerosene, agar-agar etc. which gets coated over scale forming ppts and convert them into soft non-sticky & loose precipitate which can be easily removed.

(2) Phosphate conditioning (high pressure boilers)



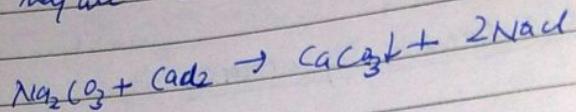
Main phosphates employed are:



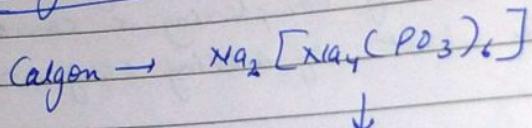
Based on pH
of water
to be treated

(3) Carbonate conditioning (Low pressure boilers)

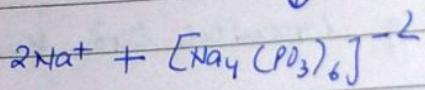
Na_2CO_3 is added to hardness causing salts to form.
They are converted to hardness carbonates.



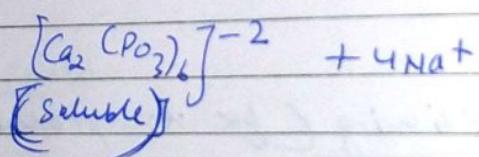
Algon conditioning



↓



↓ $\text{Ca}^{2+}/\text{Mg}^{2+}$



M

27/11/17

Strong acid + Strong base \rightarrow Phenolphthalein + Methyl orange both can be used

Strong acid + weak base \rightarrow Phenolphthalein

Weak acid + ~~weak~~ strong base \rightarrow H₂O

Tutorial Sheet D

Q2: finding alkalinity

P

$$\text{Alkaline water} \quad \text{Acid}$$

$$N_1 V_1 = N_2 V_2$$

$$N_1 = \frac{N_2 V_2}{V_1} = \frac{1}{50} \times 15 \times \frac{1}{50} \text{ N}$$

$\therefore =$

Strength = normality \times equivalent weight

$$= \frac{15}{50} \times 50 \text{ (eqwt of } \text{CaCO}_3\text{)}$$

$$= \frac{15}{50} \text{ g/L} = \frac{15}{50} \times 1000 = 300 \text{ ppm}$$

= mg/Lt.

M

$$\text{Alk. water} \quad \text{Acid}$$

$$N_1 V_1 = N_2 V_2$$

$$= \frac{1}{50} \times 25 \times \frac{1}{50} \text{ N}$$

$\therefore =$

Strength = normality \times eq weight

$$= \frac{25}{50} \times 50 \times 1000 \text{ mg/L}$$

= 500 ppm or mg/L

$$P = 300 \text{ ppm}$$

$$M = 500 \text{ ppm} \quad 1/2 M = 250 \text{ ppm}$$

as $P \geq 300$ $\text{Na}_2\text{H} \Rightarrow \text{OH}^- \& \text{CO}_3^{2-}$
are present

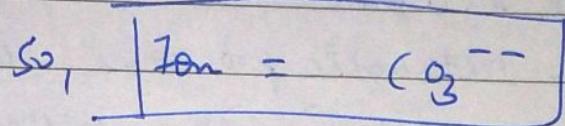
classmate

Date _____

Page _____

Here, 15 ml detected by P.
But NaO detects whole
titration. so we take
 $15 + 10 = 25$

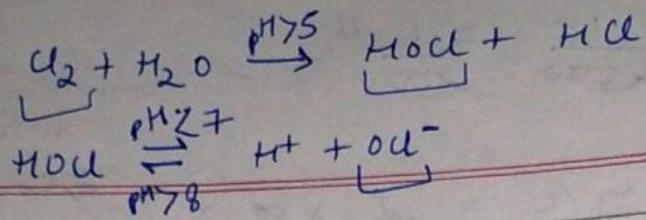
Here, $P = 1/2 \text{ M}$



Domestic water treatment

- ① \hookrightarrow screening
- ② \hookrightarrow sedimentation
- ③ \hookrightarrow sedimentation with coagulation
- ④ \hookrightarrow filtration
- ⑤ \hookrightarrow Disinfection \Rightarrow chlorination

Vिषय Disinfecting actions of chlorine



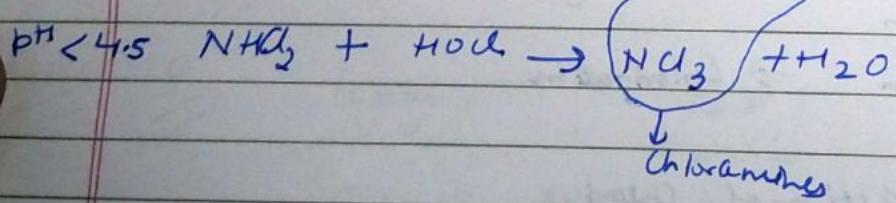
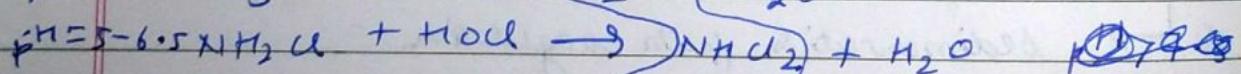
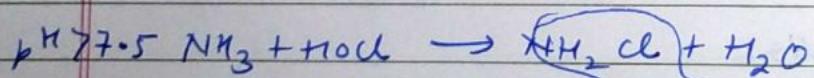
\hookrightarrow Free Cl₂

The above reaction is pH dependent. The dissociation of HOCl is most effective at higher pH values & at pH higher than 8, \Rightarrow HOCl exists.

Out of all the three species, HOCl, OCl⁻ & Cl₂ are termed as "free Cl₂". Out of these, OCl⁻ is the predominant species & HOCl is the most destructive. The pH value of water during chlorination is more maintained slightly less than 7 to prevent the dissociation of HOCl.

According to enzymatic hypothesis given by Gleent Stumpf, HOCl reacts with the enzymes in the cells of the bacteria which are essential for their growth & other metabolic processes. Due to deactivation of enzyme the bacteria gets killed.

In order to make these species stable in water, ammonia is added when various chloramines are formed.



Predominant is (NH_2Cl_2) dichloramine

classmate

Date _____

Page _____

Q. Chlorine or chloramine? which is better?

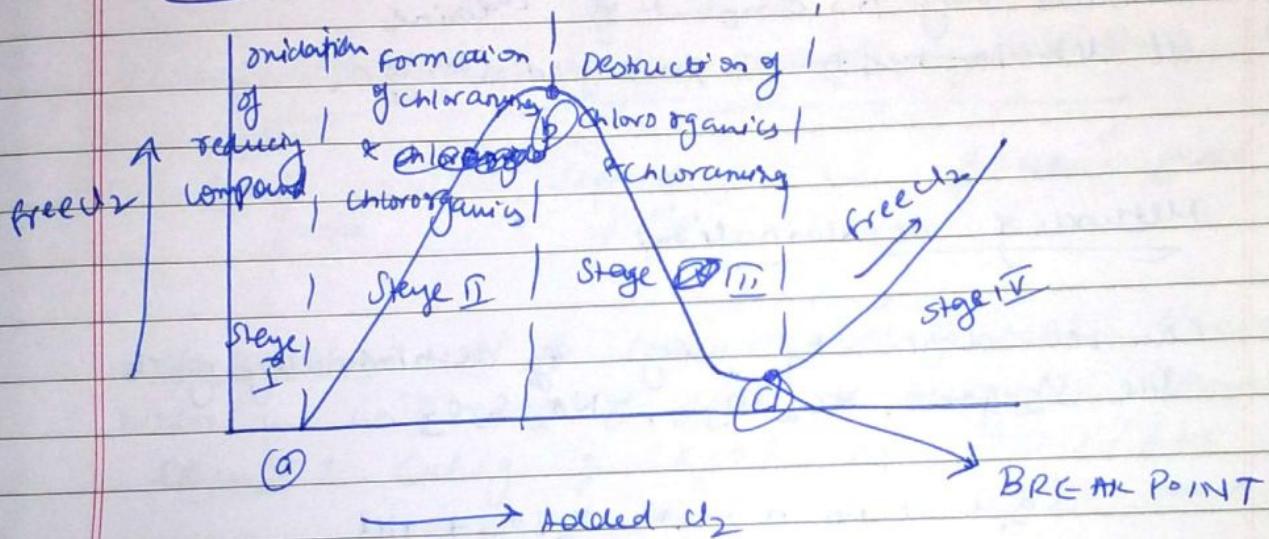
→ NH_2Cl_2 are more effective.

They act as reservoirs & are combined form of Cl_2 which is more stable & posses very good disinfecting properties.

Q. Why do we need residual chlorine?

→ we need around 0.2 ppm of residual chlorine. To prevent future contamination, it is needed.

Break point chlorination.



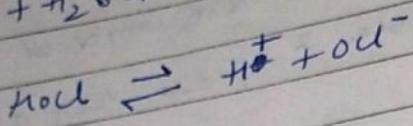
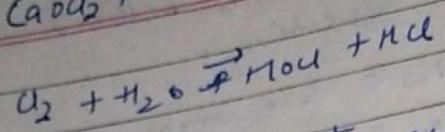
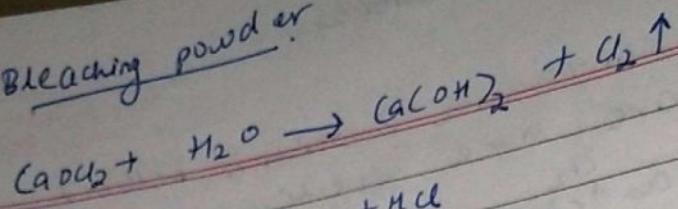
Thus, break point chlorination can be defined as chlorination to such an extent that microorganisms as well as bad taste & odours present in water are also destroyed.

Byself: Advantages of chlorination? & disadvantages

Types of method of chlorination

- liquid
- gaseous
- tablets.

Bleaching powder

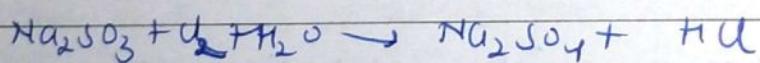
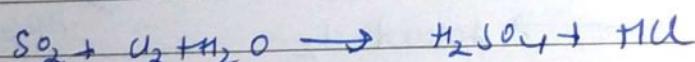


Disadvantages of using CaOCl_2

- (1) On account of lime content $\text{Ca}(\text{OH})_2$, pH of water is increased & hardness is also added to water.
- (2) Contains very low amount of chlorine.
It deteriorates on prolonged storage.

Methods of dechlorination?

Can be done by using by dechlorinating agents
 HgS_2 gas, Na_2SO_3 , $\text{Na}_2\text{S}_2\text{O}_3$



Molecular carbon.



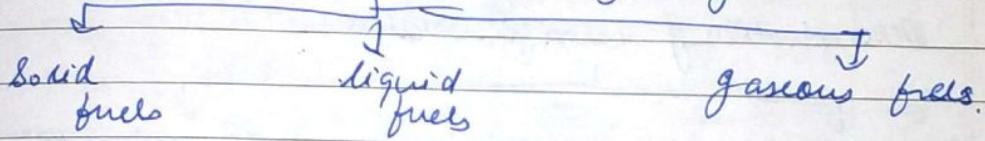
Module - I
Fuels

31 / ~~14~~ ¹⁴ page
Date _____
Page _____

Characteristics of a good fuel

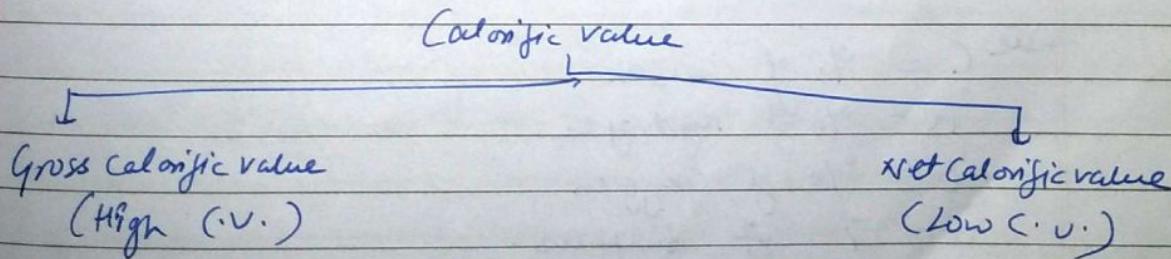
- (1) High calorific value
- (2) Moderate ignition temperature
- (3) Moderate rate of combustion
- (4) Moisture content
- (5) Free of toxic products
- (6) Low smoke
- (7) Low volatile matter content.
- (8) Low cost, easy transportation
- (9) Easy control & easy storage

Classification of fuel on the basis of physical state



Calorific value: it is the ~~amount~~^{total quantity} of heat liberated when a unit mass of fuel is burned, completely.
Its units : Cal/g ; kcal/kg, BTU/lbs
(British Thermal Unit)

Calorie: unit of heat required to raise temperature of 1kg water by 1°.

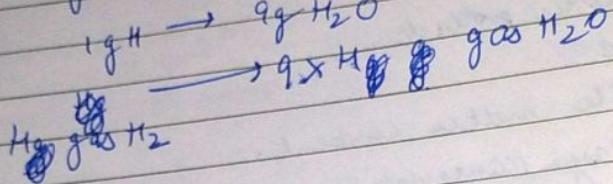
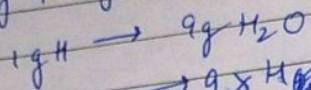
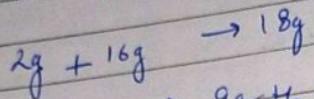
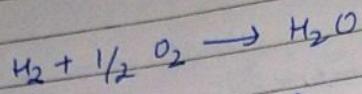


$$LCV = GCV - Q \times H \times \text{latent heat of vapourisation}$$

Date _____
Page _____

$= GCV - \frac{9 \times H}{100} \times 587 \text{ cal/g}$

where H is amount of hydrogen present in fuel.



Q. Difference b/w GCV & LCV
Ans.

Determination of calorific value.

Theoretical method

Experimental method

(Bomb's Calorimeter)

(Dulong's formula)



$$GCV = \frac{1}{100} [8080C + 34500 \left(H - \frac{O}{8} \right) + 2240S]$$

$$= \text{Cal/gm}$$

Where $C = \%$ of Carbon

$H = \%$ of Hydrogen

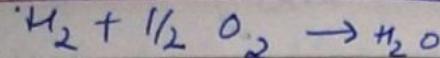
$O = \%$ of Oxygen

$S = \%$ of Sulphur.

Mechan
slime

$(H - O/8) = \text{combined hydrogen}$

$\frac{\%}{\%} = \frac{\text{combined hydrogen}}{\text{Total hydrogen}}$



$$\frac{2g + 16g}{1g + 1g}$$

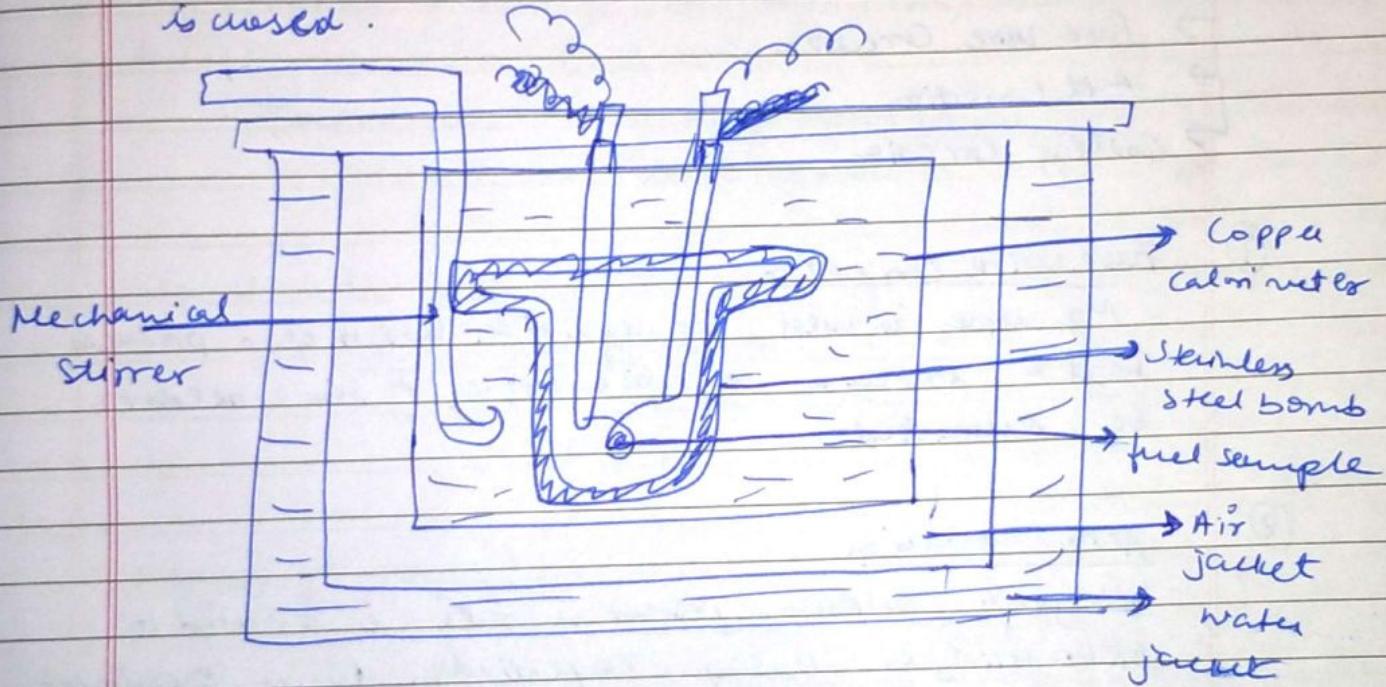
$\therefore 8g O_2 \text{ combine with } 1g H_2$

$$8g O_2 \text{ " " } = \frac{1}{8} g H_2$$

Combined hydrogen doesn't add to calorific value

Bomb's Calorimeter

We get GCV from this as the atmosphere is sealed.



PRINCIPLE:

$$\text{Heat loss by fuel} = \text{Heat gained by water} + \text{calorimeter}$$

$$\text{Heat lost by fuel} = L (\text{gross calorific value of fuel}) \times m (\text{mass of fuel})$$

$$\text{Heat gained by water} = M \times S \times \Delta = W \times I \times (t_2 - t_1)$$

classmate

Date _____

Page _____

$$\text{Calorimeter} = m \times s \times \theta = w \quad (\text{water equivalent})$$

$w = \frac{m \times s}{c_a \cdot c_v}$

$$m \times L = w(t_2 - t_1) + w(t_2 - t_1)$$

$$L = \frac{(w+w)(t_2 - t_1)}{m}$$

✓ in numbers only till here.

Errors in Bomb Calorimeter

This is also for numbers.

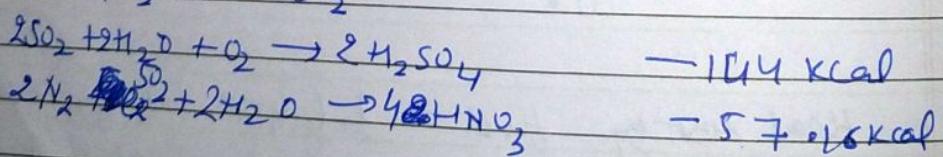
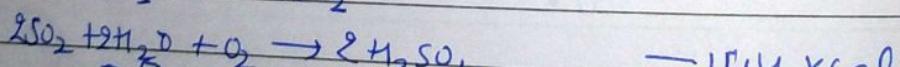
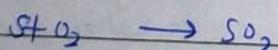
- Fuse wire correction
- Acid correction
- Cooling correction

① Fuse wire correction

Mg wire is used for ignition which also produces heat & increases effective GCV & this needs to be subtracted

② Acid correction

Nitrogen & Sulphur present in fuel is converted to H_2SO_4 & HNO_3 respectively during experiment. The conversion of both is an exothermic reaction as shown below.



The heat liberated is not obtained in practical use of coal as SO_2 & N_2 escape into the atmosphere to make the corrections, following

- 1) Amo anal
- 2) For sub
- 3) H_2 for sub
- 4) CO_2 Th heat loss to

needs to be done

CLASSMATE

Date _____

- 1) Amount of H_2SO_4 & HNO_3 in washings of calorimeter is analysed
- 2) For each ml of $N/10 H_2SO_4$ formed, 3.6 cal are subtracted
- 3) H_2SO_4 can be precipitated as $BaSO_4$ using $BaCl_2$ for 1 mg of ~~SO₂~~ Sulphur, 2.25 cal are subtracted.
- 4) For each ml of $N/10 HNO_3$, 1.43 cal must be subtracted

③ Cooling correction

The maximum temperature to which calorimeter is heated is a bit higher than that recorded due to loss of heat & hence rise in temperature is added to cooling correction ($\propto \times dt$)

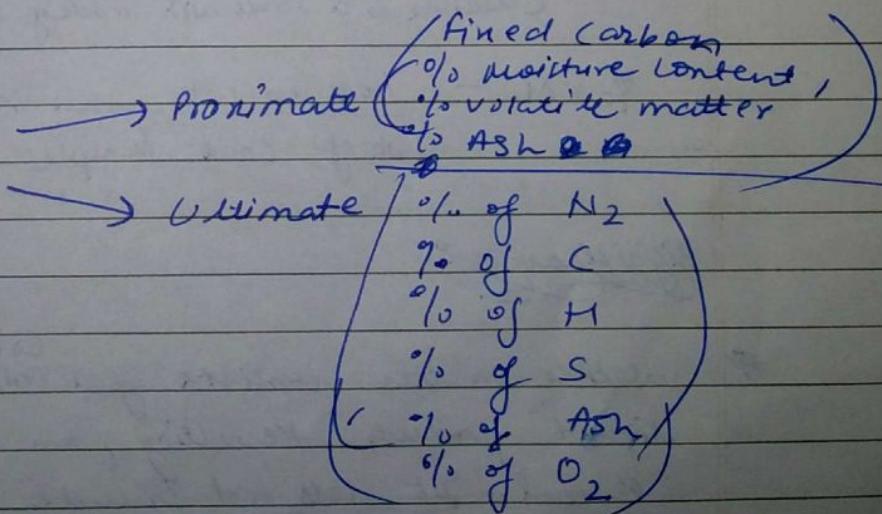
Where $dt \rightarrow$ rate of cooling
 $\propto \rightarrow$ time taken

$$GCV = \frac{(W+w)(t_2 - t_1 + \text{cooling correction})}{\text{Mass of fuel sample (m)}} - \\ (\text{Acid correction} + \text{Fused correction})$$

Example of solid fuel

coal

Analysis of coal



i) Proximate Analysis

(a) % moisture - Weighed $\xrightarrow{\Delta}$ weighed again
 Amount of coal $100 - 105^{\circ}\text{C}$
 for 1 hr

$$\% \text{ moisture} = \frac{\text{Loss in wt}}{\text{Wt of coal sample}} \times 100$$

Significance:

- It is undesirable content in coal
- It decreases the calorific value as it takes away appreciable amount of heat in the form of latent heat of vaporisation
- It makes the transport & handling difficult
- Ignition & combustion becomes difficult

(b) % volatile matter

Moisture free coal $\xrightarrow{\Delta}$ weighed again
 (weighed amount) $950^{\circ}\text{C} \pm 20^{\circ}\text{C}$
 for 7 min in

Partially open Crucible
 (Crucible is a small dish made of silica)

$$\% \text{ VM} = \frac{\text{Loss in wt}}{\text{Wt of coal sample}} \times 100$$

QUESTION

* volatile matter consists of a mixture of gaseous & liquid products resulting from thermal decomposition of coal. It does not include moisture. It mainly consists of H_2 , CO , CH_4 & other hydrocarbons.

Its significance can be stated as below:

- High volatile matter is undesirable as lot of fuel is wasted.
- It consists of non-combustible gases which unnecessarily occupy volume but do not add to the calorific value.
- Coal with high VM burns with long flames, high smoke & relatively low heating values.

7/2/17

(c) % Ash

weighed amount of fuel $\xrightarrow{\Delta}$ weighed again.
 $750^{\circ}\text{C} \pm 50^{\circ}\text{C}$
for $1/2$ hr. in an
open lid crucible

$$\% \text{ Ash} = \frac{\text{wt of Ash}}{\text{wt of coal sample}} \times 100$$

Significance:

- High percentage of ash is undesirable as it does not contribute to the calorific value of coal.
- The coal with high % of ash produces clinkers on burning.

(d) % fixed carbon

$$\% \text{ C} = 100 - \{ \% \text{ of moisture} + \text{VM} + \text{Ash} \}$$

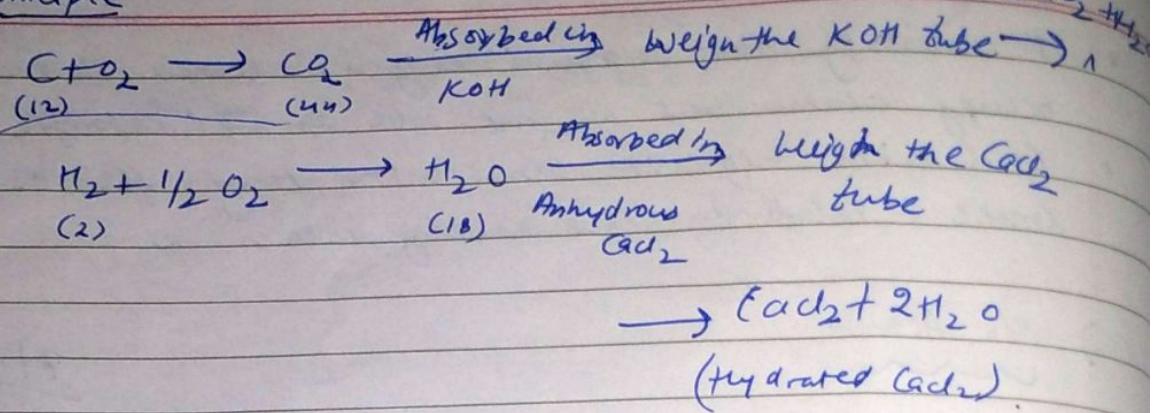
Significance:

- High % C means high calorific value of coal.

ii)

Ultimate Analysis

Principle



$$\% \text{ of C} = \frac{\text{increase in wt of KOH tube}}{\text{wt of coal sample}} \times \frac{12}{44} \times 100$$

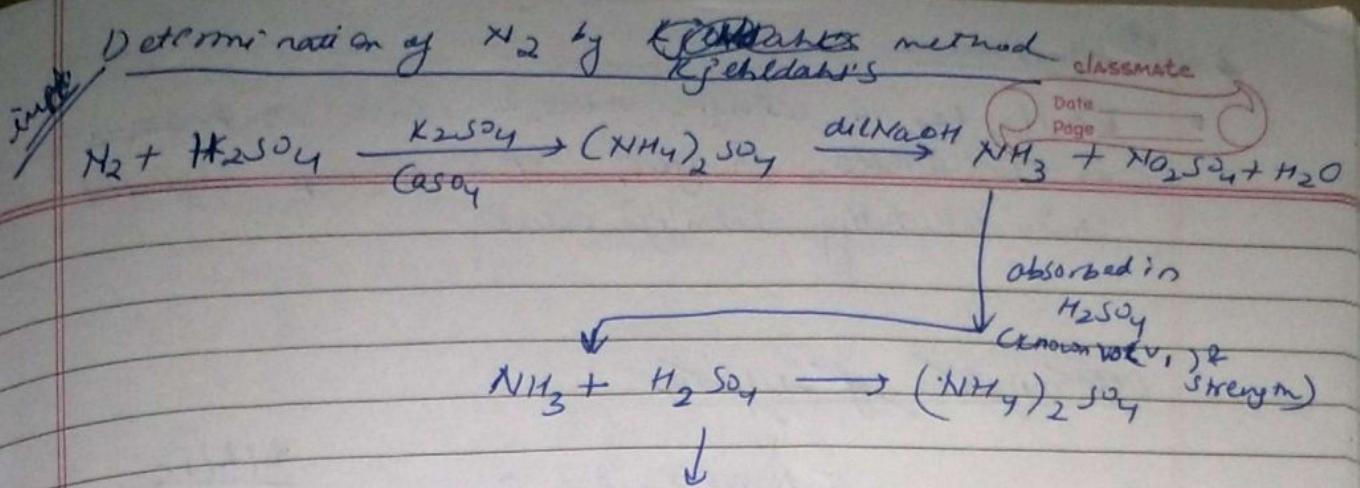
$$\% \text{ of H} = \frac{\text{increase in wt of CaCl}_2 \text{ tube}}{\text{wt of coal sample}} \times \frac{2}{18} \times 100$$

Do diagram from book

a.

classmate
Date _____
Page _____

$\text{K}_2\text{CO}_3 + \text{H}_2\text{O}$



Remaining acid is titrated against
std. NaOH \longrightarrow Used vol of Acid
 $= (v_1 - v_2)$

$$\text{wt/l lit} = N \times \text{eqwt.}$$

(Normality)

$$\text{wt of Nitrogen} = \frac{0.1 \times (v_1 - v_2) \times 14}{1000}$$

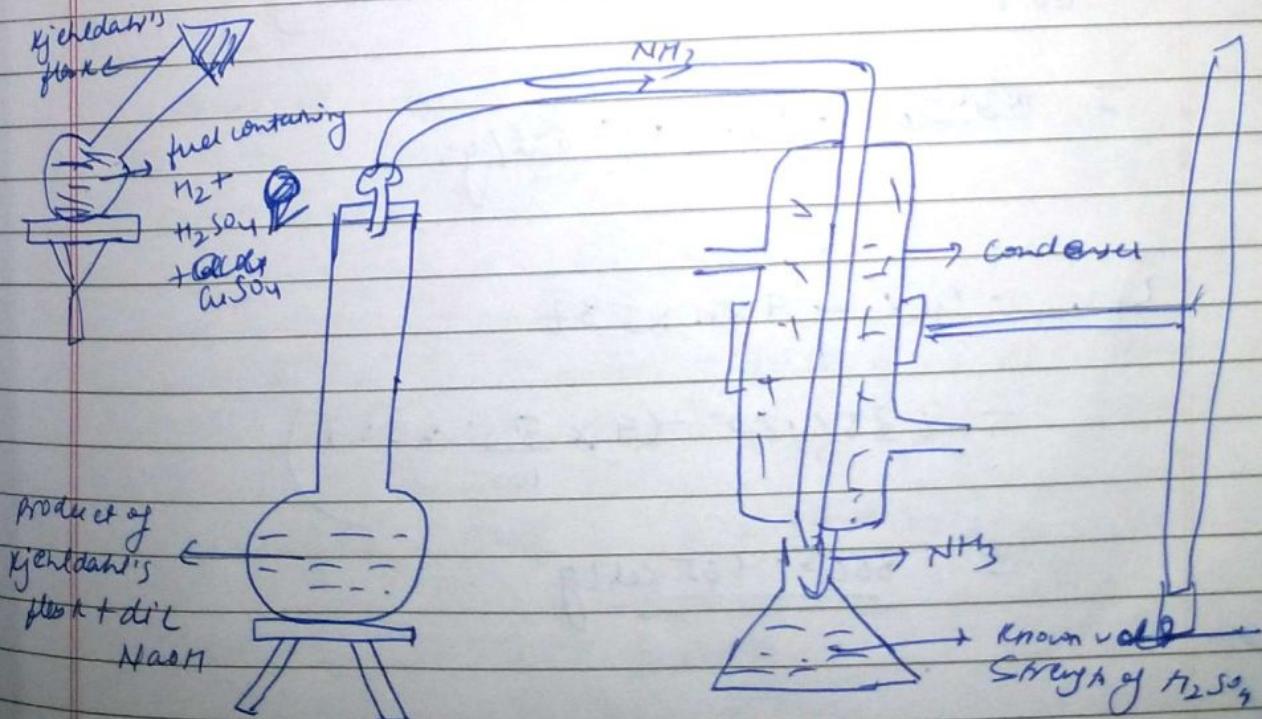
$$\% \text{ of N} = \frac{0.1 \times (v_1 - v_2) \times 14 \times 100}{\text{wt of sample} \times 1000}$$

[Volume in litres]

$$= [0.1(v_1 - v_2) \times 1.4]$$

[Normalizing 0.1 is
diluted in the eqpt]

When wt of sample = 1g.



Significance :

- NO_x has no calorific value & hence its presence is undesirable. Therefore, it is always neglected while calculating calorific value.

Determination of Sulphur

8/2/17

Tutorial Sheet - I

Fuel

No 4.) Buelong's formula

$$\text{FCV} = \frac{1}{100} \left[8080 \text{C} + 34500 \left(\text{H} - \frac{\text{O}}{8} \right) + 2240 \text{S} \right]$$

$$\begin{aligned} \text{FCV} = \frac{1}{100} & \left[8080 \times \frac{84}{100} + 34500 \left(\frac{5.5}{100} - \frac{8.4}{100} + \frac{1}{8} \right) \right. \\ & \left. + 2240 \times \frac{1.5}{100} \right] \end{aligned}$$

$\frac{100 \times 84}{100}$

$$= \frac{1}{100} \left[6787.2 + 1535.25 + 33.6 \right]$$

$$= \underline{\underline{8356.05 \text{ cal/g.}}}$$

$$\text{LCV} = \text{FCV} - 9 \times \text{H} \times 587$$

$$= 8356.05 - \left(9 \times \frac{5.5}{100} \times 587 \right)$$

$$= \underline{\underline{8065.485 \text{ cal/g.}}}$$

$$M7.) \quad w = 250g \\ w = 150g$$

classmate

Date _____

Page _____

$$t_2 = 29.1^\circ C$$

$$t_1 = 27.3^\circ C$$

$$m = 0.72$$

$$\begin{aligned} L &= \frac{(w+w)}{m} (t_2 - t_1) \\ &= \frac{(250+150)}{0.72} (29.1 - 27.3) \\ &= \underline{\underline{1000 \text{ cal/g}}}\end{aligned}$$

$$M8.) \quad C = 90\%, \quad O = 7.0\%, \quad S = 0.5\%, \quad N = 0.5\% \\ A_{SH} = 2.5\%$$

$$\text{Net calorific val} = 8490.5 \text{ kcal/g} \\ (\text{Lcv})$$

Lcv & Gcv

$$\text{Lcv} = \frac{1}{100} \left[8080 \times 90 + 34500 \left(H - \frac{3}{8} \right) + 2240 \times 0.5 \right]$$

$$Gcv = \left[727200 + 34500H - 12937.5 + 1120 \right] \frac{1}{100}$$

$$Gcv = [60902.5 + 34500H] \frac{1}{100}$$

$$Lcv = \frac{60902.5 + 34500H}{100}$$

$$= \frac{609.025 + 345H}{7.53825 + 345H}$$

$$\text{LHV} = \left(609.025 + 345H \right) - \left(\frac{9}{100} \times H \times 587 \right)$$

$$= 609.025 + 345H - 52.83H$$

$$8490.5 = 609.025 - 496.84H$$

$$H = 1.59\%$$

[we take 900 kg
100 mass of H given]
[we take 0.09
because H is to
be in %]

$$\text{LHV} = \left(7153.825 + 345H \right) - \left(\frac{9}{100} \times H \times 587 \right)$$

$$= 7153.825 - 52.83H$$

$$+ 345H$$

$$8490.5 = 7153.825 + 292.17H$$

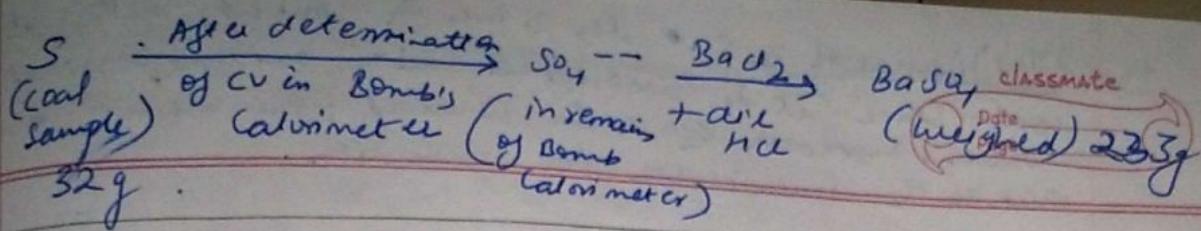
$$H = 4.57\%$$

$$\text{Ans} \quad \underline{\text{LHV}} = 8730.475 \text{ kcal/kg}$$

13/2/17

Determination of Sulphur

Sulphur can be determined by washings obtained from the known mass of coal used in a bomb calorimeter for determination of Calorific value. The washings contain sulphur in the form of sulphate, which is precipitated as BaSO_4 using BaCl_2 . The precipitate of BaSO_4 is filtered & heated to a constant weight & the calculations are done as below.



$$\% \text{ of S} = \frac{\text{wt of } \text{BaSO}_4 \text{ ppt}}{\text{wt of coal sample}} \times \frac{32}{233} \times 100$$

Significance of S.

Thick S contributes to calorific value of coal, it is an undesirable constituent. The reason for this is it produces corrosive gases.

- same as in proximate

Determination of O₂

On combustion like S_2, S_3 & H_2S which are highly objectionable. These gases also cause atmospheric pollution.

$$\% \text{ of O}_2 = 100 - [\% \text{ of C + H + N + S + Ash}]$$

Numericals on combustion.

Molecular weight of air =

28.94 g/mol.

Component	Balanced eqn.	O ₂ required by weight	O ₂ required by volume.
C (xg)	$\text{C} + \text{O}_2 \rightarrow \text{CO}_2$ 12g 32g 44g 1 mole 1/2 mole	$x \times \frac{32}{12}$	$x \times \frac{1}{1} = x$
H (yg)	$\text{H}_2 + \frac{1}{2} \text{O}_2 \rightarrow \text{H}_2\text{O}$ 2g 16g 1 mole 1/2 mole	$y \times \frac{16}{2}$	$y \times 0.5 = 0.5y$
CH ₄ (zg)	$\text{CH}_4 + 2\text{O}_2 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O}$ 16g 64g	$z \times \frac{64}{16}$	$z \times 2 = 2z$

Significance of O₂: Less is the O₂ content, better is the calorific value since it is associated with moisture & low calorific value. Moreover O₂ is in combined form with H₂ & hence H₂ unavailable for combustion.

Q1 Calculate the minimum amount of air required for complete combustion of 100 kg of fuel containing C = 80%, H = 6%, O = 5%, g = 2% & rest Nitrogen by weight.

→	Constituent	% of fuel	Avg wt. of fuel	Balanced eqn.	O ₂ required by weight
C	80%	800g		C + O ₂ → CO ₂ 12g 32g	$\frac{800 \times 32}{12} = 2133.34\text{g}$
H	6%	60g		H ₂ + 1/2 O ₂ → H ₂ O 2g 16g	$\frac{60 \times 16}{2} = 480\text{g}$
S	2%	20g		S + O ₂ → SO ₂ 32g 32g	$\frac{20 \times 32}{32} = 20\text{g}$

Theoretical O₂ req = 2133.34 + 480 + 20g = 2633.34g

Net O₂ req = 50g

∴ Air contains 23% O₂ by weight \rightarrow Net O₂.

Weight of air = $2583.34 \times \frac{100}{23} = 11231.91\text{g}$
 $= 11.23\text{kg}$

$11.23 \times 100 = 1123\text{kg} / 100\text{kg}$ 100 kg of fuel

Q2:

A gas has the following composition by volume: $\text{CO}_2 = 22\%$, $\text{CH}_4 = 4\%$, $\text{C}_2\text{H}_6 = 20\%$, $\text{O}_2 = 3\%$, $\text{N}_2 = 45\%$.

14/2/17
CLASSMATEDate _____
Page _____

If 25% excess air is used actually supplied per m^3 of the gas, find the weight of air.

→ constituent	Am't in balanced eqn ↓ ↓ of fuel	vol of O_2 required for combustion
$\text{H}_2 = 22\%$	$\text{H}_2 + \frac{1}{2}\text{O}_2 \rightarrow \text{H}_2\text{O}$ 0.22 m^3	$0.22 \times 0.5 = 0.11 \text{ m}^3$
$\text{CH}_4 = 4\%$	$\text{CH}_4 + 2\text{O}_2 \rightarrow 2\text{CO}_2 + 2\text{H}_2\text{O}$ 0.04 m^3	$0.04 \times 2 = 0.08 \text{ m}^3$
$\text{CO} = 20\%$	$\text{CO} + \frac{1}{2}\text{O}_2 \rightarrow \text{CO}_2$ 0.20 m^3	$0.5 \times 0.2 = 0.10 \text{ m}^3$ <hr style="width: 100px; margin-left: 0;"/> 0.29 m^3 \downarrow Total theoretical O_2 required.

$0.29 - 0.03 = 0.26 \text{ m}^3 \rightarrow$ Net O_2 required

$$\text{vol. of air required} = 0.26 \times \frac{100}{21} =$$

(\because Air contains 21% O_2 by volume)

[From page 82 for this step]
 $\therefore 22.4 \text{ lt}$ of any gas at NTP = its molecular weight.

$22.4 \text{ lt of air} = 28.94$ grams.

$$\frac{28.94}{22.4} =$$

$$\frac{x \times 100}{125} = 1.07 \rightarrow \text{Actual}$$

$$\frac{x \times 125}{100} = \frac{1.5475 \text{ m}^3}{(1.5475 \times 100 \text{ L})} = 1547.5 \text{ L}$$

$$25\% \text{ excess air is used} = 0.26 \times \frac{100}{21} + \frac{125}{100}$$

$$= 1.5475 \text{ m}^3$$

or
1547.5 L.

$$\therefore \frac{1 \text{ m}^3}{1000 \text{ L.}}$$

1 m^3 air is required actually,
air supplied is 125 m^3

$$1547.5 \times 2894 = 1999.8 \text{ g}$$

$$= 1.999 \text{ kg}$$

Q3:

A sample of coal was found to have the following % composition, C = 75%, H = 5.2%, O = 12.1%, N = 3.2% & Ash = 4.5%

Qii)

i) Calculate the min. air required for complete combustion of 1kg of coal

ii) Also calculate H-CV & LCV of coal sample

f →

constituent	mass in 1kg of fuel	Balanced eqn	vol of O_2 req. for combustion
C = 75%	750g	$C + O_2 \rightarrow CO_2$ 12g 32g	$750 \times \frac{32}{12} = 2000 \text{ g}$
H = 5.2%	52g	$H_2 + \frac{1}{2}O_2 \rightarrow H_2O$ 2g 16g	$\frac{52 \times 16}{2} = 416 \text{ g}$

2416g

$$\text{Net } O_2 \text{ req} = 2416 - 121 = 2295 \text{ g}$$

$$\begin{aligned} \text{Weight of air} &= 2916 \times \frac{100}{23} = 9978.2 \text{ g} \\ &= \underline{9.9782 \text{ kg}} \end{aligned}$$

$$(i) HCV = \frac{1}{100} [8080C + 34500\left(H - \frac{o}{8}\right) + 2240S]$$

$$= \frac{1}{100} [8080 \times 75 + 34500\left(5.2 - \frac{12.1}{8}\right) + 2240 \times 0]$$

$$= \frac{1}{100} [606000 + 127218.75]$$

$$= 13342.18 \text{ cal/g} \quad \underline{\underline{733.218 \text{ cal/g}}}$$

$$Lcv = Hcv - q \times H \times S$$

$$\cancel{13342.18} - \frac{q \times 5.2}{100} \times 587$$

$$\begin{aligned}
 &= 13392.18 - \left(9 \times \frac{5.2}{100} \times 587 \right) \\
 &= 13392.18 - \left(9 \times 5.2 \times 587 \right) \\
 &\approx 13392.18 - 27121.7 \\
 &= 7057.464 \text{ cal/g}
 \end{aligned}$$

27/2/17

Module III - Instrumental methods of analysis

What is spectroscopy?

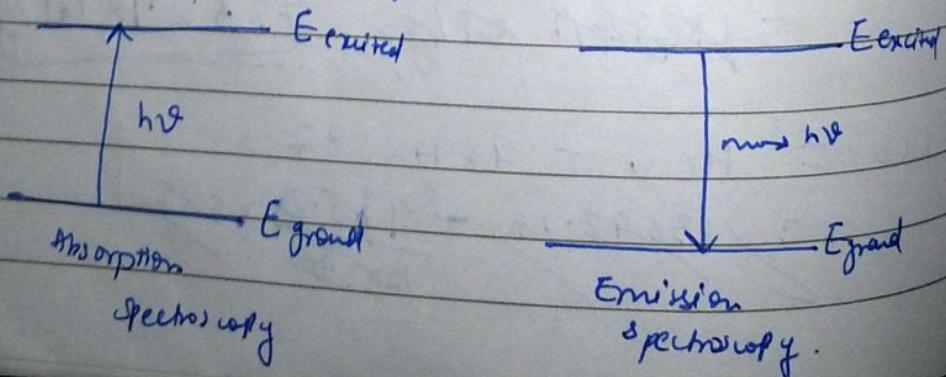
What is spectroscopy?

Spectroscopy deals with the transitions that a molecule undergoes between its energy levels upon absorption of suitable electromagnetic radiations.

There are various types of spectroscopy:

(i) Absorption spectroscopy: in this type, the transition is studied when an atom or molecule absorbs EMR (electromagnetic radiation) & goes from lower energy level to the higher energy level.

(ii) Emission Spectroscopy: in this type, the transition studied is when an atom or molecule falls from excited state to the ground state



Another type of classification is :

Atomic spectroscopy & molecular spectroscopy.

classmate _____

Date _____

- (i) In Atomic spectroscopy, transitions of an electron between atomic energy levels is studied
- (ii) In molecular spectroscopy, transition b/w molecular energy levels (rotational & vibrational) are studied

Spectrophotometer

It is an instrument used for absorption measurements & can be made to operate in UV visible, infrared etc. using suitable energy source. It has got the following components:

- i) source of EMR : to generate the required EMR various sources are used as:
 - (a) for infrared → Hg arcs inside a quartz envelope is used or electrically heated rod of rare earth oxides can be used
 - (b) for UV → a hydrogen discharge lamp is used
 - (c) for visible → tungsten filament lamp is used
 - (d) for producing radio frequency → used in NMR → electric current is caused to oscillate in coil of wire
- ii) wavelength controller : this component is a dispersing element which separates different frequencies into different spatial directions.

Eg: a glass or quartz prism or a diffraction grating

Date _____
Page _____

- iii) Sample holder's it varies with the type of spectroscopy like a test tube or a quartz cell etc.
- iv) Photodetector / Receptor unit: this unit detects & converts radiant energy into measurable electrical signal
Eg: photo multiplier tube, thermo couple detector, crystal diode etc.
- v) Amplification / recording unit: in this unit, electrical signal is amplified followed by output generation either on computer monitor or graphical printout

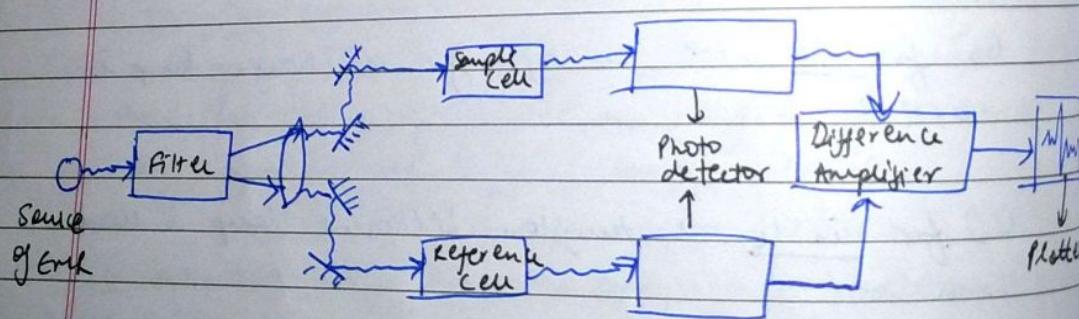
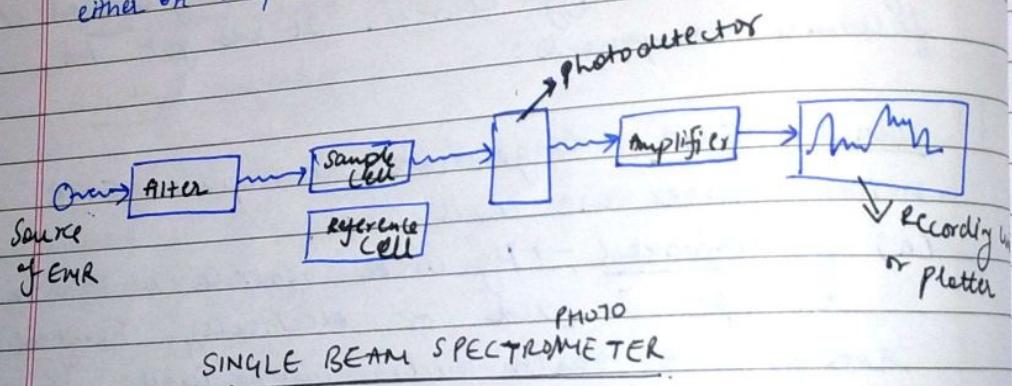


PHOTO
DOUBLE BEAM SPECTROMETER

(i)
(ii)

(iii)
B

(iv)
There
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U-V visible Spectroscopy

UV - Visible (200 - 780 nm)

28/2/17 Tuesday

Date _____
Page _____

Type of transitions. - electronic.

This is also known as electronic spectroscopy. It involves electronic transitions from ^{our} ground to excited state. The type of electrons involved may be σ , π or π^* electrons.

$n \rightarrow$ lone pair electron (non bonding electron)

$\sigma \rightarrow$ Single bond electrons

It is very useful to measure the no. of conjugated double bonds & aromatic configuration. It can distinguish between conjugated & non-conjugated systems.

When a radiation of a desired frequency is made to fall on a sample of a substance, energy will be absorbed & electrons will be promoted to the higher energy state. Thus, the radiation leaving the sample after absorption will be either less intense or its intensity may be completely lost.

There are two laws which govern the absorption of radiation by the molecules:

Lambert's

(i) ~~No~~ Beer's law

(ii) Beer - Lambert's law

(i) ~~Defn~~. According to Lambert's law, When a beam of monochromatic radiation passes through a homogeneous absorbing medium, the rate of decrease of intensity of radiation with thickness of absorbing medium is proportional to the intensity of incident radiation. Mathematically,

$$-\frac{dI}{dx} \propto I$$

$$-\frac{dI}{I} = k dx$$

$$\int_{I_0}^I \frac{dI}{I} = - \int_0^x k dx$$

$$\ln \frac{I}{I_0} = -kx$$

$$2.303 \log \frac{I}{I_0} = -kx$$

$$\log \frac{I}{I_0} = \left[\frac{-k}{2.303} \right] x$$

$$\left[\log \frac{I_0}{I} \right] = Ex$$

$$A = Ex$$

$$\therefore (A = \log \frac{I_0}{I})$$

where,

A = absorption

E = Molar extinction coefficient or molar absorptivity constant

x = thickness of medium

(ii)

Beer-Lambert's law or Beer's law: it states that when a beam of monochromatic radiation is passed through a solution of an absorbing substance, the rate of decrease of intensity of radiation with thickness of the absorbing solution is proportional to the intensity of incident radiation as well as concentration of solution.

Mathematically,

$$\frac{-dI}{dx} \propto I$$

$$-\frac{dI}{I} = k_c dx$$

$$\int_{I_0}^I \frac{dI}{I} = - \int_0^x k_c dx$$

$$\ln \frac{I}{I_0} = -k_c x$$

$$2.303 \log \frac{I}{I_0} = -k_c x$$

$$\log \frac{I_0}{I} = E_c x$$

$$A = E_c x$$

$$\therefore (A = \log \frac{I_0}{I})$$

Remember,

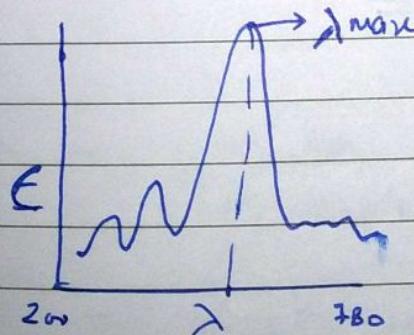
$$A = \log \frac{I_0}{I}$$

$$T \text{ (Transmittance)} = \frac{I}{I_0}$$

$$A = \log \frac{1}{T}$$

OR

$$A = -\log T$$



CLASSMATE
Date _____
Page _____

$$\% \text{ fuel carbon} = 100 - (\% \text{ H} + \% \text{ C} + \% \text{ N})$$

$$= 100 - (1.25 + 32.35 + 10.25) = 100 - 43.85$$

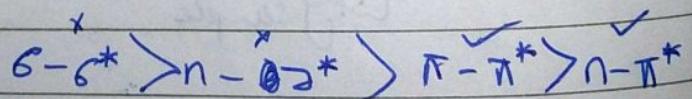
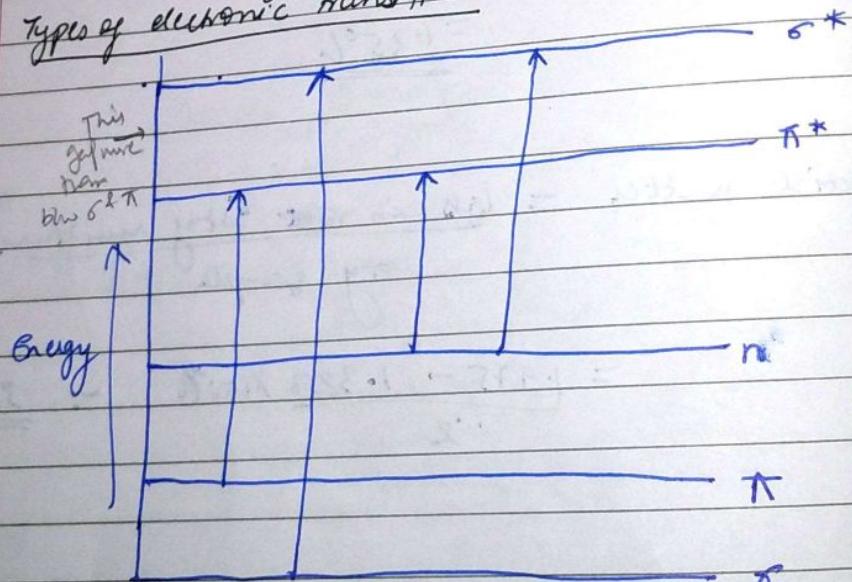
$$= 56.15\%$$

613117

Q: why broad bands are observed in UV-vis instead of sharp peaks?

→ It is due to the fact that excitation of electrons are also accompanied by the constant vibratory rotatory motion of the molecules. The vibratory rotating modes are also quantized

Types of electronic transitions



UV visible

In $\text{e}^- \text{UV}$, first two transitions are not classifiable.
Condition: It should be unsaturated (π) more than
single bond

Date _____
Page _____

① $\text{C}_2\text{H}_5\text{OH} \rightarrow$ UV went show. as $\sigma - \sigma^*, \pi - \pi^*$
 \rightarrow lone pair + π or only π .

② $\text{CH}_3\text{Cl} \rightarrow \sigma - \sigma^*, \pi - \sigma^*$

③ $\text{CH}_3\text{CH}_3 \rightarrow \sigma - \sigma^*$

④ $\text{CH}_3\text{CHO} \rightarrow$
All transitions $\pi - \pi^*, \pi - \pi^*, \pi - \sigma^*, \sigma - \sigma^*$
are possible

Chromophore Concept

It is defined as any isolated covalently bonded group that shows a characteristic absorption in UV or visible region. There are two types of chromophores.

1) chromophores in which the group contains π electrons & they undergo $\pi - \pi^*$ transitions.
e.g. Acetylene, ethylene

2) chromophores which contain both π electrons & σ electrons & undergo two types of transitions:

$\pi - \pi^*, \pi - \sigma^*$

e.g. Carbonyls, nitriles, azocompounds, nitro compounds etc.

Aunochro me:

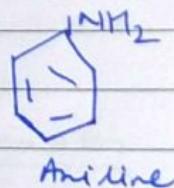
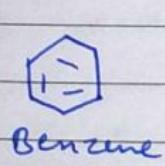
An ~~auto~~ aunochro me can be defined as any group which does not itself act as a chromophore but whose presence brings about a shift of the absorption band towards the red ~~end of the~~ ^{end of the} spectrum i.e. towards higher wavelength.

An aunochro meic group is also called colour enhancing group.

The effect of the aunochro me is due to its ability to extend the conjugation of a chromophore by sharing of ~~resonance~~ non-bonding electrons.

E.g. -OH, -OR, -NH₂, -SH etc.

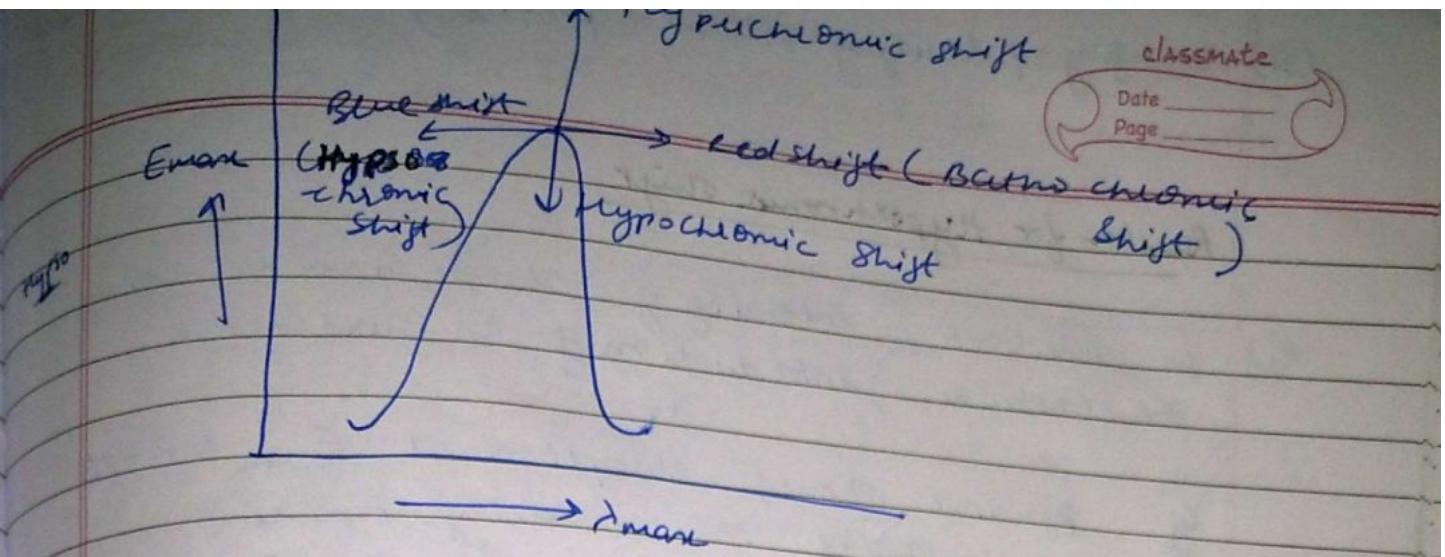
Eg. Benzene has a $\lambda_{max} = 255\text{ nm}$ whereas Aniline has a $\lambda_{max} = 280\text{ nm}$



∴ Due to ~~energy~~ resonance, energy lowers
as ~~is~~ resonance causes stabilization

$$(f) E \propto \frac{1}{\lambda}$$

Absorption & Intensity Shifts



Reasons for Bathochromic shift

Reasons for Bathochromic shift

(i) Presence of autochrome

(ii) change of Solvent.

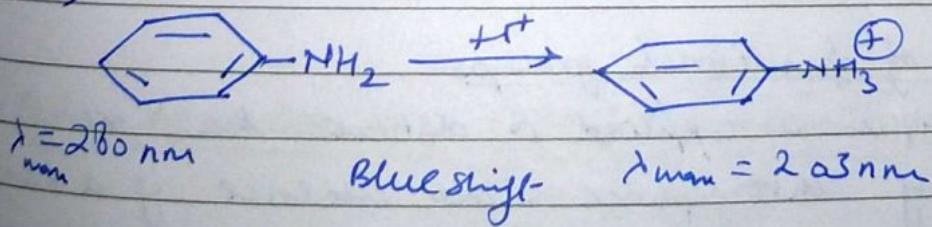
↳ When polarity of solvent is decreased
polarity \propto wavelength of absorption

Reasons for Hypsochromic shift

(i) Removal of Conjugation

↳ e.g. In acidic solution, aniline shows a blueshift.
Why?

→



due to removal of conjugation, stability decrease.

(ii) changing polarity of solvent (polarity γ)

Reasons for hypochromic shift

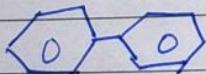
In this case, intensity of absorption is increased.
The reason is, introduction of an auxochrome.

E.g. Pyridine shows absorption at $\epsilon_{max} = 2750$
which is shifted to 2-methyl pyridine
 $\epsilon_{max} = \approx 3560$

Reasons for hypochromic shift

In this case intensity of absorption is decreased,
i.e. ϵ_{max} is decreased. The reason is introduction
of groups which distort the geometry of molecule.

E.g. Biphenyl has $\epsilon_{max} = 19000$
& 2-methyl Biphenyl has $\epsilon_{max} = 10250$ ↓ decreasing



Biphenyl

7/3/17.

Applications of UV-vis

1. Detection of functional groups

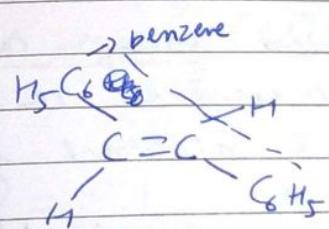
The technique is applied to detect the presence or absence of chromophore. The absence of a band at a particular wavelength may be regarded as an evidence for the absence of particular group in the compound.

2. Extent of conjugation: It helps in determining ~~extents of~~
the extent of conjugation, addition shifts the absorption to higher wavelength.

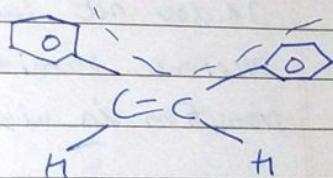
3. Distinction in conjugated & non conjugated compounds:
Eg: $(CH_3)_2C=CH-C(CH_3)_3$ } will absorb at higher wavelength due to conjugation.
 $CH_2=C(CH_3)-CH_2-C^{\ddagger}(CH_3)$

4. Identification of an unknown compound: Every compound has a characteristic ~~λ~~ max ~~wavelength~~ on the basis of which it can be identified.

5. Perturbation of configuration of geometrical isomers



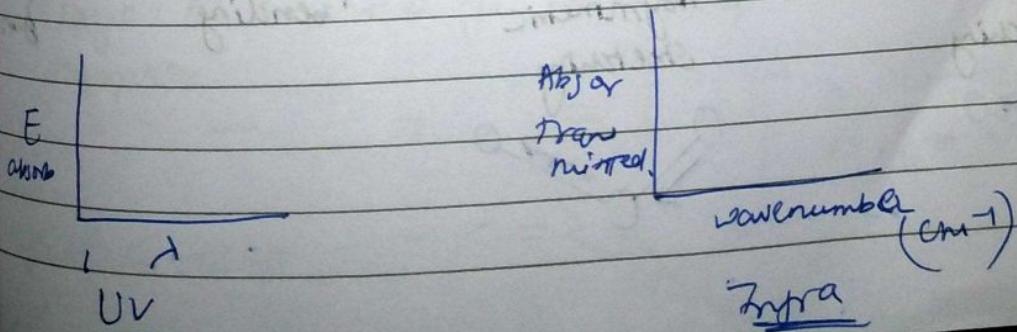
Trans-stilbene
higher λ



Cis - stilbene

There is a lack of coplanarity & hence, less stable.
Absorbed at lesser λ value!

Infrared Spectroscopy (IR): 4000 cm⁻¹ - 400 cm⁻¹



IR active: only those compounds which show change in dipole moment are absorbed in IR
R are known as IR active compounds. (CO₂ exception)

IR inactive: do not have dipole moment.
e.g. O₂, N₂

Q: Why CO₂ is IR active?
→ CO₂ is exception to above rule. Though it does not have dipole moment but certain vibrational mode of CO₂ shows dipole moment & therefore, it is IR Active.

Vibrations Types of vibrations

→ Electronic transitions are not possible in IR as IR does not have sufficient energy to cause electronic transitions & therefore IR involves transition in vibrational & rotational levels.

Types of vibrations (that can occur in a molecule after absorbing IR)

Stretching vibrations

(change in bond length)
(leads to higher energy)

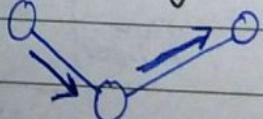
Bending Vibrations

(change in bond angle)
(involves less energy)

Symmetric stretching



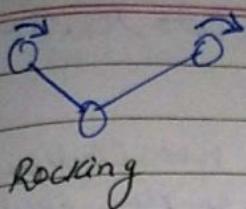
Asymmetric stretching



In-plane bending

out-of-plane bending

In plane bending

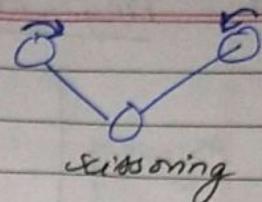


Rocking

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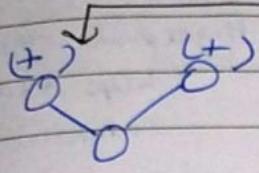
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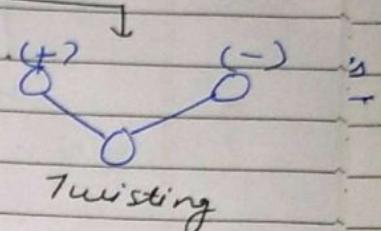


scissoring

out of plane bending



wagging



Twisting

(+) → towards you

(-) → away from you

vibrational frequency (ν)

$$\nu = \frac{1}{2\pi c} \sqrt{\frac{k}{\mu}}$$

where k is force constant depending on bond strength
& μ is reduced mass. $= \frac{m_1 m_2}{m_1 + m_2}$

where m_1 & m_2 are masses of two atoms involved.

(c , the velocity of radiation.)

Q: Arrange the monoxide of increasing wave number of absorption.
following in

- , = , ≡

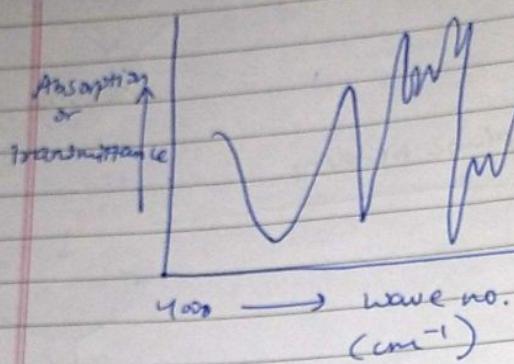
- < = < ≡

[As bond strength = K
so, $\nu \propto K$]

→ O < O < O

IR Spectroscopy

Fingerprint Region



- No two compounds can have similar spectra in this region & hence, this region is known as fingerprint region which helps to identify the unknown compounds.

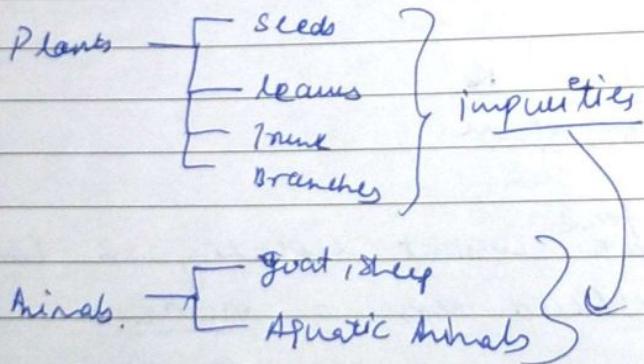
14/13/17

Lubricants

On basis of source:

(1) Natural (80%) (2) synthetic
↳ Plants, Animals, crude oil

(1) Primary (2) Secondary



Crude → (1) wax (Asphaltic impurity)
(2) fatty acids
(3) suspended particles

Ways of lubricants. (3 mechanisms)

- ① Thick film lubrication / hydrodynamic
- ② Thin film lubrication
- ③ Semi solid lubrication

classmate

Date _____

Page _____

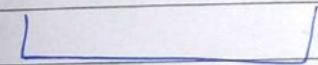
Properties.

- ① Viscosity (η)
- ② Consistency / oiliness → (most imp. property)
- ③ Thermal stability (Δ_c)
- ④ Ignition temperature → Flash point
- ⑤ Boiling point → Fire point.
- ⑥ Iodine Value (tells about unsaturated part of oil)
- ⑦ Ailine point (temp. at which oil gets immiscible with ailine)

1) Thick film lubrication

In hydrodynamic lubrication, the two sliding surfaces are separated by a thick film of lubricant (thickness of film should be $> 100 \mu\text{m}$). This film of lubricant is adsorbed on the metal surface which is held by van der waal forces. The coefficient of friction in this type of lubrication is low.

Eg: used in delicate machinery like scientific instruments, scientific clock, watches.



Adsorption.

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2) Thin film/ Boundary film lubrication

In some cases another condition of high load & low speed or low viscosity of oil, the lubricants tends to squeeze ^{down} out of the position. So, continuous film is not formed b/w two sliding surfaces. In such cases, the ~~adsorbed~~ lubricant is maintained by a

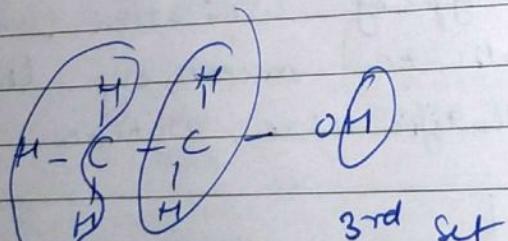
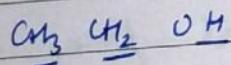
1000 *classmate*
Date _____
Page _____

thin film whose thickness is less than the lubricants may be absorbed chemically or by some physical force which results direct contact resulting lowering of friction in such case is generally too coefficient of friction is low about (0.025 to 0.15) : In this type of lubricity, lubricant must have long chain of hydrocarbons, high viscosity index, good oiliness property, low pour point.

20/11/17.

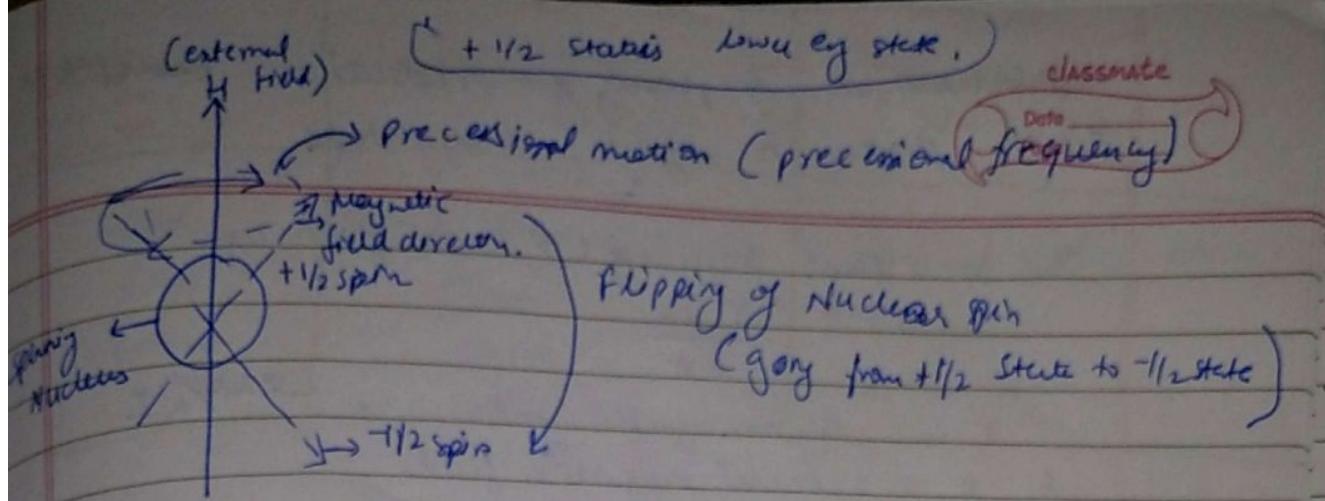
NMR Spectroscopy (Nuclear magnetic resonance)

EPR used → Radio waves
Here we study spin change in electrons.



1st 2nd set

of equivalent protons.



principle of NMR: the proton is a spinning magnet which precesses. NMR involves interaction between an oscillating magnetic field of radiowaves & magnetic energy of hydrogen nucleus or some other type of nuclei when they are placed in an external magnetic field. Consider a spinning top whose spinning axis of which moves slowly around the vertical axis of earth's gravitational field. This motion is known as precessional motion. The spin of nucleus can be compared with this motion which precesses around the axis of external magnetic field. It can either precess in alignment with external field or opposed to the external field. The aligned orientation is stable & of low energy whereas the opposed orientation is unstable & is of higher energy.

If a proton is precessing in aligned orientation, it can pass into the opposed orientation by absorbing energy of EMR (radio waves). This transition from one energy state to another is called flipping of proton.

The energy required to bring about the transition depends upon the strength of external field. Stronger the field, greater will be the tendency of the nuclear magnet to remain lined up with it &

higher will be frequency of radiation
to flip the proton to higher energy state

CLASSMATE
needed
Date _____
Page _____

The precessional frequency (ν) is given by

$$(\nu) = \frac{\gamma B_0}{2\pi}$$

& γ is Gyromagnetic ratio = $2\pi\mu/hI$
& B_0 is external magnetic field.

where, μ = magnetic moment of spinning nucleus

I = spin quantum number

h = Planck's constant.

Spin-active nuclei

Nuclei that exhibit NMR phenomenon are known as spin active nuclei. Only those nuclei will exhibit the phenomenon of NMR for which the spin quantum number (I) is greater than 0.

E.g. 1H , 2He , ^{13}C , ^{19}F etc.

Some of the nuclei that are spin-inactive are ^{12}C , ^{16}O , ^{32}S etc. As they have $I=0$.

Spin quantum number is associated with mass number & atomic number as below:

Mass no.

Atomic No.

Spin quantum number
No. (ASSUME 1/2)

Odd

Even

Even

odd or even

Even

odd

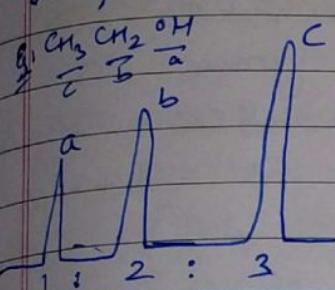
$1/2, 3/2, 5/2$ etc...

0

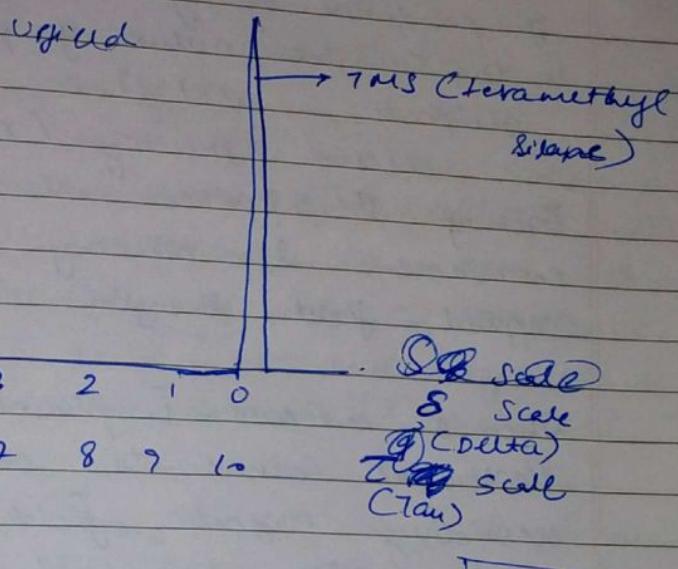
1, 2, 3, ...

Chemical Shift

Downfield

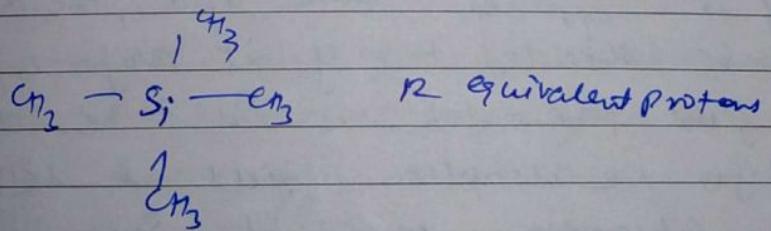


Upfield



$\rightarrow B_0$

(External magnetic field)



deshield \rightarrow downfield peak

shielded \rightarrow upfield peak

Tetramethyl Silane

No. of signals.

The no. of signals in an NMR spectrum tells the number of different sets of equivalent protons in a molecule. Each signal corresponds to a set of equivalent protons.

Eg: $\text{CH}_3 \text{CH}_2 \text{OH}$ has 3 sets of equivalent protons.

The positions of the signals

classmate

Date _____

Page _____

(i) (i) tell no. of signals

(ii) Draw NMR Spectrum.

(Deshielding occurs ^{when} ~~because~~ ~~it is more due to~~
-I)

The positions of signals in NMR spectrum helps us to know the nature of protons, i.e. aromatic, aliphatic, acetylenic, vinylic & adjacent some electron attracting / releasing group etc. Each of these protons will have different electronic environments & thus they absorb at different applied field strengths.

When a molecule is placed in a magnetic field, its electrons are caused to circulate & they produce secondary magnetic field, i.e. induced magnetic fields. ~~This~~ This field can either oppose or reinforce the external magnetic field at the proton. If it opposes the field, the proton is said to be shielded but if it reinforces the ~~field~~ external field, the proton is said to be deshielded.

Shielding shifts the absorption upfield & deshielding shifts the absorption downfield. Such shifts as compared with standard reference TMS in the positions of NMR absorptions which arise due to shielding or deshielding of protons by the electrons are called chemical shifts.

For measuring chemical shift, signal ~~of~~ ^{from} TMS is taken as a reference due to the following reasons:

- ASSIMATE
- CLASSMATE
Date _____
Page _____
- (i) It has maximum number of equivalent protons in its structure.
 - (ii) Due to low electronegativity of Si, the protons in TMS are shielded more than any other compound.
 - (iii) It is miscible with all organic substances.
 - (iv) It is highly volatile & is readily removed from the system.
 - (v) It does not take part in intermolecular associations with the sample.

Unit for measuring chemical shift

Chemical Shift positions are expressed in δ units which are defined as difference in ppm from the TMS Signal. The value of δ for a substance with respect to TMS can be obtained by measuring resonance frequency of the sample & the TMS

$$\boxed{\delta = \frac{V_{\text{sample}} - V_{\text{TMS}}}{\text{operating frequency}}} \quad (V_{\text{frequency}})$$

Another scale used for measurement of chemical shift is τ scale which is given as

$$\boxed{\tau = 10 - \delta}$$

22/3/17.

Q: For a solution of camphor & hexane in a 1 cm cell absorbance was found to be 2.52 at 295nm & $E_{\text{max}} = 14$. What is concentration of camphor?

2.52

$$\rightarrow A = \epsilon ct$$

$$2.52 = 14 \times c \times 2.2 \times 10^{-3} \Rightarrow c = 14 \times 10$$

$$c = 0.018 \text{ moles/L}$$

$$f = 1.8 \times 10^{-2} \text{ mole/L}$$

1252

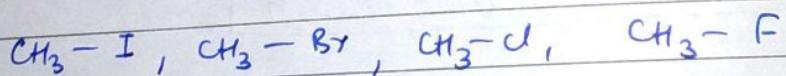
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Factors affecting chemical shift

The chemical shift is affected by shielding or deshielding of the proton by the electrons of the surrounding environment. (already discussed under chemical shift).

Shielding & deshielding occur due to the following factors:

- (i) electronegativity (-I effect)
Causes deshielding & shifts the peak downfield.



$\rightarrow + I$ effect \therefore opposite

- (ii) hydrogen bonding

Deshielding — peak is downfield.

- (iii) aromatic compounds

Causes deshielding — peak is downfield.

- (iv) carbonyl compounds

Deshielding — peak is downfield

(c) Anisotropic effects

classmate

Date _____

Page _____

(a) = bonded compounds \rightarrow deshielding - downfield

(b) = bonded compounds \rightarrow shielding - upfield.

Module - IV Corrosion (mostly reasoning corrosion)

Q Prove that corrosion is reverse of extraction.

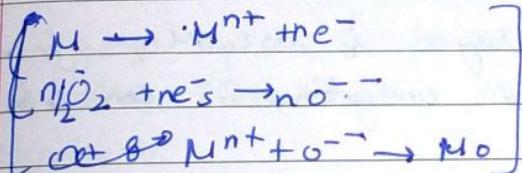
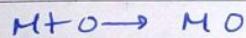
\rightarrow Corrosion \rightarrow spontaneous, extraction \rightarrow requires energy etc.

Types

Dry or chemical
corrosion

wet or electro
chemical
corrosion

→ (i) oxidation



→ (ii) by other gases

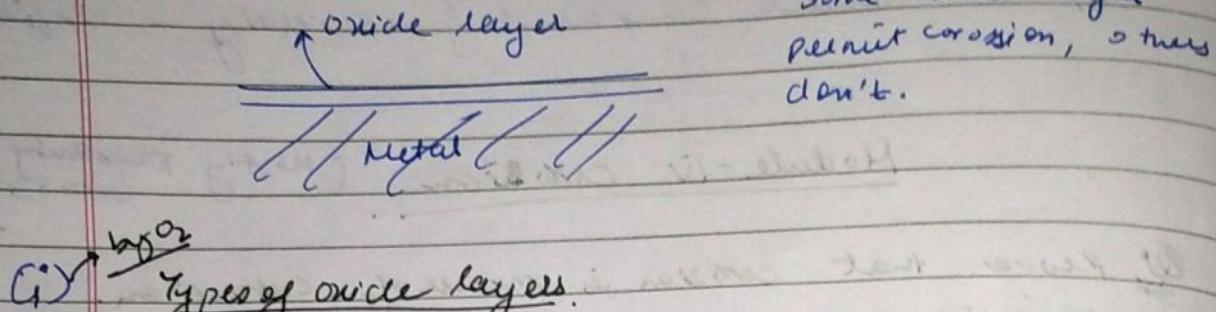
→ (iii) liquid natural
corrosion ~~gas~~

Mechanism of dry corrosion

classmate

Date _____

Page _____



(i) stable: If a layer of oxide is stable, it does not allow further ~~corrosion~~ corrosion as it becomes impervious.

Eg: Al, Chromium, Tin (Sn)

(ii) Unstable: There is no corrosion in such metals since oxide layer formed is converted back to the metal.

Eg: Noble metals like Ag, Au, etc.

(iii) Volatile: if oxide layer is volatile, fresh metal surface is exposed everytime & corrosion rate is very high.

Eg: Molybdenum oxide (MoO_3)

(iv) Porous: in this case, the porosity of oxide layer allows further ~~corrosion~~ corrosion & thus, rate of corrosion is high.

Eg: All alkaline earth metals like Fe, Ba etc.

Pilling-Bedworth rule

Acc. to this rule, if the volume of oxide is less than volume of metal, the oxide

layer is porous, & hence non-protective
E.g. Li, Na, K, Mg, Fe etc.

classmate
Date _____
Page _____

& vice-versa.

$$\text{Specific volume ratio} = \frac{\text{Volume of metal oxide}}{\text{Volume of metal oxide}}$$

by other gases.

28/3/17

(ii) Gases like CO_2 , SO_2 , Cl_2 , H_2S etc.

The extent of corrosion depends on chemical affinity b/w metal & gas involved.

Further corrosion depends on the formation of initial layer which may be porous or non-porous (discussed earlier)

One example of this is Attack of Cl_2 on Sn.

When SnCl_4 is formed which is volatile & leads to very high rate of corrosion whereas AgClO_2 film formed on Silver is protected & hence does not allow further corrosion.

It is

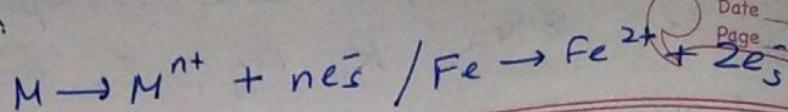
Due to chemical action of flowing liquid metal at high temperatures on solid metal or alloy,

It involves dissolution of solid metal by liquid metal or internal penetration of liquid metal into the solid metal.

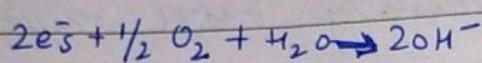


Wet or electrochemical corrosion

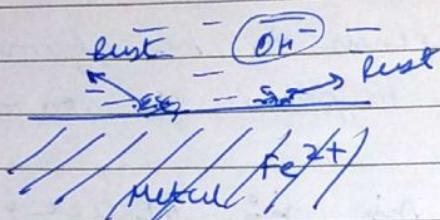
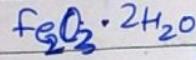
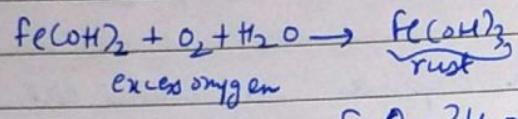
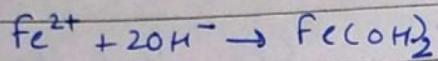
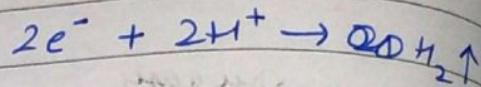
Mechanism:

At anode:At cathode:

Neutral medium



Acidic medium



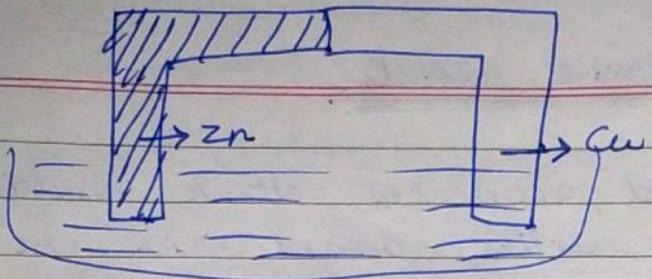
The two reactants Fe^{2+} & OH^- originate from anode & cathode respectively but their combination occurs more commonly near the cathode because smaller Fe^{2+} ions diffuse more rapidly than the larger OH^- ions & so corrosion occurs at anode but the rust is deposited at cathode.

can come in reasoning.

Corrosion is more when cathode is bigger in size than anode]

Types of wet chemical corrosion

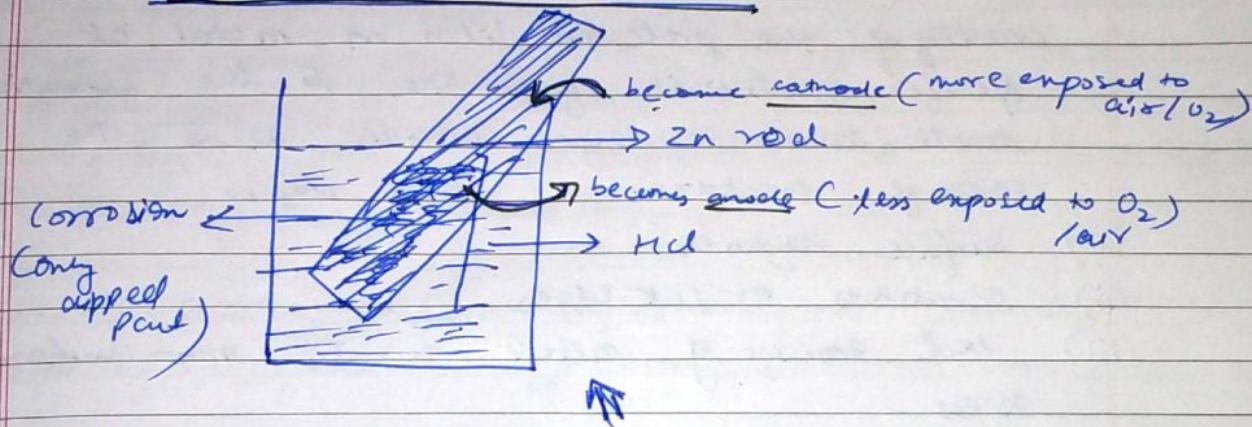
- (1) Galvanic or Bimetallic corrosion



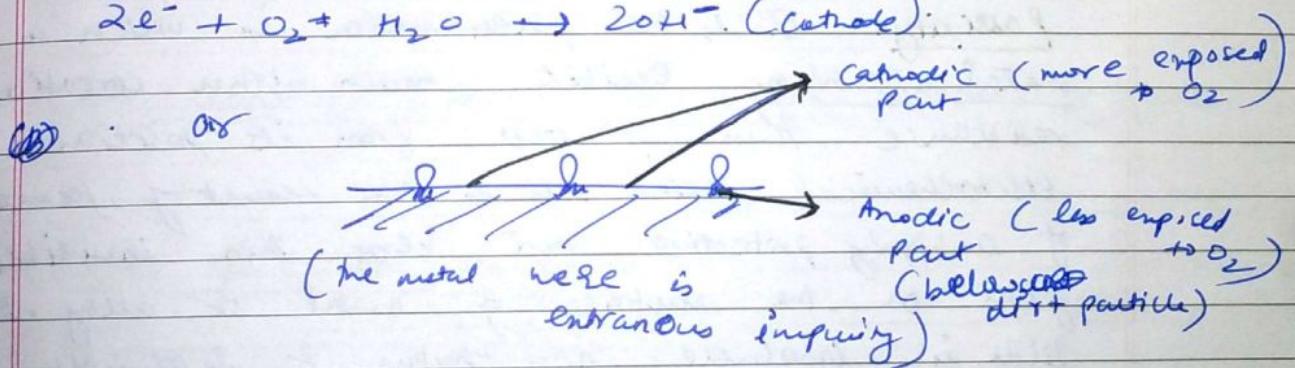
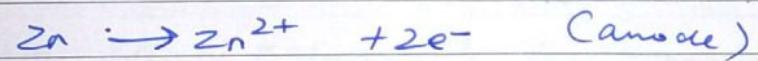
classmate
Date _____
Page _____

here two metals involved. one metal becomes anodic in comparison of other.

v. v. important
(ii) Concentration cell corrosion

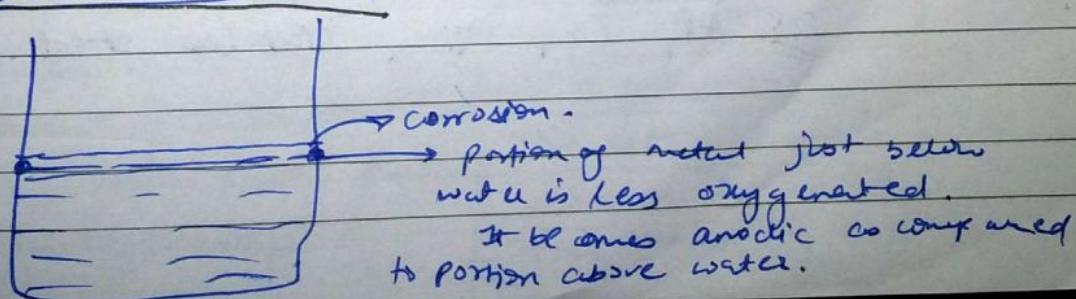


(a) Differential aeration corrosion:



Inpure metal gets more easily corroded due to formation of tiny electrochemical cells.

(b) Watertline corrosion:



V.V. Jayalakshmi

C) Pitting Corrosion.It occurs in passive metals.

It is a localized, accelerated attack resulting in formation of cavities around which the metal is relatively unattacked. It leads to reformation of pinholes, pits & cavities in the metal. It occurs due to breakdown or cracking of the protective film on metal at specific points which gives rise to the formation of small anodic & large cathodic areas. The reason of breakdown of film may be:

- (i) Surface roughness
- (ii) Scratches or cut edges
- (iii) Local straining of metal due to non-uniform stress
- (iv) Sliding under load
- (v) Chemical attack.

Passivity: it is the phenomenon in which a metal or alloy exhibit much higher corrosion resistance than expected from its position in electrochemical series. It is the result of formation of a highly protective but very thin invisible film on the surface of metal or alloy. This film is insoluble, non-porous & is of self healing nature. The passive metals are passive only (i.e. show passivity) only in oxidizing environments. But in reducing environment, their passivity is lost.

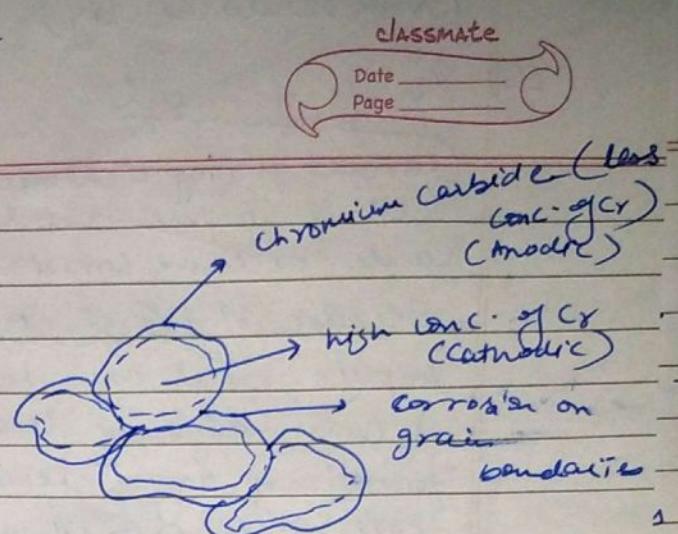
Eg: Al, Cr, Ti ; stainless steel.

(c) Intergranular corrosion

in Metals & alloys.

at micro level.

Eg: stainless steel.



Prevention:

- by heat treatment (heating to high temp & sudden cooling)
- by using low carbon steel
- on sudden cooling, layer does not deposit.
- by low carbon, ~~Chromium carbide~~ not formed.

Galvanic series: (do from book)

Q: diff b/w galvanic & electrochemical series.

Also learn positions of elements of galvanic series.

factors affecting corrosion

Nature of metal

- position of metal in galvanic series

- over voltage

Explain: in over voltage accelerates the corrosion rate & vice versa

- relative areas of anode & cathode

Nature of corroding environment (medium)

- temperature

- humidity

the rate of corrosion will increase till critical humidity after which it becomes constant.

(Anode should be big)

(v) Purity of metal

(Formation of tiny e-chemical cell in impure metal cause excessive corrosion)

Because of heterogeneity

Impure metals are heterogeneous & their heterogeneity leads to formation of tiny e-chemical cells at the exposed parts which causes corrosion

E.g.: Zn-Metal containing Pb or Fe as impurity

(vi) Physical state of metal

The smaller the grain size, greater will be corrosion.

(vii) Area under stress

Sharp corners corrode more

(viii) Nature of surface film

(Explain nature of oxide)

(ix) Passive character of metal

(x) Solubility of corrosion product

If corrosion product is soluble, the corrosion proceeds at a higher rate. On the contrary if corrosion product is insoluble, it forms a physical barrier & reduces the rate of corrosion.

E.g.: Corrosion of lead in acidic medium (H_2SO_4)

$PbSO_4$ formed which is insoluble & reduces corrosion rate.

Classmate
Date _____
Page _____

E.g. in industrial areas → presence of corrosive gases increases corrosion (CO_2, SO_2)

(xi) Presence of suspended particles in atmosphere

Two kinds of impurities may be true:
• chemically active like $NaCl, (NH_4)_2SO_4$ etc.
• chemically inactive E.g. charcoal

(xii) Influence of pH

$pH < 7 \rightarrow$ high corrosion

(xiii) Nature of ions present

V.V. Imps (Today)

Nature of ions play an imp. role in corrosion. E.g.:

presence of silicate ions leads to the formation of insoluble reaction products which inhibits further corrosion. On the other hand, presence of chloride ions destroys the protective & passive surface film exposing the fresh metal surface for corrosion.

Other examples are: increase in rate of corrosion of Fe in presence of ammonium salts. Also, traces of copper or any other noble metal in mine waters

v. inhibitor
(X)

Volatility of corrosion product

Eg: Molybdenum oxide
(MoO_3)

accelerates corrosion
of iron pipes used
for carrying such
waters.

Date _____
Page No. _____

(iii) Conductance of corrosive medium

↑ conductance, ↑ corrosion.

(iv) Formation of O_2 concentration cell

v. v. inhibitor

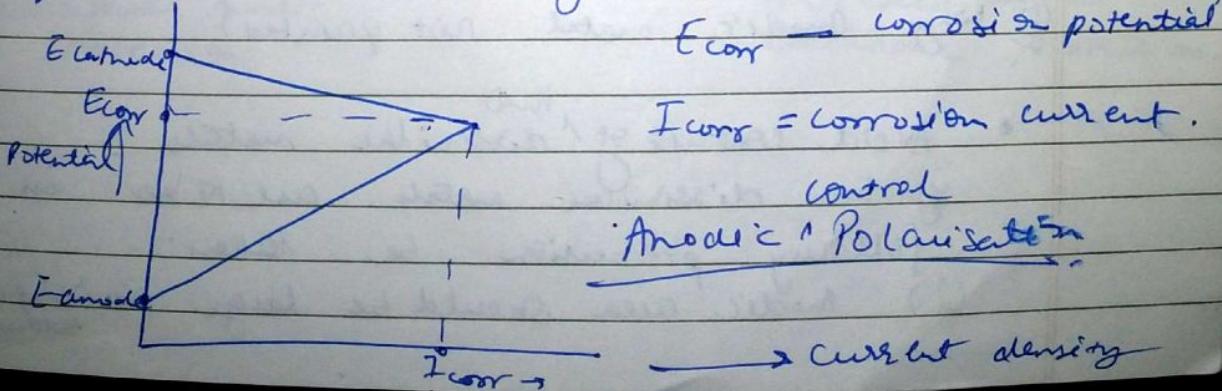
polarisation of electrodes

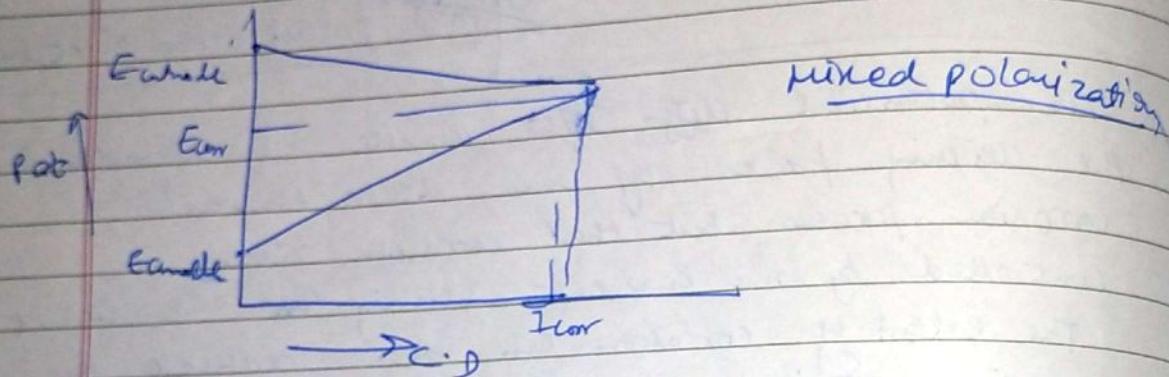
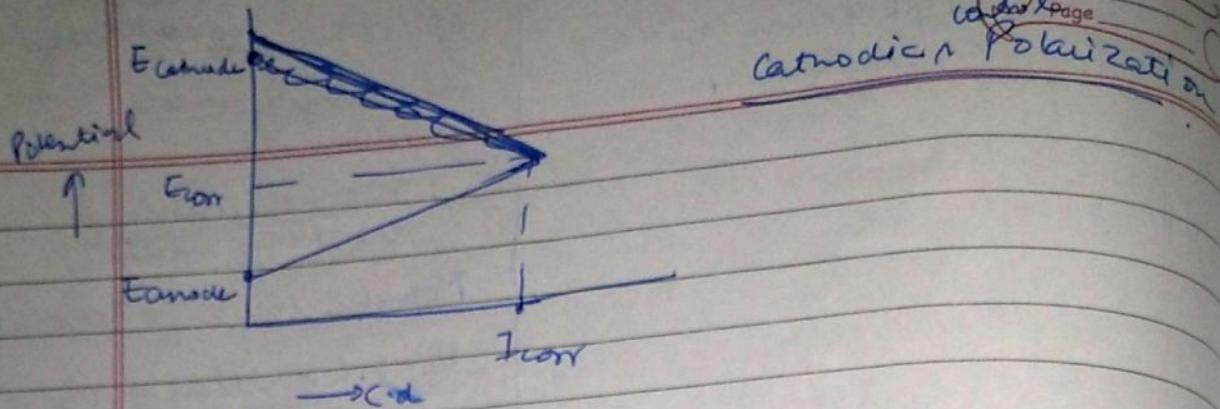
The potential diff. b/w anode & cathode is the driving force of an electrochemical corrosion process but the corrosion rate is controlled by the current flowing in the circuit.

The extent of corrosion can be reduced by adding certain organic or inorganic substances called inhibitors to the corroding environment.

These inhibitors cause irreversible changes around the electrodes which tend to oppose the direction of corrosion current. If the reaction at anode is reversed the anode becomes less anodic & is said to be polarised whereas if reaction at cathode is reversed, the cathode becomes less cathodic & is said to be polarised.

The polarisation can be understood with the help of Evans's diagrams in which potential is plotted against current density





As the corrosion reaction progresses, the PD b/w anodic & cathodic areas alters & ultimately a steady state is reached which is known as corrosion potential (E_{corr}). The corrosion pending value of current at this potential is known as corrosion current (I_{corr})

Protection against corrosion.

~~V.Vinayak~~

1) Proper designing.

Q: Why Anodic metal not painted?

- Avoid contact of ^{two} dissimilar metals if two dissimilar metals are to be in contact following precaution be taken:
 - (i) Anodic area should be large as compared to cathodic

- Date _____
Page _____
- (ii) two metals should be as close as possible
(in electrical sense)
 - (iii) An insulator fitting should be applied
b/w two metals.
 - (iv) ~~Anodic metal should not be painted or coated as it leads to excessive corrosion.~~

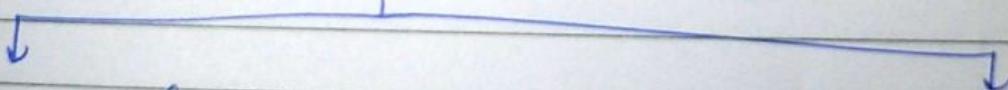
- Metal should not have inhomogeneities
~~(no crevices etc.)~~
(Avoid presence of crevices b/w adjacent parts, less use of bolts & rivets)
- Design should allow adequate cleaning & flushing (sharp corners & recesses should be avoided which may lead to accumulation of dirt or dust)
- whenever possible, equipment be supported on legs to allow free circulation of air

2) Using pure metal.

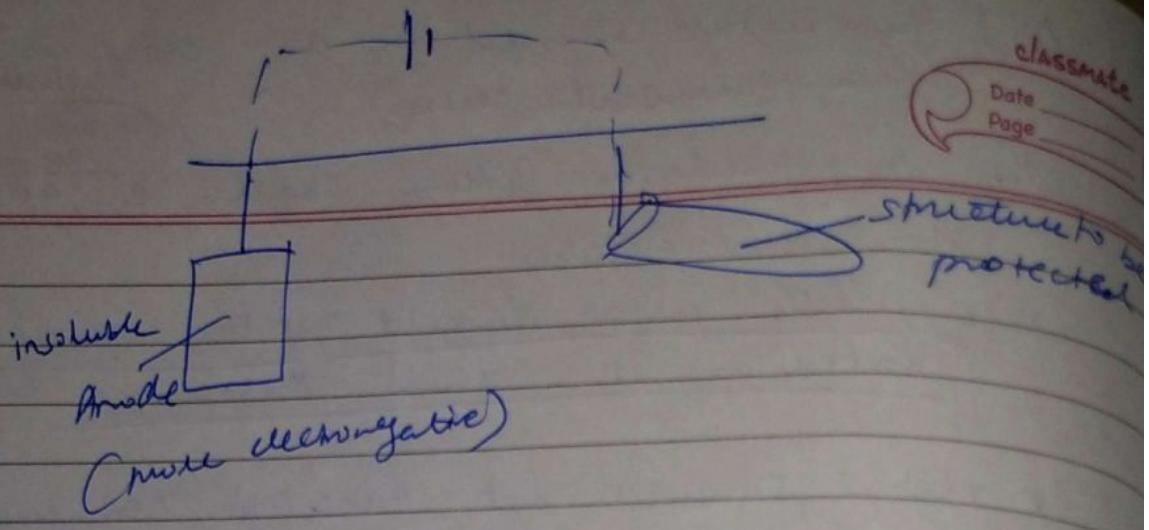
Impurities in a metal cause heterogeneity which decreases corrosion resistance of metal & therefore impure metals corrode faster than pure metals.

3) Using metal alloys.

4) ~~V.V. insp. #~~ (always comes) Cathodic protection


↓
Sacrificial Anodic protection

↓
Impressed current
Cathodic protection.



Anode

O. D. P. S.